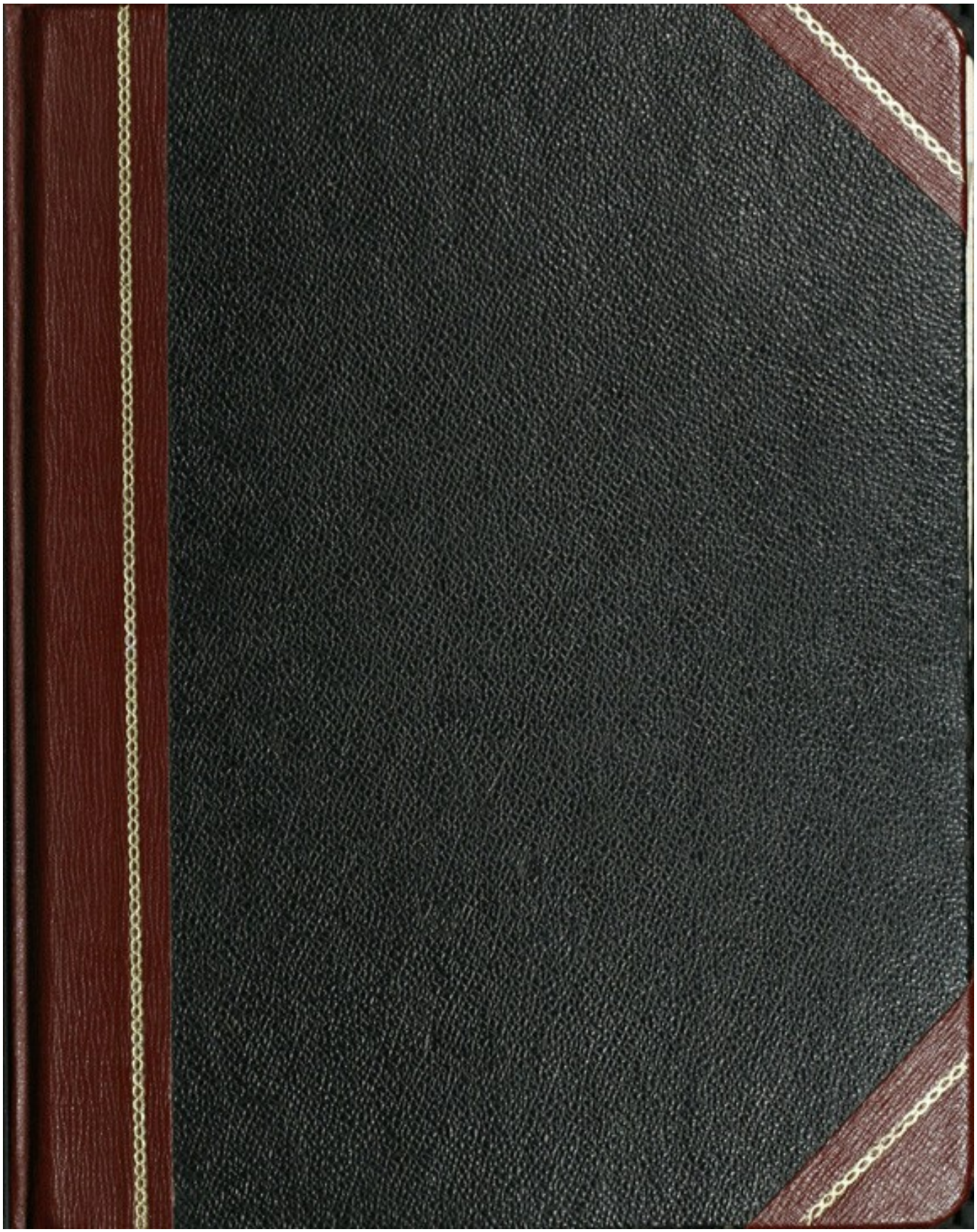


Alexander T. Shulgin
Reward for Return

[TELEPHONE NUMBER]

Synthesis

		24	25	35
CM. 4 Carbon:	NS	6:3	5:295	5:284
	IRS		5:279	
	6:4			

1 NS
3 Fe
25 HoAC
2 hrs SB

2C-T's 7 6:5

40 Al 1g $HgCl_2$
140 ml H_2O
o
60g 60ml | 76 ml 40%
ISO IPA
145 25% | 50 NaCl 140 H_2O 25 25%
53 AA
350 IPA

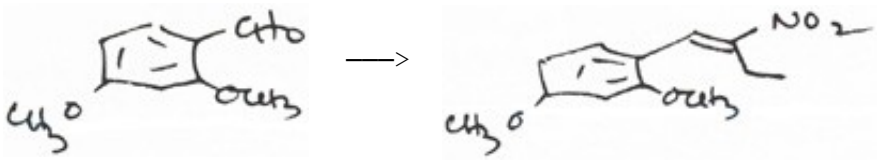
	ether	CHO	NS	NH2
		107		
Ψ 2-CT-1	99	107	NS 107	
	126	~~107~~	129	
2	129·127	~~107MN~~		
4	99	70	70	
(benzyl)	99			

2C-T-X		ether	Analytical CHO	CN	NS	$NH_2 \cdot HCl$
X	R					
2.	Et		163	164 163		164
9.	tBu		166	166	166	

MMDA Clan Lab 199->212
DMT study. 213->
N-CHOEt of T 220-221
N-Me-NIRtryptamine MIPT 222-3

(2C)G-4 (70,NS)

May 26, 1988

Attempt: 

|| page 5:295 8.3 g aldehyde , into
35 g No_2Pr add
0.85 g $(Me)_2NCH_2CH_2NH_2$ into SB 11:10AM
immediate deep yellow color.

Δ SB 2 hrs - TLC -> 90% done (no trace of nitrite). Strip -> yellow oil [with] spots of water. into 300 ml dil HCl & CH_2Cl_2 - sep CH_2Cl_2 - xtrt HCl [with] CH_2Cl_2 - strip -> heavy yellow oil.

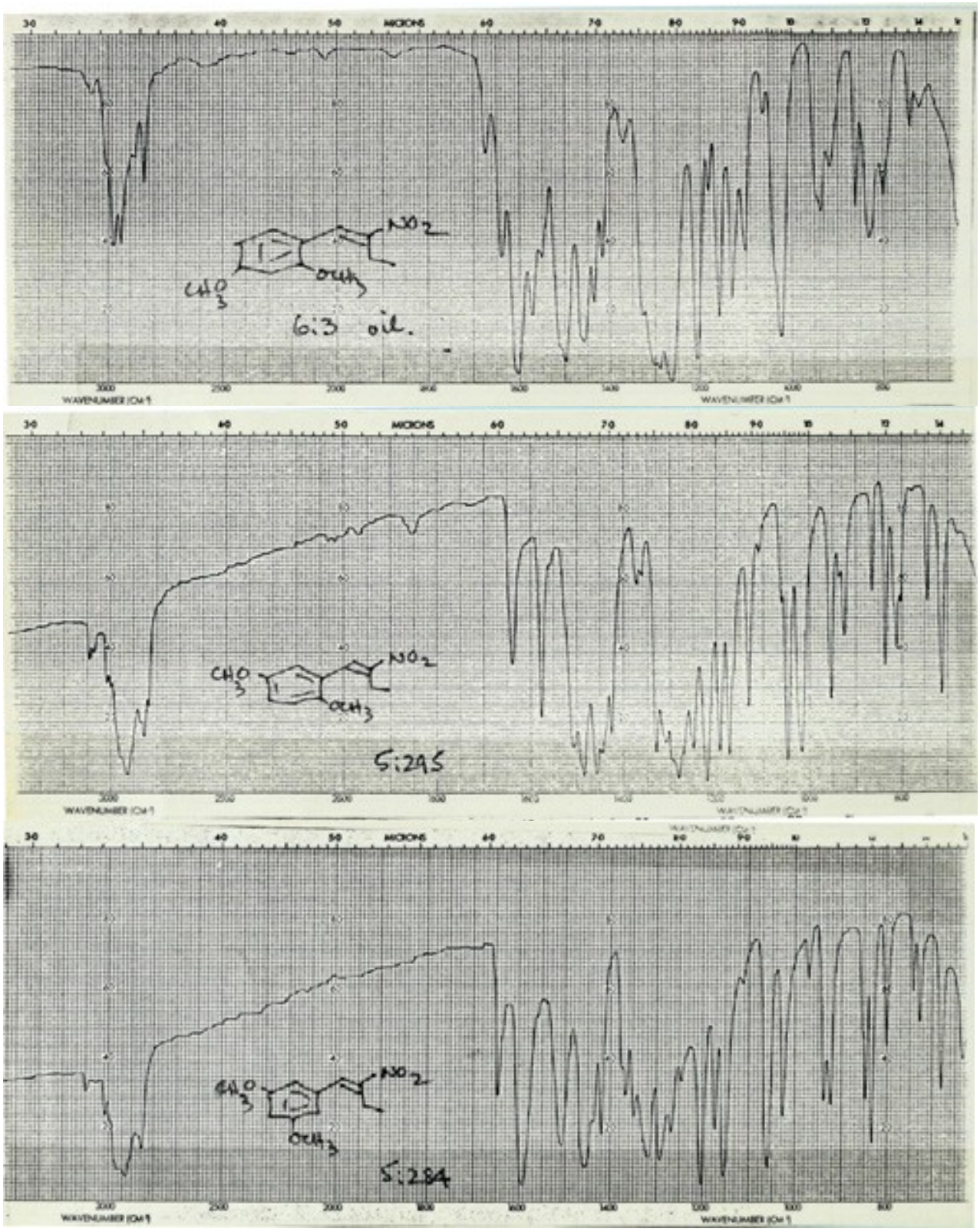
earlier tries.
5:287 dean stark
5:283 HoAC, chron.

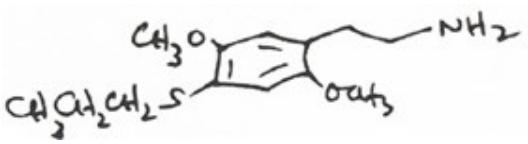
outside play -> seed - it takes ——————> 9.82 g. of fused solids

6:3 IR - next page

Rextallize from = wt of MeOH. tricky! - oils easily, very slow to xtallize, & exothermic xtalization - ∇ slowly and seed at the right time ——> excellent, brilliant light yellow xtals. 8.05g
7.5g onto Ketone 6:8

Ariadne - like nitro styrenes





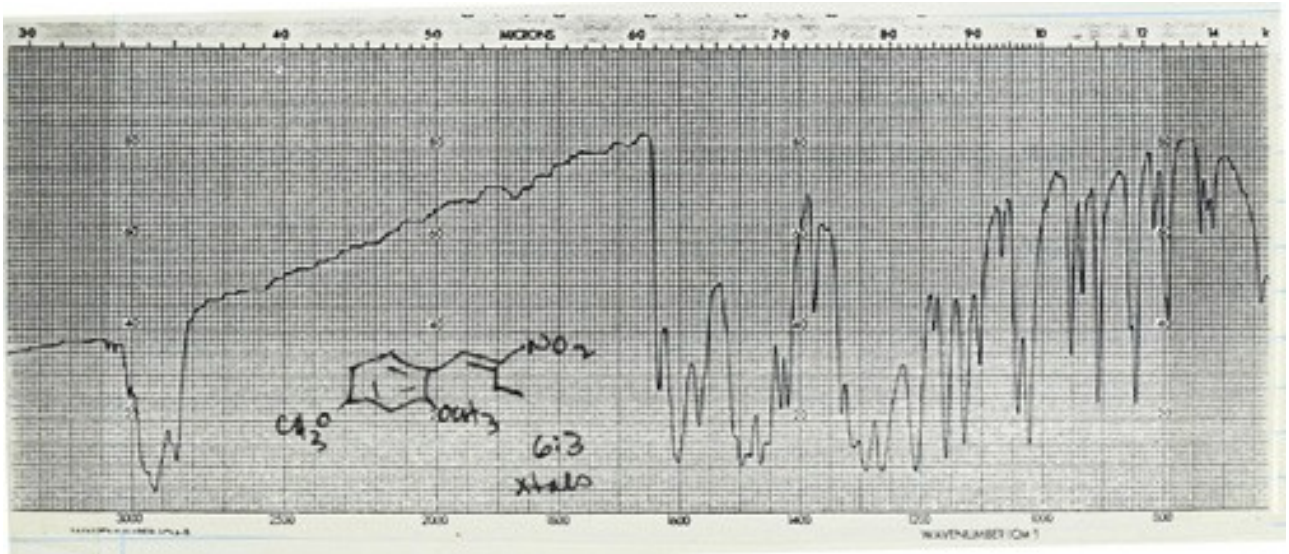
See 5:211 ether: 19.47g white oil (ex 13.6g ArS·H)

aldehyde: 31.5g $POCl_3$ 29.2g NFA Δ 25 min -> 16.27 absolute dry.
from 21.02 g wet sugar + 21 g MeOH. ML's -> brown oil. OUT

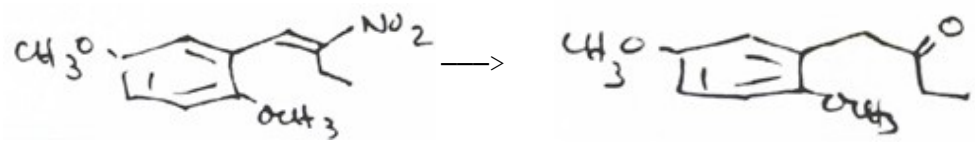
nitrostyrene: 16.27g into 50 g warm CH_3NO_3 + 2.0g NH_4OAc - on SB at 3:45 . RE at [1:15]–> spont. xtals [with] some NO_2Me left. filter wash [with] a little IPA -> 18.65 g damp. ~~rextal from IPA.~~

ML's-strip down -> orange paste - filter, wash [with] IPA -> 2.36
Σ 21g
or 20g

17.64 drier -> combine. rextal from IPA. 250ml.
↓
orange xtals. 16.76 g static-dry .



May 31,1988



7.95g { 5:279 / 5:295 / 5:29A } into 200ml HOAc. Δ to ~ 60° - add

||'ed mostly on 5:222

25g electrolytic iron - usual progression - start to bubble - cloudy - via green to eventual thick gray with deep-colored chapeau. Δ SB 2hrs.

Into 1L H_2O, filter (paper) water & CH_2Cl_2 wash.

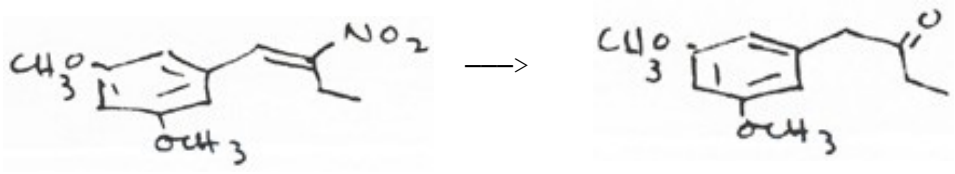
Xtrt 3 x 75 CH_2Cl_2 - pool - wash [with] 2 x 100ml 5% NaOH. (1st xtrt already basic, 2nd colorless) flash -> orange liquid.

5.32g into KR pot. distill.

→ 4.96g sl. off white clear oil

bp. 70°/50μ
↓
110°/80μ.

probably 70-85°/50 is fair.

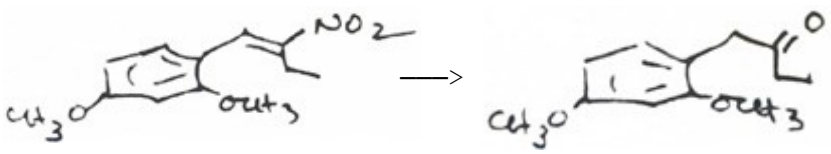


5.70g 5.284 into 130ml HoAc, Δ, add.
17g electrolytic Fe° - SB 2 hrs. usual bubble -
to solid cake on bottom - to gray - to dark chapeau-
on ~1:45 off ~4:00 >2hrs.

Into 1 L H_2O, filter (paper) & wash [with] H_2O & CH_2Cl_2 -
xtrt [with] 3 x 75ml CH_2Cl_2, wash [with] 2 x 100 ml NaOH (5%)
1st is basic, 2nd clean - no emulsions. flash on
R.E.
→ almost colorless oil. 4.40 g.

KR. ~~4.08~~ 70-90°/0.1mm.
4.12g. pale yellow oil.

Attempt.
5/31/88



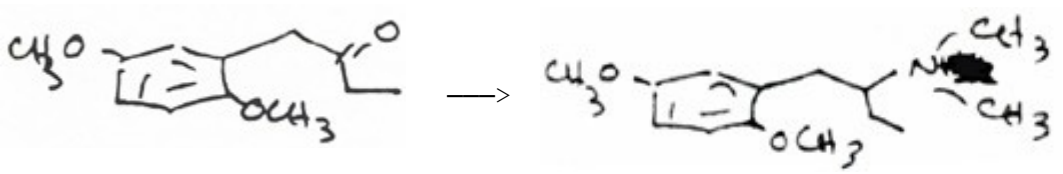
7.5g NS from 6:3 into 200 ml HOAc - warm - add
25g electrolytic Fe° - standard sequence. on SB.
on ~ 2:45PM. It looks as if it is going more slowly.
(yellow to green to gray a little sluggish - then
fine. off ~ 4:15 only 1 1/2 hrs.

Into 1 L H_2O, filter through paper, wash cake
(quite a bit of unreacted Fe - next time > 2 hrs)
[with] H_2O & CH_2Cl_2. xtrt [with] 3 x 75ml CH_2Cl_2 - pool -
wash [with] 2 x 100ml 5% NaOH. (1st extract was
already basic. Flash on R.E.

→ 5.80g yellow oil.

.075mm. to KR. ⟶ 5.37g pale yellow fluid oil.
80° no 90-105°/0.075mm.
90µs.->105°

6/19/88



To a solution of
6 g $(CH_3)_2NH$-HCl in } Δ->solu, ∇. add.
|| 5:224 20ml MeOH

1.75 g Ketone, then
0.8 g $NaCNBH_3$ - on to stir $5^{\underline{00}}$PM. neut to wet PH.
(yellow)
Add conc HCl as needed -> damp pH paper at yellow.

M +2 drops
Tu +2
W +3
Th +4
F +2

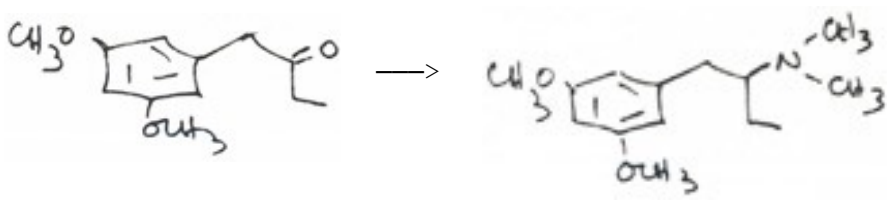
Work-up 7/1/88. into ~~1 1/2~~ 1/2 L -H_2O - basic [with] 5% NaOH - extract 3 x 75ml CH_2Cl_2 - extract pooled dichlor [with] 2 x 100 ml H_2SO_4

CH_2Cl_2
flash
→1.56g neuts.

OH [with] 50% NaOH -
xtrt 3 x 75 ml -
flash → 0.42 g.

.34 removed.

June 19, 1988

Attempt: 

To a solution of

6 g $(CH_3)_2NH$-HCl in 20 ml MeOH } Δ, ∇, add

1.75g Ketone, +
0.8 g $NaCN_3H_3$ on to stirring 5:05PM. neutral (yellow, pH.

add conc-HCl as needed to bring wet PH paper to yellow
M 4 drops
Tu 3
W 2
Th. 4
F. 3 Σ16
one more week - 3 more drops.

Work-up. 7/1/88 - into 1/2 L H_2O - basic [with] 5% NaOH.
xtrt 3 x 75 CH_2Cl_2 - pool - back extract
2 x 100ml H_2SO_4 5%
2 x 100ml 5% citric acid

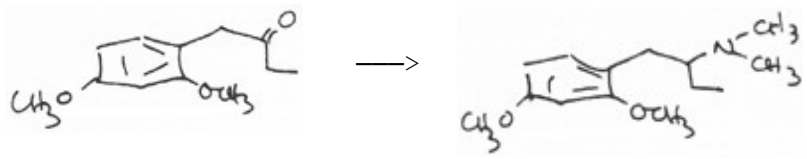
left-over CH_2Cl_2
flash
→ 1.45g
6:10A

H_2SO_4
basic [with]
50% NaOH
xtrt 3 x 75
CH_2Cl_2
flash
↓
0.45

Citrate-
basic [with]
50% NaOH
xtrt 3 x 75
CH_2Cl_2
flash
↓
0.02

pool-
hits shelf as 6:10B

June 19, 1988

Attempt: 

To a solution of

6 g $(CH_3)_2NH$-HCl in 20 ml MeOH. } add.

1.75g Ketone +
0.8 g $NaCNBH_3$ on to stirring 5:10PM. neutral (yellow to pH paper).

Add cool HCl to bring wet pH paper to yellow.
M +3 drops.
Tu +3
W +2
TH. +4
F. +2 Σ14

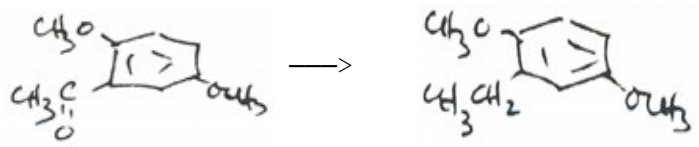
workup Friday afternoon. Into ~ 1/2 L. H_2O. 5% NaOH to quite basic - xtrt 3 x CH_2Cl_2 - back extract [with] 3 x 50 ml 5% H_2SO4 - OH [with] 50% base. xtrt [with] CH_2Cl_2 (2 x 75ml).

flash → 0.30g white oil.

CH_2Cl_2 (neutrals).
wash [with] 5% NaOH
strop,
→ 1.72g in flask.

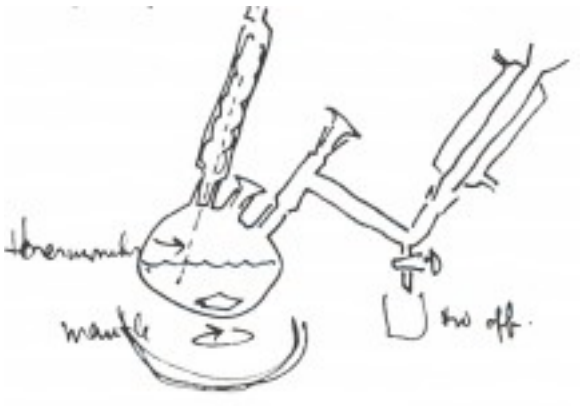
6/19/88

Repeat



28 g acetophenone (aldrich).
Seepage. 19.75 g 85% KOH pellets.
5:228 140 ml triethylene glycol
"22.4 ml 85% hydrazine hydrate" I used.
30 ml 65% hydrazine.

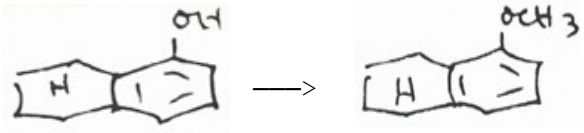
Onto reflux (takeoff) ~7PM
awfully slow to come open. Δ [with] mantle to ~60V. slow. - to 75V. slow. replace receiver [with] low D.stark take-off - very fast. Temp within 10 min to 220°- then hold at reflux. 11PM



220° for 1 1/2 hrs. off - ∇ - into 1 hr. H_2O (combine distillate) and extract [with] 3 x 75 ml CH_2Cl_2. flash -> deep amber oil.

Some used in p.14 try on Wilsmeyer. - very bad.
rest - page 19- Cl_2CHOCH_3 $SuCl_4$.- very successful.

6/19/88
Repeat



See page 5:257.

50 g Naphthol. (49.2 - contents of a new Aldrich bottle). in.
100 ml MeOH - Δ to dissolve - add
56 g MeI. add
{ solu. 24.8g KOH
  100 ml hot MeOH }
into 55° bath. white solids in ~ 10 min. - Δ 55° ~ 3 hrs.
Strip on RE -> oil + solids.
rinse out [with] a little water - ~2L.
acidify [with] HCl. xtrt [with] 4 x 75 ml CH_2Cl_2

org. → wash [with] 3 x 75 ml 5% base

org. → Flash.
48.2g. crude. black oil.

KR. 0.25mm
80->100°C.

33.9g white oil
terrible pot.
pot OUT.

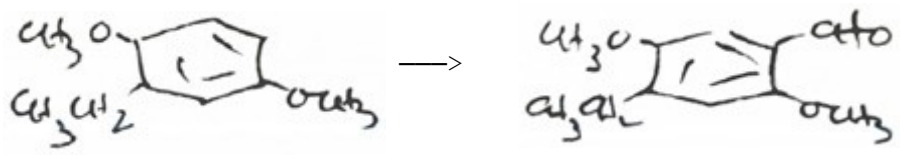
aq → H^+ to red.
xtrt [with] CH_2Cl_2

org. → flash.
17.3 crude.
black oil
KR. 0.35mm. - product over
(lots of color).
11.4 over. some brown colors
through it. Pretty good.
put on shelf as recovered
phenol
6:13 10.82g
6:13

aq OUT

aq OUT.

6/20/88

Repeat. 

Try small runs:

see 5:235
see 2:177 0.65g $POCl_3$ } SB. Δ->claret – add.
(1) 0.57g NMeFA. }
0.65g crude ether ex 6:12

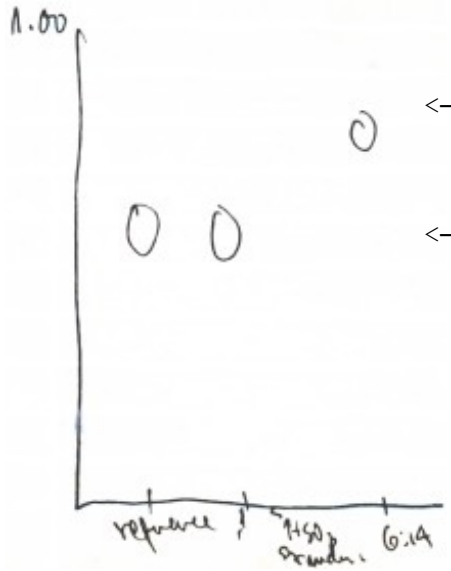
Δ SB 20 minutes - add 25ml H_2O - ~1 hr -> granular stuff. decant. xtrt solids (bad) [with] 25 ml C_6H_{14}. let stand -> curdy solids as hexane evaporates- finally - a small sludge - pov. plate -> 0.03g amber solids

(2) ≡ Δ SB 1hr. same workup (decant, boiling hexane) 0.06g. xtals.

(3) 2x that of (1), 2hr. same workup -> .64 (.44 recovered)(scoop out)

(4) as (3) 4 hrs. some workup. -> .44 (.32 xtals scooped out

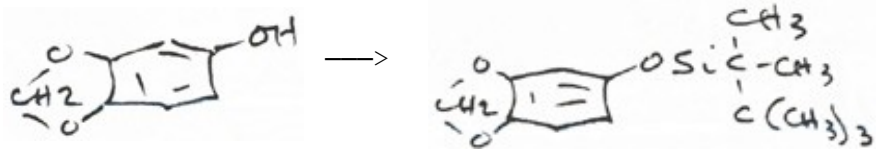
.44 #3
.32 #4
+ .06 #7
into 10 ml boiling MeOH, ∇ -> 0.22g white solids. (6:14)

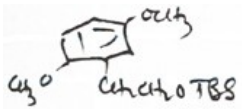


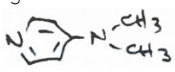
<— nothing [with] long wave

<— white flour. [with] long wave.

August 31, 1988

Attempt: 

|| Larry W.
prep of

page 117.
dilute CH_2Cl_2
wash H_2O, sat. NH_4Cl
dry, strip -> oil
80-83/0.3mm 86%

4.7g sesamol into 33g CH_2Cl_2 - add
4.2g Et_3N
.16g  (as catalyst). add, dropwise,

5.66g TBSCl
(used 5.77) in
12 g CH_2Cl_2.

Slight heating - in ~2 minutes - sudden solids. Let stir. O.K.T. Removefreder
Into 1 bilter ??.

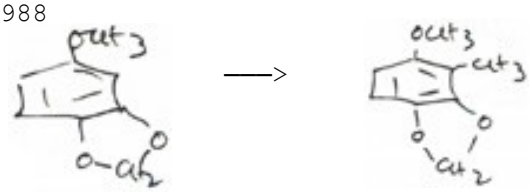
Wier 9/1/88
diluted suspension [with] 50ml CH_2Cl_2 ; washed 1 x 100ml H_2O; 1 x 100ml Sat. NH_4Cl; dried ($MgSO_4$) filtered and stripped to a gold oil.

dist 84-86° 0.75mm Hg .

8.4g isolated after distillation

NMR- in LW's standards file

August 31, 1988

Attempt- 

Solu. of 1.88g sesamol methyl ether (L.W. page 286)
in ~ 20 ml THF, add (at 0°) (and stirring) (under Arg)on

1.44g TMEDA
5.0ml 2.5M Bu Li.

Color to yellow to amber to deep amber.
Stir 1 hr. - add

1.87 (1.75 theo) CH_3I in ~ 10ml THF.

Color to pale yellow in 1st 1/4 of addition.
Let stir a while.

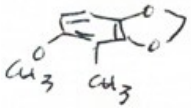
Dump into ~ 5% H_2SO_4 (250ml) a bit at a time.
Initially red-brown -dispelled by good stirring
Extract [with] 3 x 50 ml CH_2Cl_2 - pool - wash
5% H_2SO_4 - strip.

dry of $MgSO_4$ in CH_2Cl_2 - strip => 1.90g

By Larry W.
Column Chromatography
3 x 35 cm Silica
Eluted with 8% EtOAc /Hexane
Elution Volume 165-300mL

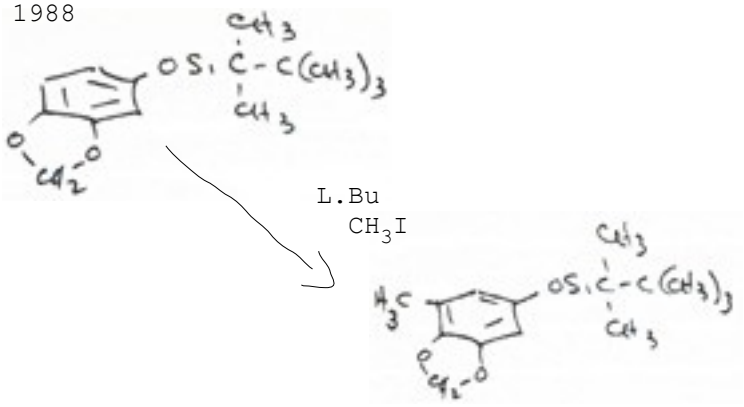
1.475g pure isolated : Solid
white / clear plates

[Editor's Note: The following is written vertically in the left margin]

purification of 

September 9, 1988

Attempt:



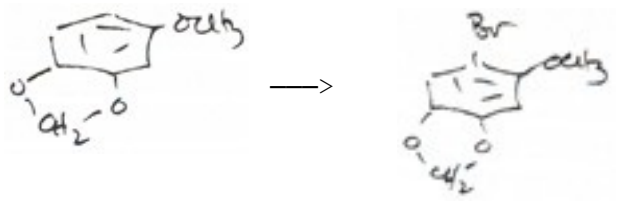
1.63 g TDS sesamol in
20 ml THF. add
0.72 g TMEDA.
∇ to ~ -20° [with] chipped ice / conc HCl. -
2.5ml 2.5M BuLi.
turns yellow to orange to deeper orange
over ~ 1/2 hr. add.

1g CH_3I in THF. discolores - white solids.
stir ~ 1hr.
dump into H_2O - acid to pH 6 [with] H_3PO_4
xtrt [with] CH_2Cl_2
wash [with] pH 6 H_3PO_4.

flash evap -> dark oil. LW KR's
no methyl by NMR.

Sept /16 1988

various
attempts

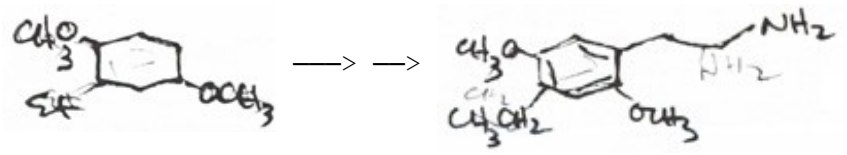


(1) in CH_2Cl_2 1.52g M.R's "95%" ether
10 g CH_2Cl_2 add
~2.0g (1.6 = theo) Br_2.

Initial add'n -> HBr↑ and immediate decolorization until about the 1/3 point - then stays dark. Let stir ~ 20 min, wash [with] lots of dithionite. evap -> dark oil that solidifies - TLC terrible. 18:1

(2) in CH_2CL_2 .76 g - as above except stop at the 1/3 point - no persistent dark. wash dithionite flash -> white xtals! IR [with] small sharp OH
18:2

Oct. 9, 1988



2C-E

|| smedchem 16 #5 480 (1973)

A solution of 8.16 g ether (6:12) into 30 ml CH_2Cl_2 - ∇ to ~ 0° - good stirring - add 11.7 ml anh. $SnCl_4$. - then add

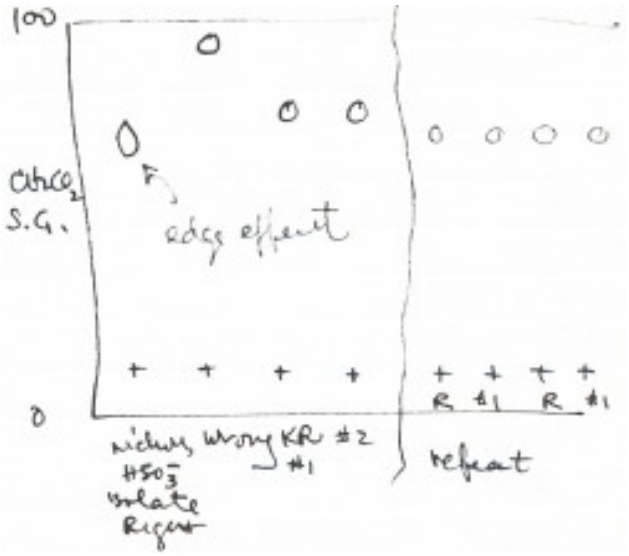
3.95 ml Cl_2CHOCH_3 dropwise over ~1/2 hr.

Then up to RT - to S.B. ~1 hr. into water, xtrt CH_2Cl_2 - wash dil HCl. flash CH_2Cl_2 ->10.8g . KR whole mess (dark)

↳ off white ~~sol~~ oil that solidifies. (some in trap #2)

5.64g .
oily .
Σ5.91

mp nichols Insulfate 47-48
my KR'ed. 46-47.

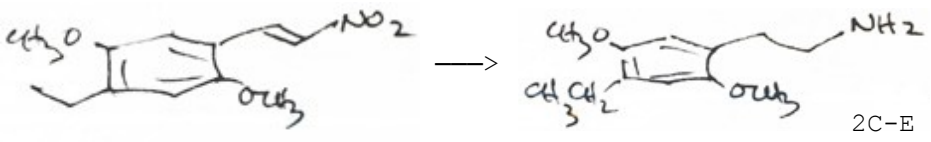


See Book #2
page 179 mp 99-100°
to nitrostyrene

5.9 g aldehyde (all of above, save a bit for mp.) (use James's
25 g CH_3NO_2 SO_3^- for ref)
0.5 g NH_4OAc. SB. (old ref black xtals!)

TLC 20 min ~ 1/2 1/2
Silica 45 min done
CH_2Cl_2 off at 1 hr. strip -> orange solids 7.33 wet rextal of MeOH (total of 50 ml solution - ∇ in ice ~ 1hr -> yellow-orange xtals 5.93g air-dry. save 0.10g rest next page.
mp 99-100°.

Oct 16, 1988



2C-E

120 ml 1.0 M LAH in THF into a 3 neck 500 ml
RB [with] good stirring. ∇ 0° [with] lots of ice.
See Book 2 221 Under He. — add.

3.0 ml 100% H_2SO_4 over 1/2 hr. - freshly made from new bottles. No clearring. Becomes quite cloudy [with] white solids. — add

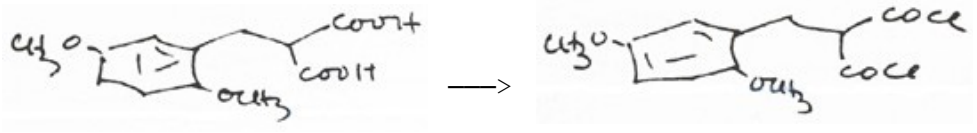
5.83 g NS 6:19 in 40 ml THF, over 20 min.
stir 1/2 hr.
Δ SB 1/2 hr.
∇ RT - add.

12 ml IPA dropwise to kill excess. AcH_3.

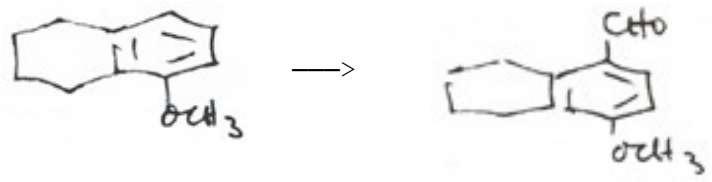
2.83 crude + some 5% base - added ~ 4.5 ml - looks like good
1.8 KR cottage cheeze - filter - wash [with] THF. flash -> 2.83g
90-100 .25 crude - KR -> 1.8g white OIL.
15 ml IPA 90-100/.25mm. into 15 ml IPA.

White solids - resuspend in THF, add another 15 ml 5%
2nd crop. NaOH - filter-wash THF -> 2.8g crude base again
2.8 crude KR as above → combine. +15 more IPA + HCl ∝ external
KR HCl (solids) + ~ 50 ml ether → magnificent white solids. air dry.
3.87g 2C-E

Oct 28, 1988



3.6g recovered -not-too-good acid p 5:280 +
32g $SOCl_2$ - slow to dissolve in SB. much bubbling -
then all in solu. deep red but good red.
IR -> no COOH & new but broad C=0

Oct 30, 1988 

parallel·

5:258 33.9g ether, from page 13. add to
43.17g $POCl_3$ (wanted 38.52 but over shot 33.9)
38.0g NMeFA

heated on S.B.~10 min -> deep claret.

Δ all on SB 2 1/2 hrs. — into 1 1/2L H_2O - stir during dinner. filter (coarse funnel) wash [with] H_2O - suck dry -> 38.1g wet cake. suspend in 22g MeOH, grind up. filter, wash sparingly [with] MeOH, ~~filter~~ suck dry -> 25.6 damp pale green solids - let air-dry

24.76
drier all mL's etc - xtrt [with] CH_2Cl_2, wash [with] H_2O, then 5% base - flash -> 16.1g black oil.

23.28
over/110-130°- RK. 0.4mm 2.33 *

1st fraction to 110° - liquid
2nd fraction to 130° ~~6.19 g~~ heavy oil - sets to pale yellow solids. scrape out 6.1g solids.

.25

~~22.96g~~

22.96. 22.96g pale yellow solids.
6.19.

1st crop

1st fraction

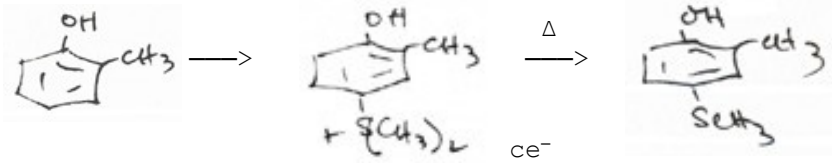
2nd fraction. 6.19g combine

Σ29g ~~ea~~ good products.

Tally.

good aldehyde 29.0g TLC fine (3:1 CH_2Cl_2/hexane
fair aldehyde * 2.3g. TLC - some NMeFA. aldehyde 0.6)

Nov 4, 1988.



64.8g o-cresol into
56g DMSO . add
300ml ether. ∇ 0° [with] good stirring. add.
40ml } $CeSO_2OH$
70.8g }
dropwise over ~ 1/2 hr.

up to RT. - shake - stir [with] rod. - finally (1hr).
decant ether. grind under 300ml IPA -> eventually
solids - filter, wash [with] 150ml IPA -> white solids.
let air-dry a week.

wet. 22.65g white solids with the slightest hint of pink.

IR on 6:26

Nov 11, 1988.

22.65g dry sulfonium salt was pyrolyzed with an open flame. there was effervescence on melting, and the melt, when quiet, was heated up until there was distinct browning - wt. of cooled, fused salt is 16.71g.

into 250ml CH_2Cl_2 - xtrt [with] 3 x 75ml 5% base

16.81 CH_2Cl_2 Stripped. 0.4mm. 0.35mm 80° start. to 115° some res.

aq. @ [with] HCl - 3 x 75ml CH_2Cl_2 -> flash -> 16.81g - KR 0.35 80/115°

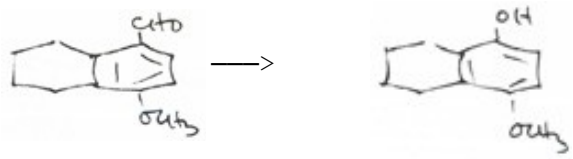
CH_2Cl_2 flash

1st receiver 13-90 almost white oil
2nd receiver. xtals. same stuff- .90

19.80g IR on 6:26

theo 17.09
yield 87%.

Nov 6, 1988
Attempt:



Trial

10MM.
1.9g aldehyde from 6:22. - dissolve into
3.7g HoAc. SB -> solu. - ∇ to almost RT. add

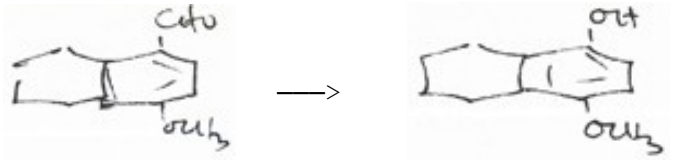
2.4g 32% HoAc.- at end, exothermic -> deep brown
solution - extremely exothermic. - stand to RT

Add H_2O 100ml - xtrt [with] 4 x 25ml CH_2Cl_2 flash on
SB -> black oil. add

10ml= 20ml 5% base. 25mm. - on SB. 11:00 PM. - off at 25 min.
12.5mm. add 100ml. H_2O (still basic) - xtrt [with] CH_2Cl_2 - 3 x 25ml-
make aq. @ [with] HCl. , xtrt 3 x again (difficult). flash
acid CH_2Cl_2 ->

125°/.25mm

.32g.



Trial

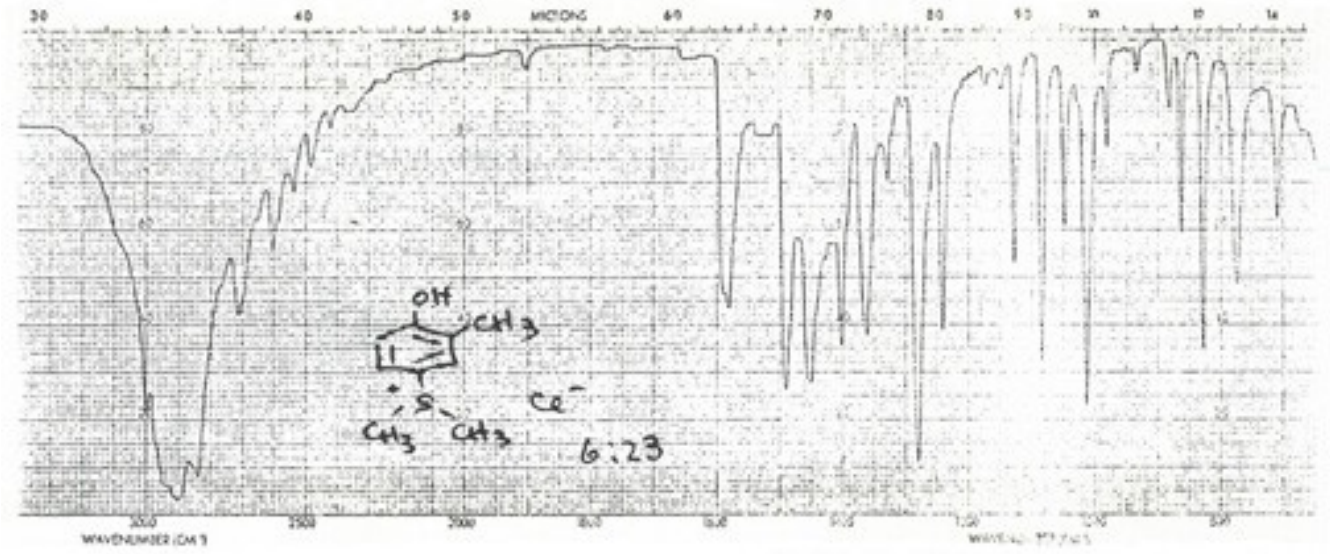
1.9g (10mm) aldehyde - into
6g CH_2Cl_2 - solution . add.

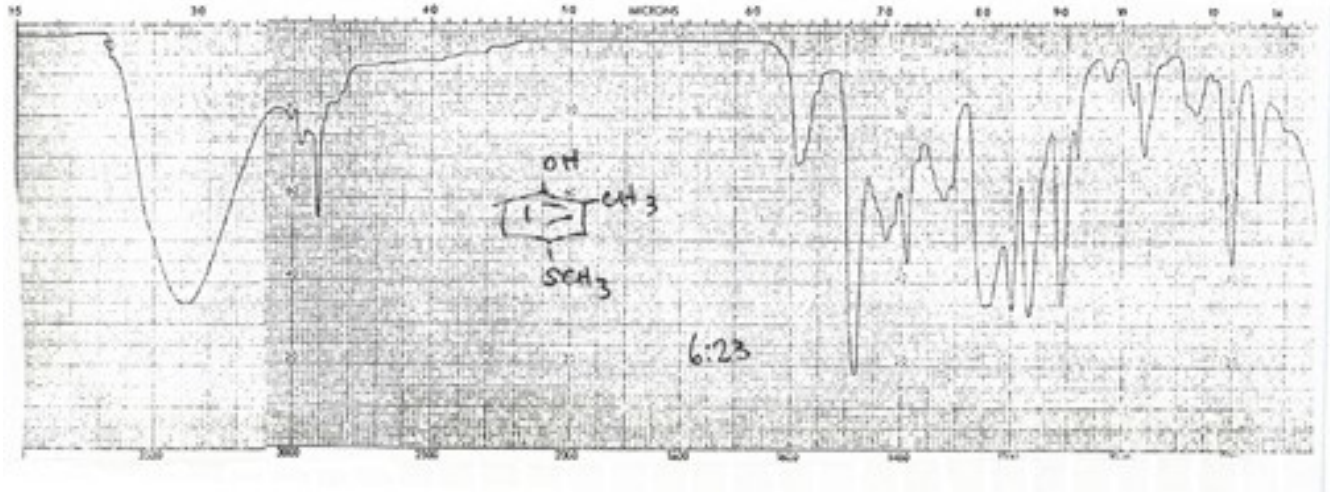
2.4g 32% HoAc. - to reflux. - Keep on SB. for a couple of hours - add CH_2Cl_2 as needed. Slowly from yellow to brown to black. ~ 2 hr reflux. Off, +100ml CH_2Cl_2 - extract 2 x 50ml H_2O. flash the CH_2Cl_2 - add 20ml 5% NOOH on SB.

.3 into H_2O - partition between H_2O (base) & CH_2Cl_2 -
1.46 extract OH^- [with] CH_2Cl_2 - . wash CH_2Cl_2, & 5% NaOH.
crude.

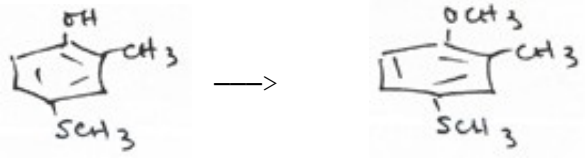
flash - distill . 90-120°/0.3mm Hg.
white solid. solid crap in pot.

[Editor's Note: The following graphs were originally vertical on the page]





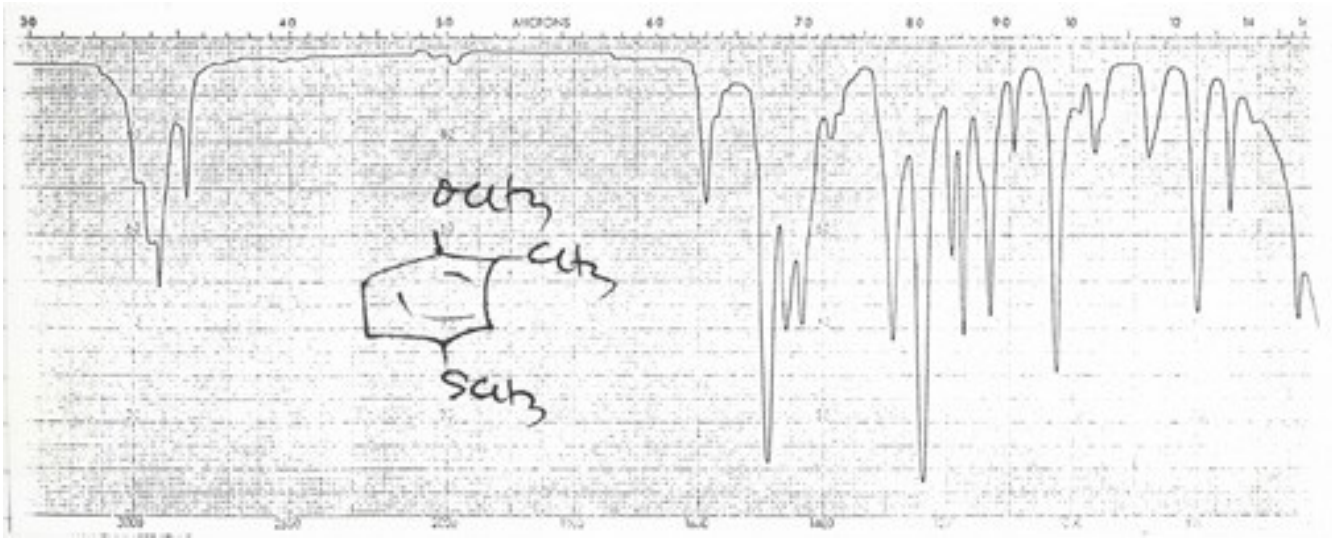
Nov 11, 1988

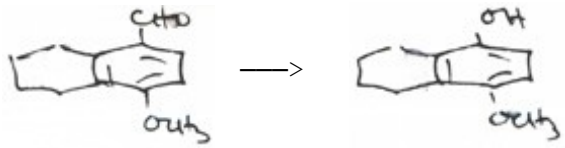


14.8g phenol - page 6:23, into warm methanol (~60ml). add
7.0g KOH (85%) in ~60ml warm MeOH. add.
7.2 ml CH_3I. onto reflux.
~ 1/2hr - white solids ppt.
~1 1/2hr - work up - into ~ 1 L H_2O- add base until blue pH paper. xtrt 3 x 75ml CH_2Cl_2 - wash [with] 5% NaOH

aq. dichlor
@ [with] HCl. xtrt, flash → flash ->
—> small amt phenol. 5.70g amber oil.
1.85 where did everything go?
5.48 transfer to KR

Distil ~ 100°/.15mm
3.28 1st bulb.
4.83 both bulbs.



11/13/88 

25.11g (the rest of the naphthaldehyde) 6:22 dissolve in
|| to page 100 ml CH_2Cl_2 - add.
2:144 25g m-chloroperbenzoic acid (10% xs, 85%).
spontaneously up to reflux - add peraid at a rate
commensurate [with] exotherm. swirl. When 1/2 in -
solids start out - into 1 L flask. won't stir - add
CH_2Cl_2 to ~ 300 ml CH_2Cl_2 - stir OK - add rest
of peraid over 20 minutes

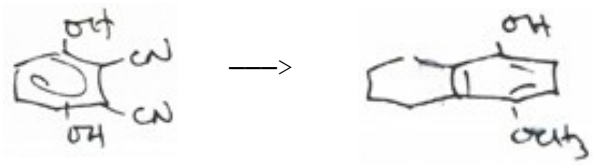
Onto gentle reflux [with] stirring - heavy solids - 1 L.
6:00PM. heating mantle. off at ~ 2AM. stand 1 week ->
Sunday. heavy white xtals of ArCOOH. filter - ~~sa~~
~~whesh~~ wash [with] a little CH_2Cl_2 —> solids.
Wash [with] 50ml sat $NaHCO_3$ <— save.
—> aq. A^+ -> white
out
flash -> 20-30g amber oil.
add 100ml MeOH
add 40ml 25% NaOH - dark - homogeneous - onto
1 L H_2O SB.
@ - solids off at ~ 1hr.
wash H_2O

into 1 L. H_2O., add HCl -> acid -> solids. - filter - wash [with]
H_2O. Wet· 39.5g. Try to K.R. - wont go over - but becomes very
dry. Wt. 27.27g - use as is for ether synthesis. - no - try
KR-again - all the little bits of 6:24 & 6:25.

39.5g
Crude KR. 0.2mm. (melt first) at ~120-170°. small residue
see
5:262 —> 21.44g off - white solids. slightly waxy.

Rextallize ~20mg at
1 ml Hexane
—> marvelous xtals
white.

Attempt (again)



11/13/88

20MM

3.2g ← dicyanohydroquine (aldrich) into 40 g acetone, add

See 7.0g reasonably finely ground K_2CO_3, anh. add

5:151 25%x5 1 for 1

5:155 7.~~?~~ g CH_3I. onto SB at reflux ~ 8$^{\underline{PM}}$ good reflux - then

none in 2,4. bumps.

first try in 25%x5 1 for 1 off (how long?) stand 1 week. Into

Vol. 1 or 3. 200ml H_2O. - filter off solids

aq. solids. → 3.07 wet.

xtrt·[with] CH_2Cl_2 -> trivial solids. 6:29-A

@ [with] HCl. xtrt [with] CH_2Cl_2

→ trivial solids.

16g remaining dicyano - into 200ml acetone.

35g K_2CO_3 ground up. add.

35.5g CH_3I reflex ON. off in AM. Stand 1 week.

Into 1 liter H_2O - Strong base.- filter -> slate solids

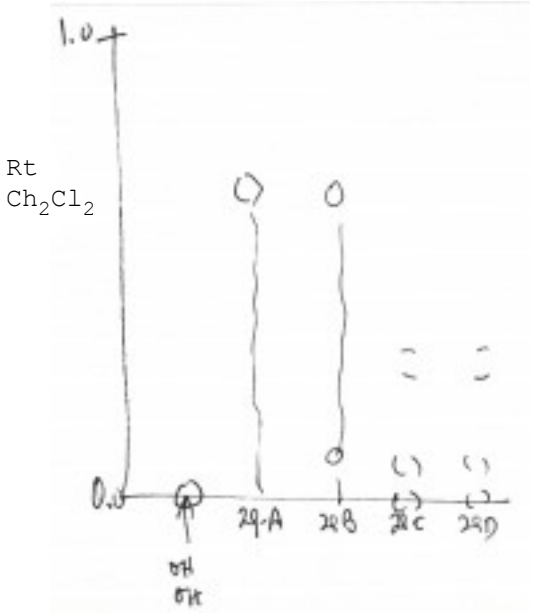
17.0g wet 6:29-B

ML

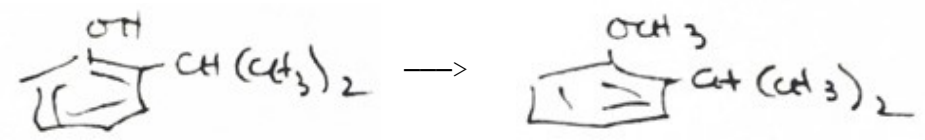
↓

H^+-filter ->slate smudge. → 6:29-C

ML's of sludge- xtrt [with] CH_2Cl_2 slate solids. → 6:29-D



11/18/88



27.2 g o-isopropylphenol (MW 136, 200mM). into

{ 16.0g 85% KOH
150 ml warm MeOH } 20% xs. then, add

36g CH_3I. Onto reflux (SB). ~1 30. xtals of KI in ~10 minutes. off at 3 1/2 hrs. into about a liter of water (still basic) xtrt 3 x 100 ml CH_2Cl_2

org.

wash once with 50 ml 5% NaOH. (some color is removed). flash

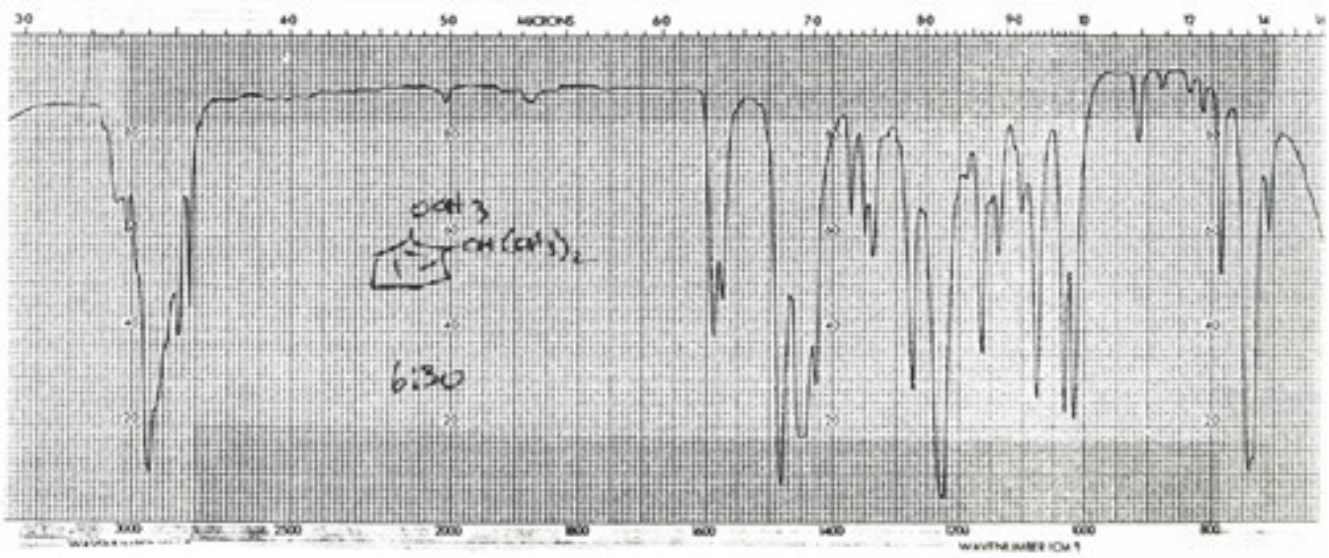
> 23.56 amber oil.

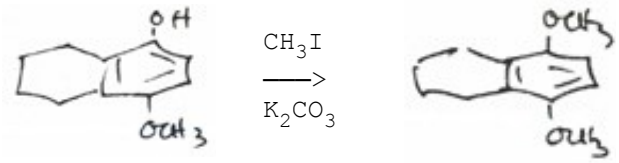
aq. add conc HCl xtrt [with] 3x75 CH_2Cl_2

KR. too volatile · ~60-70°/0.5 over and up snorkle.

save a bit in vial for reference. 6:30

rest to page 32





|| 5:272

21.44 g KR'ed phenol. [6:28] into
100 ml CH_3COCH_3 - add.
25g K_2CO_3 powdered anh. K_2CO_3. - 1 liter flask.
26g CH_3I - onto S.B. 9^{15}. ~~A~~ P.M.

off at 11^{15} PM. - into 1 L. H_2O - strongly basic - extract [with]
3 x 60ml CH_2Cl_2

aq. ← organic. → wash one time [with] 50 ml NaOH

aq. ← organic

base.
H^+ ->clear
solu.
->cloudy.
but still acidic.
xtrt [with] CH_2Cl_2
→ 4.55 g
recovered phenol.

flash
→ 20.17 g.
waxy red xtals.

into 20ml acetone.
+5g ground K_2CO_3 anh.
+5g CH_3I.
on SB. 12^{30}AM.
off neg. yield
out

grind under
14g hexane

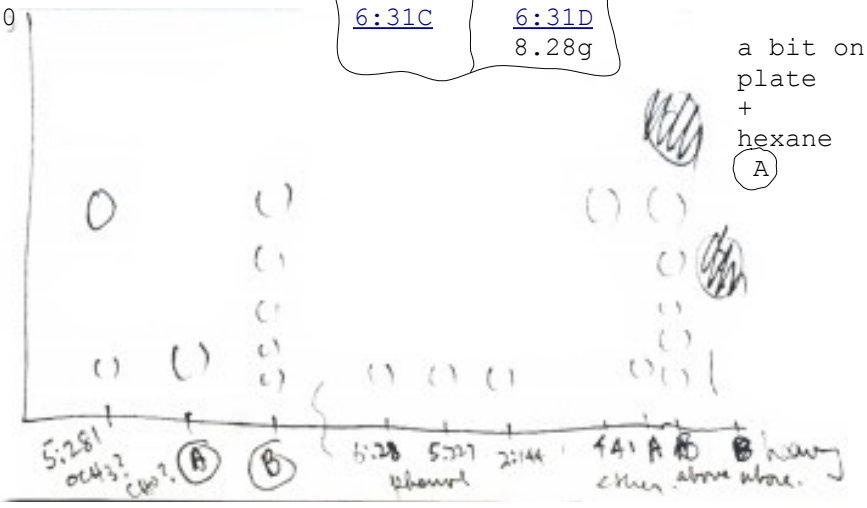
solids	ML
6.41g white solid. 6:31C	~pale amber oil. 6:31D 8.28g

KR. 90-130° / 0.3mm
→ 14.10g waxy, oily white Solids.
crude (B)
a bit on a plate + hexane (A)

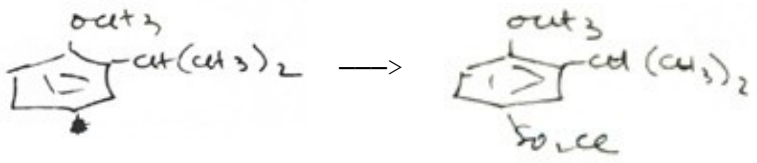
19.66
13.56
~~19~~
~~13.93~~
14.10

1.0

3/1
hexane
CH_2Cl_2



12/2/88



3.0g anisole - add, [with] good stirring
5.0g $ClSO_2OH$ - neat.

At 1/2 way point, the frothing quiets down. all is very hot. let stir 20 min - into cracked ice > lower phase that finally xtallizes. IR -> SO_2Cl, not SO_2OH.

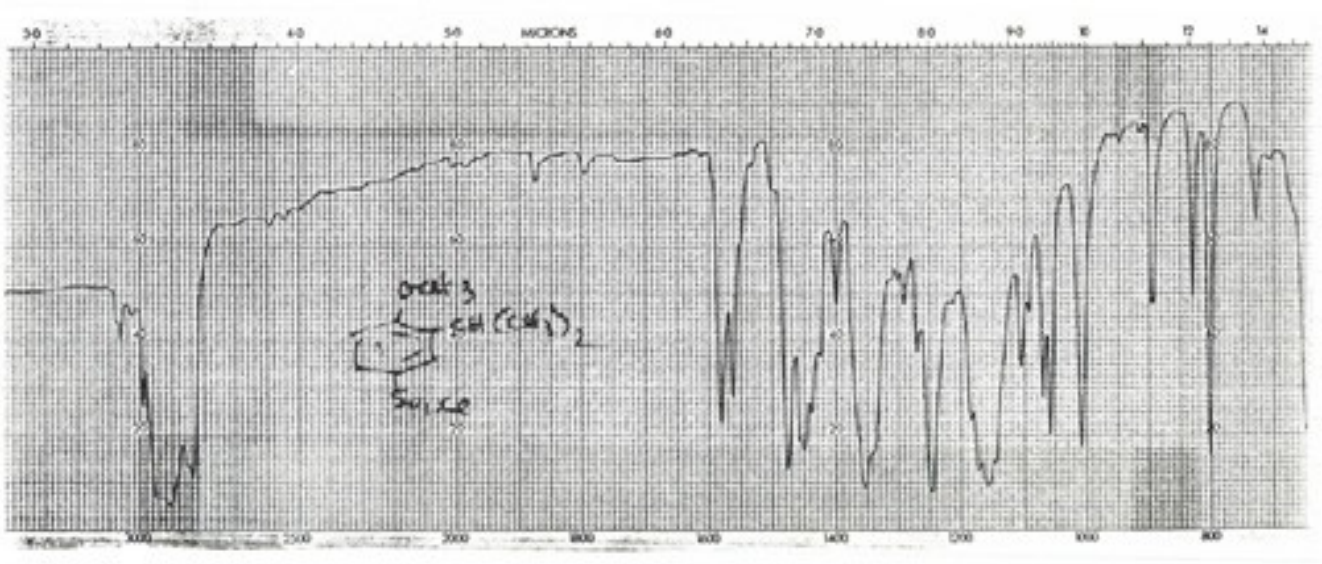
16.63g anisole - good stirring +
27.7g $ClSO_2OH$. very hot. foaming (gas ↑) up to 1/2 way - then quiet - 20 minute stir. Quiet dark- into ice-water slurry. Immediate xtals. filter - wash [with] H_2O. pale pink- 31.10 wet. (from both)

Small amt ex. Hexane -> white xtals [with] hint of pink.
6:32A.

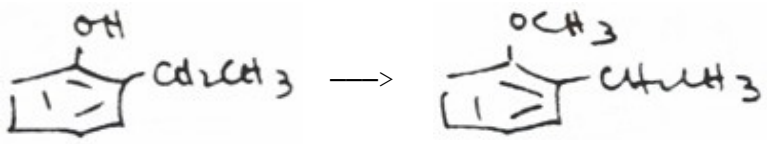
25.23 when air-dry.

to page 35

save a few mg.



12/2/88



16.0g 85% KOH. in
150 ml warm MeOH. add.

24.4g o-Ethyl phenol. - then.
36 g CH_3I - onto SB. - Salts show in 10 min.
reflux. 2 1/2 hrs.
strip on R.E. - into 1 L. H_2O (quite basic).
extract 3 x 75ml CH_2Cl_2

aq.

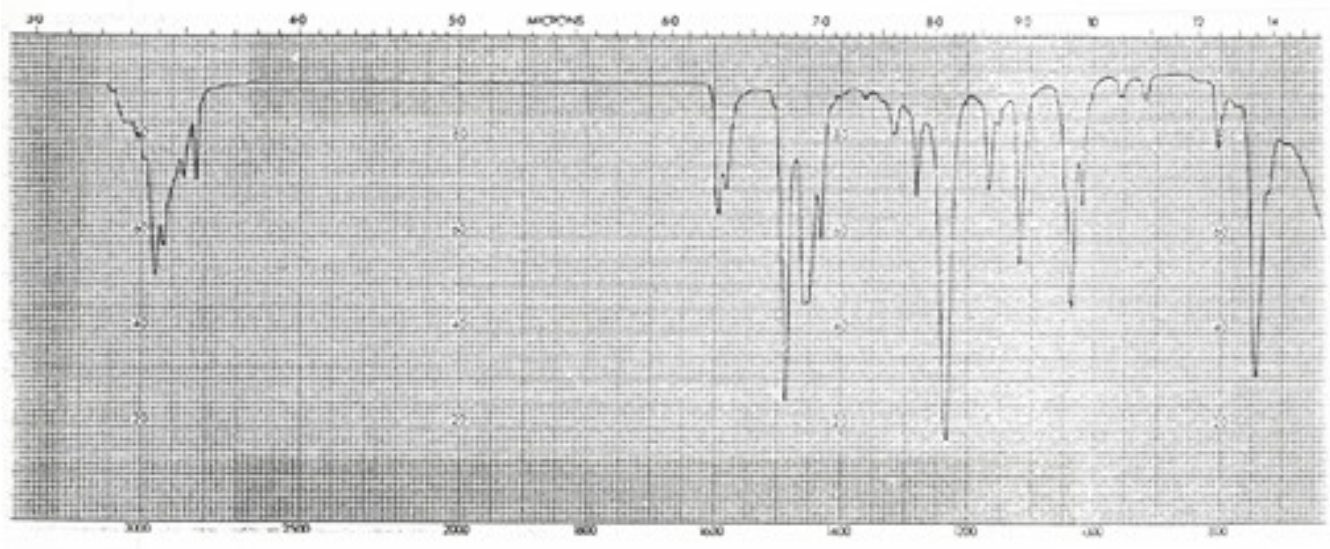
wash [with] 2x50ml
5% NaOH

aq

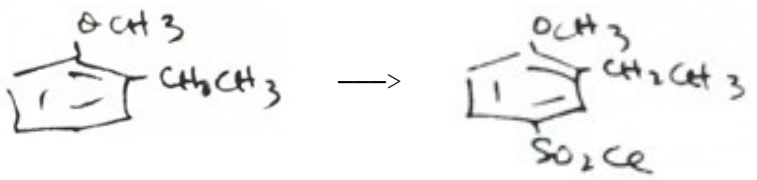
pool - H^+ -> ~~deep~~
cloudy.
xtrt [with] CH_2Cl_2
strip.
8.56g
dark oil
onto shelf.
8.10g.
decanted

flash CH_2Cl_2
-> 13.33g fluid
deep amber liquid

IR below. onto SO_2Cl



12/9/88



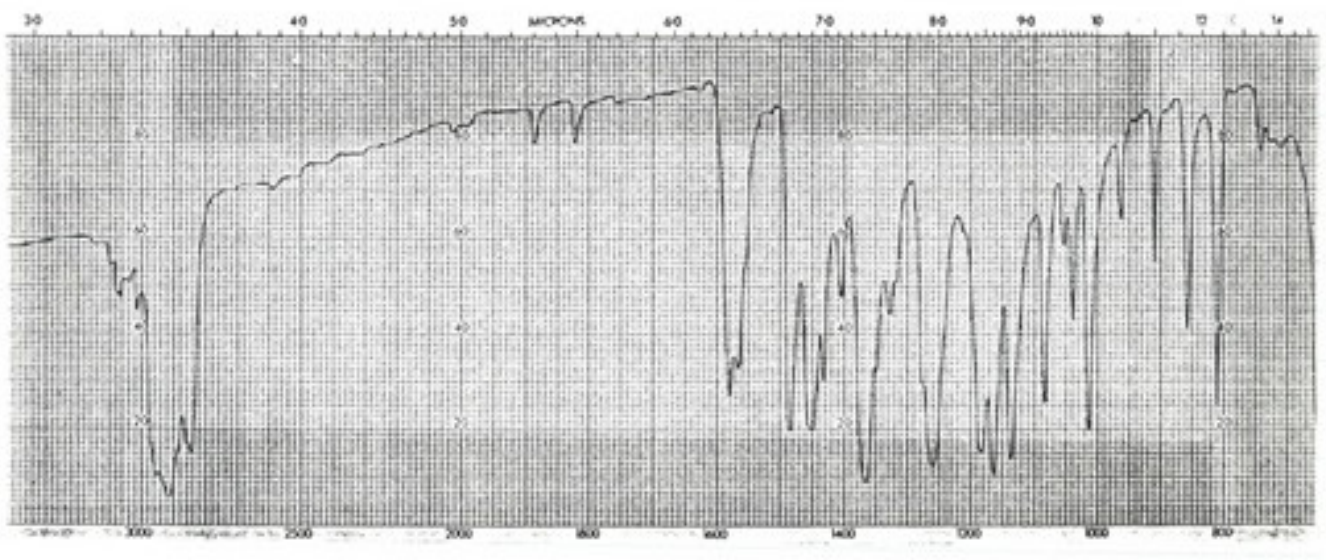
13.3 g crude amber oil. add, dropwise with good stirring:

24.5 g $ClSO_2OH$.

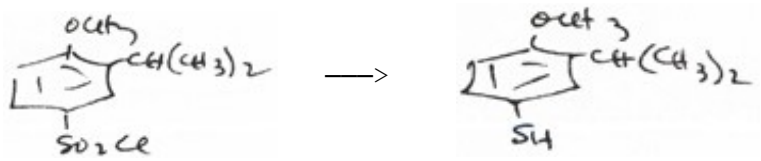
quite exothermic - not as much foaming as [with] isopropyl. . let stand ~1/2 hr. into 200 ml wet ice ⟶ lavender solids. Rextal a bit ex hexane -> IR of $ArSo_2Cl$.

19.6 g wet.

17.37 g air dry to constant wet. slate colored.



12/9/88

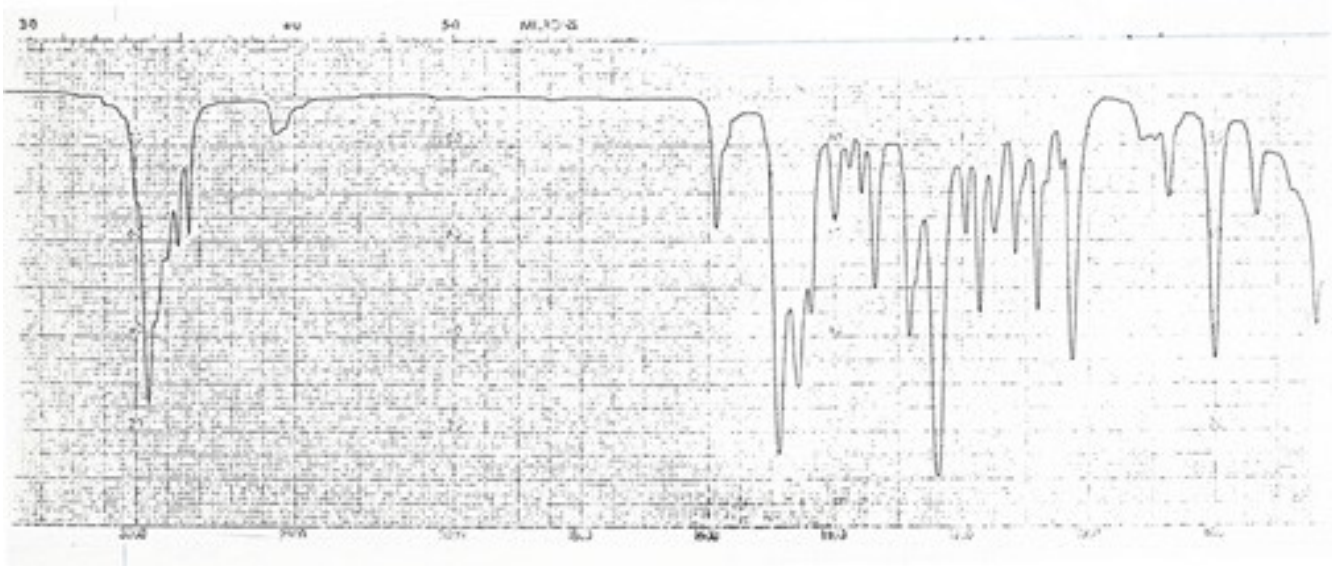


2.0g Scale.
2.0g dried SO_2Cl. page 32 - into 20 ml 6 N HCl. Δ to S.B.
add
2.1g Zn. good H_2↑. - let go a while - then [with] good stirring
2.2g Zn more. let stir 10 min - into H_2O , CH_2Cl_2 (Rx!)
separate from Zn. save over week as 2 phase 6:35
separate- ~~wash~~ xtrt aq . [with] 50 ml CH_2Cl_2 - pool.
wash CH_2Cl_2 [with] H_2O. flash → 2.20 wet pale yellow liquid .rather wet.

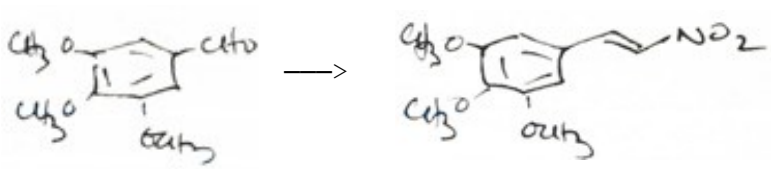
2.20 wet pale yellow oil.

23.28g (rest of the) dried SO_2Cl. in 200ml 6N HCl. Δ on SB.
add 50g Zn to the hot, stirred suspension.

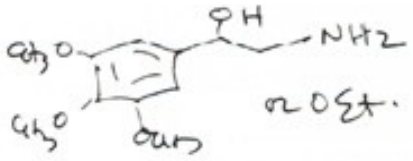
Oil generated, goes to top - 1/2 way through quite green, then lighter & lighter. Almost colorless at the end. Stir back to RT. (~ 20 min). filter through paper - wash quickly [with] CH_2Cl_2 - ML's in funnel flask to sep. funnel - separate CH_2Cl_2 - xtrt (gently . slow separation) [with] 2 x 75 more CH_2Cl_2 - pool, flash → 10.32g ~~white~~ oil. pale amber. looks quite dry.



12/11/88 Explore yield, purity.



(1) Explore various ways of making NS's . eventual
72 g ArCHO into
250 ml so-so CH_3NO_2 , add
7.1 g NHaOAC. onto SB 3:00PM.



TLC.	[:20] - slow - some low stuff.	pale yellow
	[1:00] - more - more low stuff.	yellow
	[3:00] 75% done - static low stuff	red-orange
	[6:00] done - static low stuff.	dark red.

Onto R.E. -> heavy black oil - add 150 ml hot EtOH. let stand ON

ML

filter solids → wash lightly [with] EtOH, air dry. not too good looking.

evap RE -> black oil that sets solid.

air dry -> 49.36 g, (6:36A)

41.79 g (6:36B)

dissolve in small amt. of some solvent (acetone?)- filter. strip -> 44.78g of good looking yellow solids.

Recrystallize from ~ 120 ml boiling MeOH
12/20/88 -> 34.77 g yellow xtals. (6:36M)

ML's evap -> dull off-white Solids

(2) 36 g ArCHO OUT
125ml new, excellent CH_3NO_2
1 ml $(CH_3)_2CH_2CH_2NH_2$ - onto SB. 4:36PM

TLC [:35] (5:10) 1/2-1/2 (deep orange)
[1:10] off - strip (dull brown & turbid)

Add 125 ml hot MeOH - let stand ON -> partly xtals.
filter (slow even through course) -> wet cake wash lightly [with] MeOH let air dry (2-3 days)

ML-+H_2O-let stand,

17.15 so so xtals

dissolve in 4x acetone - (spin) cloudy super, + 4x again acetone, filter [with] filterade -> red oil.
underwent - evaporate.

[Editor's Note: The preceding 3 lines originally continued on the next page but have been moved here for clarity]

Properties of 

See
5:272
5:274
5:192
2:153

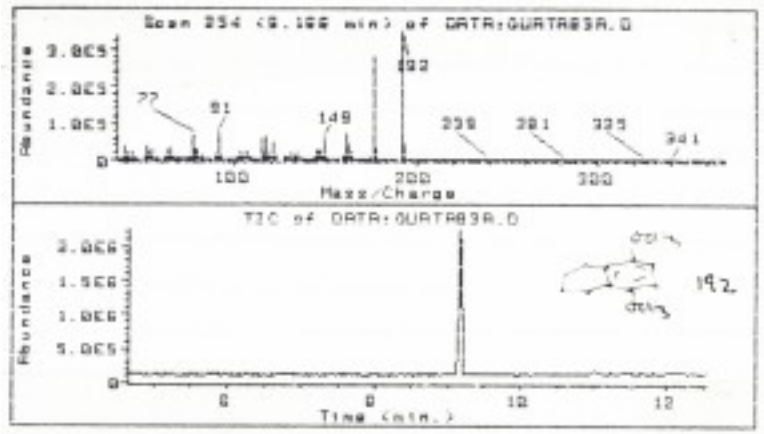
(mp. 38-39)

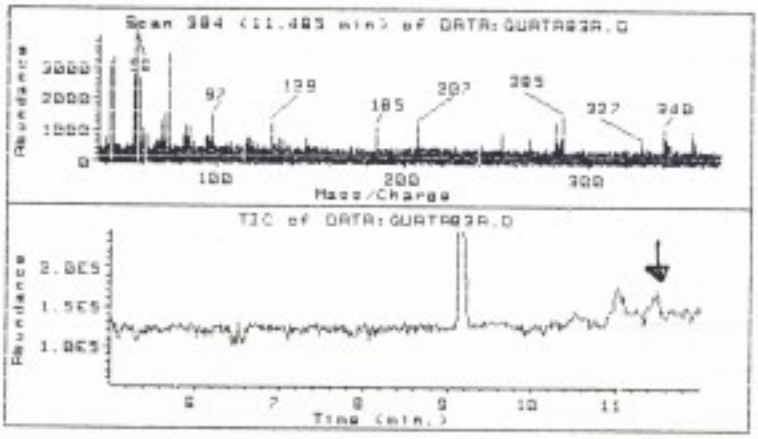
remelt-
12/17/88-
SLOW
44-45°

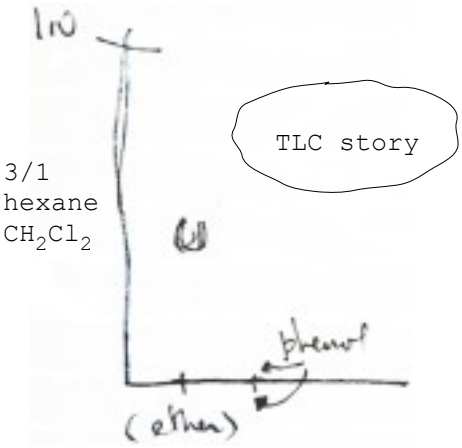
ref.
sample.

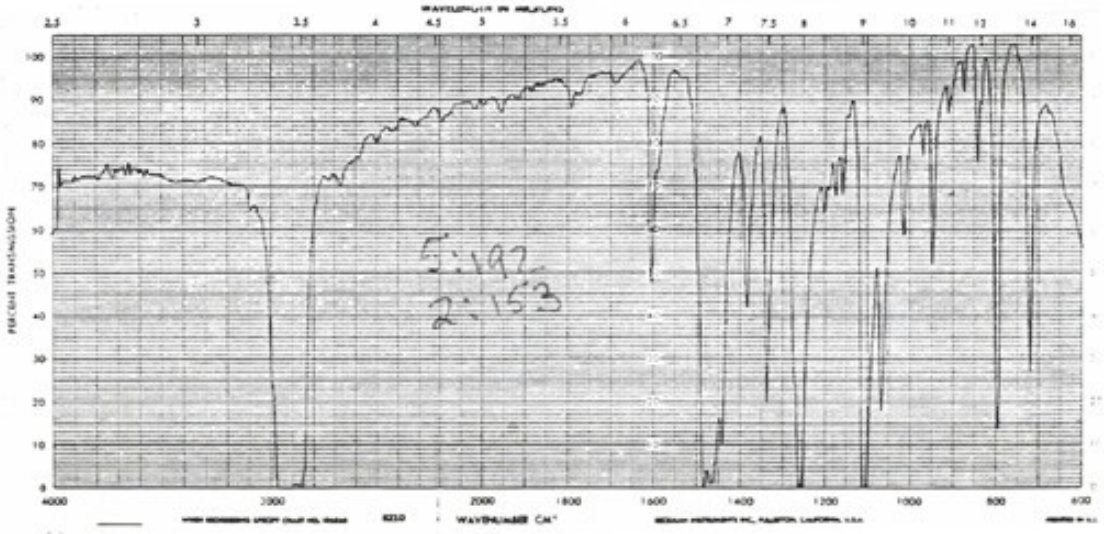
GCMS 5% phenylmethyl silicone.
12 meter.
TProgram S-350
70° -> 230°

20°/min.

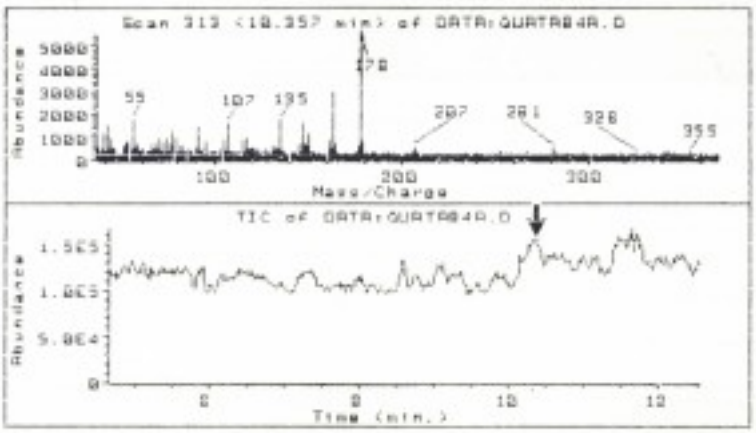


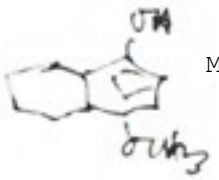






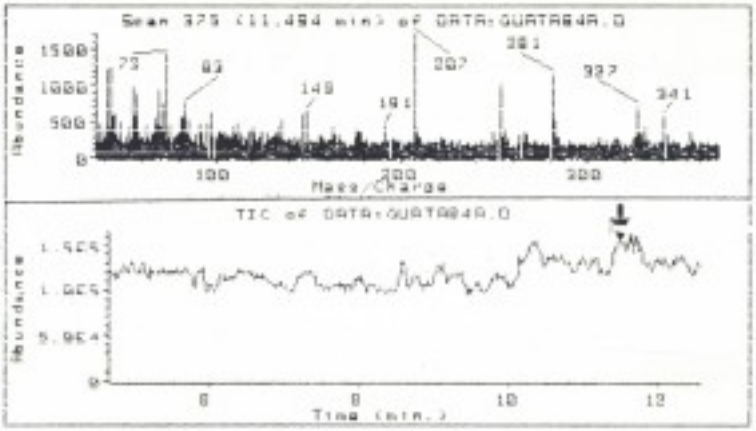
Properties of

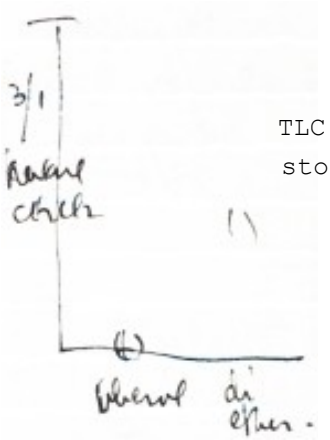




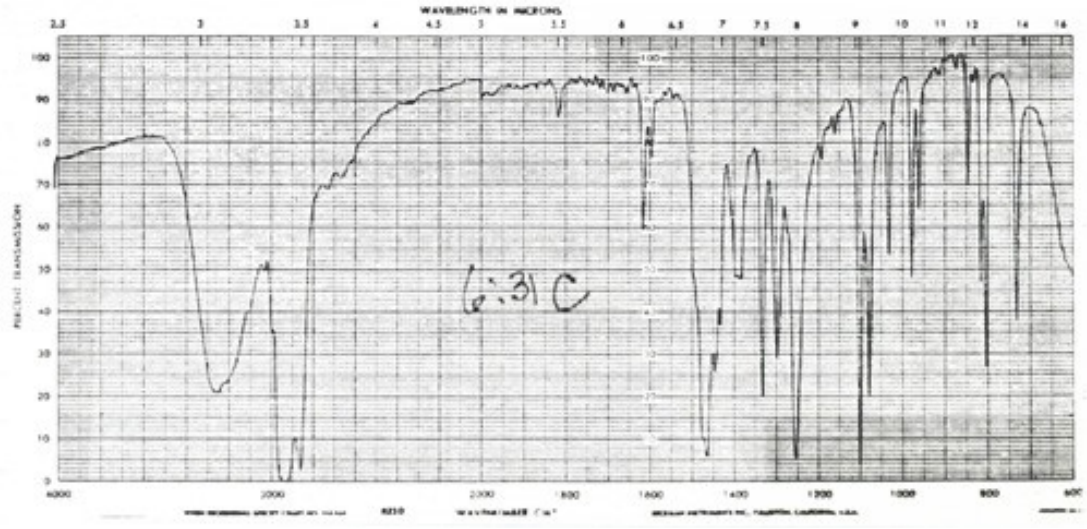
MW
178

6:28
mp 115-116°

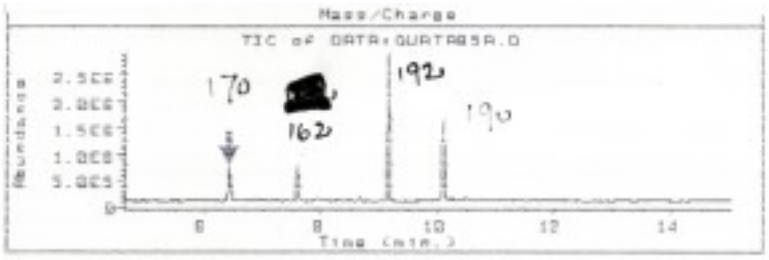


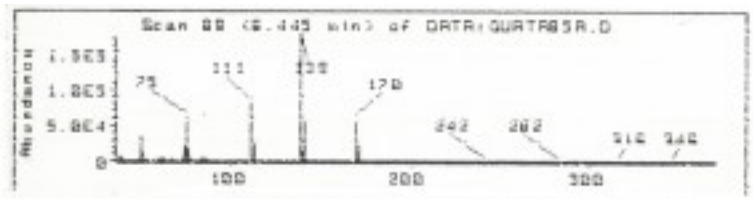


TLC
story

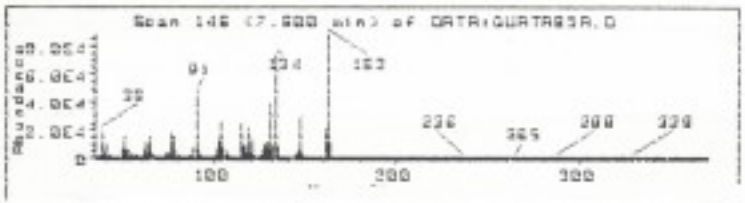


Properties of ML. 8.28g.

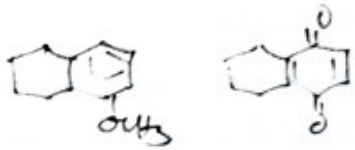


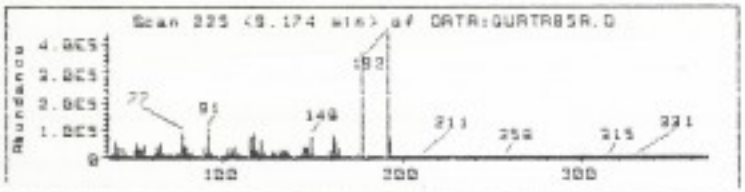


170

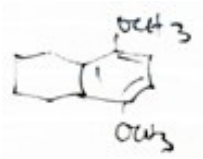


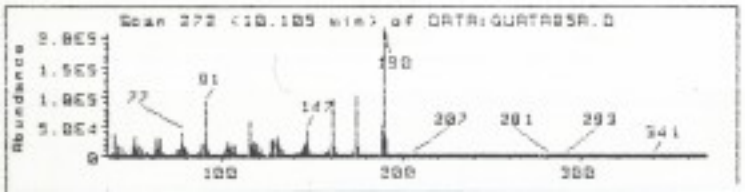
162



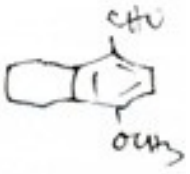


192

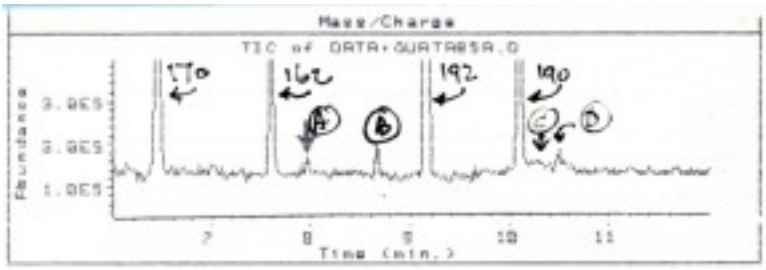


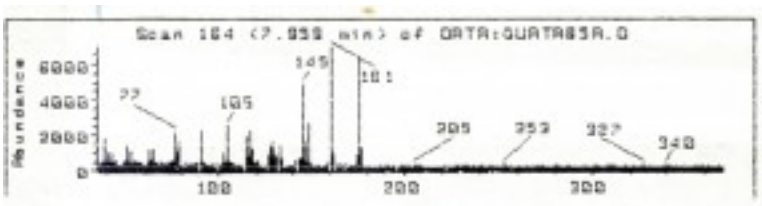


190

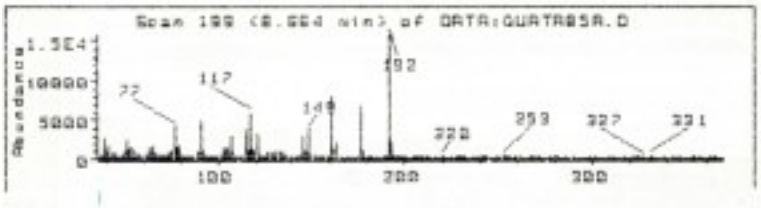


small stuff- see next page.


Mass/Charge
TIC of DATA:QUATR85A.D
Abundance
Time (min.)


Scan 164 (7.959 min) of DATA:QUATR85A.D
Abundance

A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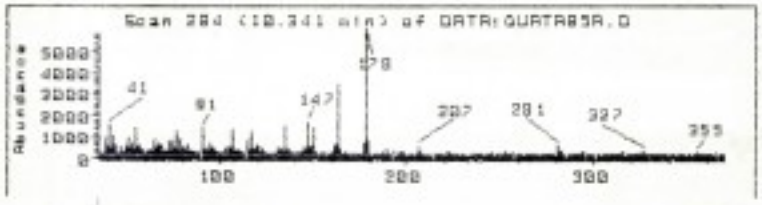
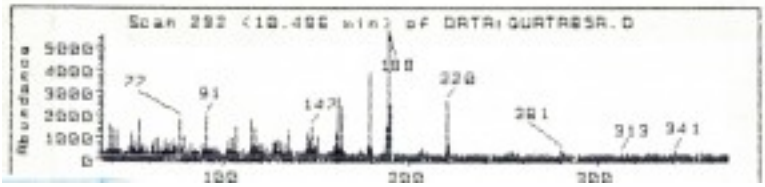
Abundance

192

B


Scan 284 (13.341 min) of DATA:QUATR85A.D
Abundance

"C"


Scan 292 (13.486 min) of DATA:QUATR85A.D
Abundance

"D"

Workup of 8.28g 2C-G-4. ether. 6:31D.

GCMS spectra - 6:39->6:40.

8.28g. ML's from xtalline phenol
up to
25ml Hexane. [with] (17ml Hexane)
xtrt [with] 100mg KOH/MeOH solution.

200 ml MeOH + 20g KOH solution, all

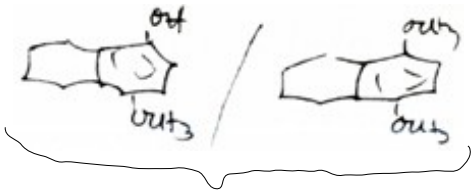
2Φ
org.
+ 100ml KOH
1Φ!
add
aq.
1 phen. flash all ——> ~50ml pale amber oil.
aq. 5ml.
41:A

Jan 1 1989. dissolve. ~150ml H_2O -> very cloudy.

extract [with] 3 x 75ml CH_2Cl_2
CH_2Cl_2
aq.
pale yellow
wash [with] 50 ml 10% KOH
flash. -> 6.54 g brown oil. seed does not take.
aq.
deep orange-red

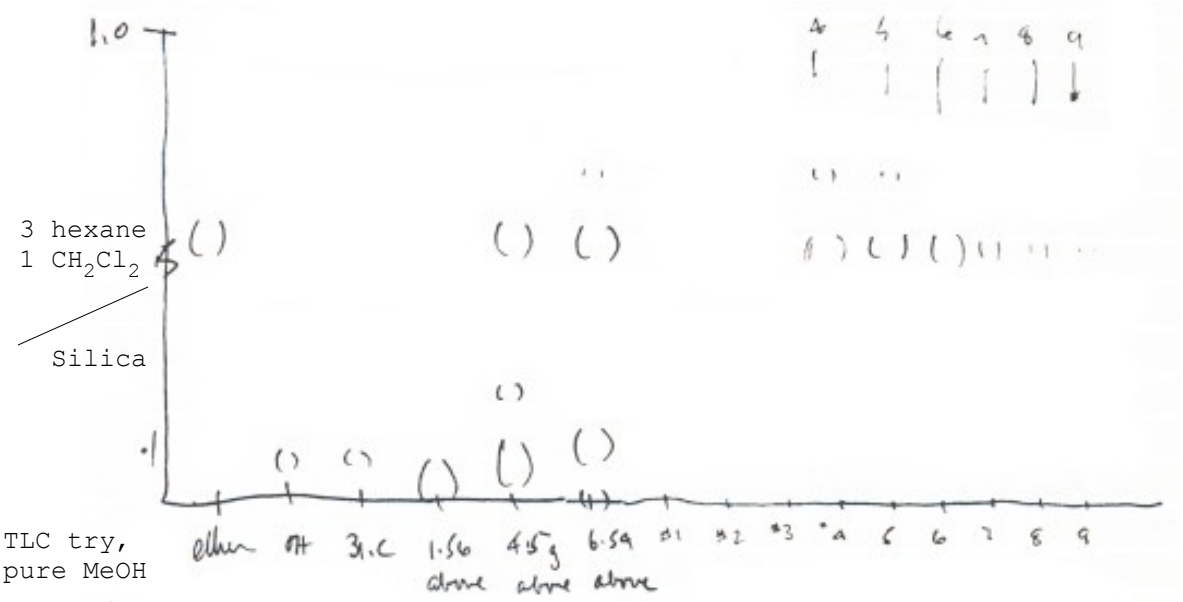
presumably the dimethoxy tetralin 6.54g

add conc. HCl -> red.
xtrt [with] CH_2Cl_2 (50ml x 3)
pool, evap -> 1.56g amber oil. -sets to gummy solids.

Assay of 

Jan 1, 1989.

[page 41](): 6.54 g - ether ex KOH
[page 41](): 1.56 g - recovered phenol.
Page ? : 4.5 g " recovered phenol.



TLC try, pure MeOH

nothing below 0.7Rf.

Dissolve 6.54g above in = vol 3:1 hexane/CH_2Cl_2 - dropwise to ~ 1" column (3" diameter) in course funnel - wash them [with] 3:1 - take 40 ml cuts.

pool cuts 4 through 9. - RE -> almost white oil. 3.86g

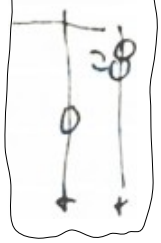
50 MeOH
50CH_2Cl_2
way up there

suspend in 1 ml CO_3 - cold hexane. filter - air dry

-> 2.40g glistening white plates

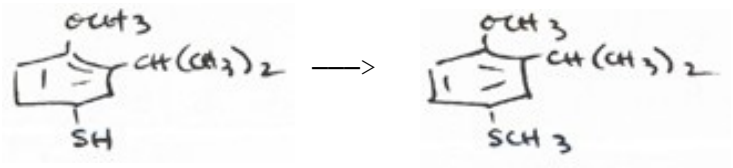
ML <-

pure CH_2Cl_2



[6:31 C](): ML

Jan 6, 1988



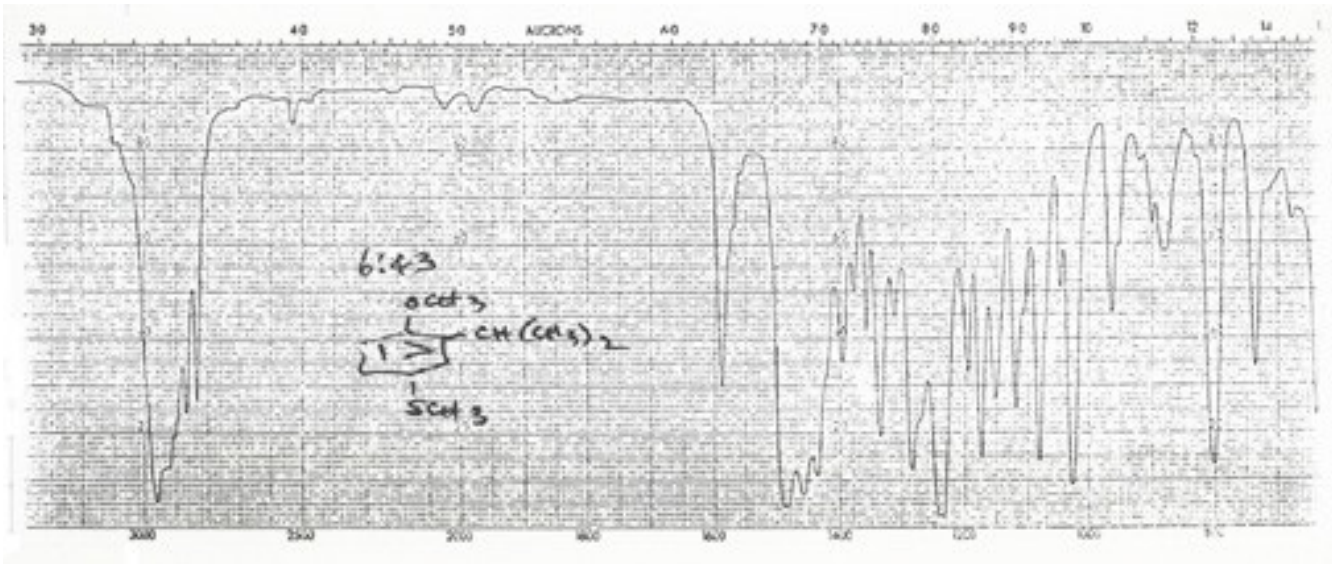
|| page 27

12.5g thiophenol (combine both from 6:35 - save a little bit as reference, and weights are certainly less).

add ~ 20 ml MeOH
add 5.2 ml CH_3I 12.5 g ~20% xs.

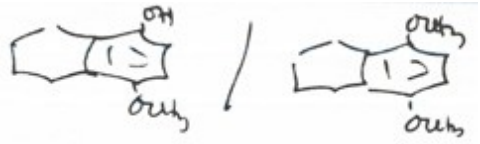
add solu. of { 5.0g KOH 85% / 50 ml MeOH } hot. quite exothermic.
onto SB. 3:40 PM. under reflux.
at [40:] add 2 ml more CH_3I.
at 2 hrs - off - into ~ 300 ml H_2O - is not basic - add 5% NaOH -> strong base xtrt 3 x 50 ml CH_2Cl_2 - pool - wash one time with 5% base. flash
↳ 10.20 g pale yellow oil.

10.20g.



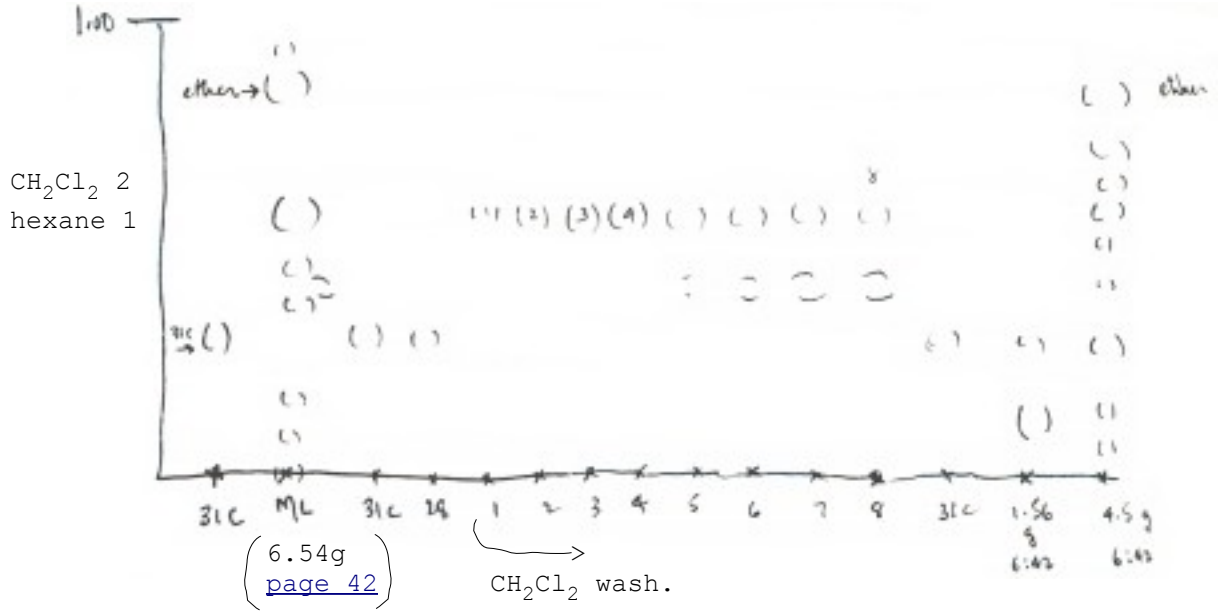
Jan 8, 1989.

continue TLC & other isolations in the



problem.

Set up TLC method.
continue from page 42
good system

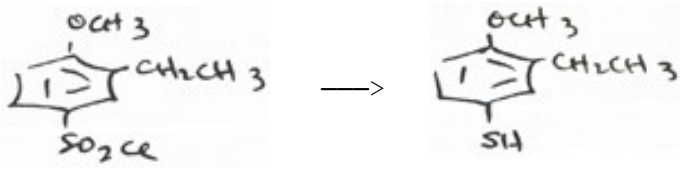


wash silica parted column now [with] 40 ml portions of CH_2Cl_2

cuts 1,2,3,4,5 ⟶ 12345 - pool -
take to dryness -> solids.

cuts 6,7,8 ⟶ 678 ⟶ pool
take to dryness -> solids.

Jan 13, 1988



17.37 g of the slate - grey acid chloride 6:34. add to

200 ml 6N HCl. Δ on S.B. add.

50 g powdered Zn a gram or 2 at a time - over 20 mins
Δ S.B. for ~ 2 hr. (Zn down, deep amber oil up).
filter (paper) wash [with] H_2O -> aq.

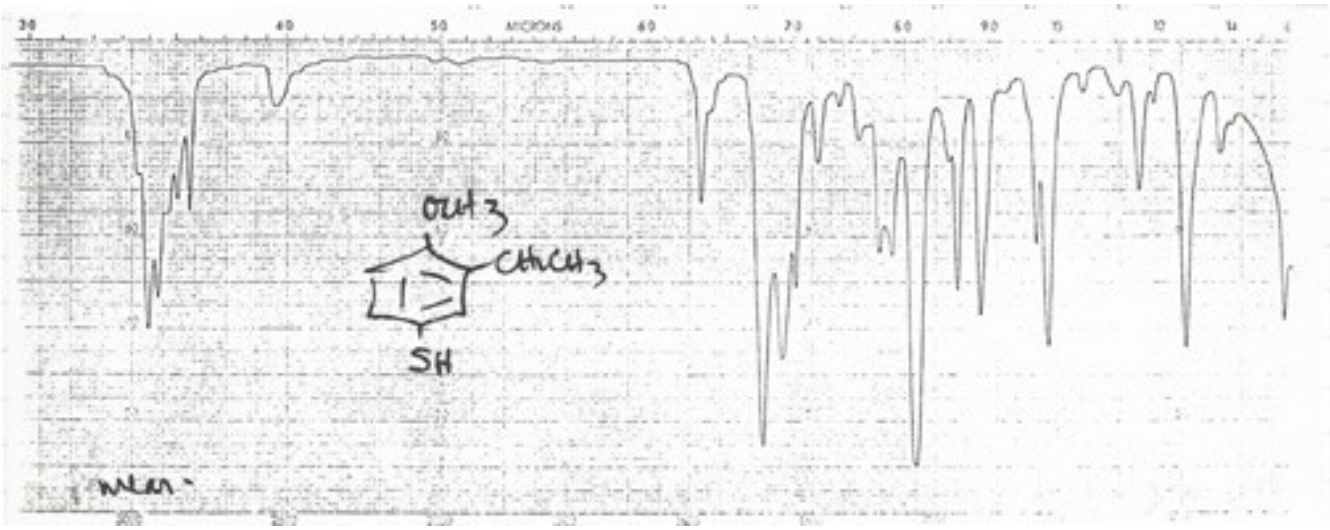
wash Zn
[with] MeOH

yellow sol.
evp -> 2.77g -> Combine
xtrt [with] CH_2Cl_2

flash
6.61g deep
brown

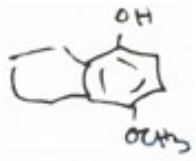
KR @. 0.6mm/Hg.
70-85° -> water - white oil.

5.91 in ist trap.
0.16 in 2nd trap

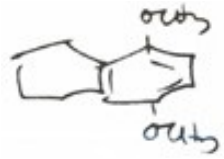


Separation of

Jan 16/89

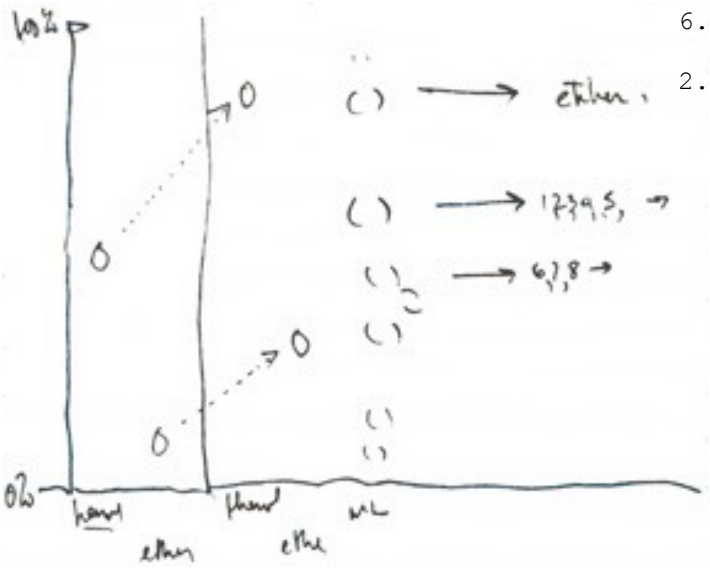


and



phenol ether

page 42 page 44
3/1 hexane 2/1 hexane
CH_2Cl_2 CH_2Cl_2



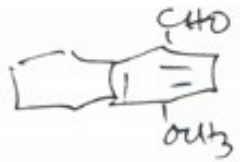
6.54g page 42 on column.

2.40g +ml. = oil, a trace solid.

Isolation of 1-5 - pool fractions, flash -> yellow solids
1.12g. - rextallize from 4x volume of hexane
↳ 0.70g pale yellow xtals. (6:46)

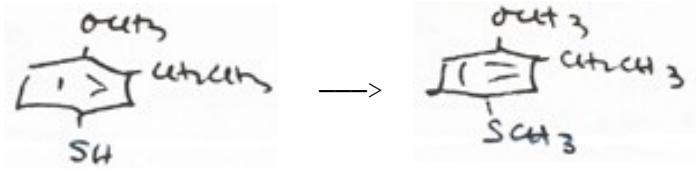
Isolation of 6->8 - pool fractions, flash -> .30g bright yellow xtals. rextal 0.8ml -> 0.16 g yellow xtals - IR ≡ to 1-5.

See pages 58-59 for GCMS,
very possibly



small amt 6:31C
into Ac_2O+pyridine
Δ [with] flame -∇
↳ white solids.
onto p.plate · to M-S.
6:46A.

Jan. 27, 1989.

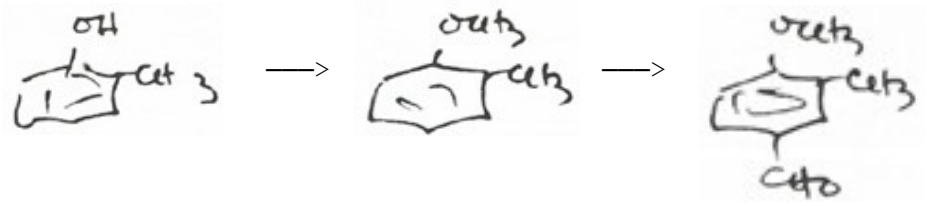


To a solution of
3.6 g (3.49 = 50% xs) in ~ 40 ml MeOH. Δ to dissolve
∇ to go on:

mw 168 = 35.1mM.

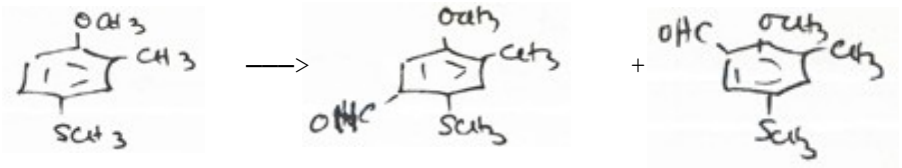
add
5.91 g anisole 6:45 , then
3.3 ml CH_3I (7.5g = 50% xs)
onto SB 3:30 PM.

Fed. 3 1989.



|| page 30

17.15 g KOH 85% into ~ 150 ml hot methanol
+ 23.15 g puriss . o-cresol which is deep brown!
add.
39.7g CH_3I - onto SB. 2:05PM. 5:05 off - strip-
into H_2O

2/3/89 

A solution of 4.83 g ether 6:27 in ~ 50 ml CH_2Cl_2
∇ [with] stirring to 0°
add.

6.8 ml (15g) (2 fold) $SnCl_4$. dropwise . · Immediate dark brown color [with] each drop, that despells to light yellow. All gold-colored at end of addition. add (still at 0°)

2.61 ml (3.31 g) Cl_2CHOCH_3 dropwise. Color progresses from gold to dark, and finally deep rich purple. to RT · - finally to warm water bath. - thence on to steam bath. 5:15 PM quite (most) of CH_2Cl_2 gone in 1/2 hr. ∇ - (some solids coming out of needle vent) - into water. a very ugly mess - deep red oil -> orange solid that don't dissolve in either H_2O OR CH_2Cl_2. let stand.

2/12/89.

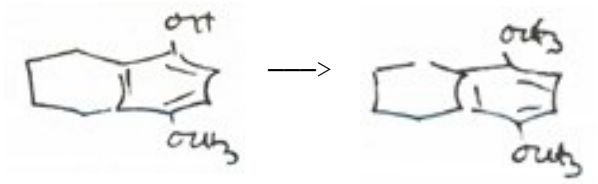
Add much more CH_2Cl_2 - separate (lots of solids not soluble in either solvent). xtrt aq. [with] 3 x 50 ml CH_2Cl_2 pool - filter through paper -> clear CH_2Cl_2 (deep yellow) and some aq. - remove mechanically.

2.32g. ex R.E. 100-130 0.8mm.

Strip on R.E. -> 2.32 dark heavy oil. 2.32g to KR -> 100-130°/0.8mm -> pale yellow-orange distillate that partially crystallizes.

Press on p.plate -> excellent yellow xtals. 0.44g.

Feb 5, 1989 Repeated, for 30th time!



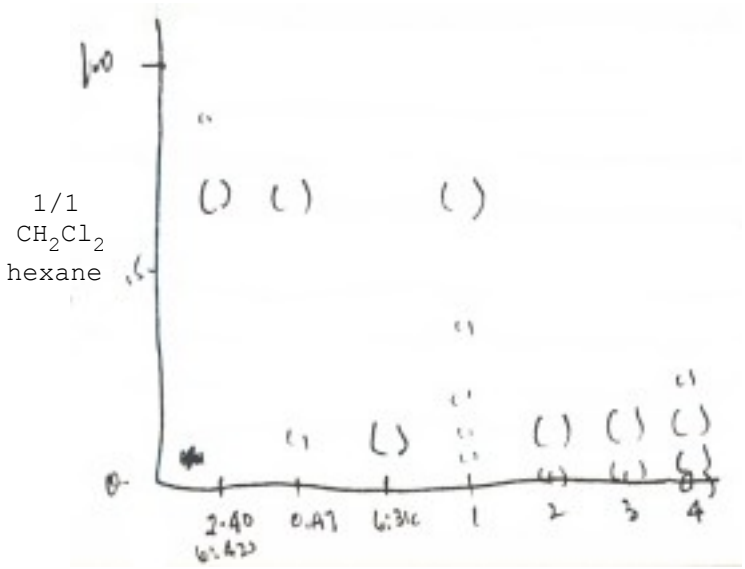
7.96 g phenol (6.26 6:31C and all of 5.277 (1.70g))
into
35 g MeOH. - dissolve [with] a little warmth.
add
4.2g KOH 85% in ~ 40ml hot MeOH, 50% xs
then
4.0ml (9.0g) CH_3I · 50% xs.
onto steam bath. 6:30PM.
off steam bath ~ 11PM -> 4 1/2 hrs.
(basic)
Strip on R.E. - into 150 ml H_2O. add
150 ml 5% base -> > 2 1/2% base.
xtrt 3 x 75ml hexane
-> A 1.76g - sets to xtal. ->
(LARGELY DIETHER)

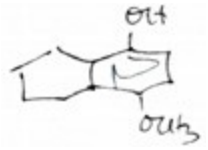
xtrt 2 x 75ml CH_2Cl_2
-> B 0.94g -> immediate white solid
(LARGELY PHENOL)

make H^+ -> ppt.
stand, filter -> C 8.33g wet xtals ->
(PHENOL + polar)

xtrt ML's [with] 3 x 75ml
CH_2Cl_2 -> D. trace gummy goo.

COMPLEX-
(PHENOL)
(no diether)
70mg OUT



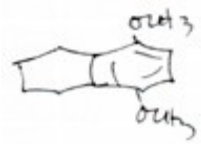


"A"
5.10g "B" 6.04g combined.
0.94g

flash over [with] KR - propane torch
at ~ 0.5mm
↳ 4.86g phenol.

——————> rextallize from 1.8 ml hexane, ∇ CO_2 —> xtals -
onto p.plate. —> 1.34 pale amber xtals. diether. (6:51A)
wash beater [with] cold hexane -> + 0.05 -> 1.39. combine.

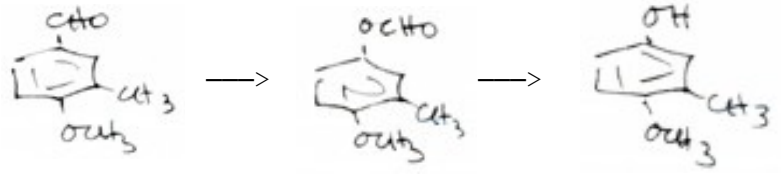
——————> dry 5.10g.



1.34g 6:51A
2.40g 6:42 4.12g combined -
0.47g 5:281 distill

distil 105-115°/0.3mg Hg.
4.10g sl. pink
xtals.

(6:51)

Feb 12, 1989 

10 g aldrich 3-methyl-p-anisaldehyde, into
50 ml CH_2Cl_2 - add
23 g 50-60% meta-chloroperoxybenzoic acid.
CHL
clear, endothermic solution. - onto S.B. and
in ~ 1 hr -> bright yellow sol & white solids
everywhere. Stay at reflux ~ 3 hrs. off.

Let stand 1 week - heavy whitish curdy
xtals in deep yellow solution. filter - wash
[with] CH_2Cl_2 -> white solids.

|| 6:28

OUT.

6.26g.

ML's -

extract [with] 3 x 50ml sat.
$NaHCO_3$ (extremely dark-
final extrt light amber)

organic.

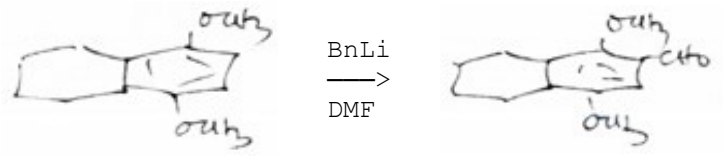
deep brown <

solu. H^+ ->
yellow solids.
OUT

CH_2Cl_2 -> R.E. to
9.98g deep amber residue
dissolve in 50 ml MeOH, add
20 ml ~25% base. - cook
on steam bath for 1 hr. - strip on
R.E -> residues - into ~~CH_2Cl_2~~ 800ml H_2O - very
strongly basic. xtrt [with] 3 x 25 ml CH_2Cl_2-
trivial color removal - @ [with] conc. HCl. xtrt [with]
3 x 75 ml CH_2Cl_2 - flash ⟶ 7.46 g residue -
KR @ 0.7mm - 95-120° ⟶ pale amber oil -
6.98 g - to Larry Wier.

Feb. 19, 1989

Attempt:



4.10 g . ether (6:51) 21 mM (21.3 mM). in RB 3 neck,
|| MB add.
5:57 40 ml ether (diethyl.) - add.
$SeCH_3$ 3.2 mL TMEDA. - cool to - 80° [with] good stirring under He.
crystals of ether come out of solution. add
8.5 ml 2.5 M BuLi in hexane. - allow to come up
to RT. ——> slow but eventual dissolving. At
RT. add.

3 ml DMF. some exotherm. no appreciable change.
~~left~~ let stir for ~ 2 hrs. - into ~ 300 ml dil.
H_2SO_4 - ~~extr~~ separate ether, extract [with] 2 x 50 ml
CH_2Cl_2. - flash —> 5.01 wet & almost colorless oil.

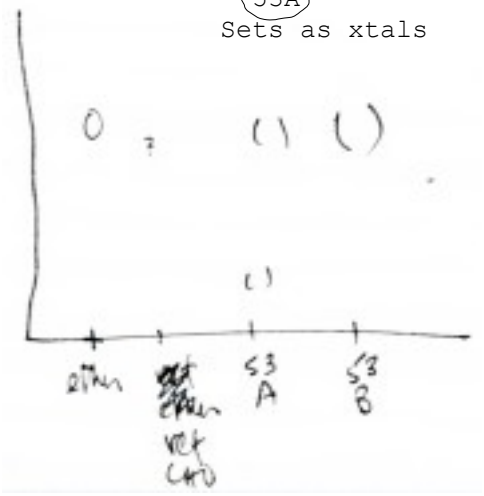
to KR.
0.25mm. ——> 3.69g white oil. 0.25mm/Hg 100-115° C.

53A

100-115° TLC Sets as xtals press a little on plate - +MeOH

53B

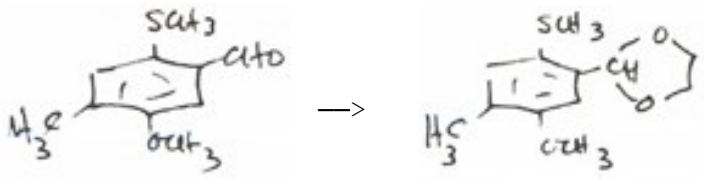
1 CH_2Cl_2
2 hexane



All recovered stuff in starting ether. (by IR). try the Cl_2CHOCH_3 method. page 6:55

(oil [with] xtal)
onto
(plate.)

Attempt.
Feb 24, 1989.



parallel to 0.44 g 6:49- in 40 ml ΦH add.
0.21 (.14 theo) glycol - and
~1 mg TSOH hydrate.
reflux in D.S. at ~ 3 PM.
off ~ 6PM. Stand 1 week.

March 3, 1989
strip ΦH -> sl. cloudy oil, most of yellow color gone. Into ~ 150 ml ether - wash [with] 5% KOH - evap -> cloudy white oil.

KR 0.2mm 110-130°
-> 0.46 g white oil. (6:54A)

0.46 g.

4 g RaNi Ventron into
50 ml 5% KOH
+ 0.45 g Acetal in 10 ml EtOH.

exotherm, H_2↑.

1/2 hr. xtrt [with] CH_2Cl_2
wash dil NaOH, H_2O

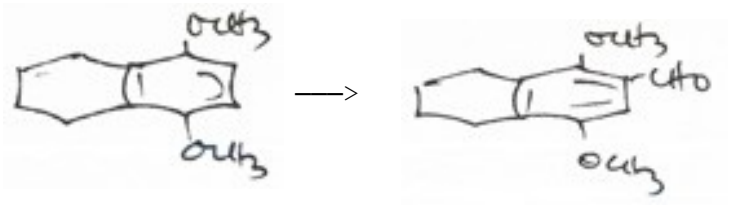
flash -> white oil.
≡ IR, save trace as (6:54B)

7.8g RaNi into
40 ml 25% NaOH. !

foam-
vigor -

+ recovered acetal in EtOH.
once quiet - onto S.B. 1 hr.
off - cool.

Feb 26, 1989.

Attempt: 

See page 53 for BuLi

3.69 g recovered ether (page 53) which has a little carbonyl unit - by IR. - into
35 ml CH_2Cl_2 - dissolve, cool to 0° [with] ice, under He.
add. dropwise - or a least squirt wise

See page 49 for example

4.5 ml anh. $SnCl_4$.^ Some color development - which quickly fades to residual yellow. homogeneous solution. add as slowly as a leaky syringe will let me -
1.73 ml Cl_2CHOCH_3 - probably used 2 ml.

Immediate dark, bubbly - looks terrible - stir 0° a while - then to RT. then to light reflux [with] steady stream of HCl ↑ into ~~lab~~ lab.

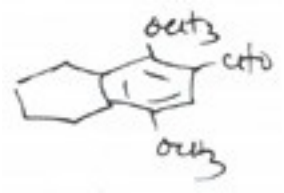
Into 200ml H_2O - separate CH_2Cl_2 - xtrt aq [with] CH_2Cl_2 - ~~whash~~ wash pooled CH_2Cl_2 [with] 3 x 50 ml 5% NaOH (yellow aq, H^+ -> loss of color but no cloudy, OUT) flash CH_2Cl_2 - KR -> white oil over 0.3mm, at ~130° (say 120-140°). no xtals. MS perfect - see page 56-57.

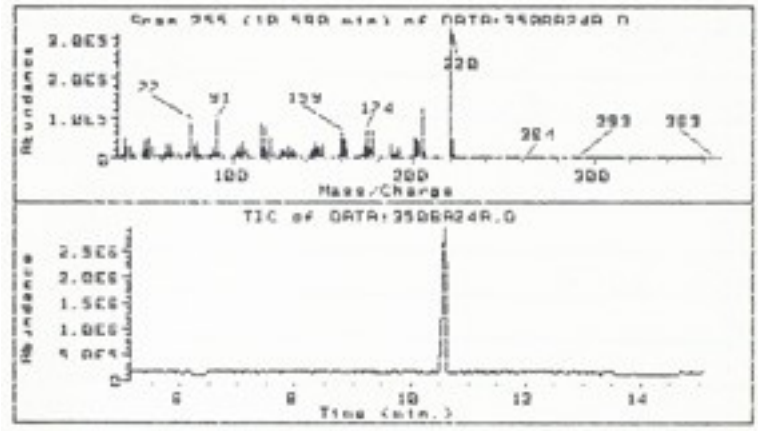
Spontaneously xtallizes in receiver. 3.19 g almost white xtals

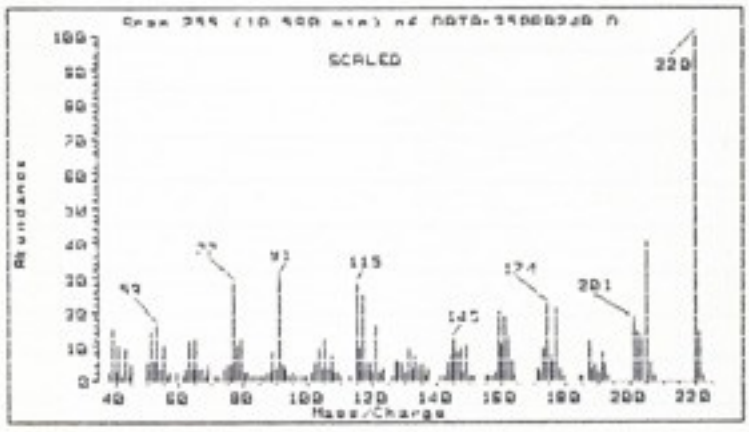
mp- as is - sulfate -> suit 67-	mp 70-72	to NS's-
mp- ex MeOH (wasteful) suit 67	mp 73-74	6:60
mp- ex hexane	mp 74-75°.	6:61

0.18 g total left-over-

recrystallize from 1 ml hexane
↳ 0.12 g fine white xtals into reference


OEt3
OEt3

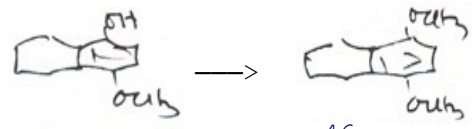

Abundance
Mass/Charge
TIC of DATA:
Abundance
Time (min.)


SCALED
Abundance
Mass/Charge

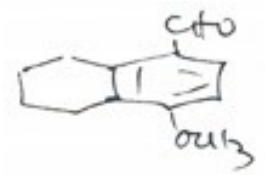
Scan 255 (10.590 min) of DATA:350BA24A.D
KRed GANESHA-4 ALDEHYDE EX DICHLOROMETHYL METHYL ETHER

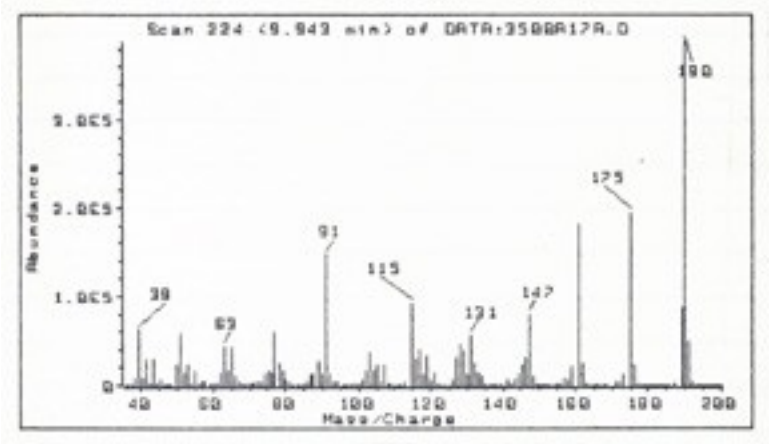
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
38.10	2	79.10	12	118.05	5	159.10	20
39.10	15	80.10	2	119.05	5	160.10	10
40.10	2	81.10	2	120.05	2	161.10	18
41.10	10	82.00	1	121.05	16	162.10	13
42.10	1	83.10	1	122.05	2	163.10	6
43.10	9	85.00	1	123.05	3	164.10	1
44.10	1	86.10	1	126.05	1	171.05	3
45.10	4	87.00	2	127.05	6	172.05	2
50.05	5	88.10	2	128.05	6	173.05	9
51.05	14	89.10	8	129.15	5	174.05	22
52.05	6	90.10	3	130.15	2	175.05	7
53.05	16	91.10	30	131.15	9	176.05	6
54.05	3	92.10	4	132.15	3	177.05	21
55.05	10	93.10	3	133.05	7	178.05	3
56.05	1	94.10	1	134.15	4	179.05	1
57.05	2	95.10	2	135.15	4	184.15	1
59.05	2	96.10	1	136.15	1	185.05	1
61.15	1	98.10	1	137.10	3	187.05	11
62.05	3	99.10	1	141.10	1	188.05	3
63.05	11	101.10	2	142.10	1	189.05	4
64.05	3	102.10	5	143.10	5	190.05	2
65.05	12	103.10	9	144.10	7	191.15	8
66.05	3	104.10	3	145.10	12	192.05	4
67.05	3	105.10	12	146.10	8	193.15	1
68.15	1	106.10	3	147.10	9	201.10	17
69.05	4	107.05	7	148.10	2	202.10	14
71.05	1	108.05	2	149.10	10	203.10	13
72.05	1	109.05	2	150.10	1	205.10	40
74.05	3	110.05	1	151.10	1	206.10	5
75.05	4	113.05	1	155.10	1	207.10	1
76.15	4	115.05	28	156.10	1	220.10	100
77.00	28	116.05	9	157.10	1	221.10	14
78.10	10	117.05	25	158.10	2	222.10	1

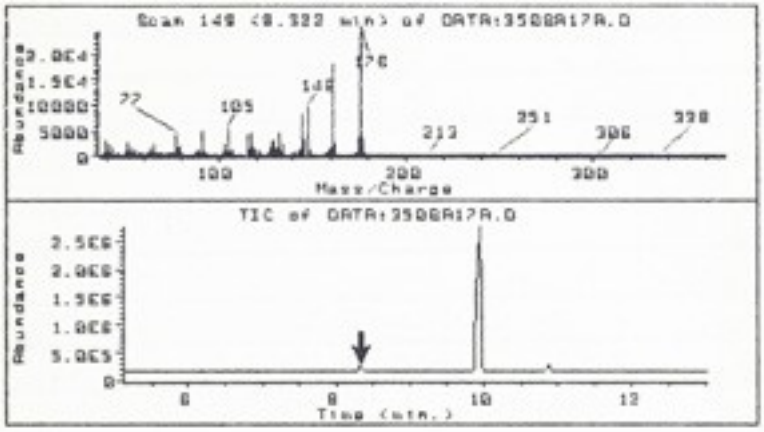
GCMS data on isolated yellow xtals

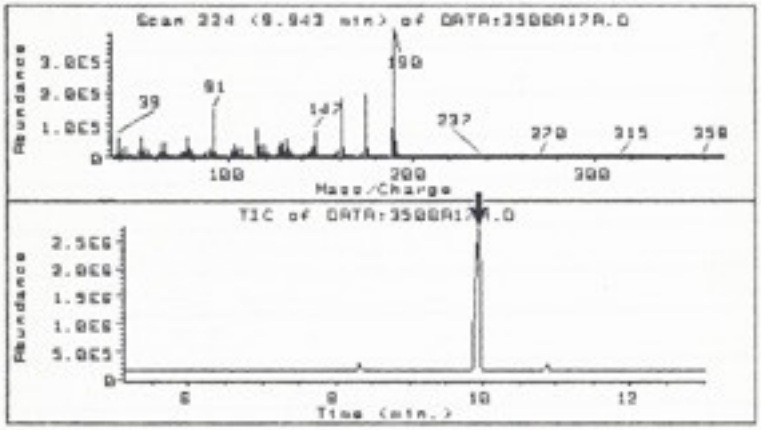
ex 

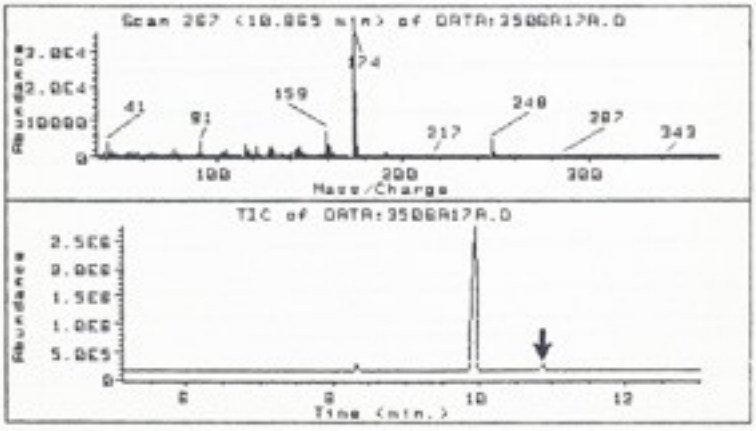
page 46.

possibly  mw. 190

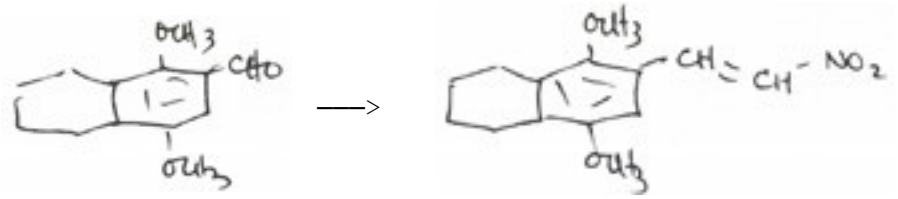



Scan 148 (8.322 min) of DATA:3508R17A.D
Abundance
Mass/Charge
TIC of DATA:3508R17A.D
Abundance
Time (min.)


Scan 334 (9.943 min) of DATA:3508R17A.D
Abundance
Mass/Charge
TIC of DATA:3508R17A.D
Abundance
Time (min.)


Scan 367 (10.865 min) of DATA:3508R17A.D
Abundance
Mass/Charge
TIC of DATA:3508R17A.D
Abundance
Time (min.)

March. 5, 1989



1.5g distilled aldehyde 6:55-
20g NO_2CH_3
.14g NH_4OAc - onto SB 6:15PM.

TLC at 50 minutes (CH_2Cl_2, silica gel) almost all as NS (CHO Rf. 0.70, NS Rf. .95). Strip on RE -> spontaneous xtals —— scrape out - filter

rextal trace from MeOH - excellent. solvent. add to suspend on right side of page

~ 5 ml ML. smell of NO_2CH_3 deep but nice gold color

yellow xtals suspend in ~1 ml MeOH filter again

ML

combine to dryness- onto good vac pump to residue suspend in ~ 1ml MeOH. onto p. plate

yellow xtals 1.67g fine-curdy 6:60A mp 151.5-152.5°

0.14g loose yellow powder

rextal from ~2ml boiling MeOH decant solids

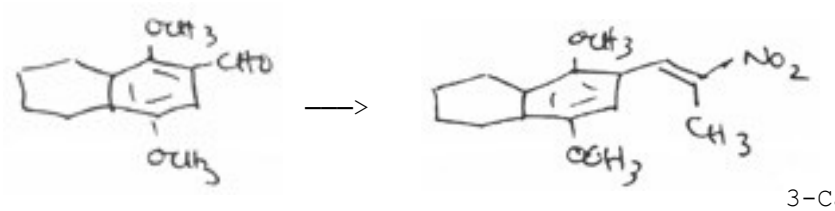
page 70 anal

cool to RT. onto p. plate brilliant yellow xtals 6:60B mp 148-9°

into 1ml boiling hexane, ∇

p. plate trace brilliant yellow xtals 6:60C mp 148-9°

6:60A 1.67
6:60B .06
6:60C .01
1.74 -> remove 0.02 anal neg. 1.65 on to [H]



3-Carbon
G-4.

page.

1.5 g distilled aldehyde 6:55
20 g NO_2 Et
0.13 g NH_4OAc. onto SB. 6:40PM

TLC at 30 min. starting material (this CH_2Cl_2, silica).
again at [2:40] → 1/2 & 1/2. Leave on SB. over night.

AM. off. let stand a week. Strip on R.E. with heat up to ~ 80° ⟶ heavy red oil - spent - xtals - Knock out of flash ⟶ 1.98 g deep - rust-colored solids.

Recrystallize from ~15 ml boiling MeOH

→ 1.33 g dull gold xtals.

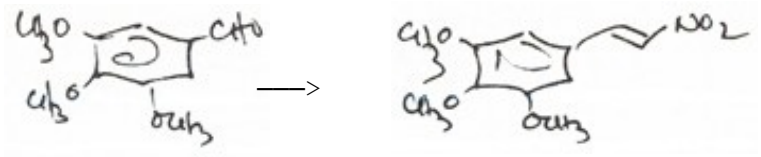
rextal small amt methanol

→ ~ 40mg gold.
mp 94.5- 95-
analytical.

94-94.5°

page 70 ANAL

[Editor's Note: Page 62 is blank]

Try MB's method. 

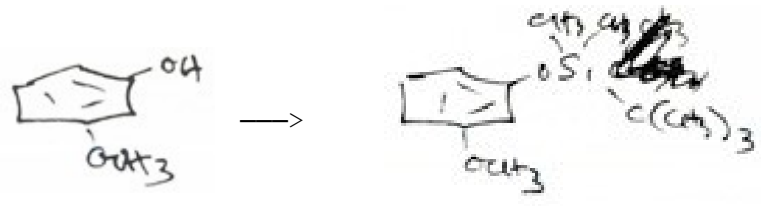
In 100 ml HoAc, add
10 g ArCHO
20 g NO_2Me -> solution add
10 ml cyclohexylamine
Onto SB. - TLC every hour, at 3rd hour, into
125 ml H_2O [with] stirring -> fine yellow xtals - filter
water - wash, air dry -> 7.37g fine looking xtals.
6.32g when looked at.
a few months later.

dissolve in 6.3g CH_3CN hot. clear solu decant -> yellow solu.
∇ -> xtals

was the 2nd crop. 1.77g? dissolve in 1.77g CH_3CN

1.73g. into 1.7g CH_3CN hot. sol. ∇ - xtals filter -

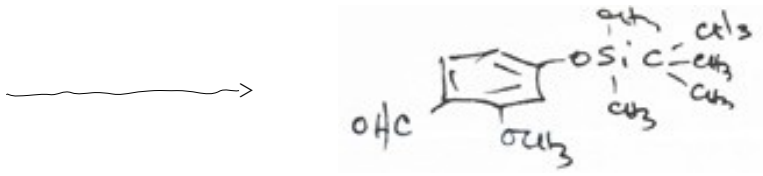
See page 156



|| JMG.395
p 51
2/24/89.

9 g meta-methoxyphenol in
30 ml CH_2Cl_2
8.8 g triethylamine
0.35 g 4-dimethylamino pyridine - then add, a bit at a time
11.5 g tert-Butyl dimethyl silyl chloride.

Stirring continued at ambient T. for 2 hrs.
Strip the CH_2Cl_2 - replace [with] ether - wash [wish] dil HCl. Strip
-> 15.48 g crude oil. spilled some.
distill [with] KR.
75-90° /0.2mm -> 14.66 g white liquid



10 mmol scale.

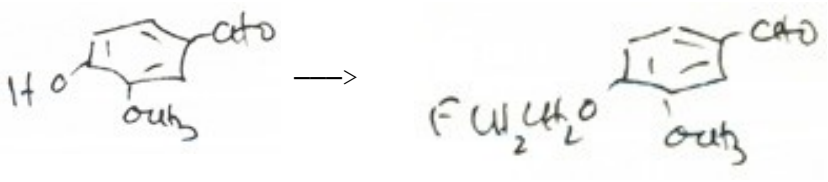
2.38 g silyl ether. in 25 ml anh. THF. stir, under Argon - ∇ to -75° [with] CO_2 acetone. Add.

7.7 ml 1.3 M see BuLi in cyclohexane - generate light color. stir a white- add

1.0 ml DMF (.75~ = theo). Not much sign of Rx. to RT. Stand 3 weeks -> dull brown gelatenaceous liquid.

April 28, 1989

Attempt:



5.1 g 85% KOH pellets- dissolve in 75 ml boiling MeOH
11.6 g vanillin in 25 ml MeOH. add
-> yellowish solution.
add
10.1 g $BrCH_2CH_2I$ in ~ 10 ml MeOH - color pretty much goes - onto reflux. color. slowly returns.

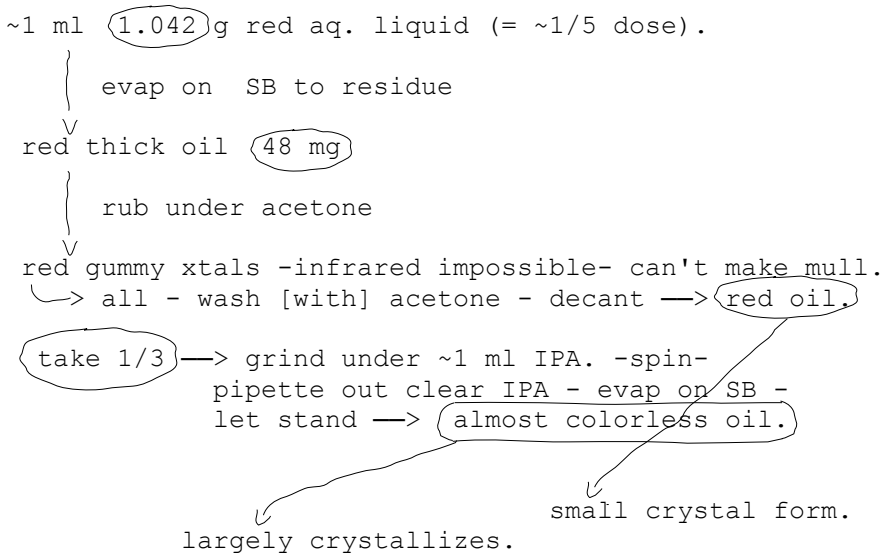
5/5/89 stand a week - strip off solvent. -> white solids [with] various colors. into 400 ml H_2O - basic to green on pH paper.
xtrt 3 x 100 ml CH_2Cl_2 - pool - wash [with] 5% KOH solution - all color goes.
evap CH_2Cl_2 -> scaly solids. ~ 0.6g 0.6g.

0.60 rextal a bit from MeOH

crude. rextal

on to page

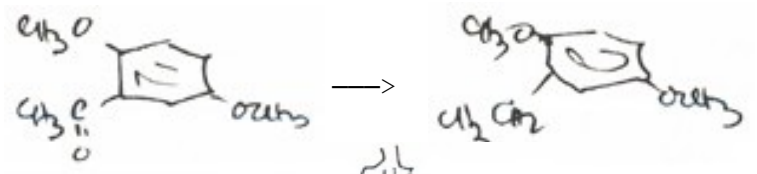
Assay of "MDMA" from Andrew Tilley - the Miami caper !!!



IR = hydrate of MDMA·HCl.

May 3, 1989.

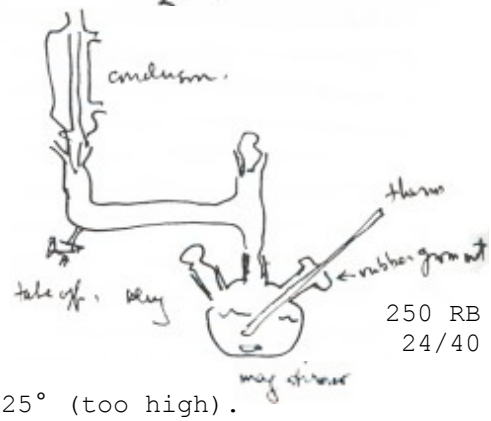
Repeat.



See 6:12

17.2 g KOH (85%)
See 6:73 60 ml triethylene glycol
24.3g dimethoxy-
acetophenone (all)

30 ml 66% hydragine
60 ml triethylene glycol



stir - up to reflux.
take off to bring temp.
~~of~~ up to 210-220°. as high as 225° (too high).

Reflux 1 1/2 hr. - let cool to RT. All into 1 L H_2O, including-the take-off. Xtrt 4 x 100 ml CH_2Cl_2 - pool, flash -> 22.4 g ~~cle~~ fluid deep brown oil

22.4.
May 7,1989 KR [with] water pump (~25" mercury). distills ~100->170° and even then, only 2/3 over.

white distillate -no- very pale yellow 11.23g.

pot -very black. but fluid at R.T.

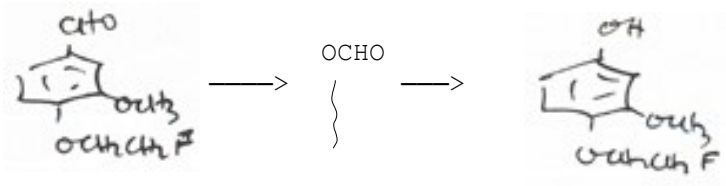
add 100 ml hexane. - extract [with] 2 x 100 ml H_2O

200ml H_2O
xtrt [with] 40ml hexane

hexane.
100 + 40

repeat 6:73

flash on R.E.
6.0g pale yellow oil.

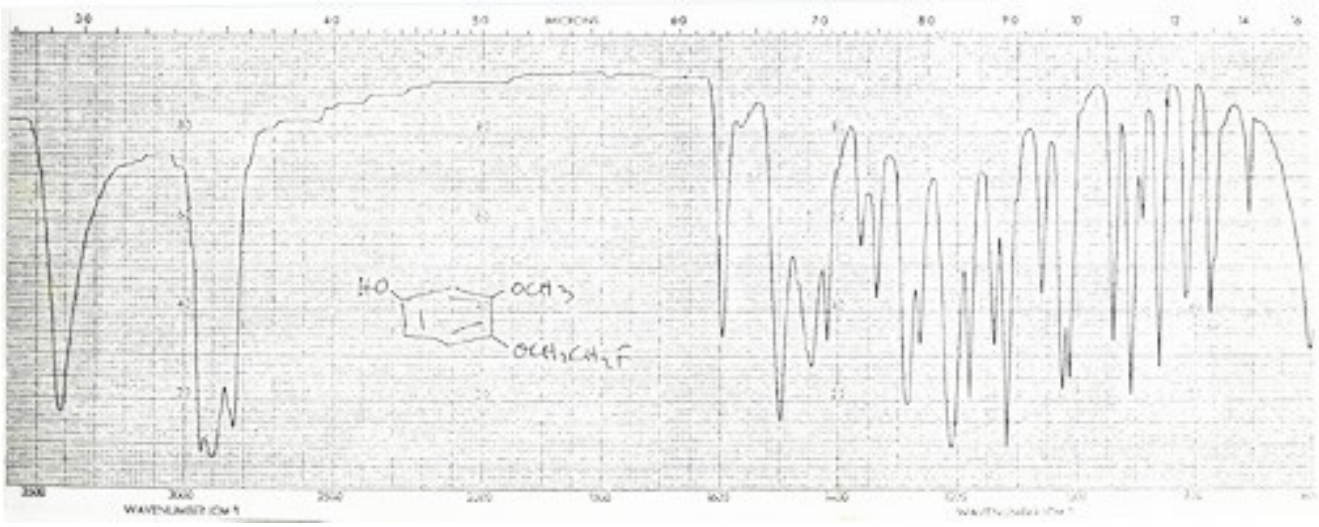


|| page 52

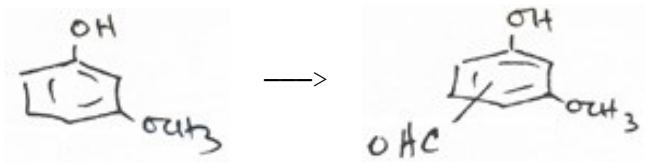
May 6,'89 0.6 g aldehyde - into
5 ml CH_2Cl_2 - add.
0.7 g 80% meta-chloro peroxy benzioc acid.

Heat briefly to boil. Substantially clear solution becomes quite cloudy, even at boil - reflux ~ 1/2 hr - then stand at R.T. a week.

filter - wash sparingly [with] CH_2Cl_2
-> solids . OUT
organic .
flash - 0.53g.
add 25% KOH
Δ in R.evap, bath 55° ~ 3 hrs.
stand 1 week - into water. very basic -
xtrt [with] CH_2Cl_2 - @ -> no solids.
out.
xtrt [with] CH_2Cl_2
-> organic
evap -> heavy
solids.



		theo,	found	their no.
ATS 6:60				
C 14	= 63.8626	C=63.86	63.84	F.6540
H 17	= 6.508561	H= 6.51	6.50	
N 1	= 5.320491			
O 4	= 24.30835			
MW IS	263.284	2C-G-4 NS		
ATS 6:61				
C 15	= 64.9634	C=64.96	65.02	F.6541
H 19	= 6.906351	H= 6.91	6.90	
N 1	= 5.051387			
O 4	= 23.07887			
MW IS	277.31	G-4-NS		
MB 6:78				
C 19	= 66.0574	C=66.06	66.03	F.6543
H 23	= 6.711401	H.6.71	6.68	
N 1	= 4.055095			
O 3	= 13.89524			
S 1	= 9.280862			
MW IS	345.442	Ψ 2C-T-4 (S) anie		
MB 6:75				
C 13	= 55.10457	C=55.10	55.35	F.6542
H 17	= 6.047985	H=6.05	6.06	
N 1	= 4.943989			
O 4	= 22.58818			
S 1	= 11.31527			
MW IS	283.334	Ψ 2C-T-4 (S) NS		

Attempt. 

May 26, 1989.

(10% xs) 1.70 g $POCl_3$ and.
(10% xs) .80 g DMF
goes pink, Δ on SB -> claret - ∇ 0°.
add.
1.24 g m-methoxy phenol. - gets very hot again.
Δ SB for ~ 20 min - well controlled - not too much color - into 150 ml H_2O. xtrt [with] 3 x 50 ml CH_2Cl_2 flash

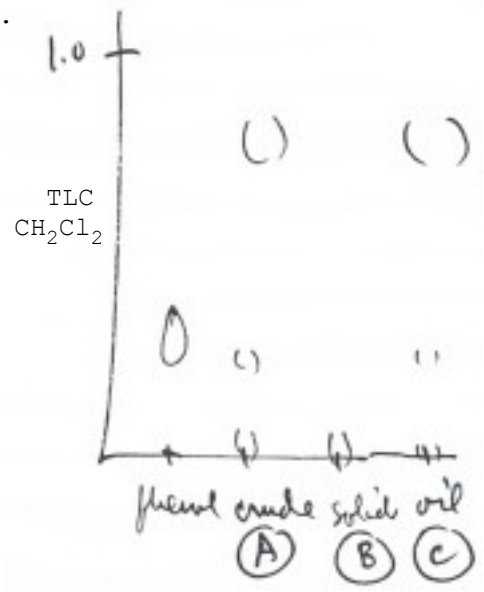
wet solids - off white (A) under hexane

hexane lots of white oil. (C) 0.20g.

-> solids - onto plate fine, white 0.10g. (B)

Where did everything go?

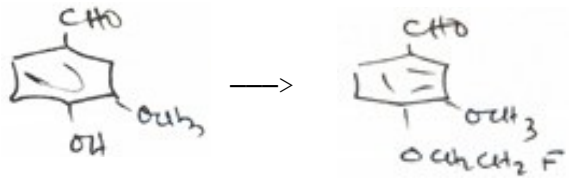
TLC CH_2Cl_2



54.78
54.58
tarem

Repeat.

May 26, 1989



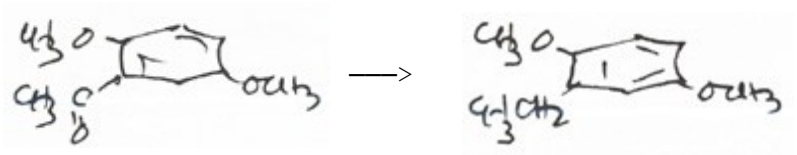
See page 66

for KOH base. K_2CO_3 here.

15.1 g (13.8g theo) K_2CO_3 anh. somewhat ground up, add
60 g acetone. +
15.2 g vanillin (sets to some solids on bottom -break up. add.
12.7 g $BrCH_2CH_2F$.

onto SB, reflux - actually open flask, so renew acetone regularly.
where does BrCCF boil?

off S.B. 2 hrs.

Repeat 

June 6, 1989.

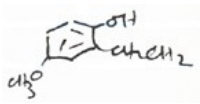
See p68

To 500 ml triethylene glycol. in a 2L BB [with] plastic thermometer. add.
71 g 85% KOH pellets.
stir as best possible - then add
100 g acetophenone (actually 99.25g - entire Aldrich bottle - then add
125 ml fresh 66% hydrazine.
Δ to reflux - take off condensate to allow temperature to climb. start at 133°- take off over ~ 3 hrs up to 145°- stay on 100% reflux overnight, 7 AM 145° and another [1:40] needed to hit exactly 210°. Hold at reflux there for 4 hrs. let stir while cooling -> very viscous deep amber oil. into ~3 liters of water.

Extract [with] 3x100ml Hexane
→ wash H_2O
flash ⟶ 22.0g pale, pale straw liquid.
excellent diether by TLC
see next page.

Extract [with] 2x100ml CH_2Cl_2
→ flash ⟶ 7.0g amber oil
no TLC - probably TEG?

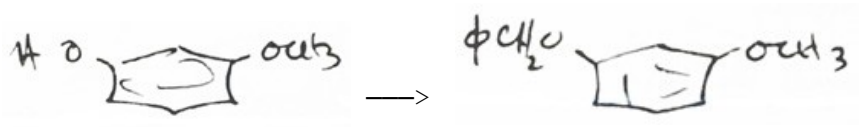
Acidify [with] Conc.HCl → rich oily phase - xtrt [with] 3x100 ml CH_2Cl_2
flash
→ heavy black oil 78g.
KR. 0.5mm 75° nothing 90-105 most (to 110°) orange-amber oil 67.4 g. TLC - 2 things a about where my of 15 years ago ran. - no trace of starting material or of hydroxy phenone by TLC. TR - trivial C=0. This is a single fraction - I bet that GCMS will give both hydroxy ethyl anisols. IR similar, not ≡ to 15 year old fraction. methylate (save 0.4g)



⟶

Attempt:

June 24, 1989



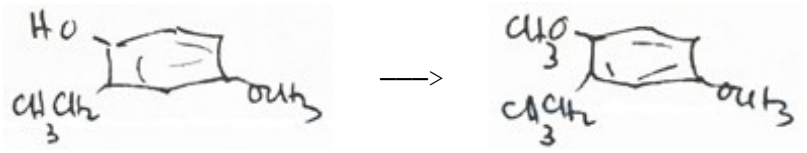
A solution of
3.3 g 85% KOH pellets in ~
100 ml MeOH - Δ to solution - off of boil-
add:
6.2 g phenol
8.6 g ΦCH_2Br } in the warm KOH
~25ml MeOH

some slight blue color - onto SB. - at reflux white solids out ~ 3 minutes - heavy bumping - reflux for 1hr. off - stand RT.

notes from my #96:
conc H_2SO_4 29g to
1,3- dimethoxyΦ 27 g
over 15 min. stir 1hr
into 250ml sat aq. K_2CO_3
ppt. filtered.

Recovery -

June 25, 1989.



67g recovered phenol , distilled, - tight fraction. added to ~~34.8g~~ 34.3g KOH in 200 ml boiling MeOH. - let cool a bit- add. (under reflux condenses)

69g CH_3I in ~ 20 ml MeOH.

reflux on Steam Bath under double reflux. - solids in ~20 minutes - full xtals of KI in ~ 1hr. add

20g more CH_3I in =vol MeOH. - probably no more solids. off ~4 hrs. stand ON -AM- strip MeOH ⟶ salty residue - into 3 L. H_2O. (pH strongly basic) - xtrt [with] 3 x 75 Hexane. Cloudy. wash [with]

H_2O ⟶ 28.3 g amber oil.

IR ≡ [with] 22g of 6:73

Aqueous phase - acidify [with] HCl -> pH acid, - heavy white - extract [with] 3 x 75ml CH_2Cl_2 (flash CH_2Cl_2).

-> 39g black fluid oil

39g

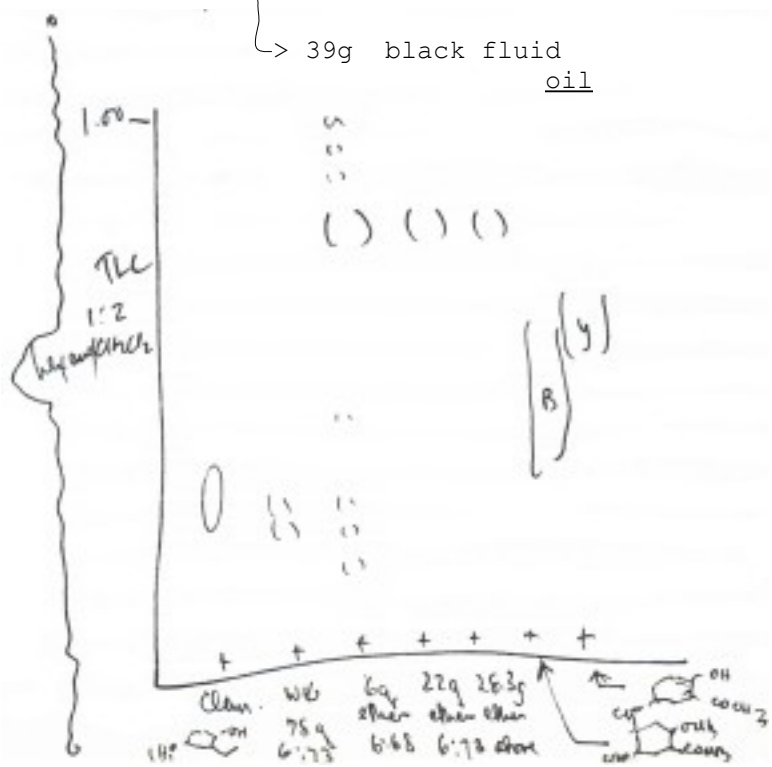
See page 19.

39g - at KR - distill- 90-130°- broader than before - and darker!

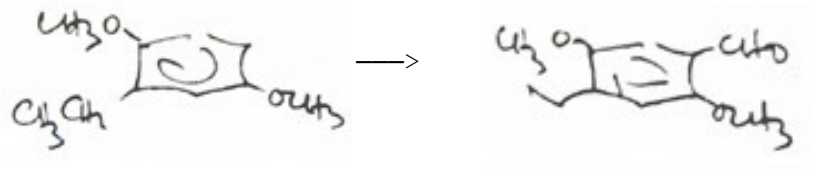
this distillate has been sitting around for a few months.

NO chromatograph at 6:75 C

24.8g. orange-red oil



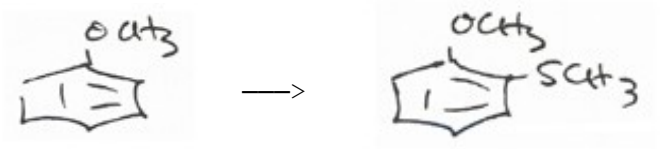
August. 6, 1989.



A Solution of 50.3g dimethoxy ethyl benzene
(combined 6:73 (22.0g) & 6:75 (28.3g)- into
200 ml CH_2Cl_2. ∇ to 0°. Add.
72.5 ml anh. $SuCl_4$. with good stirring - Initially
some dark, then clear solution. add
24.5 ml Cl_2CHOCH_3 over the course of ~1/2 hr, at 0°
Immediate dark color. Towards end, a
greenish cast everywhere.
Come up to RT.- heat at SB ~ 1 hr. during dinner. (10PM)

Into 3 L. H_2O. -extract [with] CH_2Cl_2 (3x100)
~~backwash [with] dil HCl~~.
~~(strip xxxxxxxx xxx xxx)~~
backwash [with] dil HCl
strip CH_2Cl_2 ⟶ 60.2g heavy black oil.
to KR.

	0.7mm	no
	0.5/40°	no
60.2	70°	no
	100°	start - xtals as it comes.
	110°	full bore - colorless - hot oil.
	115°	done ~~49.7~~ g white solids
		45.9

Attempt: 

August 11, 1989

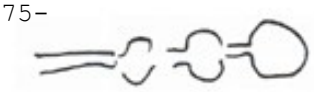
A solution of:

10.8g anisole (0.1mole)
12.1g TMEDA in
200 ml 30-75° pet ether. ∇ to 0° [with] stirring under Ar.
add.
42 ml 2.5M BuLi in hexane - slow development of white granules. Stir ~1 hr. add

10 ml (9.0 theo). CH_3SSCH_3 - turns from light white granular to creamy white. Stir 1/2 hr at 0°, then up to RT [with] another 1/2 hr stir. Next time more vigorous, as there were some yellowish globs on the sides that were dissipated by vigorous swirling. Into 500 ml dil H_2SO_4 [with] good stirring. Sep phases - xtrt aq. [with] 2 x 100ml ether. combine, flash ⟶ 16.7g bright yellow oil. Distil

16.7 br.g.
~~16.52~~
crude
pre KR

(.25mm)
70° up to 70° -> blush of liquid - up the snorkle - anisole?
out.
.25mm 70-90° (.3mm)⟶ white oil over [with] a small bit left in pot.
white
0.3/75-



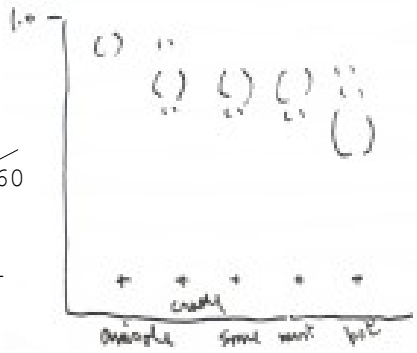
some must trace

combine most & some — off white white

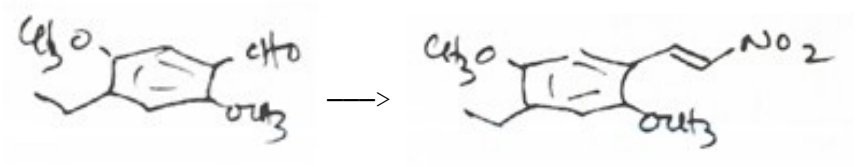
GCMS- page 80 main fraction — 9.95 g — off white

page 82 - pot

TLC CH_2Cl_2 40/60 hexane

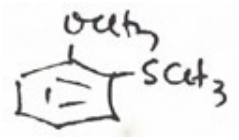


TLC CH_2Cl add to front.

August 14, 1989. 

45.9 g ArCHO from 6:76 - into
160 g NO_2CH_3 - add
8 g NH_4OAc. on the SB. to yellow -> deep orange.
TLC shows some at 1/2 hr. all done at 2 hr.
strip on RE. Pour red oil (hot) into 200 ml warm MeOH. xtals anyway. Dissolve in boiling MeOH - ~ 350 ml needed - ∇ in ice water.

45.4g.

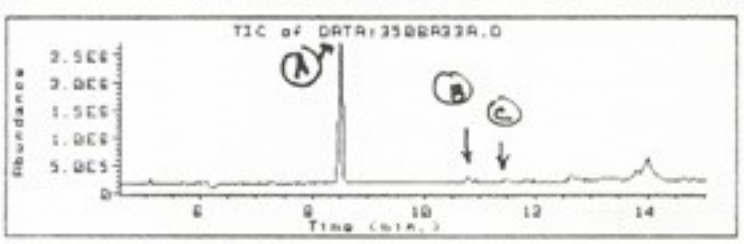
August. 18, 1989 picrate of 

About 1 g Solid picric acid, dug out from under a puddle of water in a 40% water P.A. from Fluka. Dissolved (mostly) in 5 ml warm 95% ethanol

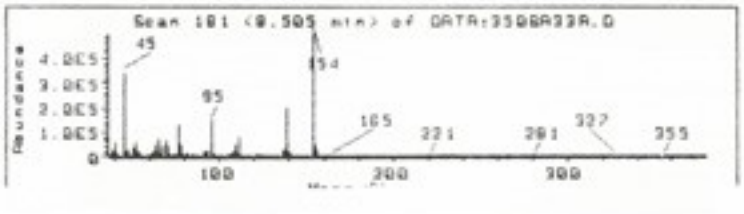
Add ~ 1/2 g thioether. red color - add water to turbid - scratch -> deep tomato xtals. filter-wash [with] 50% EtOH plate-dry.

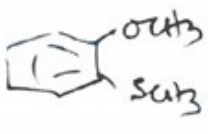
GCMS - main fraction
350B A33A

page 6:77

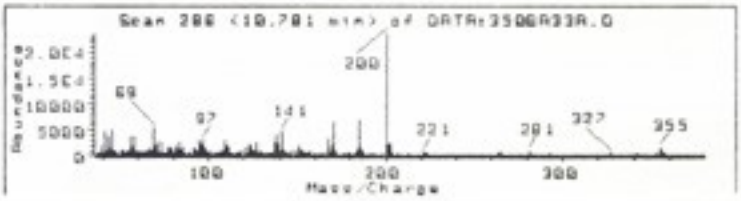


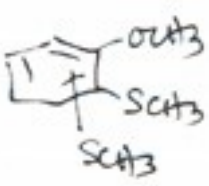
A



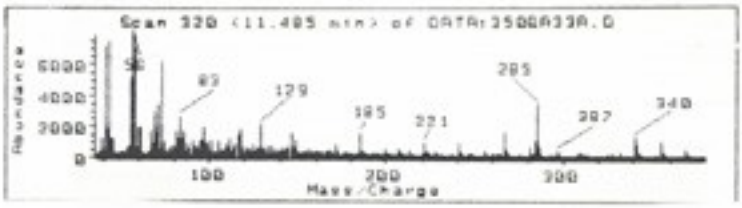


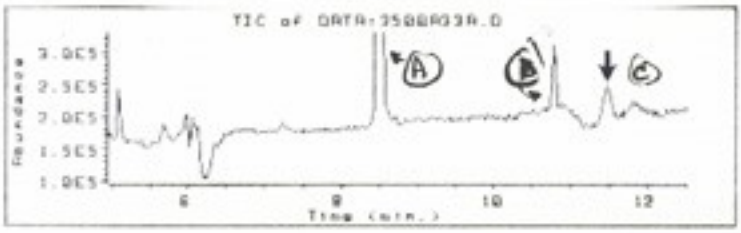
B

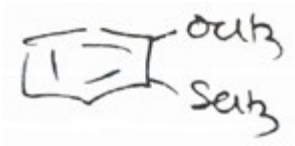




C

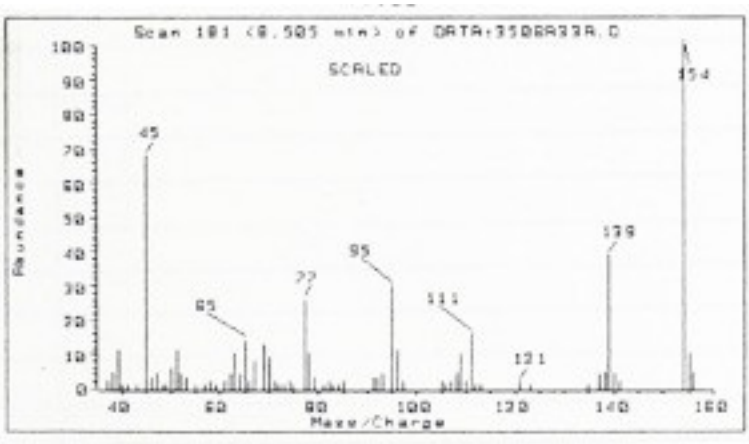




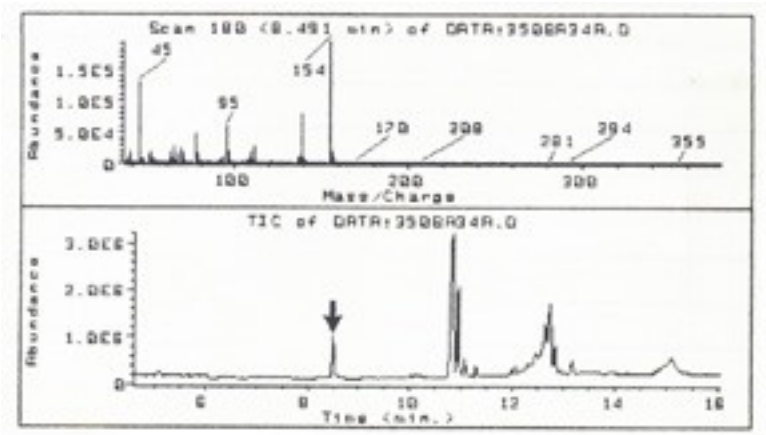
details of 

Scan 181 (8.505 min) of DATA:350BA33A.D
2-METHYLTHIOANISOLE 6:77 DISTILLED FRACTION

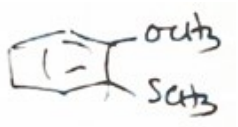
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
37.10	2	58.10	2	78.05	10	109.00	10
38.10	5	59.05	1	79.05	3	110.10	2
39.10	11	61.05	2	81.05	1	111.00	16
40.10	1	62.05	4	82.05	2	112.00	1
41.10	1	63.05	10	83.05	1	113.00	1
43.10	1	64.05	4	84.05	1	121.00	2
45.00	68	65.05	14	85.05	2	123.00	1
46.10	3	66.05	2	91.15	3	135.00	1
47.00	5	67.05	8	92.05	3	137.05	4
48.10	1	68.95	13	93.05	4	138.05	5
49.10	1	69.95	9	95.05	30	139.05	39
50.10	6	71.05	2	96.05	11	140.05	4
51.10	11	71.95	1	97.00	2	141.05	2
52.10	4	73.05	1	105.00	2	154.05	100
53.10	3	74.05	2	106.00	1	155.05	10
55.10	1	75.05	1	107.10	2	156.05	5
57.00	1	77.05	26	108.00	4		



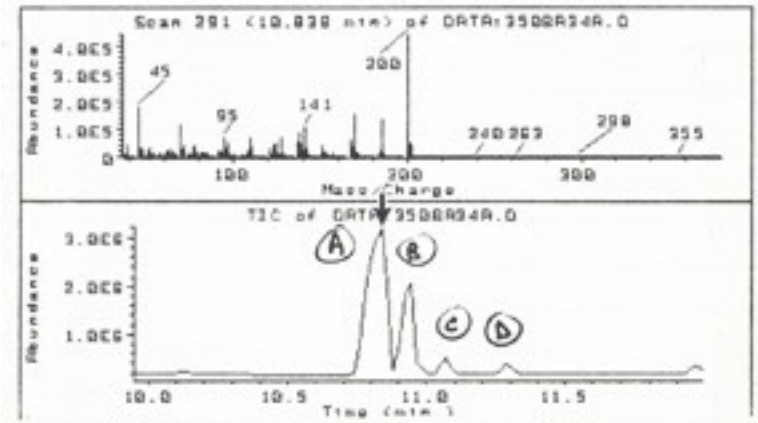
GCMS pot from 6:77

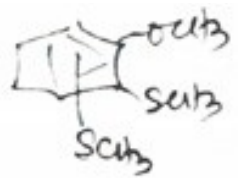


verified



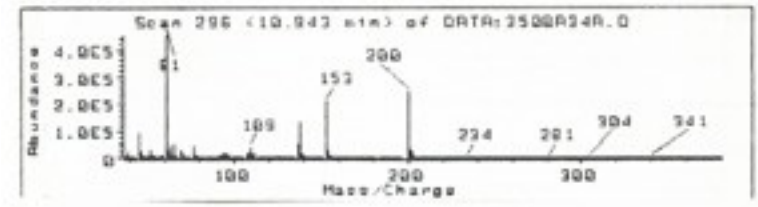
A

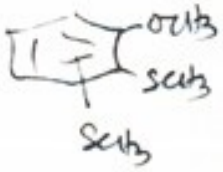




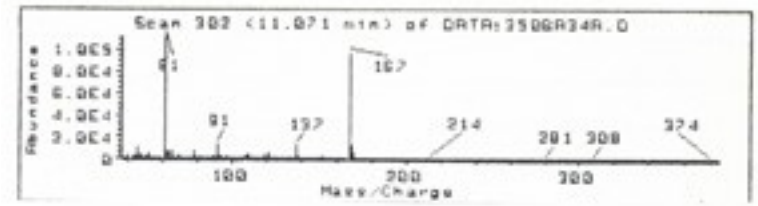
1

B



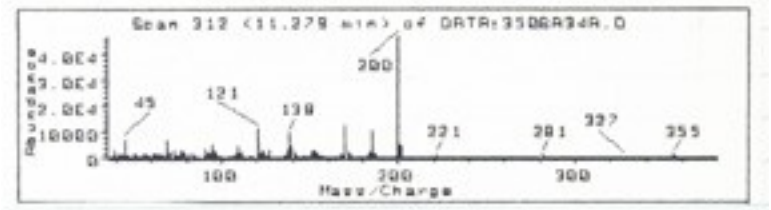


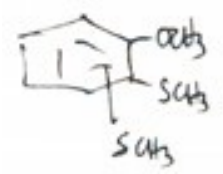
C

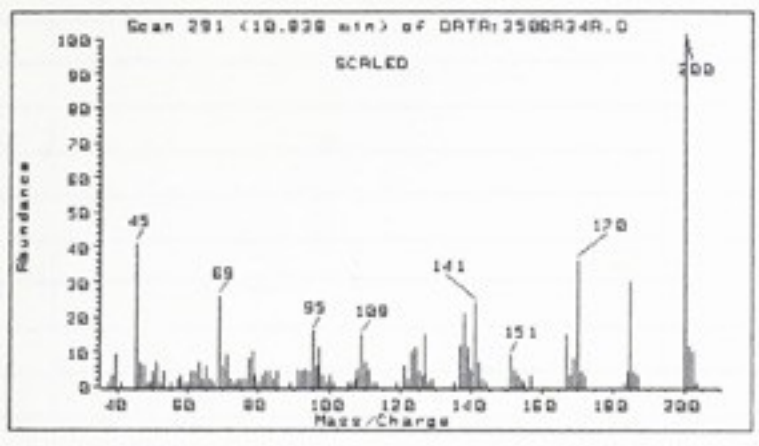


?
(nitrogen?)
(mass-1?)

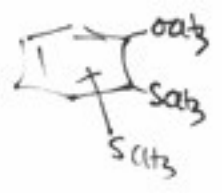
D







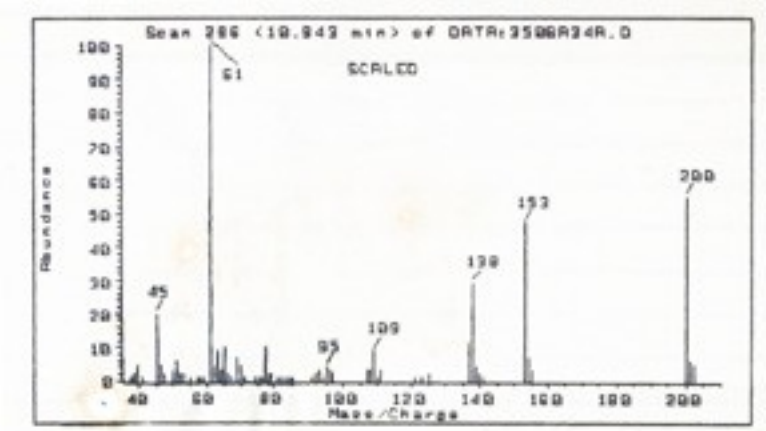
details
on

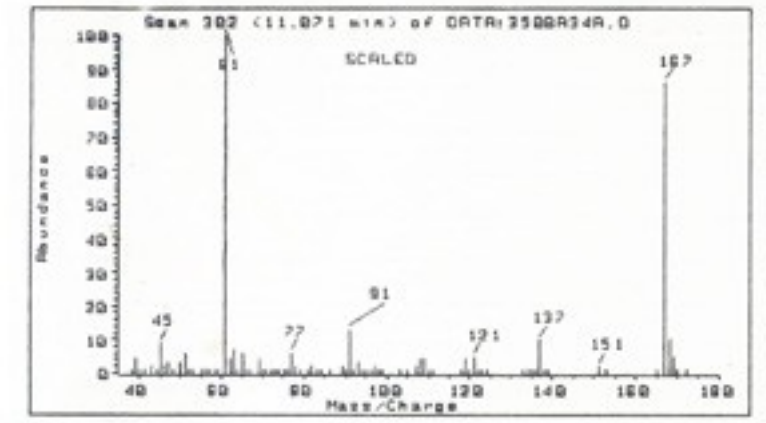


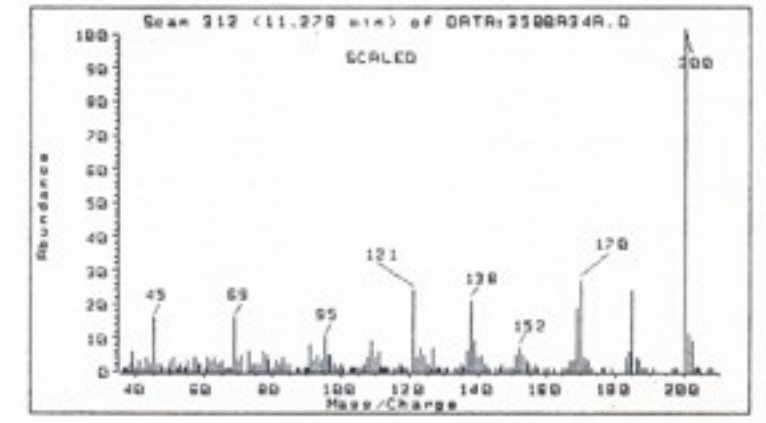
Scan 291 (10.838 min) od DATA:350BA34A.D
2-METHYLTHIOANISOLE 6:77 POT RESIDUE (WITH SLOW SPOT)

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
37.10	1	70.05	6	100.00	3	141.05	24
38.10	3	71.05	9	100.90	1	142.05	7
39.10	9	71.95	2	105.00	1	143.05	2
41.10	1	73.05	1	106.00	1	143.95	1
45.00	41	74.05	2	107.10	2	151.05	9
46.00	7	75.05	2	108.00	5	152.05	5
47.00	6	76.05	2	109.00	15	153.05	3
48.10	1	77.05	8	110.00	7	154.05	2
49.10	1	78.05	10	111.00	5	154.95	1
50.10	4	79.05	3	112.00	1	157.05	3
51.10	7	80.05	1	113.00	1	167.05	15
52.10	1	81.05	3	119.10	1	168.05	3
53.10	4	82.05	4	121.10	6	169.05	8
55.10	1	83.05	4	122.10	2	170.05	36
57.10	2	84.05	2	123.00	10	171.05	4
58.00	3	85.05	4	124.00	11	172.05	3
59.05	1	89.05	1	125.00	4	183.00	1
60.05	1	91.15	5	126.10	3	184.10	4
61.05	4	92.05	4	127.00	15	185.00	30
62.05	4	93.05	5	128.00	1	186.00	4
63.05	7	94.05	4	129.00	2	187.00	3
63.95	2	95.05	16	135.10	1	200.00	100
65.05	6	96.05	6	137.05	12	201.00	12
66.05	2	97.00	11	137.95	21	202.00	10
67.05	1	98.00	3	138.95	11	203.00	1
68.95	26	99.00	1	140.05	5		

blow-ups of page 6:82





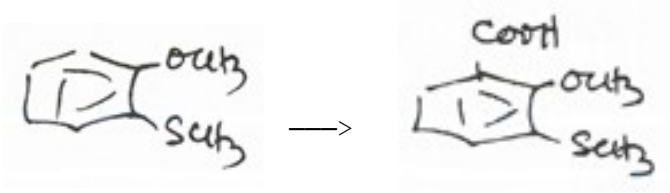


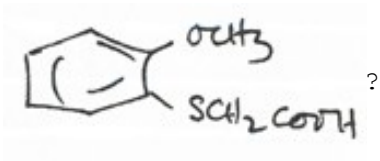
61=

$[CH_3SCH_2]^+$

Attempt:

9/~8/89.



or  ?

8.40 g starting ether [6:77](#) , into.
120 mg 30-75° pet ether, ; add
6.61 g TMEDA. stir- under argon,
cool externally [with] wet ice bath.
add:
23 ml 2.5M BuLi in hexane. -added rather quickly.
color to off-white - some solids form. Stir at
0° for an hour - then pour into:
~200g dry ice, powdered, in ~200ml anh. ether, with
good mechanical stirring.

Let come up towards room temperature. Extract [with]
200ml water (pH ~ 8 or 9) - a second time [with] water
[with] a few g. NaOH in it. Pool.

aq. organic.

@ [with] conc HCl. -> yellow oily upper crust - stir a while and all goes to white solid. filter,

flash on R.E. -> amber oil.

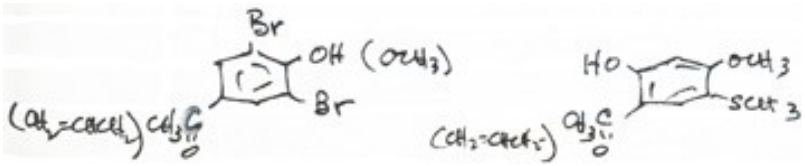
wash [with] H_2O, let stand in air.

6.02g. mp 94-110°

small amt MeOH
107° stir. 113-115°
small amt ΦCH3
107° stir. 111-114°

spectra
[page 87](#)

discussion idea inter-mediates (Maurice, Larry W.)



[Editor's Note: The following was written on a Post-It note and stuck to page 85]

st.
8.40 ether

120 ml 30-75
pet
ether

6.61g TMEDA

ice bath

23 ml BuLi
2.5M
hexane

200g dry ice in 200 ml ether.

Reduction

9/10/89  ——> 2C-E

(45.43g NS p 6:78)

Put 2L new THF into 5 L. 3 neck; mag. stir, argon.
add 38g $LiAlH_4$ (new form, as pellets) - slow to
dissolve - ~2/3 in - up to reflux. - Δ of solution quite large. Keep stirring.
when pellets ~1/2 gone- $H_2\uparrow$ slowing down- add

Δ5.4g NS
38 g H_2O
38g 15%Na^+OH^-
114g H_2O

45.4g NS in 250ml THF - dropwise over ~2 hrs. Set up for gentle reflux ON [with] heating mantle. 2:00AM Monday AM.
Reflux to ~ mid night monday - 22 hrs. cool to RT ON

15->25
26->38

Kill hydride [with] IPA.
35 ml required.
add 38 ml H_2O - Some more $H_2\uparrow$
add 38 ml 15% NaOH.
add 114 g H_2O. ——> Course solids. filter - wash [with] THF - and finally [with] MeOH (bad!).
Refilter filtrate of some fines, flash -> residue of pale red oil (~100ml). into 2 L. H_2O, acid [with] HCl - no solids - xtrt 3 x 100 ml CH_2Cl_2 - all color out

aq.
OH^- [with] 25% base
3 x 100 ml CH_2Cl_2

deep red extracts

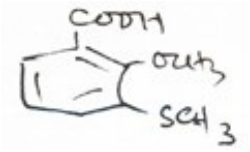
flash -> pale amber oil 22.8g. - lots of CH_2Cl_2

distill, 0.4mm. - almost 6-10g product comes over 90-130° - first in a white oil, and then crystallizing as it comes.

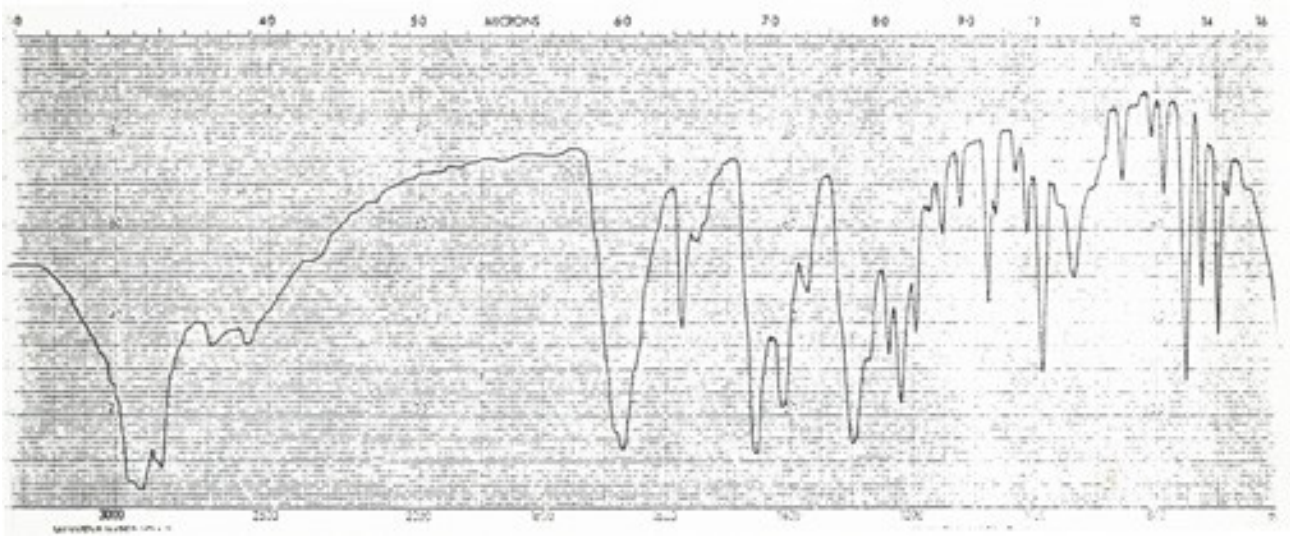
-> Fraction "A"
to page 89

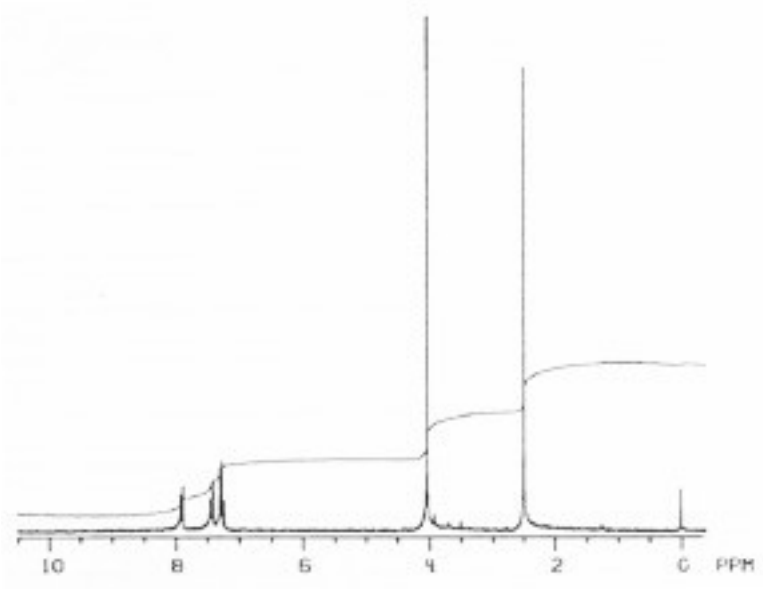
put in clear amber glass- push over at up to 200° oil & some solids (white)

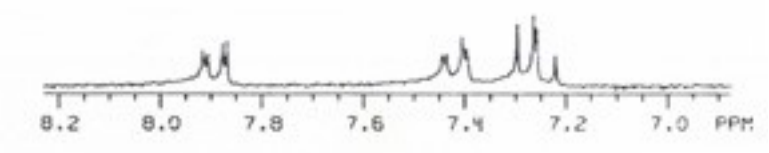
-> Fraction "B"
to page 98

spectra of 

See page 85

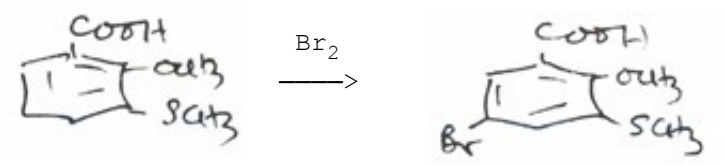




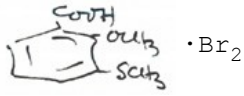


Bromination

9/15/89



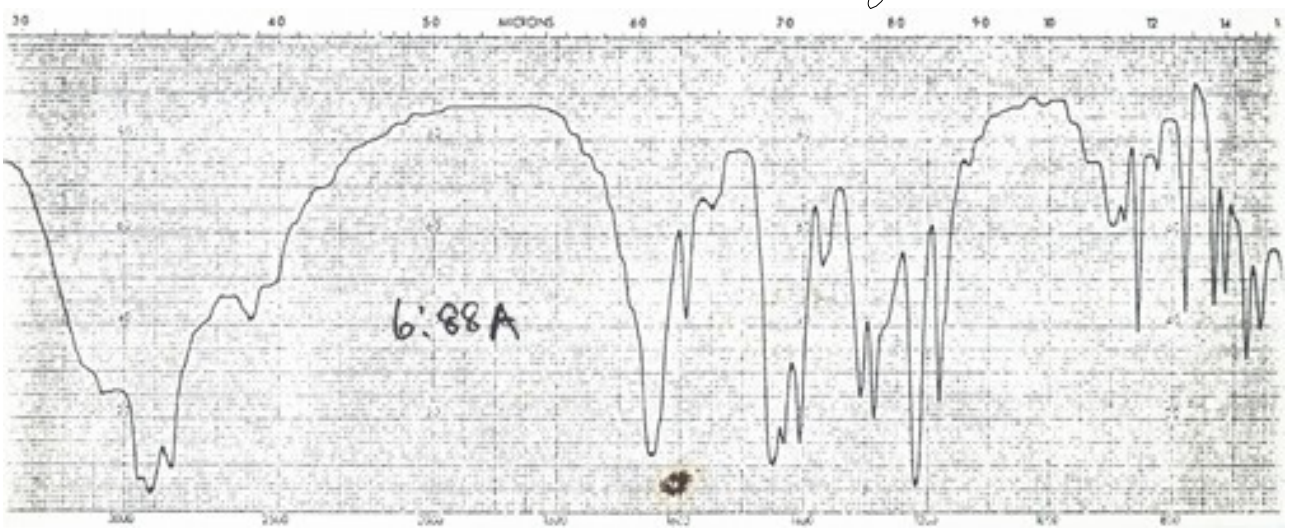
1.98g acid (page 6:85) into
27g acetic acid. - solution complete.
add.
1.76g Br_2 (10% xs). - stir at RT - slow drop out of Brown xtals. rub on plate, the color slowly disappears, and IR is that of starting acid, therefore



hold at reflux 2 1/2 days. stand at RT 4 days ->
whitish crystals. 6:88A - a new acid by infra-red.
filter-
Carboxy looks fine. air-dry -> 0.92g

recrystallize from
Methanol (at boil).
+ H_2O -> turbid - ∇ in
ice -> off white Solids

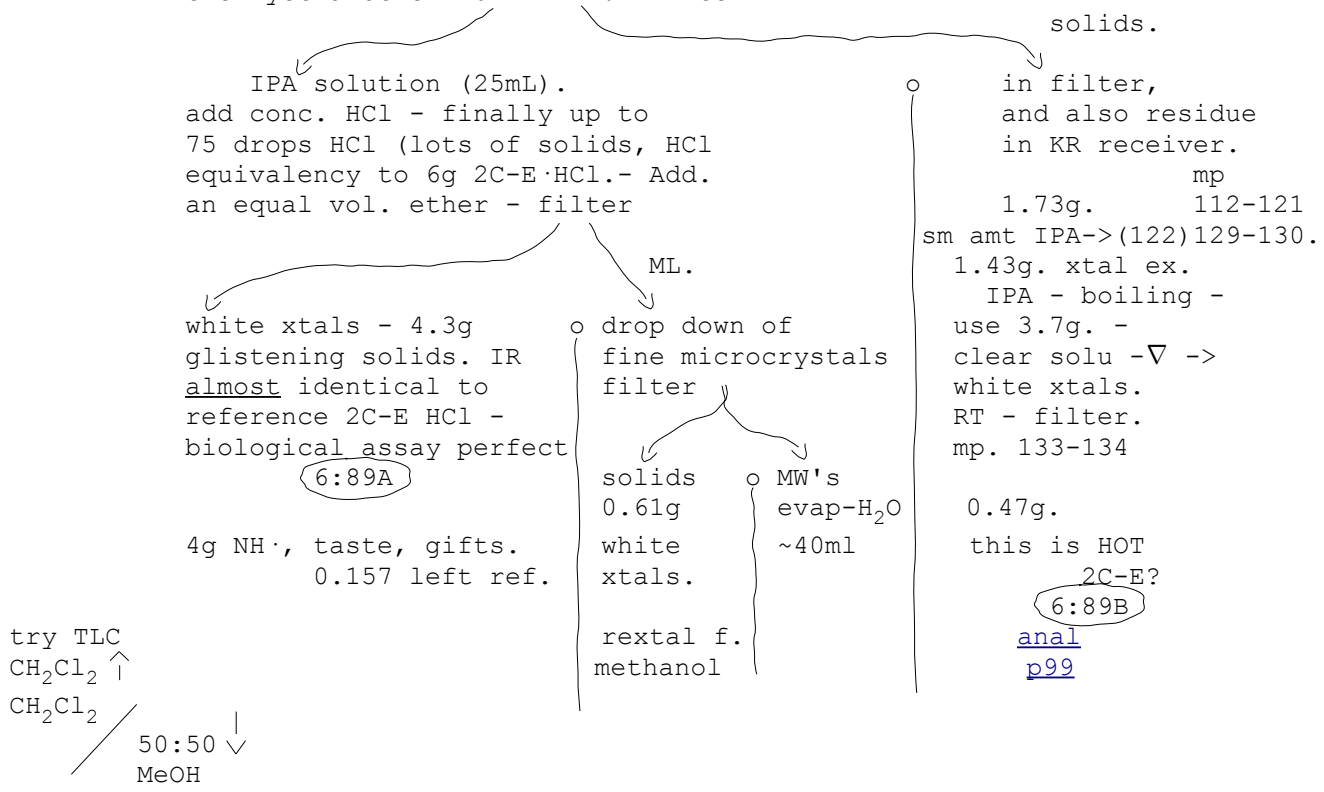
small amt ex ΦCH3 0.51g mp 203-205
mp 205-206
small ex CH_3SO- too small. IR NMR page 90

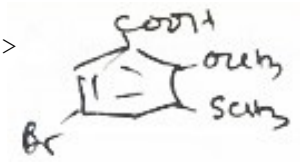


Work-up of 2C-E from 6:86

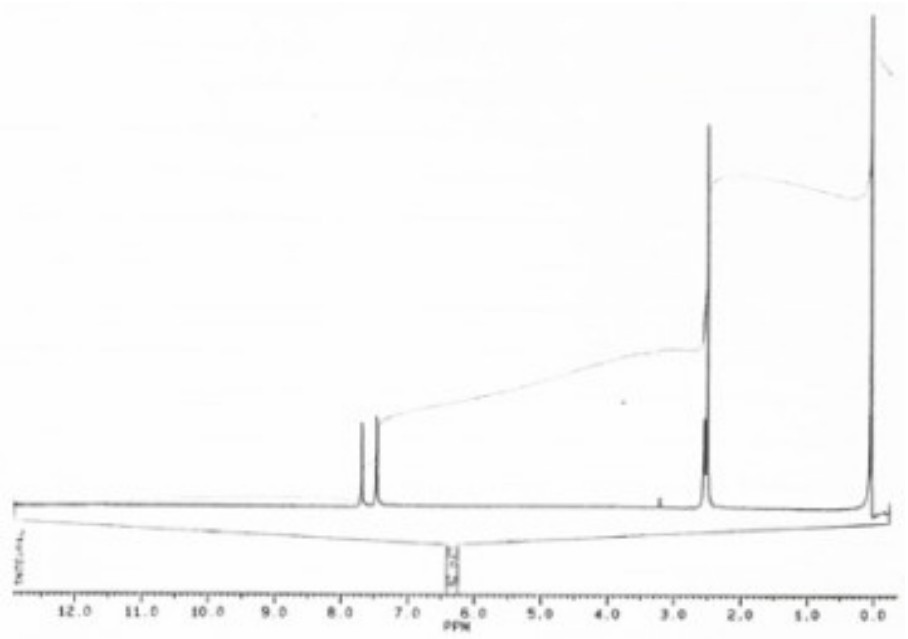
Fraction A. KR of crude basic 2C-E prep. - low boiling out - maybe 90-130°. solids came over late - the early fraction was an oil that on standing overnight set up to a thin crystal matrix.

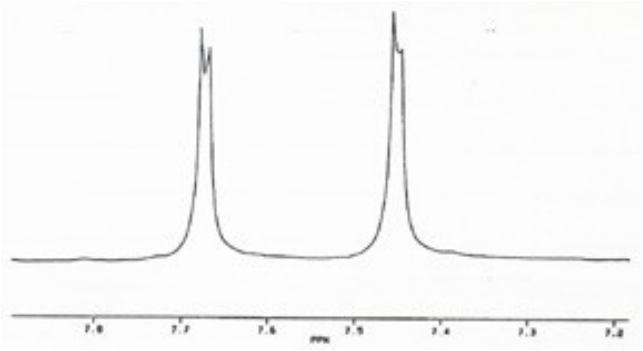
Wash out [with] 10 ml IPA, then 5 ml more IPA, and then yet another 10 ml IPA. filter



Attempt to make-> 

from page 88





NMR (in $(CD_3)_2S{->}0$) - no OCH_3

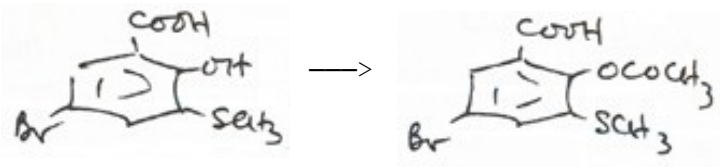
SCH_3 OH

2 ring H's OH

where is CO<u>OH</u>

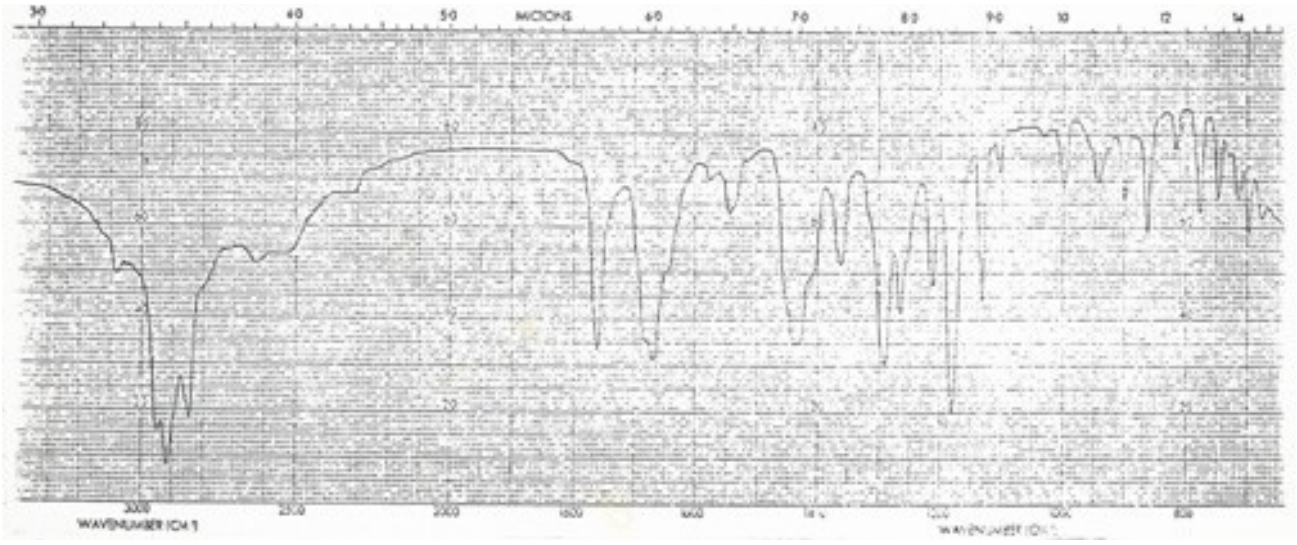
could it be the phenol?

Attempt:



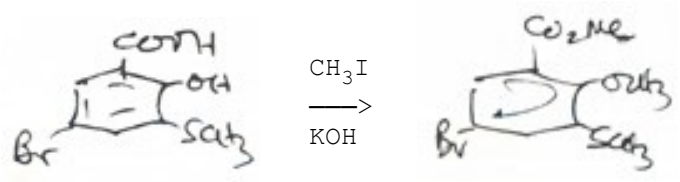
Sept 29, 1989

~20 mg wrong acid 6:88A.
~1/2 ml Acetic Anh. insol!
Δ -> sol
∇ -> xtals.
~1/2 ml pyridine - slight discolor - - Δ [with] flame
keep hot ~ 5 min - kill [with] 5 ml H_2O (sl-turbid)
+ conc. HCl -> white solids. onto plate.
IR -> new carbonyl.



Attempt:

October 6, 1989



(almost)
To a solution of 0.7g KOH (85%) in 25 ml MeOH - add
~~1.7g~~
0.38g Salicylic acid.
hot into solution . K salts insol- should have
dissolved in MeOH first. oh, well- add

1.7g CH_3I. onto S.B. -reflux ~3 hrs.

stand week-

filter - wash [with] MeOH
ML
washes-
evap.Rot.evap.
-> 1.47g white solids
into 100 ml H_2O pH 7-8 -
(light green on pH paper)
@ [with] Hcl -> pH red- slowly
becomes yellow colored
xtrt 3 x 50ml CH_2Cl_2
flash -> 30mg yellow
film (solids?).

OUT

-> white solids.
0.58g.

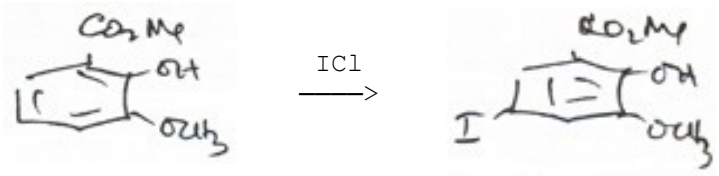
into 40 ml H_2O - not sol!
neutral pH- acidity [with] HCl
->slightly more turbid -
excellent white solid.

filter- wash H_2O - air dry
-> 0.30g white beautiful
~~xtals~~ solids

IR ≡ starting bromo
salicylate - no tx.

save a bit for ref.
rest page 96

Attempt:



10/13/89.

Following Matthew's notebook observation pp 41-43-45

etc.

MW	whole Ratios	Dissolve	
182	1	1.0g	3-methoxy-methyl salicylate (from L.W's stash) into 50 ml warm CCl_4 - into solution - let ∇ ~ 30°. add.
84	2·1	1.0g	$NaHCO_3$ (fine powder) - then
162	1·12	1.0g	ICl (freshly melted from polymorph)

Stir at ambient (30->25°) check 10 min (1/3 done)

check 25 min (1/3 done?)

Δ 35° from [:35] to [1:10]

25° check 1:10 hr. 50:50?

onto steam bath 3:30PM.

off. 4:00PM still 50:50

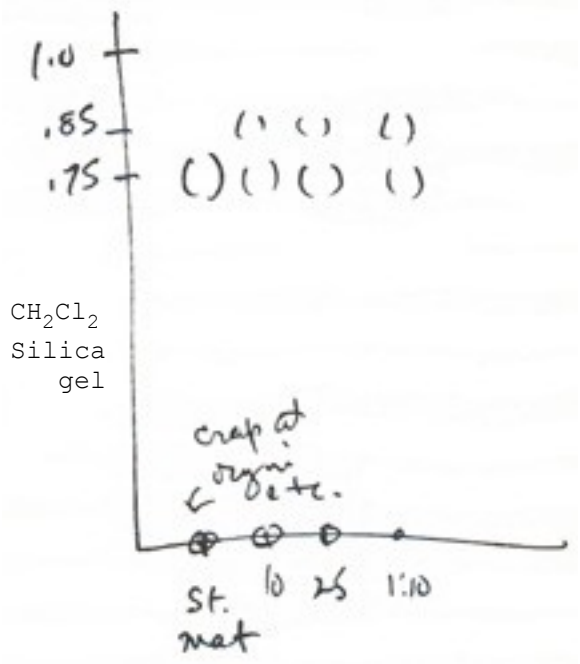
185.86

184.25

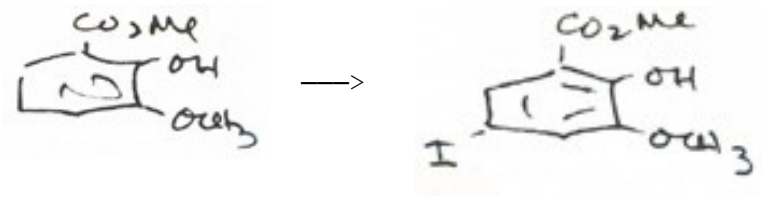
crude oil.

CH_2Cl_2

Silica gel



Repeat:
of page 93

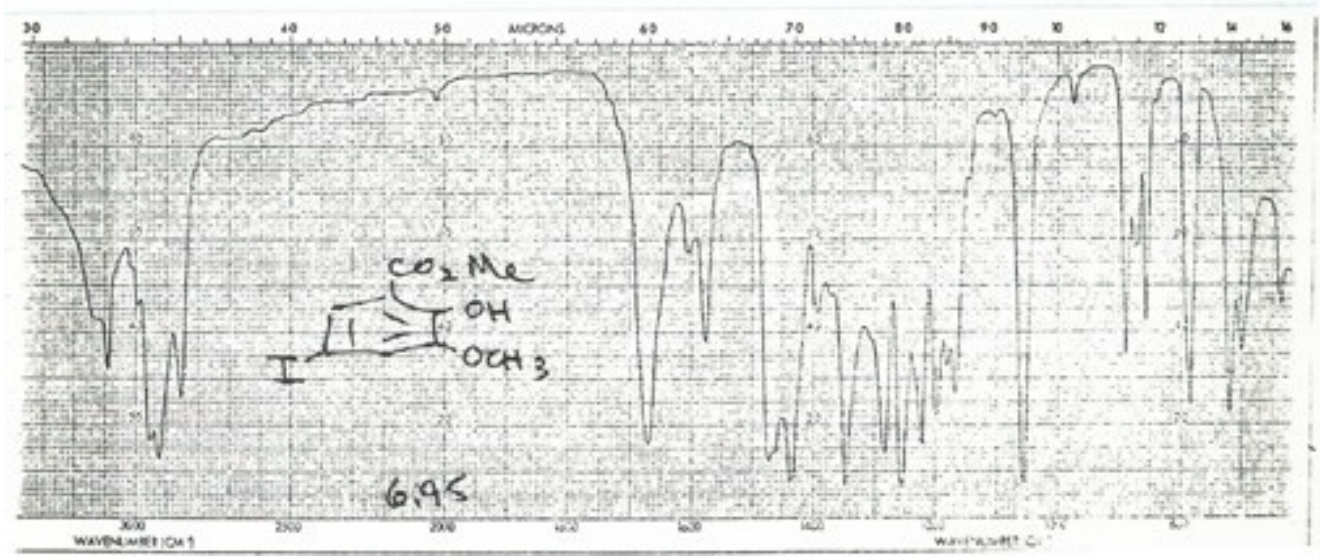


Into 100 ml methylene chloride, add

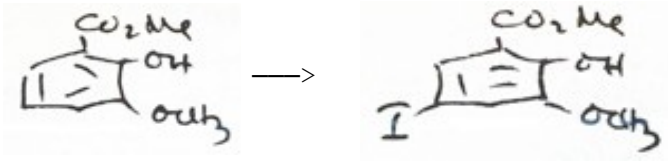
9.88 g Larry W's ether - (he thought 10.135g)
7.g $NaHCO_3$ (150%)
11.6 g ICl. (130%) - Stir 1 1/4 hr. RT. then:

3.5 g (75%) $NaHCO_3$
5.4 g (60%) ICl.

Stir another hr. Into 300 ml H_2O - add dithionite, shake -> pale yellow. Separate - ~~wash~~ extract 100 ml more CH_2Cl_2 - wash [with] H_2O -> dichlor solution . LW works up.



Repeat:



10/27/89

~0.5g recovered ~ 2:1 stuff from L.W. page 93-
dissolve in
20 ml HoAc - Δ a bit -> sol. add
1 g ICl (big excess) - onto SB ~ 1 1/2 hrs.

into 250 ml H_2O ⟶ dark purple + brown stuff-
add spatula full of dithionite - shake ->
pale yellow + solids everywhere.

filter ⟶ brownish solids 0.62g. ← crude-TLC-NO ST.MAT.
rextal a bit from MeOH -> light tan.

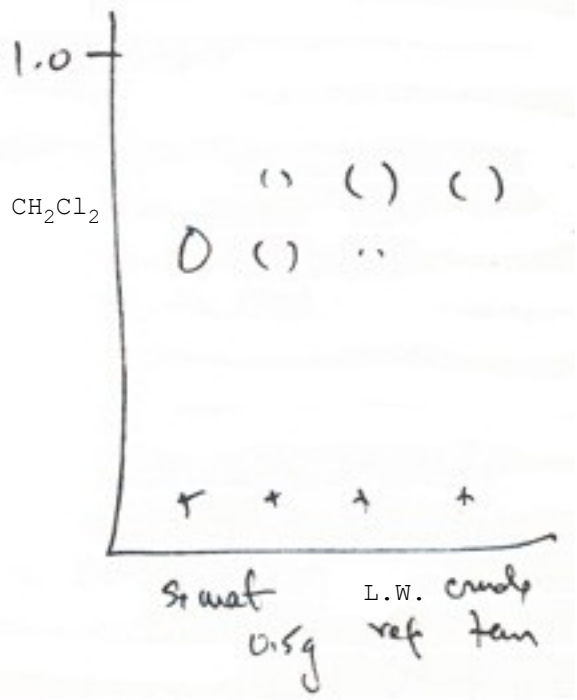
dissolve in 10 ml CH_2Cl_2 - through 6 cm x 6 cm
silica gel. CH_2Cl_2 wash

-> 40 ml - almost nothing. #1
+ 40 ml -> heavy spont. xtals #2
pale yellow
+ 40 ml -> trace more #3

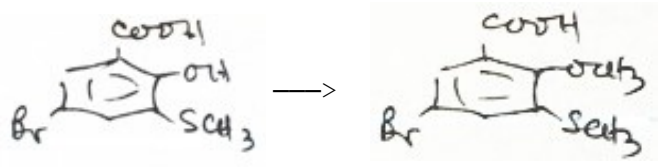
flash
0.47g.

small-ex MeOH
105-106
small-ex ΦCH_3
105.5-106.5
EtOAc 106-108
L.W ex hexane

all \ ex MeOH
6:95



Attempt:
10/29/89.

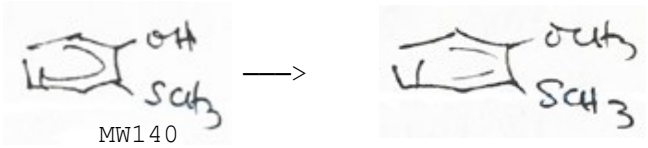


MW263.

0.3g recovered phenol from page 93 - into
10ml DMF -add
0.3g methyl sulfate
0.3g KOH- reflux [with] mantle - 3 hrs - let stand a week.

work up -> 0.19g same phenolic starting material

6:96
190mg
to
L.W.

Reaction. 

11/17/89 MW140

To 10 g KOH 85% pellets in 100 ml methanol. Δ to sol.
∇ RT.

See page 79. 77.

add a mix of

21 g CH_3I
14 g Phenol
} ⟶ yellow solu + some exotherm.

Onto SB. white solids in a minute or so. Reflux 1/2 hr. stand R.T.
Work up - almost no methylation - - into water 800 ml- strongly basic still - xtrt [with] 3 x 50ml CH_2Cl_2
@ [with] HCl 4 x 75ml CH_2Cl_2

12.4g deep amber oil

1.85g light amber oil. out

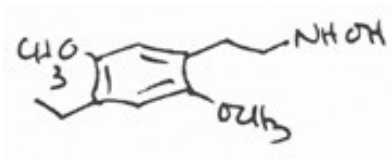
Another 10 g KOH in 100 ml. MeOH
+21 g CH_3I - onto reflux 2:30PM 12/1/89.

again - mostly acidic product -
everything OUT

High Boiling HOT-2C-E from page 86

All the 2nd high-boiling fraction of 2C-E distillation scraped out - into storage - MS below. small amt rubbed under EtOAc -> sl.gummy solids. RX f. EtOH -> oil.

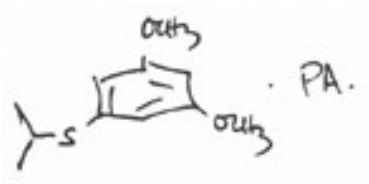
6:89B



			found.
		I-9945	
C	12 = 63.97372	C	64.33
H	19 = 8.501421	H	8.73
N	1 = 6.21804	N	6.22
O	3 = 21.30682		

MW IS 225.28

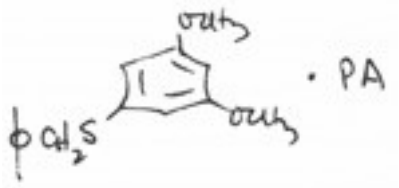
MB VI-86



		I-9946	
C	17 = 46.25447	C	44.58 ; 44.45
H	19 = 4.338863	H	4.20 4.19
N	3 = 9.520488	N	9.46
O	9 = 32.62303		
S	1 = 7.263155		

MW IS 441.406

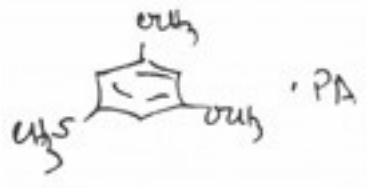
MB VI-85



		I-9947	
C	21 = 51.52969	C	51.21
H	19 = 3.912996	H	3.89
N	3 = 8.586035	N	8.43
O	9 = 29.42102		
S	1 = 6.550263		

MW IS 489.446

✓MB VI-84

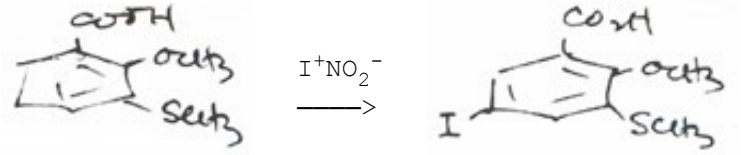


		I-9948	
C	15 = 43.5825	C	43.48
H	19 = 3.657882	H	3.63
N	3 = 10.16659	N	10.04
O	9 = 34.83697		
S	1 = 7.756064		

MW IS 413.354

Dec 1, 1989

Attempt:



A solution { 0.76g $AgNO_2$; 100 ml warm water } A.

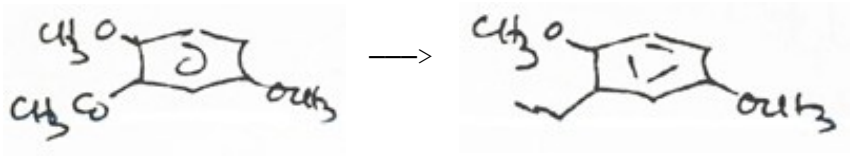
A Solution { 0.5g 6:85 ; 1.27g I_2 ; 75ml Ch_2Cl_2 } B.

Stir A rigorously (~30° temp). and add B all at once. Stir a while - light solids, but dichlor stays purple. then shake vigorously - separate bottom phase - extract aq [with] 3 x 50 ml Ch_2Cl_2 - 0.27g wash [with] aq. $Na_2S_2O_4$ -> pale yellow - strip -> 0.27g xtals. IR ≡ to starting acid.

OUT.

December 3, 1989.

repeat · 6:73



500 ml triethylene glycol.
71 g KOH 85% pellets (~/3 added, so stirrer will still go
99.64 100 g acetophenone (99.64g total aldrich bottle)
125 ml 66% hydrazine.

Δ [with] mantle [with] take-off under reflux condenser. At ~ 100° - add rest of KOH. - stirrer OK. Take off up to 210°-
190 off. (~2 hrs, 190ml off). Hold there a while. (8:~~20~~ PM 8:20)
Δ off at 1AM, let stir ON. - let stand until

Jan 4, 1990 deep black - very viscous oil - into 3 L water
(follow page 73)

Extract [with] 3x100 ml hexane. —aq.→ acidify - xtrt [with] 3 x 100 ml CH_2Cl_2

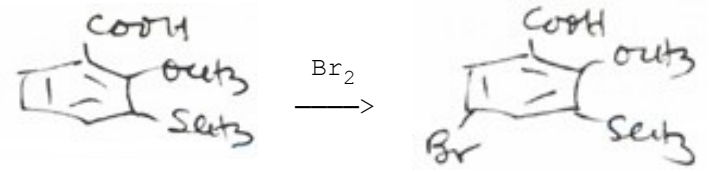
flash ↓

~~22~~ 21.2g water -white fluid oil.
6:101 A

~~flash~~ water wash
flash
0.3 mm/95-110°
↳ 60.2g
6:101B. yellow oil.
bad tar residue out.
see page 105

Attempt:

12/8/89.



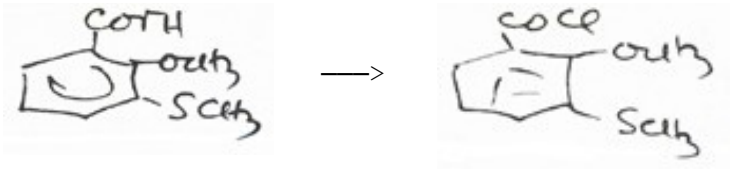
0.5 g 6:85 - into 25 ml $CHCl_3$. add:
2.5 g $NaHCO_3$ - stir vigorously.

dissolve 0.5g Br_2 in 20 ml $CHCl_3$
(25% xs)

add a few drops ⟶ orange-red color in $CHCl_3$
(~2ml?)

stir for ~ 2 hrs → colorless

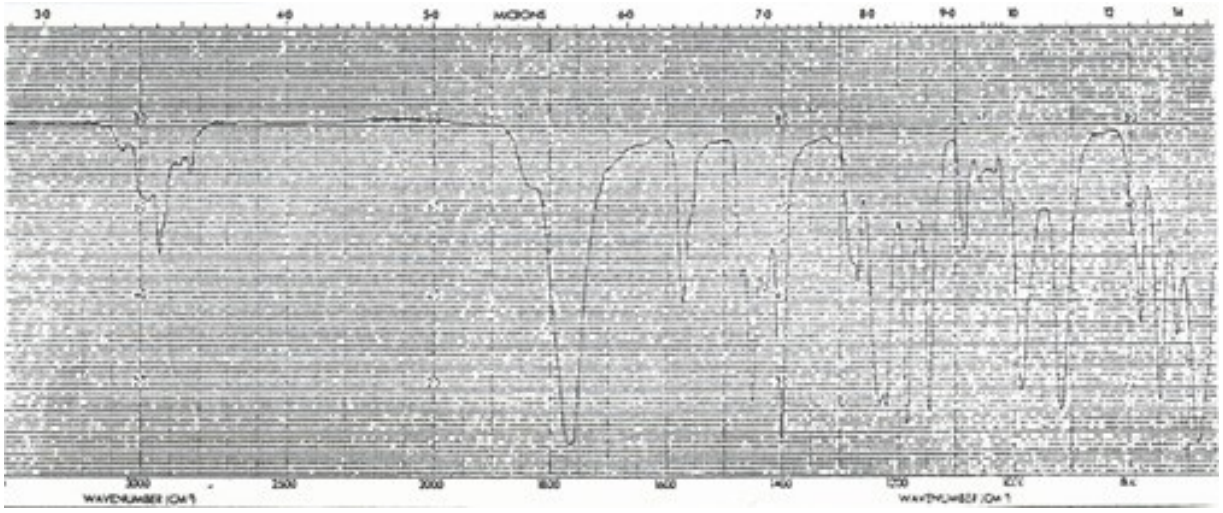
add the rest of the bromine. stir at R.T.



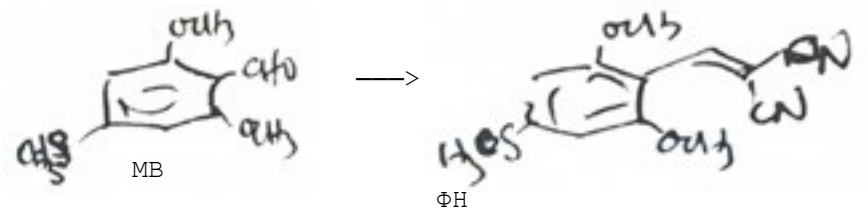
1.0g of the acid 6:85 - add
1.0g 6.5g $SOCl_2$ - on SB for ~ 4 hrs. then boil to dryness.
6.5g 1.29g crude deep brown oil -
$SOCl_2$
distill at KR. 0.3mm ~140° ⟶ pale yellow oil.
0.90g -
1.29.
superb IR.
0.90. all TLC -> streaking [with] ArCOOH formation.

white solids as residue

0.1mm
120-140°



Attempt:



MB ΦH

12/9/89 ±.
Friday.

~20mg aldehyde - MB 2/out of 3. intermediate qual.
dissolve in 1/2 ml iso PA

~50g
$CH_2(CN)_2$ in 1/2 ml IPA.

combine - add 1 drop Et_3N
20 seconds, then yellow xtals.

onto plate ⟶ fine light yellow xtals.

mp ~~138~~-133-138
133-158

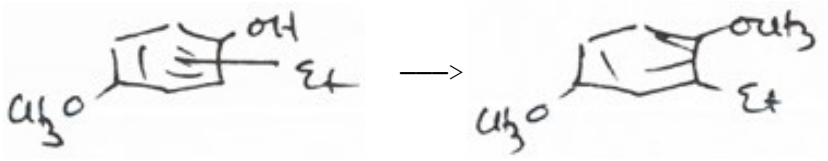
Recrystalline from Ethanol
mp 144-145°- wt ~ 20mg.
just right for ~~non spxxx~~
for analysis

6:104.

Methylation.

1/6/90.

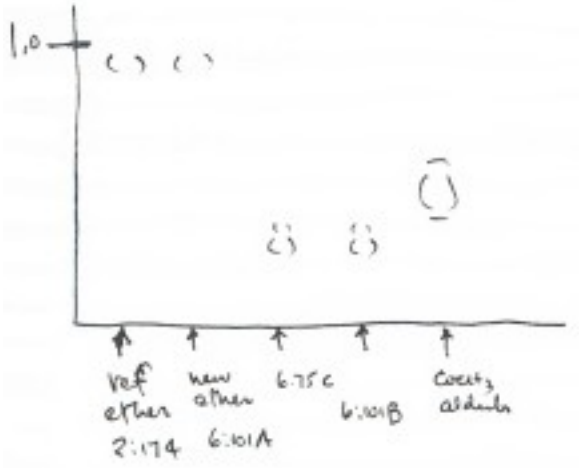
Attempt. Me_2SO_4



TLC tidy-up & IR standard taking!

rf.

1:2 hexane CH_2Cl_2 on Silica



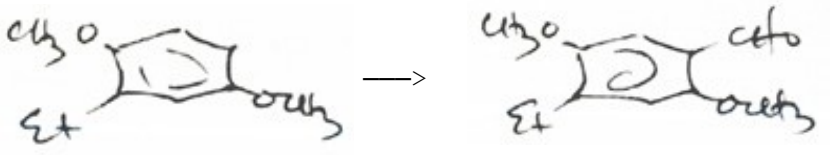
combine phenols!

6.75 C	24.8g
6:101B	60.2g.
	85 g.

Δ 85 g recovered. mixed phenols on S.B. -add
+ 100 ml 25% NaOH - ~~sl~~ becomes cloudy, then clear.
+ 71 g Me_2SO_4 - over an hour - finally no longer basic -
+ 40 ml 25% NaOH basic
+ 20 g Me_2SO_4 - still basic. total heating ~ 3 hrs.

Into 2 L H_2O - add additional base -> deep blue pH paper - extract 3 x 100ml hexane - wash [with] dil NH_4OH - flash -> 80.0 g amber, fluid oil. all, next page

Aqueous - H^+, xtrt [with] CH_2Cl_2 - flash ->

1/6/~~89~~90, 

See page 76

All of p 105 80.0g
All of 6:101A. now 20.0g -> 100g

100g ether.
into 400 ml CH_2Cl_2 ∇ 0° under He. add
~~145 ml~~ $SuCl_4$.
used 70 ml (+ more, below) · (why 2 x xs on 76?)

add 55 ml Cl_2CHOCH_3 over 1/2 hr - gas out the lab [with] HCl. -get two fans. Color to deep blue or green. * Stir to RT. Stand outside ON.

last 7 ml [with]
no HCl ↑, so
add 30 ml 1M $SuCl_4$ in CH_2Cl_2 - no more HCl.

To RT- overnight - add to 4 L. H_2O. Separate CH_2Cl_2-
extract aq. [with] 3 x 100ml CH_2Cl_2
→ 1 h. CH_2Cl_2! wash [with] H_2O 1x
(not enough - there was HCl in vac distil. next time [with] NaOH)

1000ml
126.5g.

1.3
120° Start
Solids

0.5
135° slow?

0.8mm
blush 70°

0.8 powdery 0.4* first
130° 135 s?alter

1.0mm no
80°

pale yellow stop
solids + liz

1.2mm back
95° ????

1.5mm 0.7
100° 90
bla?

1.0 still-
130 oil dil
hot

0.8
100 as

0.6
130° still

yellow [with]
sli.arid gr.

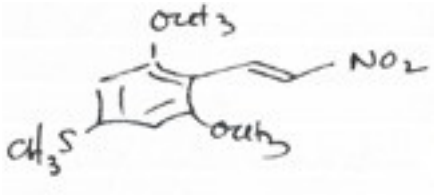
0.5 still
130°

76.88
+rec.
78.20

flash -> 126.5g black oil.
distill at KR.
see track record
final best value
130-140°/.05 mm

into beaker - immediate xtals. 79.2g.
rextal. a bit from MeOH 45-46°
and then, that, from hexane 47-48°
save MeOH reference as 6:106
rest to NS p 108

MB-VI-100

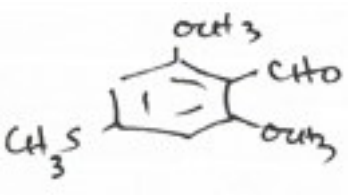


		theo	found
C 11 = 51.75062	C	51.75	51.59
H 13 = 5.133147	H	5.13	5.11
N 1 = 5.487265			
O 4 = 25.07032			
S 1 = 12.55866			

mp 157-158.5

MW IS 255.282

MB-VI-96

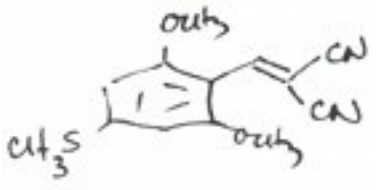


		theo	found
			55.45
c 10 = 56.58262	C	56.58	55.89
H 13 = 5.698779	H	5.70	5.62
O 3 = 22.6142			5.62
S 1 = 15.1044			

mp 86-87°

MW IS 212.256

ATS 6:104

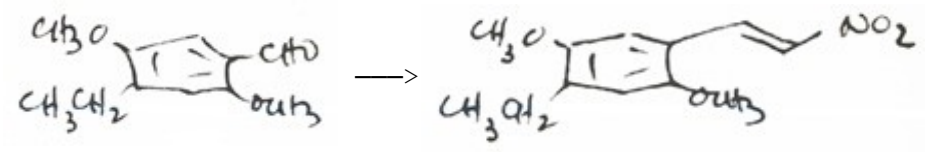


		theo	found
c 13 = 59.98033	C	59.98	59.66
H 12 = 4.64691	H	4.65	4.63
N 2 = 10.76288			
O 2 = 12.29341			
S 1 = 12.31646			

mp · 144-145°

MW IS 260.302

Jan 14, 1990



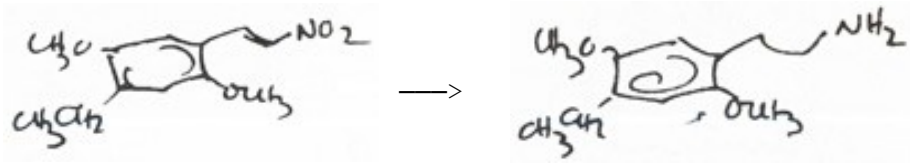
Repeat ·

[See 6:78](#) 77 g distilled aldehyde [6:106](#). into:
250 g CH_3NO_2 - Δ to dissolve - add
13.6g Ammonium acetate.
Δ SB. in 1 L. RB. 24/40.
1/2 hr. TLC says almost all to NS.
194->237 1 hr. off.
77->94 strip CH_2NO_2 on R.E. - spnt. xtals
theo Grind under 100 ml RT. MeOH.
81.6=87% filter - wash lightly [with] MeOH - air dry.

ML (108A) (87%Y) scrape out more. 81.48g
81.64 (final) <— yellow powder.
Strip to residue - red oil - add MeOH - no xtals - strip again.
+20g No_2CH_3
+ 1g NH_4oAc
} back on SB. 6:10PM
on SB. 1hr. gf - strip.

Jan 14, 1990

Attempt:



Into. 100 ml THF. absolutely anhydrous. add.
30.4 (actually 32ml) $(CH_3)_3SiCl$. = 26 g
no reaction.
add.
4.6 g Ma B H_4. - no Rx.
Keep at reflux. 2 hrs. then add,

13.4 g. NS· as a solid - no discoloration-
~~keep at reflux~~ keep at reflux. 11PM overnight

108A added as solid.
Keep at reflux overnight-

purple -> lighter -> bright yellow.
reflux. ON·

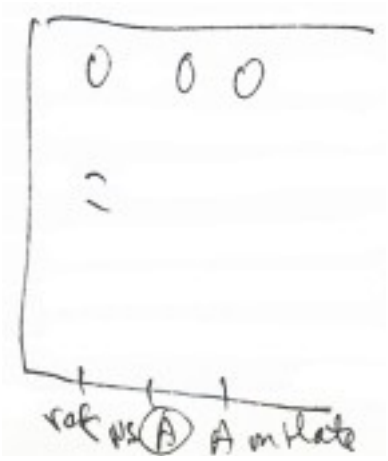
Next day - rubber septum dissolved - dropped in flask - color to deep brown -black. Reflux 2 more days - off - stands RT 3 days. [with] good stirring - add - MeOH 10 ml -> vigorous foaming + 10 ml- OUTSIDE- fumes - then quiet - + 20 MeOH - nothing more- strip on RE to smudge. - into water 300 mL. dark- with chunky at the top. acidify - ~~wash~~ extract [with] CH_2Cl_2 3 x 100

to dryness ->

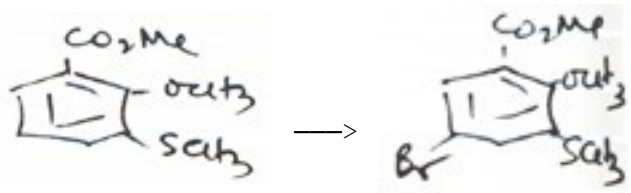
13.45g dark (A) xtals

press some on plate + MeOH
recovered NS by TLC. use again

OH-
xtrt-CH_2Cl_2 3 x 75ml
flash -> smudge.

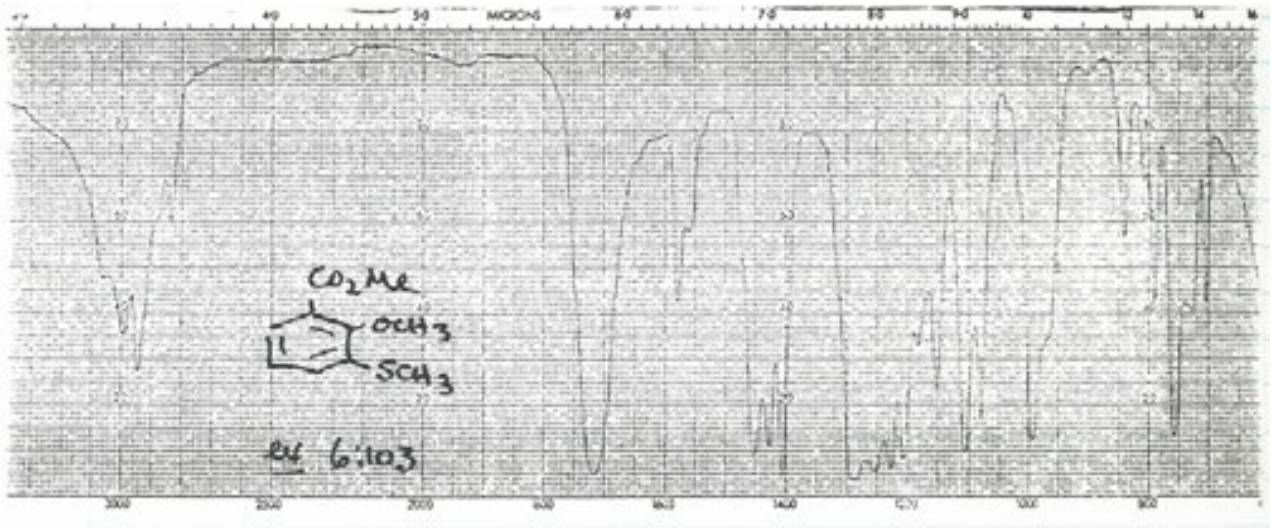


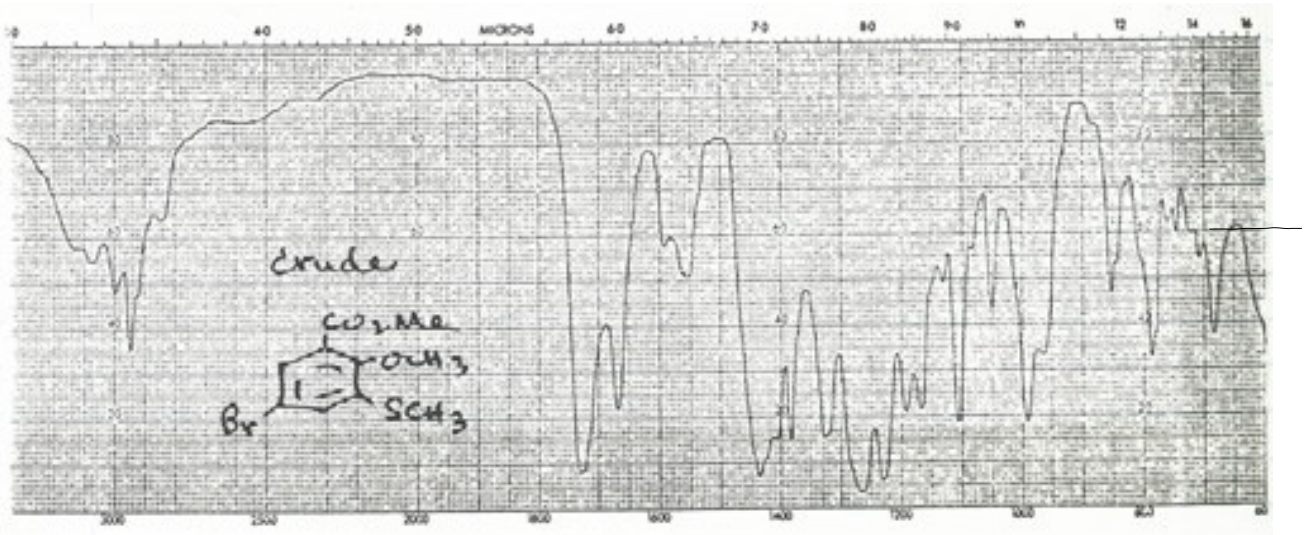
January 19, 1990 ·
Attempt:

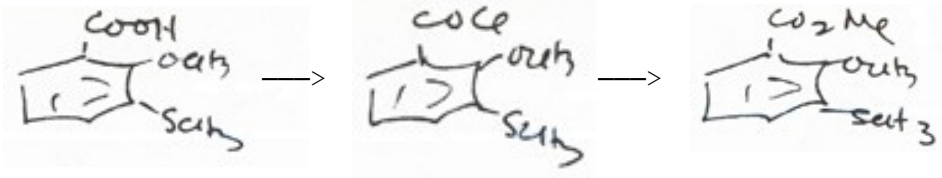


0.29 g ester (MW-212) theo 0.22g Br_2 (MW160)

Brominate [with] 30% xs - in HOAc - Δ SB ~ 2 hrs - add water, sep funnel [with] CH_2Cl_2 & dithionite - flash CH_2Cl_2 ⟶ oil that has 2 faster TLC spots.





Repeat: 

[see 103](#)
1/26/90

2.0g (remaining [6:85](#), minus trace reference).
add 15 ml $SOCl_2$ - S.B. ~ 6 hrs (replace boiled out $SOCl_2$ - strip to dryness - KR 0.2mm - 110-125°

15 ml
6 hrs
125°

—> 2.06 g COCl.

add to 5 ml dry MeOH- let stand a week.
strip —> yellowish oil.

2.06 g
KR
0.2mm

KR 0.15mm 95-100°

—> 1.78 g white oil.
no residue!
([See 103](#))

GCMS
this ester

2 major peaks. 6:111
212 - starting material
242 - by product.
284 trace .

[See page 116](#)

————> GCMS of this crude [6:110](#)

4 major products

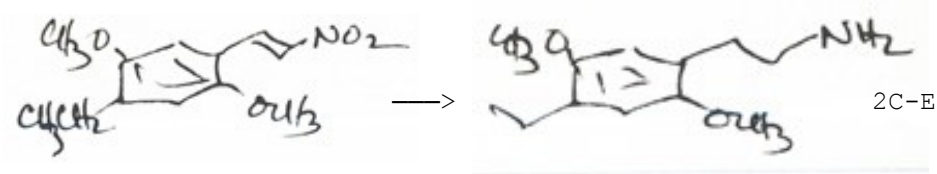
[See page 114-115](#)

290/292 correct product - 2 peaks, ∴ isomers
211 starting material -!
276/278 free bromo phenol.
trace bromo, methyl thio phenol.
starting material
290-/292 -1 product isomer .

NOT SAME AS STARTING MATERIAL

Attempt:

(again)
1/28/90



2C-E

Into a 2L. RB [with] reflux, adding funnel-stirrer and under He, heating mantle.

1 L. anh. either. - then
13.5 g of the Aldrich pellets of LAH. - Δ to near reflux. add.
~~15~~ 13.45 g recovered NS from page 109.
Δ at stirred reflux 24 hrs. goes very creamy-let cool ON- add (23g H_2SO_4 to 460ml = 5% H_2SO_4)
initially extremely violent.
it takes ~ 1/2 day to get maybe 15 ml of the H_2SO_4 in there - until the vigor is done and the exotherm is done.
Then add rest. It looks as if the lower aq is still basic - 2 phases - quite a bit of fine white solids in aq., ether is yellowish (pale)

(should have added more H_2SO_4 -> clear aq, but

filter as best possible [with] big buchner & paper
wash [with] 2 x 25ml ether

ether + cloudy aq.
separate aq -> fine white solids
wash ether [with] aq. (Sulfate & solids)
ether xtrt [with] 2 x 200ml 10% HCl

ether
flash -> small amt foul smelling oil

HCl
make basic [with] 25% NaOH
xtrt 2 x 75ml CH_2Cl_2

~1g - some xtals.

add 200ml 5%
200ml 5%
100ml 10%
10g more Σ ~60g H_2SO_4 - finally all
in solu- except for a scum on top. -
residual ether?

extract 2 x 200 ml ether. → ether

aq. add. 25% NaOH
100
100
100
100
finally >9 pH.

xtract. 3 x 100ml CH_2Cl_2 86.5
flash -> 8.27g. 1M=30g/L
0.5mm.
110-130°C. 5.2g. @ 209 HCl @ 12N-> 37% = 37g/L
24.9 MM

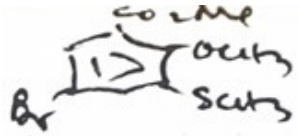
2.08mL theo 36.5MW -> .91 ~~37M~~ ~~37%~~ ~~3~~

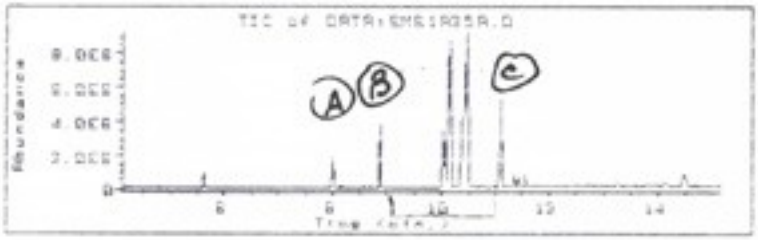
2.0 not enough.
2.1 - too much.

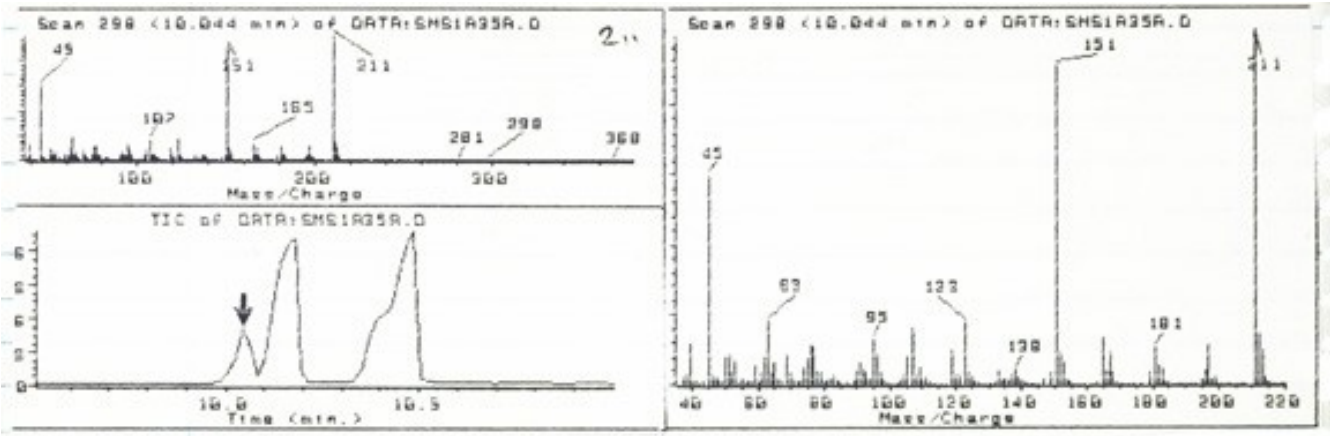
12M = 1L
1M = 83 ml
25mM = 2.08

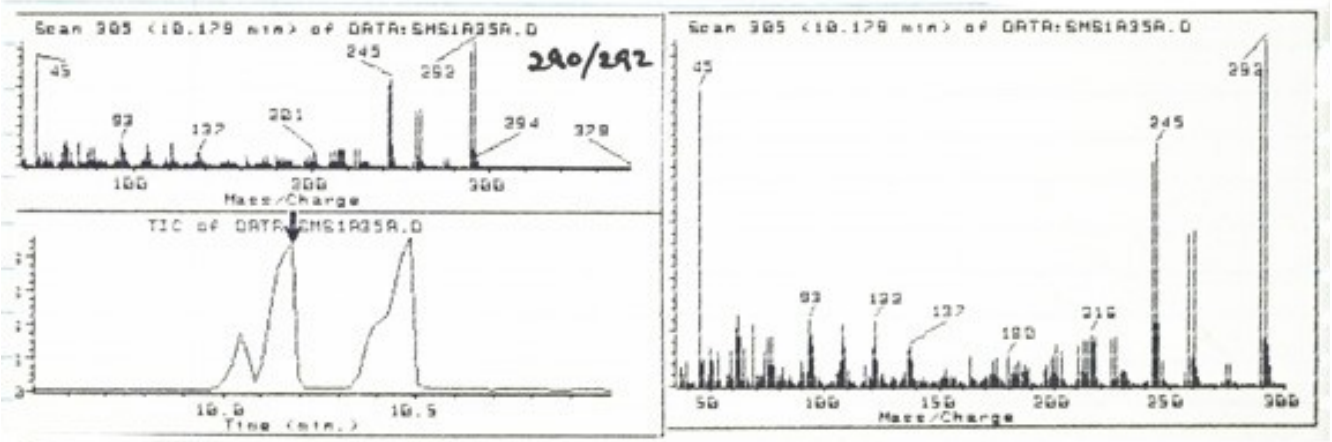
HCl salt. 6.0g white solids.
2C-E - HCl. +much ether
filter
ether wash -
air dry
5.71g
little 3.70g 2 to MS

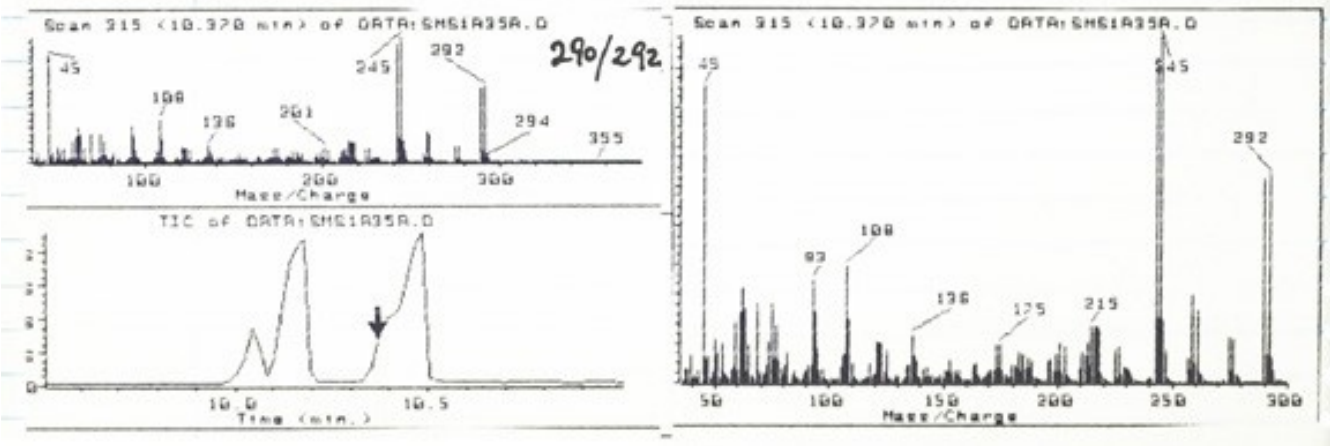
GCMS from page 110 - crude

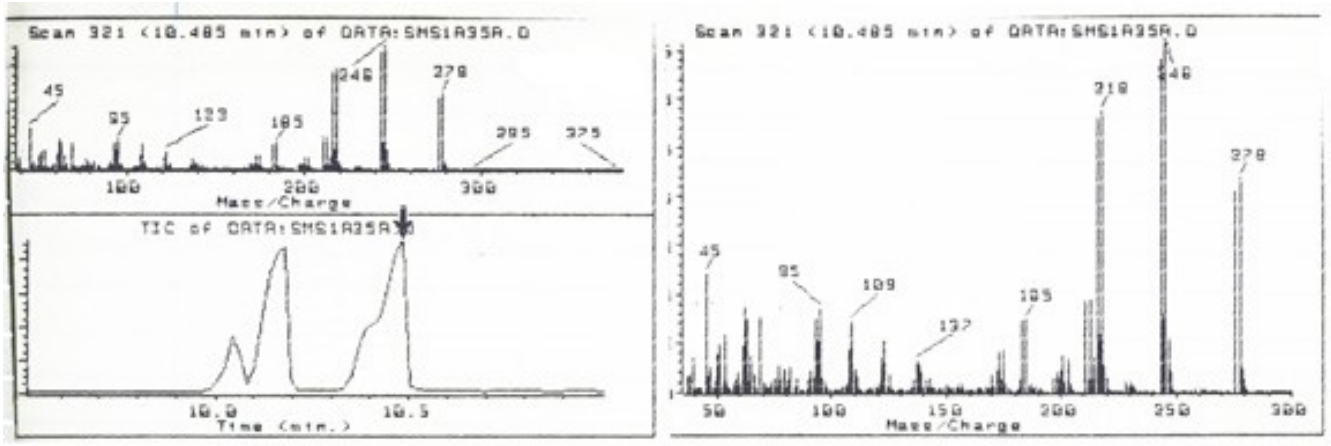




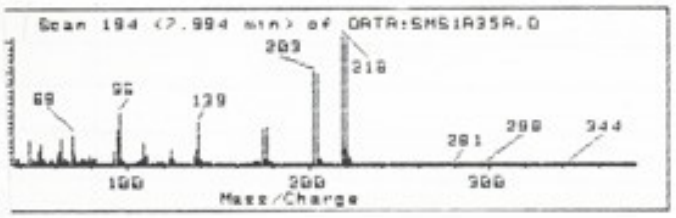


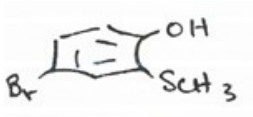




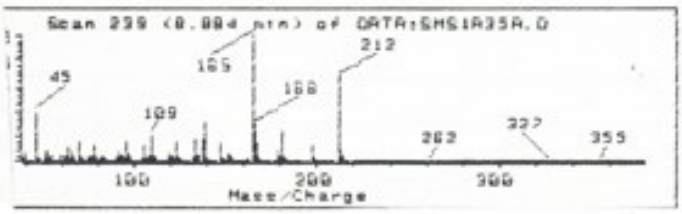


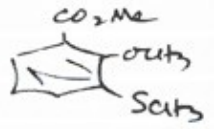
A





B

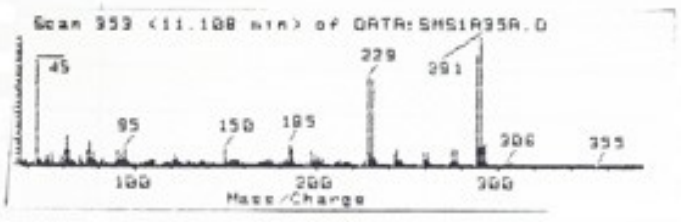


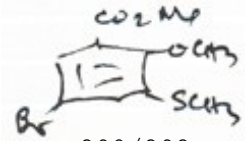


9-minute peak

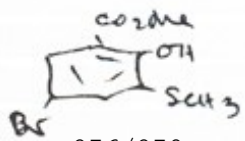
See page 116

C



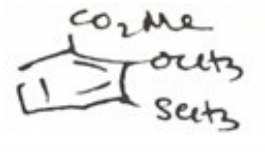


290/292

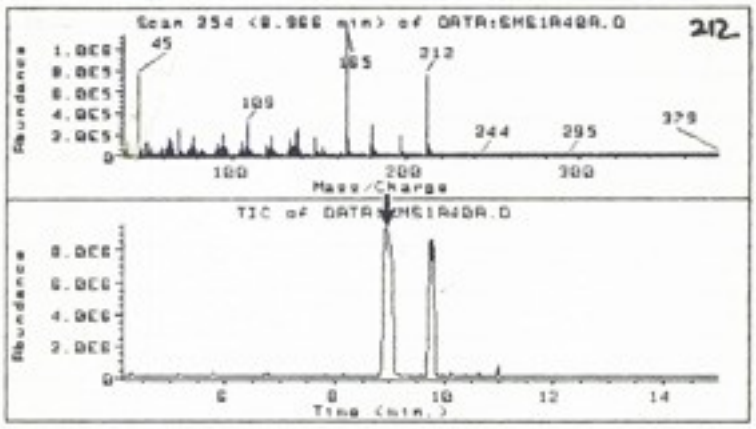


276/278

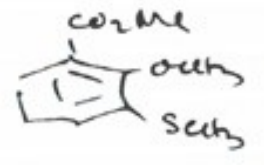
Crude



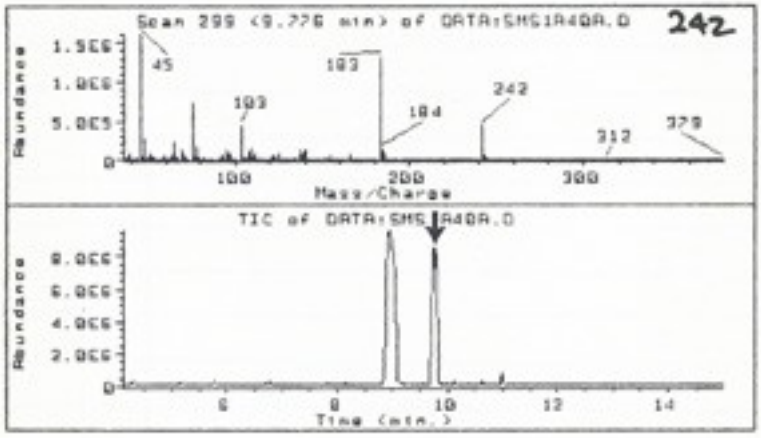
p 111

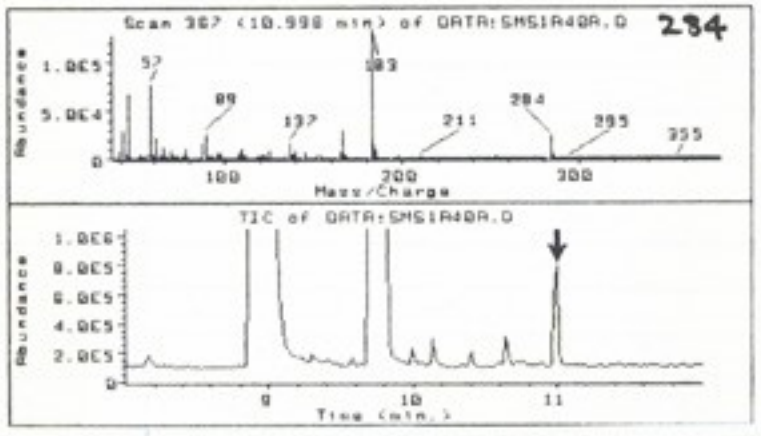


valid

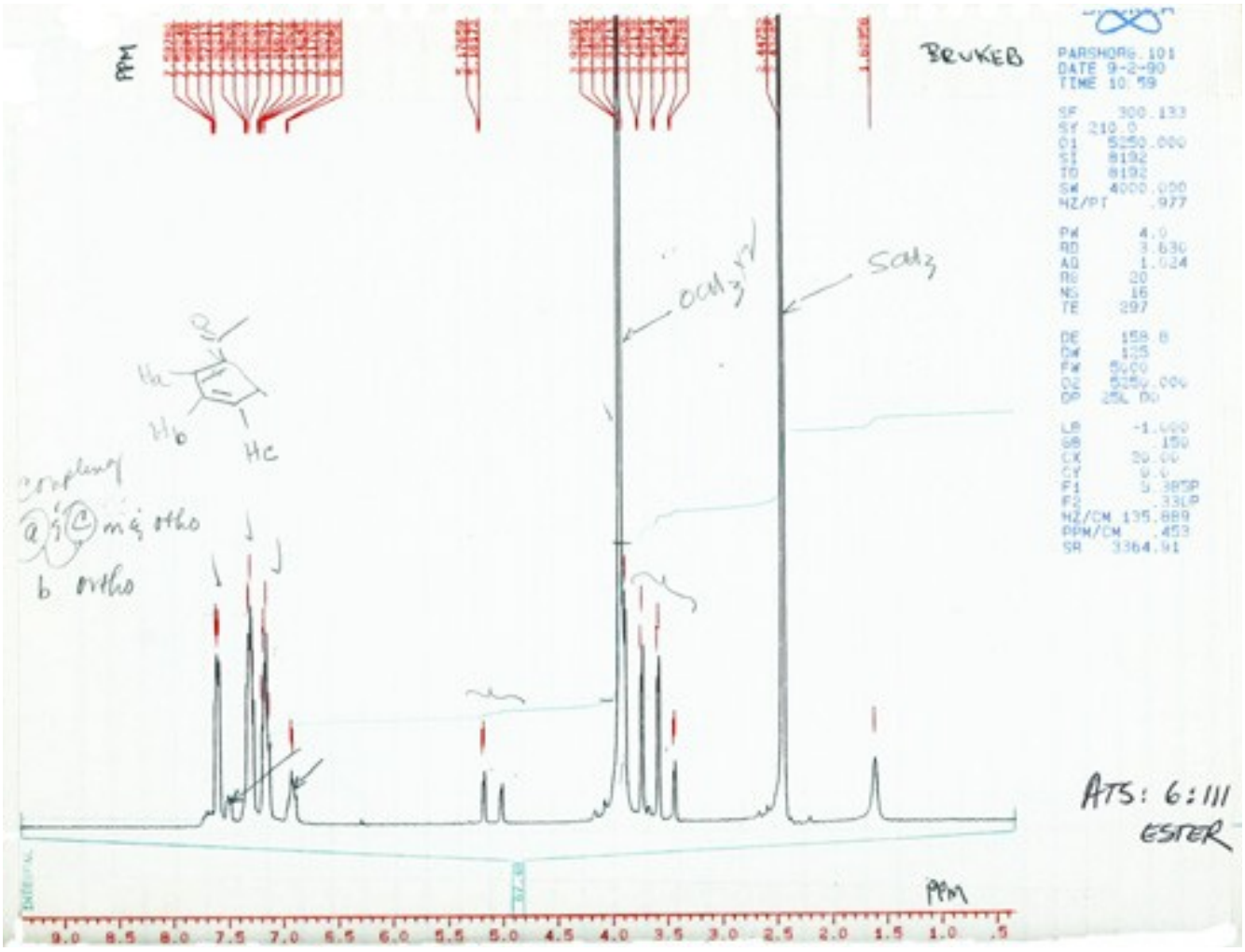


nine-minute peak-
See page 115





[Editor's Note: The following was originally vertical on the page]



Methamphetamine assay-

2/12/90 Received from Alexander M. Carr, Pub. Def. McNeely
two samples of meth. for analysis:

8.0g sample 4-089-2150 GB 2/7/90 Removed from 5A
light salmon - beige colored.
on cover - YE 15000-89 8 gms AGW

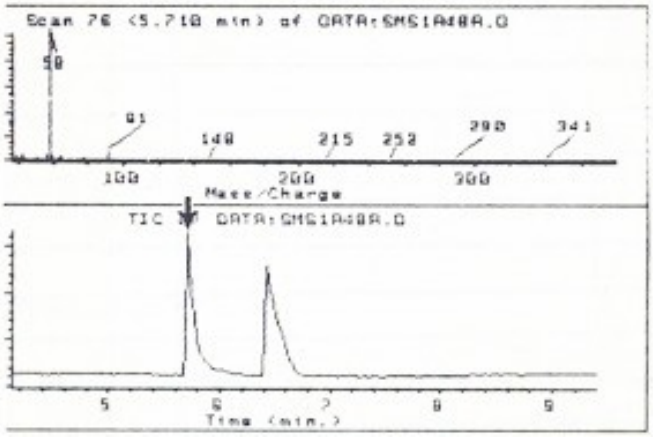
3.7g sample 4-089-2150 GB 2/17/90 Removed from 4A
pale ivory color
on cover YE·14987-89 3.7gms AGW

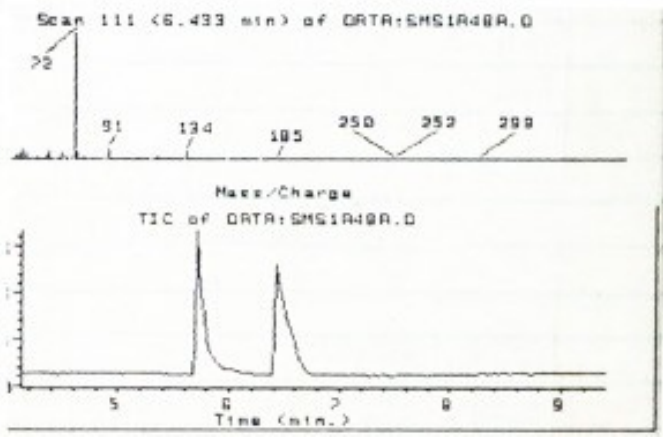
make up 2mg/ml solution, in water, of
A ⟶ 8.0g material (9.9 mg/4.95 H_2O)
B ⟶ 3.7g material (8.1 mg/4.05 ml H_2O)
C ⟶ α-Et N-Me PEA. (4.5 mg/2.25 ml H_2O)
D ⟶ ref.meth.HCl (dl,ATS) (5.2 mg/2.60 ml H_2O).

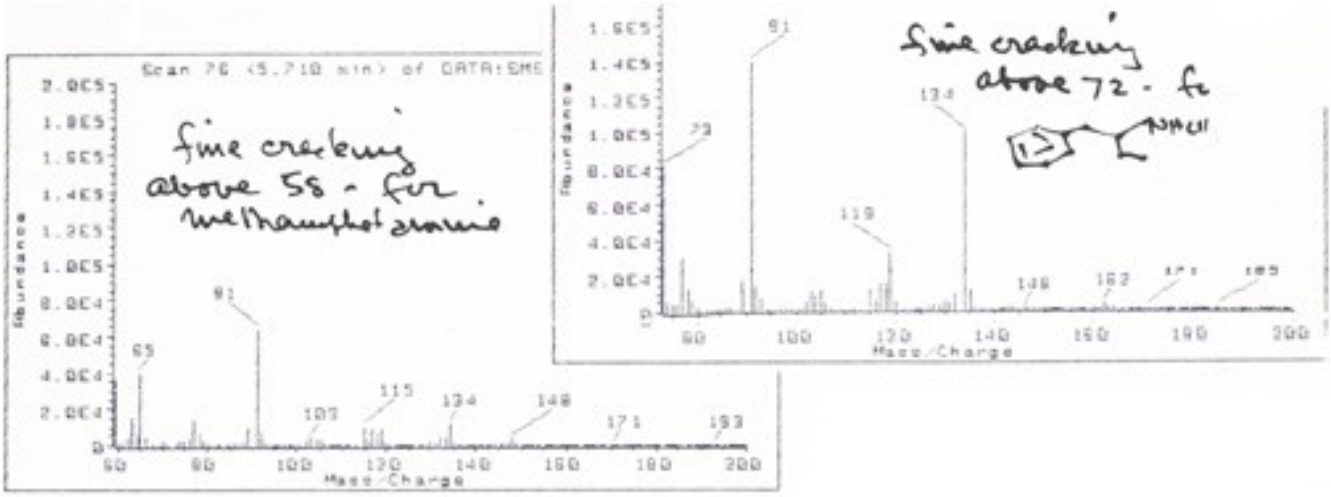
toluene
"std" ← add 1/2 ml C, 1/2 ml D, 3 drops 8 N NaOH, 3ml 90/10 BuOH
"8.0" ← add 1/2 ml A, 1/2 ml C, " " " "
"3.7" ← add 1/2 ml B, 1/2 ml C, " " " "

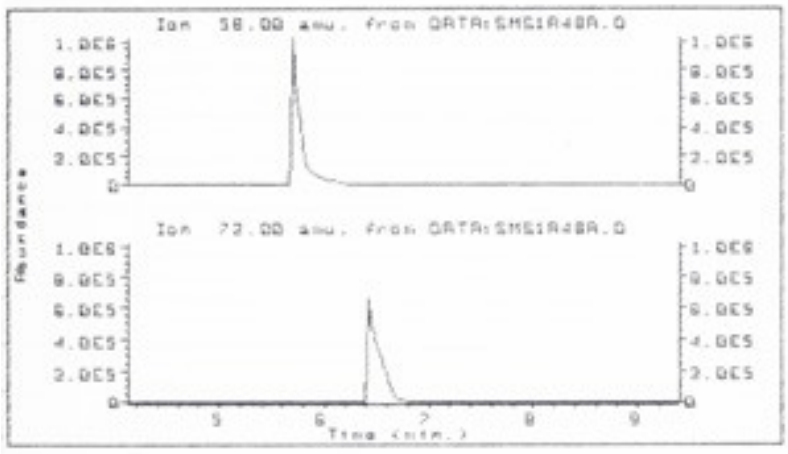
shake, spin, remove org for GCMS
5890 GC } HP.
5970 MSD }

12 Meter column 0.2mm i.d. cross - linked
5% phenyl methyl Silicone









SIM 58 (ref meth)

SIM 72 (internal Sta)

TIC of DATA:SMS1A48A.D
STANDARD: METHAMPHETAMINE PLUS ALPHAETHYL

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.716	PB	0.127	79731292	5.478	6.237
2	6.435	BV	0.130	90965117	6.349	6.902

Ion 58:00 amu. from DATA:SMS1A48A.D
STANDARD: METHAMPHETAMINE PLUS ALPHAETHYL

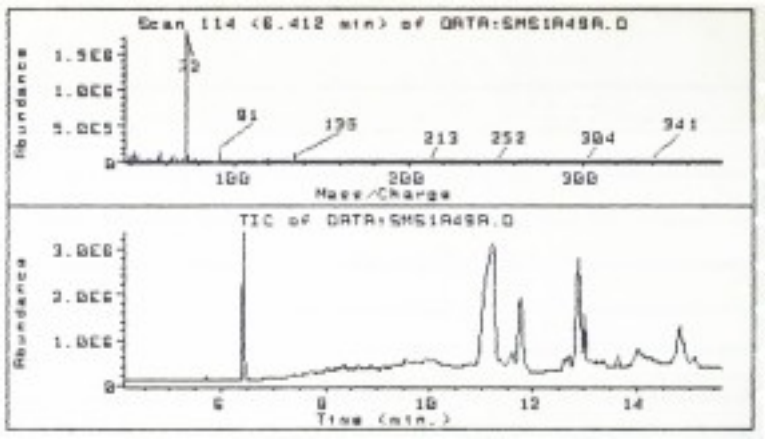
Peak#	Ret Time	Type	Width	Area	Start Time	End Time	integ of meth SIM
1	5.716	BB	0.083	53411399	5.654	6.278	

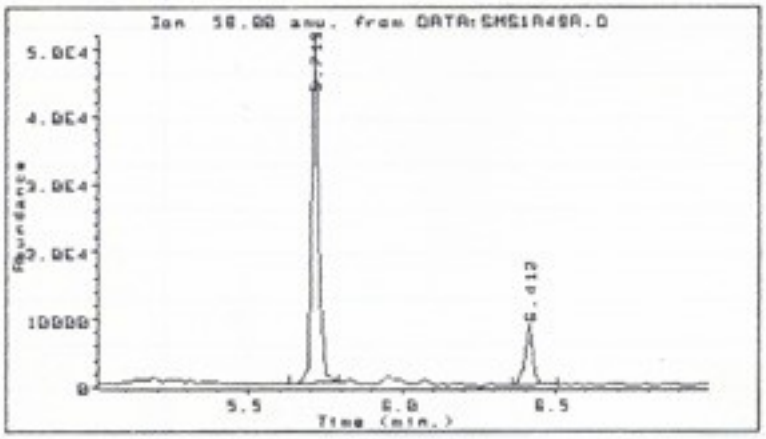
Ion 72:00 amu. from DATA:SMS1A48A.D
STANDARD: METHAMPHETAMINE PLUS ALPHAETHYL

Peak#	Ret Time	Type	Width	Area	Start Time	End Time	integ of I.S. SIM
1	6.435	BB	0.129	49686155	6.360	6.861	

$$\frac{58.14}{49.69} = 100\% \text{ (equal weights, as HCl's).}$$

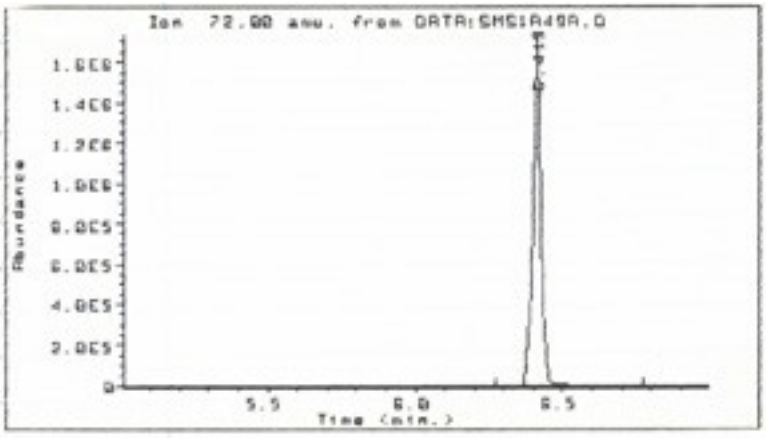
8.0g sample.





Ion 58.00 amu. from DATA:SMS1A49A.D
SAMPLE FROM 8.0G SEIZURE

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.713	BV	0.027	822779	5.634	5.795
2	6.412	BV	0.044	162382	6.357	6.505



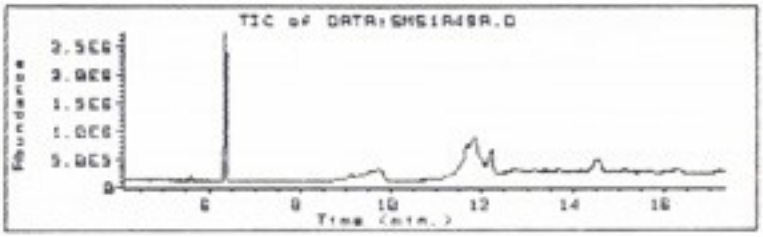
31.72M ——> "34.09"
for 100%
meth.

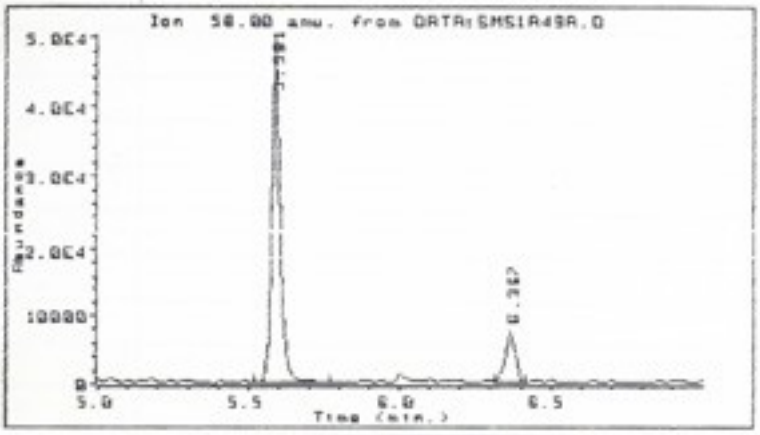
0.823
=
2.4%

Ion 72.00 amu. from DATA:SMS1A49A.D
SAMPLE FROM 8.0G SEIZURE

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	6.413	PV	0.072	31716730	6.271	6.771

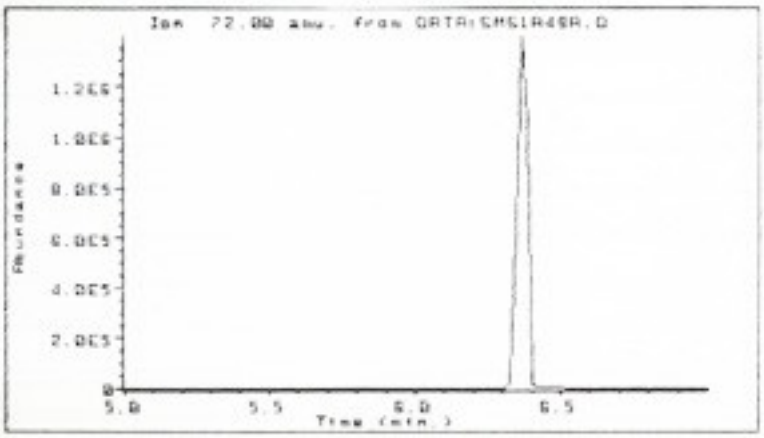
reinject 8.0g sample





Ion 58.00 amu. from DATA:SMS1A49A.D
SAMPLE FROM 8.0 G SEIZURE

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.591	BB	0.033	881699	5.517	5.767
2	6.367	VH	0.041	181512	6.316	6.412



31.45 M –> "40.25"
for 100%

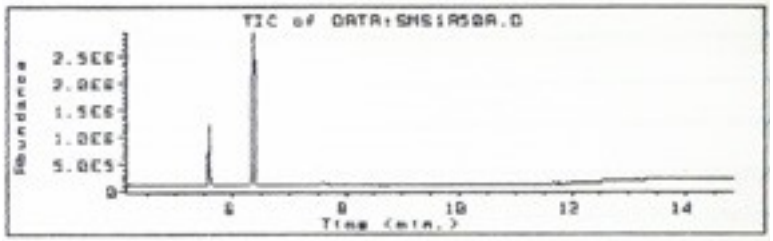
0.882
=
2.2%

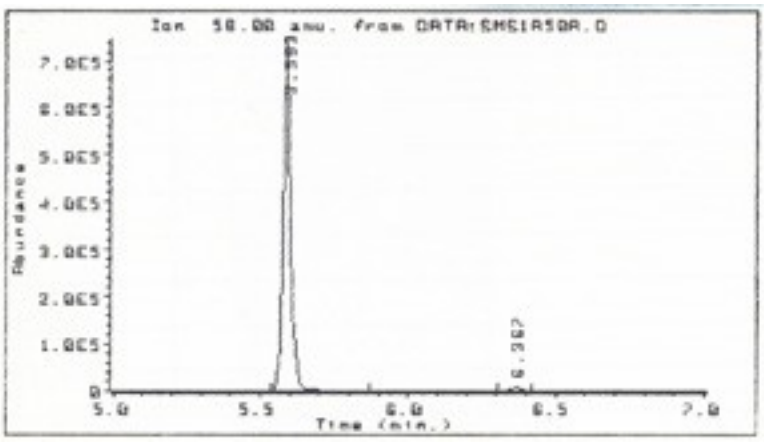
Ion 72.00 amu. from DATA:SMS1A49A.D
SAMPLE FROM 8.0G SEIZURE

2.2%

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	6.368	PV	0.045	37454003	6.261	6.641

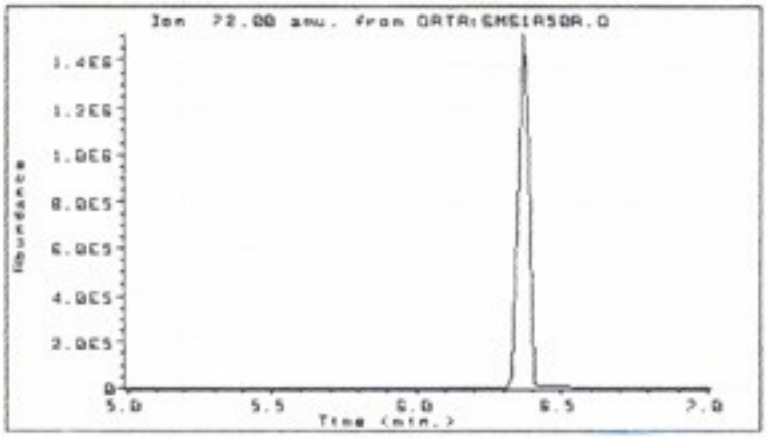
3.7g sample





Ion 58.00 amu. from DATA:SMS1A50A.D
SAMPLE FROM 3.7 G SEIZURE

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.593	BV	0.051	12176081	5.535	5.871
2	6.367	PV	0.046	192820	6.303	6.422



39.09 M ⟶ "42.02"
for 100%

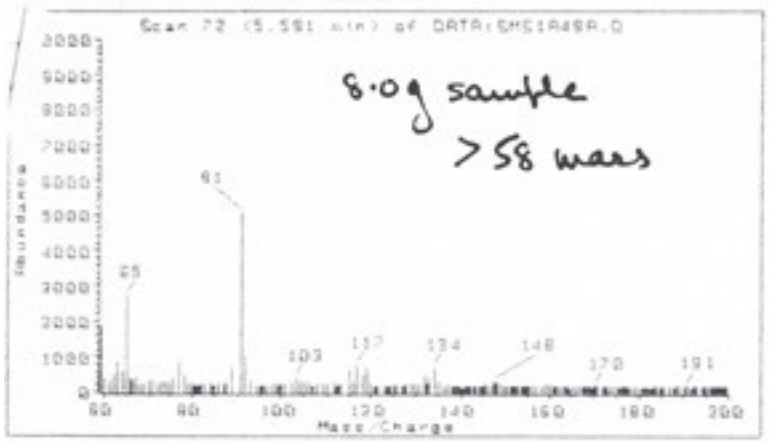
12.17
=
29%

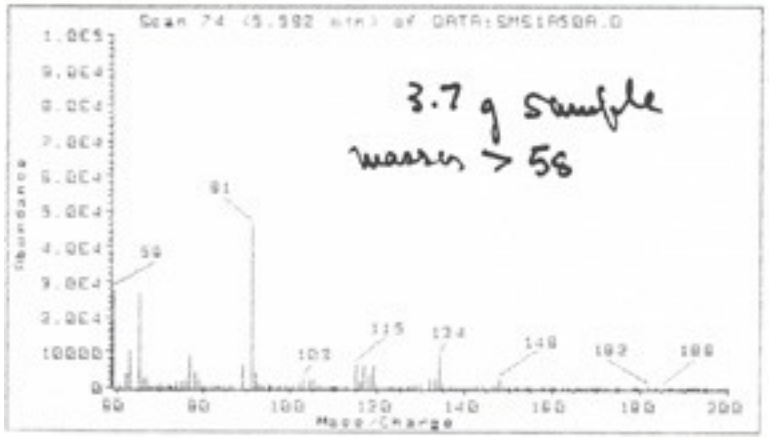
Ion 72.00 amu. from DATA:SMS1A50A.D
SAMPLE FROM 3.7 G SEIZURE

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	6.368	BBA	0.045	39094408	6.295	6.966

if the original wt. of 8.0g sample was 127.5g
there is 2.9g meth. present

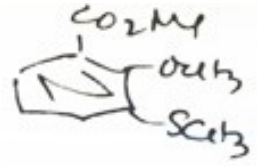
if the original wt of the 3.7g sample was 30.5g
there was 8.8g meth present.





mass frequents
>58 mass.

both are
Methamphetamine

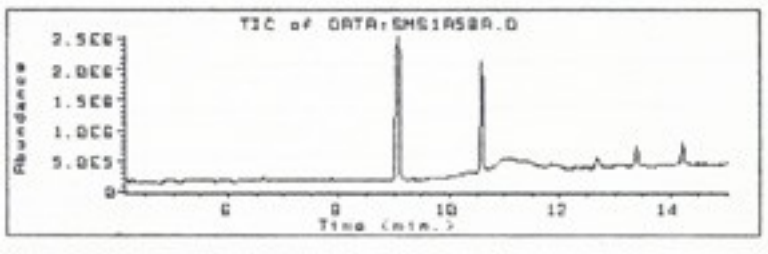
2/16/90 Purification of impure 

1.66g 6:111 - in ~5 ml CH_2Cl_2 - onto packed column 70-230 mesh silica gel (0.63-0.200mm)

Collect many fractions [with] CH_2Cl_2 as solvent:

all of the earliest spot (TLC) collected until #2 breaks through - discard rest.

let evaporate -> ~ 1g clear oil. see page 128 for Bromine B

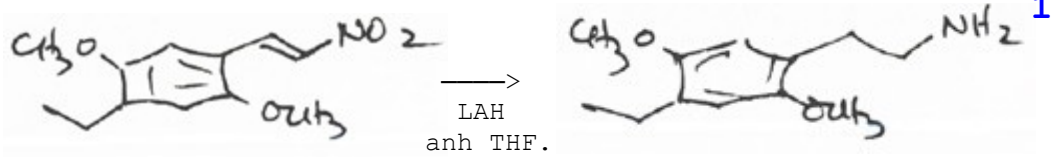


This is single - spot - chromatographically pure ester!.

9 min. peak - clearly right stuff.
(see Mass spectra - page 124)
(see earlier GC of crude 6:111 on page 116)

10.5 min peak MW 254!

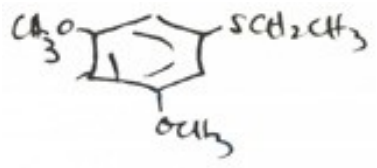
see brommation, page 128.

2/18/90. 

To a three neck flask, 300 ml, mag stirrer, He atmosphere,
add:

60 ml fresh, anhydrous THF from Na Ketyl.
add:
3 pellets LAH (just over 3g).
reflux ~ 1/2 hr -> grey suspension - much in solution
add:
3.0g nitrostyrene in 20 ml dry THF (all by syringe.)
exothermic, immediate discoloration. -
hold at reflux ON.

add ~ 13 ml IPA - Kill LAH.
add 10ml 5% NaOH, filterable-
1.3g base. filter.
wash [with] THF. _ strip.
5ml IPA distill KR. 0.3mm. 120-140°/.3mm
-> 1.3ml base. (1.3~~mg~~g base)
1.8g salt. 5ml IPA., HCl, ether.
2.38 wet HCl
1.56 salt ~~1.6~~ 1.56 g base · HCl.
dry.

March 11, 1989 Characterize, 

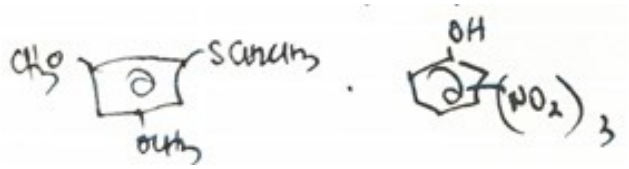
MB. VI-92 , ~ 1g. yellow oil.

MAKE PICRATE dissolve 0.3g picric acid 90% (10% H_2O)
in 1.2g anhydrous EtOH.
clear hot, xtals cold, clear hot

add 0.2g Ethythio cpd in 2 drops EtOH.
∇ - to RT - no xtals - touch [with] glass
→ xtals.
tomato-red xtals.
filter - ——> pale orange stuff on filter (orange)
deep tomato in flash.
→ onto plate.
(tomato)

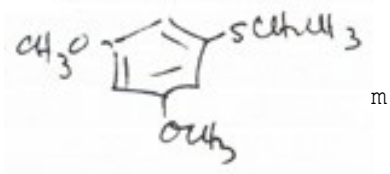
Sinter~ ~~155~~ 55
mp. ~ 60°.
hard to see-
too dark.

114° sinter.
116-117 mp.
Picrate = 122°,



[Editor's Note: A large amount of scratched out writing appears in this location]

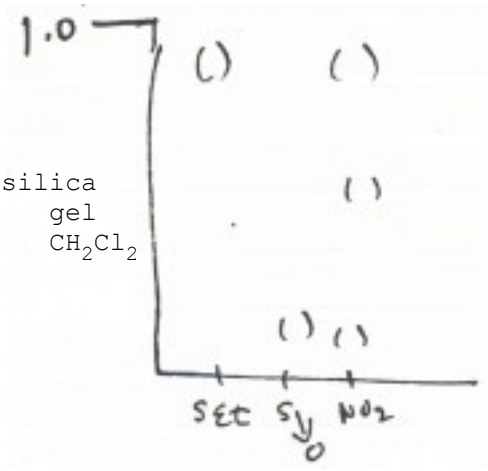
Characterize:



m.w. 208

Try to make sulfide:
0.21 g VI-92 in 0.2 g MeOH
0.25 g 35% H_2O_2 (20% xs).
2 phases - add another
0.35 g MeOH , Δ S.B. -> one phase.
stand 2 hrs - flash -> oil.
TLC - add slow.
Distill at 0.15/130-140° -> 1 large droplet white oil. CO_2 -> solid, ~ 0° melt. I cannot capture.

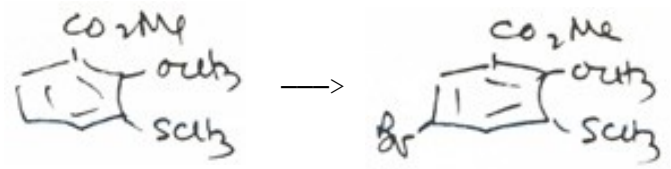
Try to make nitro.
0.21 g VI-92 add
1.0 g hexane. add.
1.0 g 70% nitric —> immediate tar. Let stir anyway. —— 2 hrs - decant hexane -> yellow oil - no xtals.



To make sulfine
0.21 VI-92 - add
——————> 1g H_2SO_4 - some amber, OK!
+ 1g dropwise 35% H_2SO_4 - spit, fume, tar . let stand stir [with] 10 ml methylene chloride.

March 16, 1990

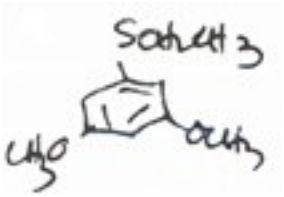
Try again:



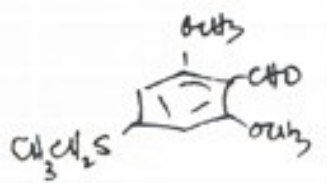
Solution of
0.39 g in 1.0g pyridine -add
0.35 g Br_2 (20 % xs). spits back -
stand an hour - does not lighten.
TLC [with] slow mover.
Δ steam bath 2 hrs. in dichlor
-> solids.

Run #2 0.68 g (rest) of 6:124. in.
27 g $CHCl_3$ - stir. add.
0.24 g Br_2 in 26 g $CHCl_3$- stir RT 3 hrs -
TLC - all gone - two slow spots.
see GCMS page 135
no bromination products

Tally on Ψ-2C-T-2

ether. 

VI-92 MB 6:126-127. sulfoxide 127.
VI-99

CHO 

$C_{11}H_{14}O_3S$

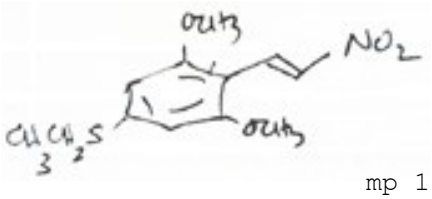
MB-VI*103 ~~mp~~
mp virgin: ~~103-106~~ 85-86°
mp 1x MeOH 85-87°
mp 2x MeOH 82-84°
off white VI-129A

.05g ICHO
.10g MN
~.2ml EtOH
1 drop Et_3N
scratch->xtal

-> ML 103-106° 6:129A
xtal MeOH -> 112-114°
canary-yellow xtal.
VI-129B

$(CN)_2$

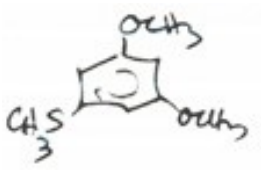
$C_{14}H_{14}N_2O_2S$ 6:129B

~~CW~~
N.S. 

$C_{12}H_{15}NO_4S$ 6:129C
33/33° MB: VI:110 ⟶ 1.80g.
6:129 C orange xtals.

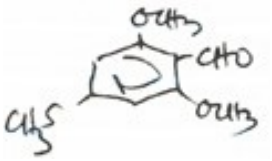
mp 118-119.5
ex MeOH mp 118-119° this is 6:129C

Tally on Ψ-2C-T

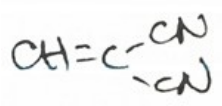
ether. 

VI-82

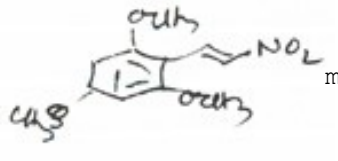
picrate: VI-84-anal ↑ -into ±m

aldehyde 

mp. 86-87°. Anal bad. 6:~~107~~ 96 ↓ VI98,97,83
anal 6:107 6:97



mp. 144-145 Anal ↑ 6:107 6:104

2C-NS 

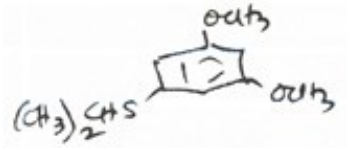
mp 157-158.5 MB-VI-100 Anal. ↑ 6:107

2C-HCl. 6:130D

VI-115. no mp, no anal.

mp-235-237°. To microanalysis.
$C_{11}H_{18}ClNO_2S$.

Tally on Ψ-2C-T-4 isopropyl

ether  VI-60,63,64,65,66,67,70,72

·picric acid. VI-86. Anal ↓

aldehyde VI-81 VI · 68,73

anil: VI-78

VI-75

2C-NS

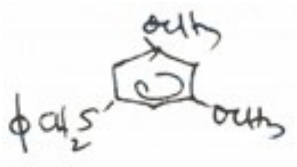
AC-NS VI-77

HCl. VI-79

VI
anil 79

4CNS 77
2CNS 75

Tally on benzyl.

ether. 

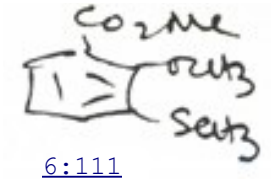
VI-80

picrate VI-85 anal ^

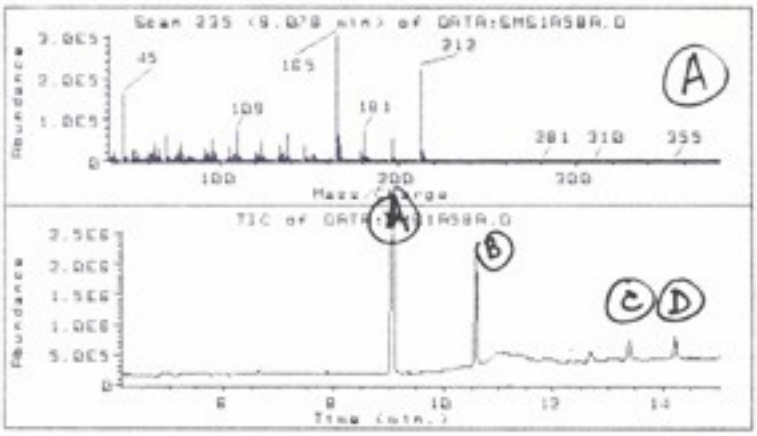
tally on Ψ t.butyl ether. VI-69.

tally on Ψ-phenyl VI-59.

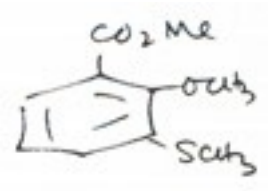
MS. from page 124 Chromatographed



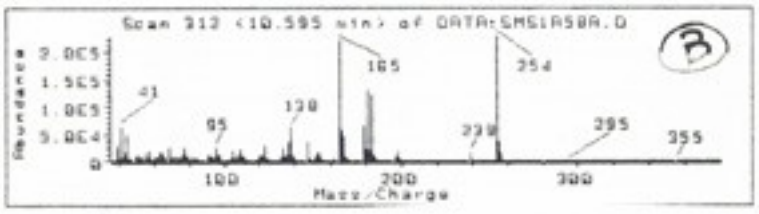
6:111



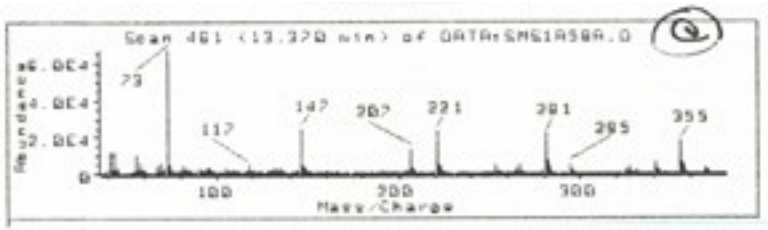
212



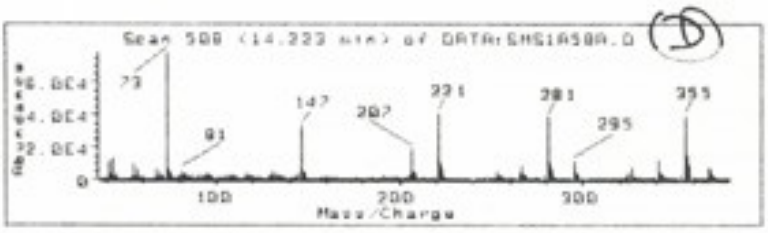
<— the major peak at 9.8min, in the crude is NOT HERE
MW 242



254

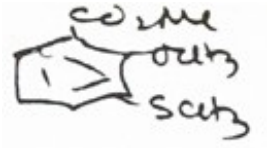


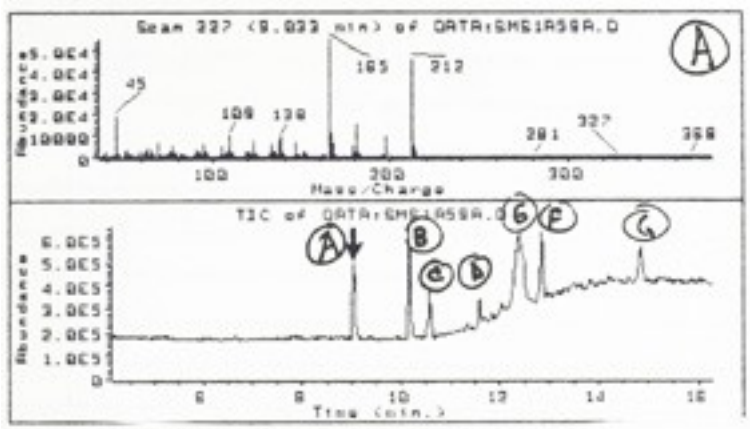
356



356

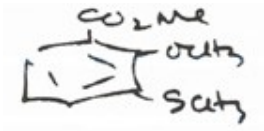
MS. for page 128 - Run #2 Bromination of

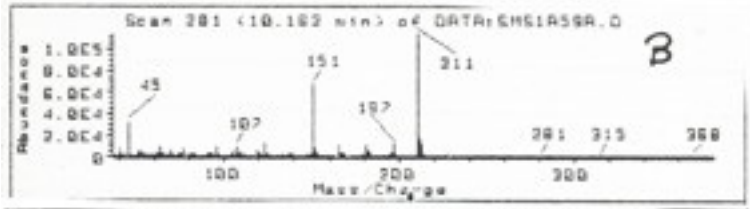




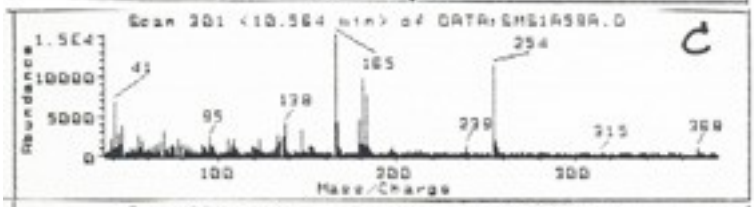
212

unreacted

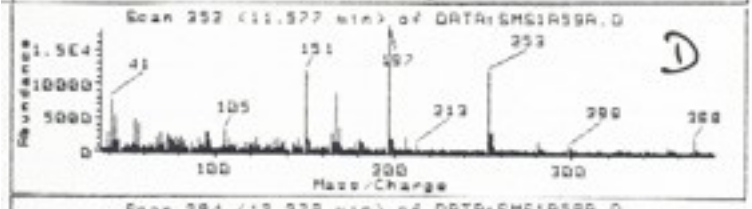




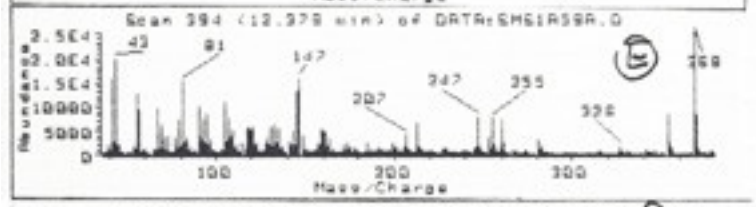
212



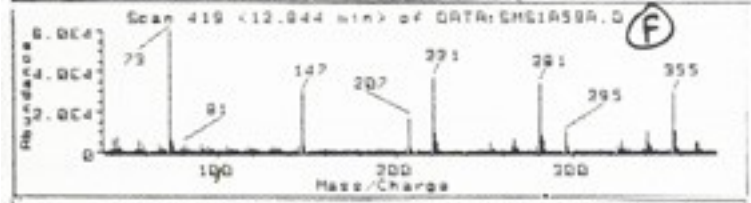
254 unreacted co-chromotographed contaminant. see other page



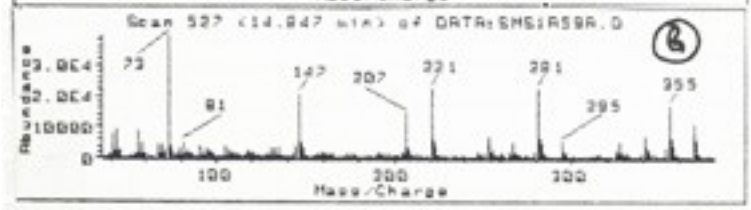
?
368?



368

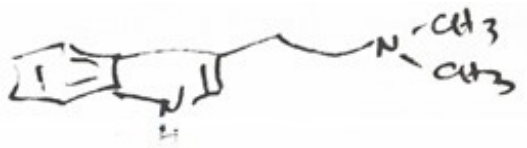


356

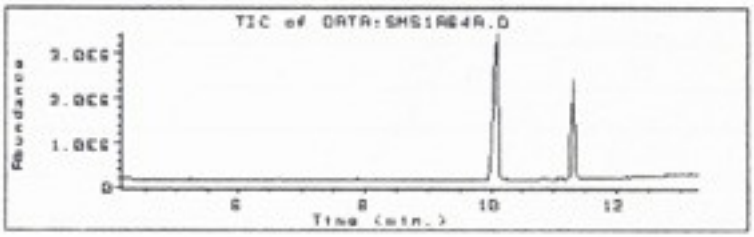


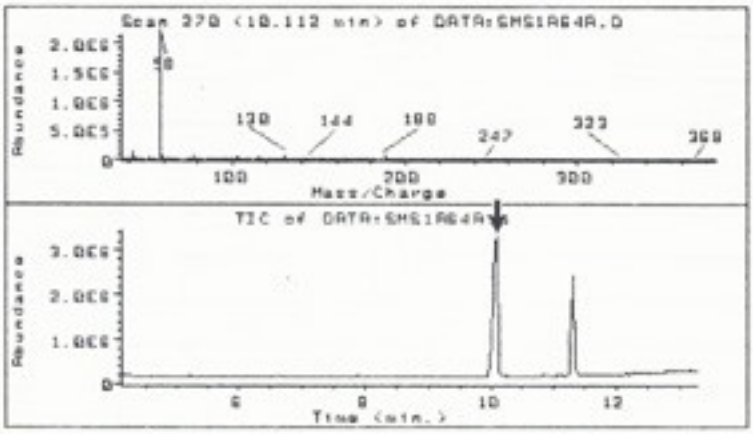
356

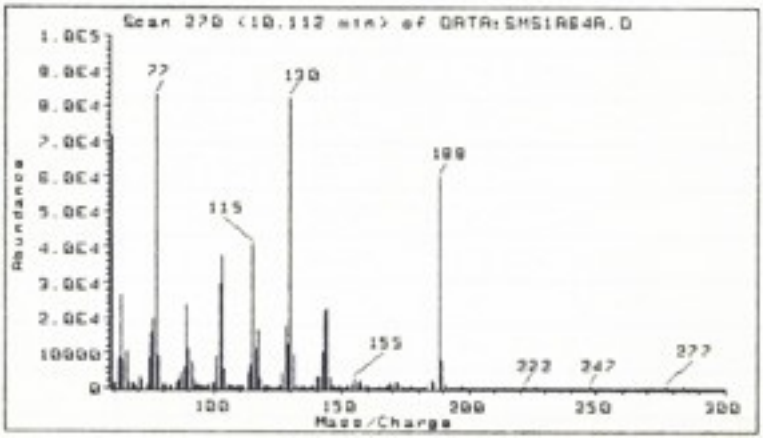
3/26/90 GCMS



underivatized

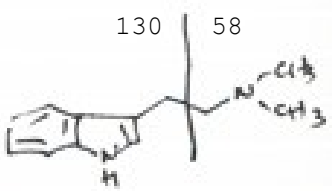


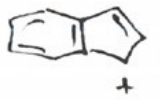




188

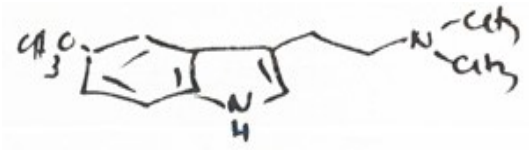
130 58



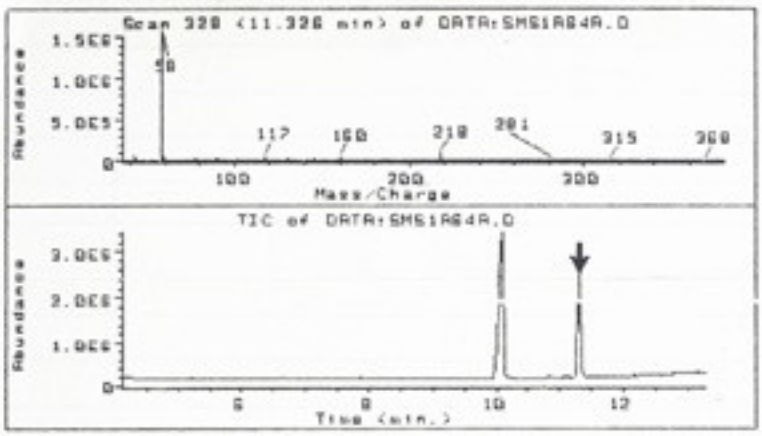


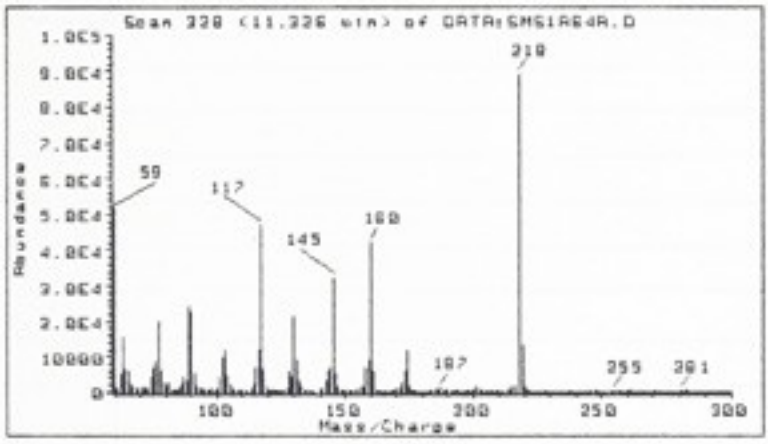
115

3/26/90 GCMS

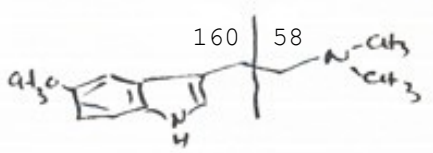


underivatized

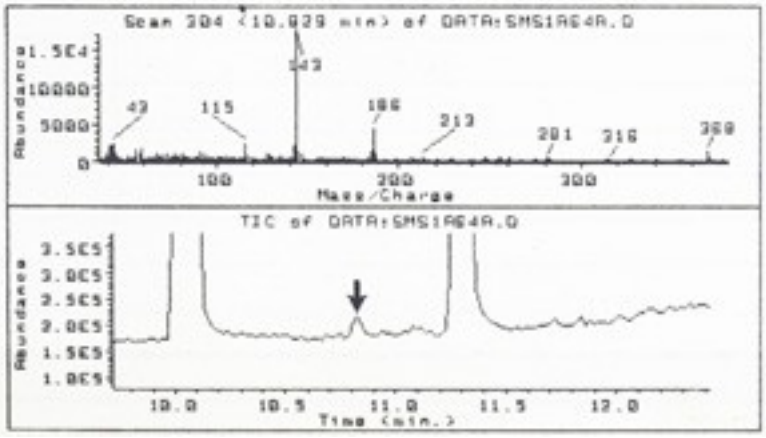




218

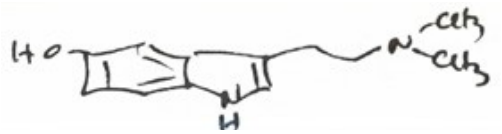


145



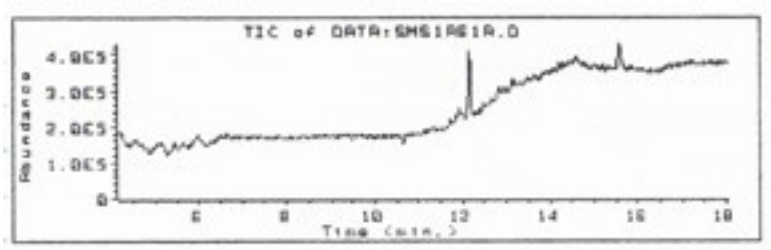
186

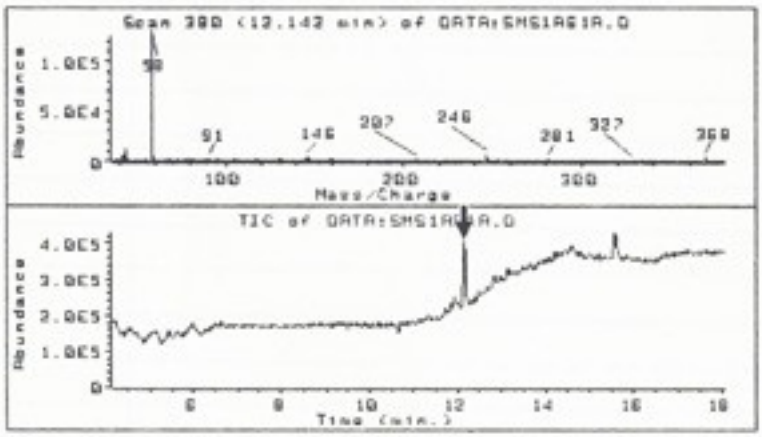
impurity in one of the two cpds.

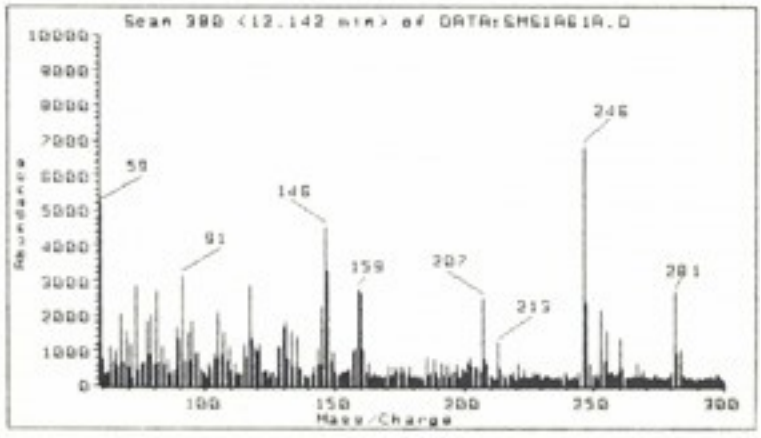
GCMS. 

3/26/90

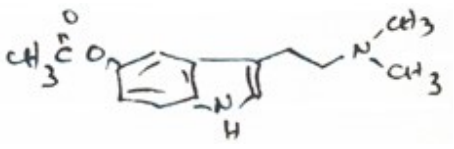
~5mg oxalate, ex Sigma +2 drops pyridine + 2 drops acetic anhydride - #Δ SB 20 min. ∇ - lots of water (2ml) then ~20mg bicarbonate (fizz) and extract [with] 1 ml 90/10 ΦCH_3 BuOH. Originally dil 1:10 but almost no spectrum - run again as is - i.e., 10x what I think it should be.







248

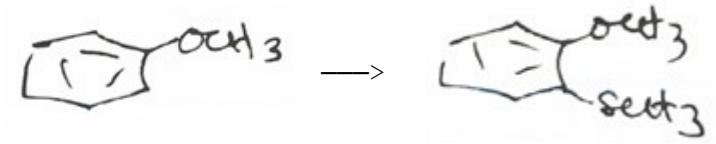


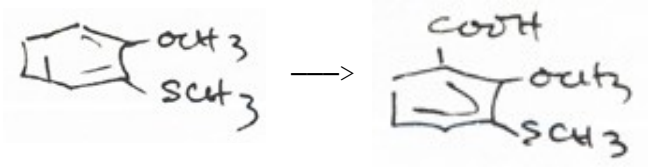
~5 mg oxalate, + 2 drops pyridine + ~5mg dimethyl-t-butyl silyl chloride - SB 10 min, ∇, 2 ml H_2O - shake [with] 1 ml ΦCH_3, dilute 1:10 ΦCH_3.

June.

April ~10, 1990

Repeat:



Repeat: 

see page 85.

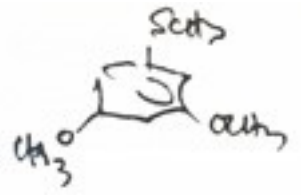
10.0 g ether from page 140 - dissolved in
200 ml pet-ether 35-60° - add
83 ml TMEDA
stir, under Argon. ∇ to 0° [with] ice.
add
27.4 ml 2.5M BuLi in hexane.

color off-white - solids form - stir 2 hrs then up to RT 1 hr. then pour all into a suspension ~ 200g CO_2 powder in 200 ml ether. GOOD STIRRING OF CO_2.

Let stand until CO_2 gone - add = volume of H_2O (~400 ml) - and stir until both phases are completely clear. Separate.

11.70
crude
wet.
9ml
MeOH
6.45g
6.17 dry.
6:141A

0.78 #2



$\xrightarrow{Br_2}$ $\xrightarrow[HNO_3]{}$?

0.12g distilled thio ether.
into.
1.0 g HOAc - add.

~~1.2~~ 0.12 g Br_2 -
decolorization—
HBr ↑ - then,
+ 0.12 g Br. (2 moles)

spont. xtals

xtals
pale cream

ML,
$+H_2O$
↓
brown
xtals

ex hexane.

save

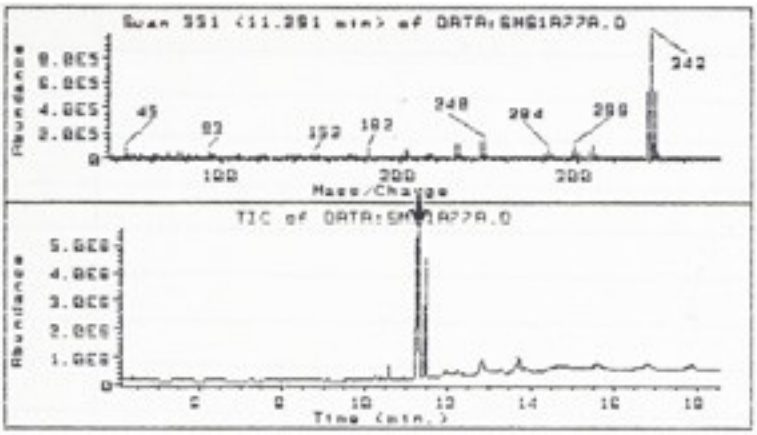
white-

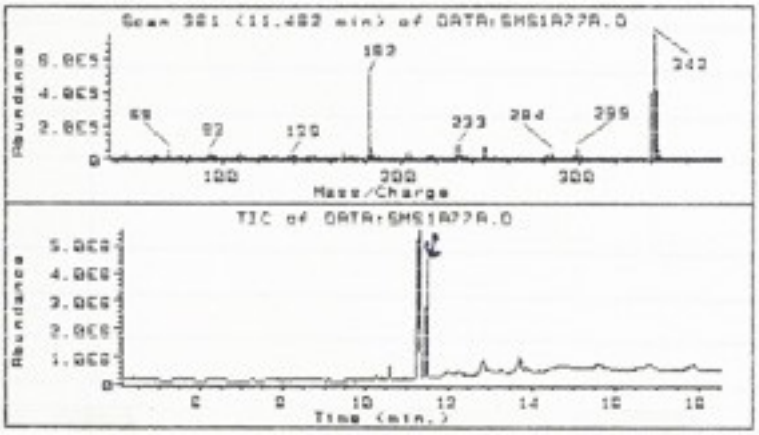
* chik the te -
stand 1 ml ??

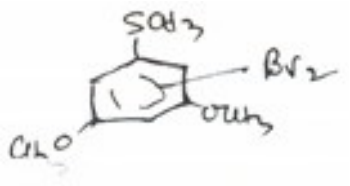
Vrotgmi

0.12g thio ether.
into.
1.0 HOAc,
add,
0.12 g 70% HNO_3 -
dark -add 3ml H_2O
junk
OUT.

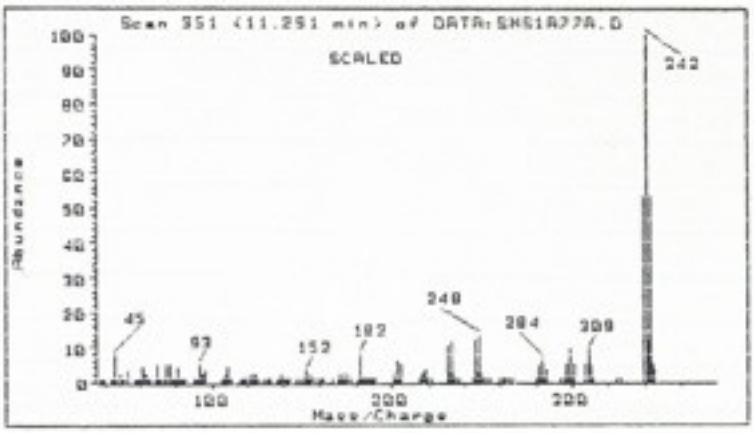
GCMS of 6:142


Scan 551 (11.281 min) of DATA:SMS1A77A.D
Abundance
8.0E5
6.0E5
4.0E5
2.0E5
0
45
83
132
182
248
284
299
342
100
200
300
Mass/Charge
TIC of DATA:SMS1A77A.D
Abundance
5.0E6
4.0E6
3.0E6
2.0E6
1.0E6
0
8
10
12
14
16
18
Time (min.)


Scan 521 (11.482 min) of DATA:SMS1A77A.D
Abundance
6.0E5
4.0E5
2.0E5
0
68
82
120
182
233
284
299
342
100
200
300
Mass/Charge
TIC of DATA:SMS1A77A.D
Abundance
5.0E6
4.0E6
3.0E6
2.0E6
1.0E6
0
8
10
12
14
16
18
Time (min.)

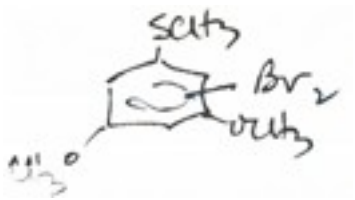


See page 142

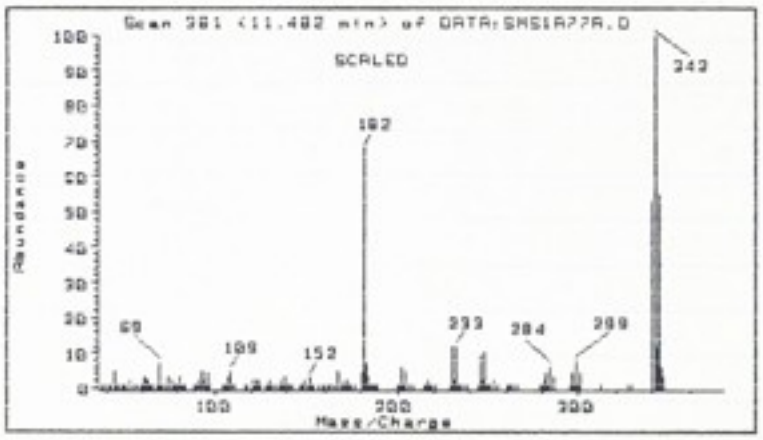

SCALED
242
45
97
152
182
240
284
299
100
200
300
Mass/Charge
Abundance

Scan 351 (11.291 min) of DATA:SMS1A77A.D
BROMINATION OF 3,5-DIMETHOXYTHIOANISOLE

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
37.00	1	91.90	1	158.80	1	245.85	12
38.00	1	92.90	5	159.80	1	246.85	2
39.00	1	93.90	2	161.80	1	247.85	13
43.00	1	95.00	2	166.90	1	248.85	2
44.00	1	95.90	3	169.90	1	249.85	1
45.00	8	105.00	1	170.90	2	250.75	1
46.00	2	105.90	1	171.85	1	252.75	1
47.00	1	107.00	1	172.75	2	254.75	1
48.95	2	108.00	2	173.85	1	259.85	1
49.95	1	108.90	4	174.75	2	261.85	1
50.95	1	109.85	1	176.75	1	262.85	1
52.95	3	110.95	1	180.95	1	264.75	1
56.95	1	115.85	1	181.95	8	266.70	1
57.95	1	116.85	1	182.95	1	280.70	1
58.95	1	117.85	1	183.95	1	281.70	4
59.95	1	118.85	1	184.85	1	282.70	1
60.95	4	120.95	2	185.85	1	283.70	6
61.95	2	121.95	1	186.85	1	284.80	1
62.95	2	122.85	2	187.85	1	285.70	3
63.95	1	123.95	2	188.85	1	293.70	1
64.95	1	124.85	1	189.85	1	295.80	1
68.05	1	127.85	1	200.85	2	296.75	5
68.95	5	129.85	1	201.85	1	297.75	1
69.95	1	130.85	1	202.85	6	298.65	9
70.95	1	132.85	1	203.80	1	299.75	1
72.95	1	136.95	1	204.80	5	300.65	5
73.95	1	137.95	1	214.80	1	306.75	5
74.95	5	138.95	2	215.80	2	308.75	9
76.05	1	139.85	1	216.80	2	309.75	1
76.95	5	140.80	1	217.80	3	310.75	4
78.05	1	141.80	1	218.80	1	311.75	1
79.00	1	142.80	1	220.80	1	324.75	1
79.90	1	146.80	1	230.80	10	326.75	1
80.90	4	148.90	1	231.90	2	339.70	53
81.90	1	150.90	1	232.80	11	341.70	100
82.90	1	151.90	3	233.80	2	342.80	11
83.90	1	152.90	1	234.75	1	343.70	53
84.90	1	153.90	2	236.75	1	344.70	5
89.90	1	154.90	1	244.85	1	345.70	3
91.00	1	156.90	1				



ex page 142


Scan 381 (11.482 min) of DATA:SMS1A77R.D
SCALED
242
192
69
109
152
233
284
299
Abundance
Mass/Charge

Scan 361 (11.482 min) of DATA:SMS1A77A.D
BROMINATION OF 3,5-DIMETHOXYTHIOANISOLE

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
37.10	1	92.90	5	156.90	1	232.80	12
39.00	1	93.90	2	158.90	1	233.80	1
41.00	1	94.90	1	159.90	1	234.75	1
43.00	1	95.90	4	161.80	1	236.75	1
44.10	1	97.00	1	162.80	1	238.65	1
45.00	5	104.90	1	164.90	1	244.85	1
46.00	1	105.90	1	166.80	5	245.85	9
47.00	1	106.90	1	167.90	1	246.85	2
48.95	1	108.00	3	169.90	1	247.75	10
49.95	1	109.00	5	170.90	2	248.85	1
50.95	1	109.95	1	171.85	1	249.75	1
52.95	2	110.95	1	172.85	2	250.75	1
55.05	1	116.85	1	173.75	1	252.75	2
57.05	1	117.85	1	174.85	1	254.75	1
58.95	1	120.95	2	176.85	1	269.85	1
59.95	1	121.95	1	180.95	4	260.85	1
60.95	3	122.85	2	181.95	68	261.85	1
61.95	2	123.95	2	182.95	7	262.85	1
62.95	2	124.85	1	183.95	3	264.75	1
64.05	1	127.85	1	184.85	1	266.70	1
65.05	1	128.85	1	185.85	1	278.70	1
68.05	1	129.85	2	186.85	1	279.70	1
68.95	7	130.85	1	187.85	1	280.70	2
69.95	1	132.85	1	188.85	1	281.70	4
70.95	1	134.85	1	200.85	1	282.70	1
72.95	1	135.95	1	201.95	1	283.70	6
74.05	1	136.95	2	202.85	6	285.70	3
74.95	3	137.95	1	203.90	1	295.80	1
76.95	2	138.95	3	204.80	5	296.75	4
78.05	1	139.85	1	206.80	1	297.75	1
78.90	1	140.80	1	208.70	1	288.65	8
79.90	1	141.80	1	214.80	1	299.75	1
80.90	3	142.90	1	215.80	1	300.75	4
81.90	1	146.80	1	216.80	2	311.75	1
83.00	1	148.00	1	217.80	1	326.75	1
83.90	1	148.80	2	218.80	1	328.70	1
89.00	1	150.90	1	220.80	1	339.70	53
90.00	1	151.90	3	228.90	1	341.70	100
91.00	2	152.90	1	230.80	12	342.70	11
92.00	1	153.90	1	321.90	2	343.70	55

6/26/90 Sample of white solids - said to be fully equivalent to MDMA, but different structure. 125 mg = 1 dose - short, less after effect. Different starting intervals - and easier to get, Out of Oregon, but original source somewhere about here in Bay Area.

——> IR = something like a carboxylate salt. Explore.

——> physical - extremely fine, white sl. electrostatic. extremely water soluble - 100 mg in 3 drops RT neutral Rx - ∴ not a bisalt of a dibasic acid

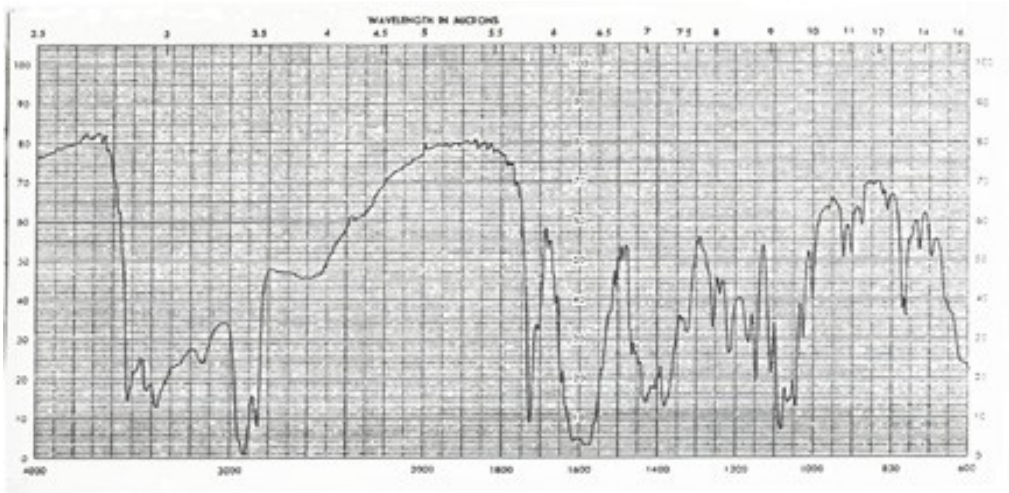
——> add 5% base; -> pale yellow color - no turbid! stand ~ 1 hr -> solids (B) IR looks like water, largely with a 7.5 μ band. $Ca(OH)_2$ & $Ba(OH)_2$ have different IR's.

——> remove several extracts [with] boiling IPA - evap -> oil that sort of xtallizes.

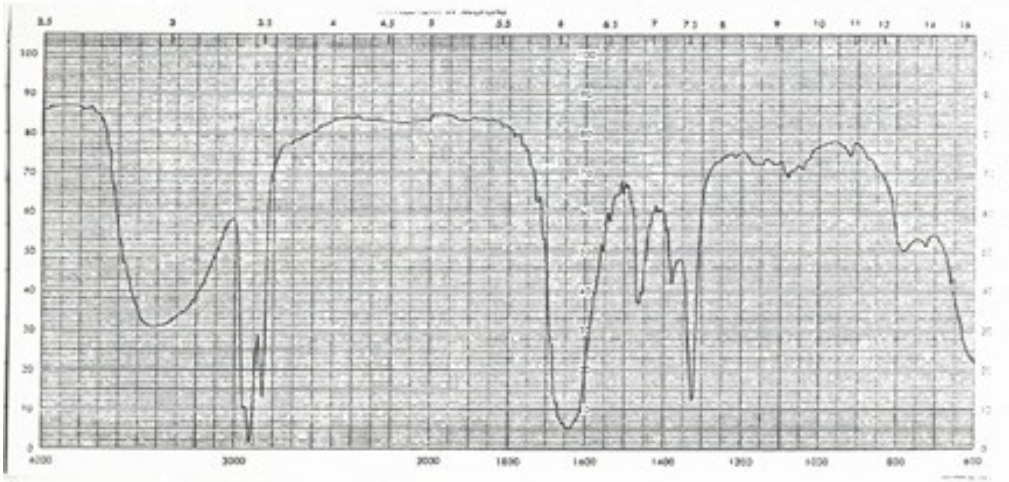
——> TLC of H_2O sol [with] 1.5% NHaOH in MeOH -> Rf at front. Keep exploring re Pemoline. TLC in CH_2Cl_2 - no movement.

——> make H_2O sol. basic [with] K_2CO_3 - xtxt CH_2Cl_2 gives an exhait solid [with] simple IR - still heavy OH - nearly organic? (C)

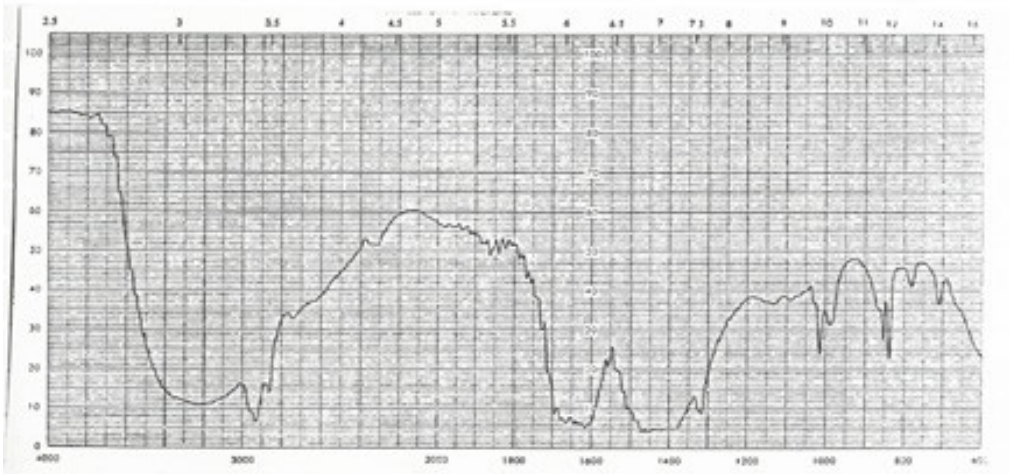
hexane wash.



white
Solids.

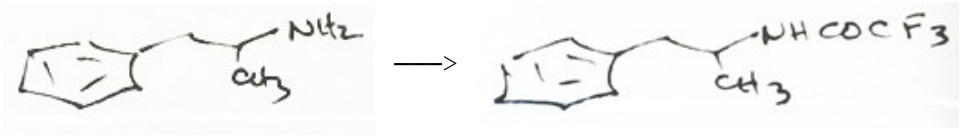


Solids ex
5% NaOH
(B)



CH_2Cl_2 xtrts
ex CO_3=
(C)

Aug 3, 1990



(+)

To 5 g pyridine - add
1.35 g d(+)amphetamine
10mM mag stirrer - cover [with] Al foil.
with good stirring, add

1.7 mL trifluoroacetic anhydride – drop wise.
1.7ml = 2.52g (2.10 theo, ∴ 20% xs).

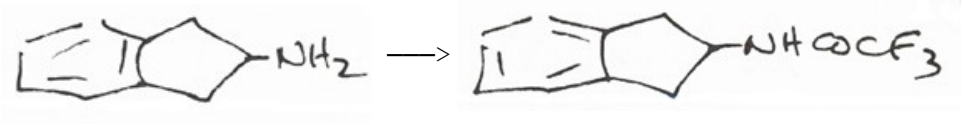
gets quite warm. - becomes quite yellow. Δ on SB ~ 1/2 hr. To RT - add H_2O up to 100 ml -> solids. ~~remove by filter~~ add dil HCl to pH red on paper. no evident change. remove by filtering.

→ 2.43g wet crude amber solids.
IR fine (NH, CO).

Rextal ex = wt MeOH, Δ sol ∇ ice
filter.

→ 1.32g dry - off white.

ML's of rextal into original aq. ML → Solids -
Save as 2nd crop
~ .5g yellow.

August 3 1990 

One 5 g bottle of aldrich 2-amino indane HCl
had 4.95 g white solids (29.1 mM)

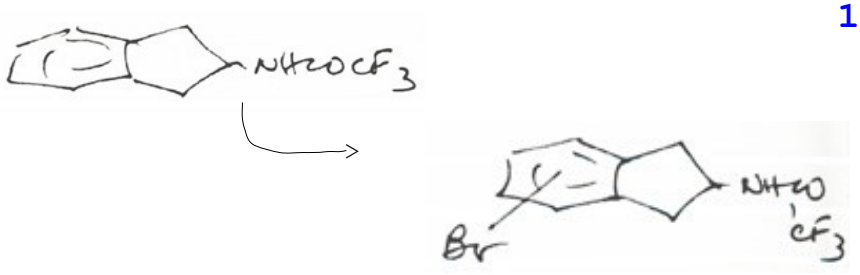
4.95 g B·HCl into ~100 ml H_2O - add aq. NaOH
to give heavy oil phase & pH paper
at deep blue - xtrt [with] 2 x 25 ml
CH_2Cl_2 - to residual oil on
steam bath - dissolve oil in
15 ml pyridine - mag stirrer - into E-flask
[with] Al cover. Add, [with] stirring, dropwise
5.1 ml TFAA
gets hot - and pale yellow. Δ SB
for 1/2 hr. ∇ - flood [with] H_2O ->
very fine solids _ @ [with] dil HCl
(color fades to paler yellow -
filter - wash H_2O
-> 7.7 g wet white solids

Rextal from 25 g MeOH, ∇ ice filter - wash
lightly [with] cold MeoH
-> 4.97 g fine white xtals

xtal ML & original ML - left in filter flask
over near the hood -

August 10, 1990

looking at:



M.Robinson. amide in CH_2Cl_2 [with] Br_2 & Ag_2SO_4, 1.5h.
and some kind of work up -> 1.2 g of oil - complex HPLC [with] 2 very close-running products in 3:1 ratio.

My TLC st.mat
crude oil
wash [with]
a little ΦH

Benzene wash looks cleaner on TLC, but going the wrong way by HPLC

Also · Brommation of free amine (Ag_2SO_4, CH_2Cl_2)
→ two peaks 10:1 ratios.

Brommation of free amine in HOAc - chews up.

Eventually H_2O [with] dilute NaOH (pH 10) in MeOH or IPA
Δ a while

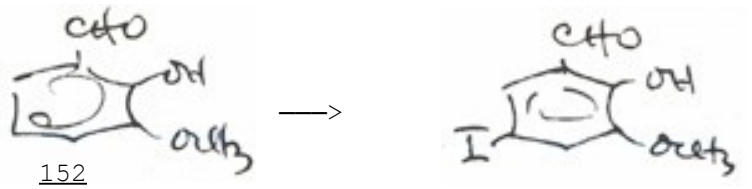
After base & IPA & flame
Small amt acid/based -> no recognizable product by HPLC.

Try brommation of page 152 in acetic acid.

0.46 g amide (2mM) in
8 g HOAc - not 100% in solution. Mostly.
add
0.38 g Br_2 (20% xs) in
2.0 g HOAc

stir R.T. 2^{20}PM.
10 minute sample 1/2 1/2 st mat faster product

Aug 16, 1990



152

A solution of

15g o-vanillin
into

140 mL 100% EtOH
∇ to 0°.

add -
a bit of one
a bit of the ot

25 g I_2
20 g HgO

alternately,
over the course of
the day- (6 hrs).

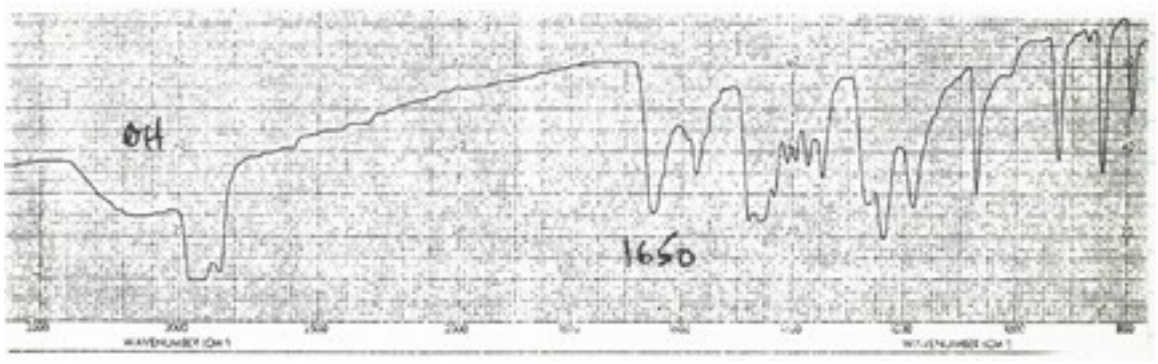
Controlled oxidation of organic compounds with cerium(IV). II. The oxidation of toluenes. Walter S. Trahanovsky and L. Brewster Young (Iowa State Univ., Ames). *J. Org. Chem.* 31 (6), 2033–5(1966)(Eng); cf. *C.A.* 64, 627*b*. The oxidn. of toluenes to benzaldehydes was reported. Also in anhyd. AcOH cerium ammonium nitrate oxidized toluenes to benzyl acetates. The mechanism of the reaction was discussed. The oxidn. of the *p*-halotoluenes in anhyd. AcOH gave a large amt. of the corresponding benzyl alc. and benzaldehyde. B. K. Wasson

o-Vanillins and novovanillins. VII. Preparation of 5-iodo-o-vanillin and production of β-nitrostyrenes. E. Profft and M. Pannach (Tech. Hochsch. Chem. Leuna-Merseburg, Ger.). *Arch. Pharm.* 299(7), 633–40(1966)(Ger); cf. *CA* 63, 17947*f*. An improved preparative method for 5,2,3-I(HO)(MeO)C_6H_2CHO (I) is described. I, 5,2,3-Br(HO)(MeO)C_6H_2CHO (II), and 5,2,3-I(MeO)$_2C_6H_2$CHO (III), which did not undergo an Ullmann condensation, were condensed with $MeNO_2$ and $EtNO_2$ to yield the corresponding nitrostyrenes. 2,3-HO(MeO)-C_6H_3CHO (15 g.) in 140 cc. EtOH treated with cooling and shaking during 1 day alternately with 25 g. iodine and 20 g. yellow HgO in small portions, filtered, and evapd., the residue triturated with aq. Na_2CO_3, and the aq. ext. acidified with HCl yielded 12.5 g. crude product; the mother liquor dild. dropwise with H_2O and the ppt. extd. with Na_2CO_3 soln. gave an addnl. 2.5 g. crude product; the combined crude fractions recrystd. from aq. MeOH yielded 14 g. pure yellow I, m. 130°. II (4.6 g.), 20 cc. MeOH, and 2.5 g. $PhNH_2$ refluxed on a water bath gave the light red 5,2,3-Br(HO)(MeO)C_6H_2CH:NPh, m. 89° (MeOH). gave similarly 5,2,3-I(HO)(MeO)C_6H_2CH:

14g = 51%

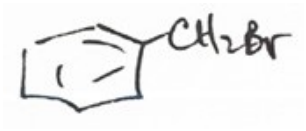
Stand 2 weeks. filter, wash inorganics [with] EtOH
flash on RE . Residual extracted [with] 20% Na_2CO_3 aqueous.

1st xtrt, acid, filter -> 0.20 g; 2nd, acid, filter -> 0.10 g- xtrt aq [with] CH_2Cl_2 -> sm. amt product & st. mat. (CH_2Cl_2, silica gel TLC). Combine, xtals ~1ml MeOH -> 0.02 g light off-white xtals to L.W. for NMR.

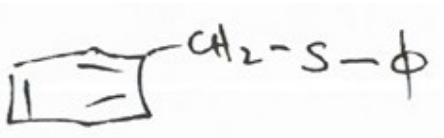


[Editor's Note: Pages 155 & 156 are missing from the original document]

Sept ~30,1990
Sunday.



ΦSK ——>



A solution of 3.9 g KOH 85% pellet - into 40 ml boiling MeOH.

While still hot, stirring - add a mix of:

7.6g ΦCH_2Cl
5.5g ΦSH
} a squirt at a time

ΦSH	~~100%~~ 50mM
KOH	20% xs
ΦCH_2Cl	20% xs

this brings it all back up to reflux. insolubles immediate stir ambient (still hot) a while

Onto steam bath - 1 hr.
Into 800 mL H_2O - stir to RT -> globs of waxy solids.

9.31 wet
7.5g Hexane
1.6g NaCl.
7.61 hexane wet.

filter - tamp dry ——> 9.31 g wet white solid.
into 7.5 g hexane - to boil - some silt, & some turbid . add
1.6 g NaCl. - At boil - it clears - decant -
to 10° [with] ice bath - seed -> xtals.

5.5 after xtal

filter - wash [with] ice-cold hexane -
air dry -> 5.5 g $\Phi CH_2S\Phi$ white xtals.

Oct 15, 1990  ——————> ?
$(CH_3)_2S \cdot BH_2Cl$

In a RB flask, under He - RT - magnetic stirrer - add

4.2 ml (actually ~ 5 ml) ~ neat $(CH_3)_2S \cdot BH_2Cl$
(40mM +) stirring vigorously - add a few drops at a time:

2.83 g NS (~10mM) in 10 ml CH_2Cl_2

with each drop -> deep green, then -> pale yellow. somewhat later -> deep brown -> yellow. cool [with] external RT water. bubbling & exothermic. Stir ~ 1/2 hr - no further change.

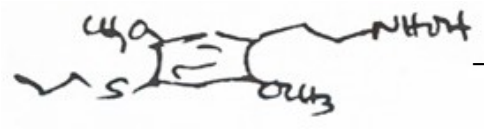
Out - squirt in 50 ml H_2O - + 20 ml CH_2Cl_2
separate - xtrt aq (very acid) [with] CH_2Cl_2

CH_2Cl_2
evap in air -> pale yellow solids,
2.68g.

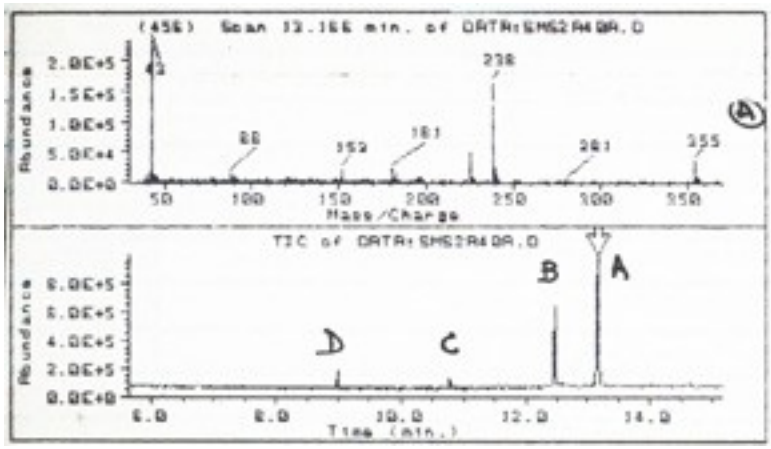
wash [with] MeOH- very soluble - almost white
wash [with] $(CH_3)_2CO$ - very sol. trace
wash [with] EtOAc -> not very sol. pale cream.
rextal f·EtOAc + a little MeOH
gorgeous white xtals.

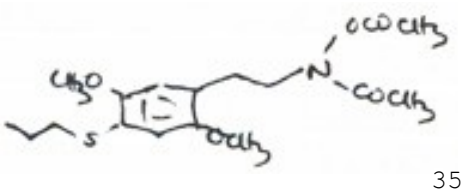
-> aq- +
5% NaOH to strong basic, cloudy - extract [with] CH_2Cl_2
flash -> 0.65g
Black oil

Rextal. all ~~from~~ (2.45g left) from 7x wt (17.2g EtOAc) - diluted with 1 wt MeOH (2.45 g) hot -> white xtals 2.45 g wet
1.76 g dry.

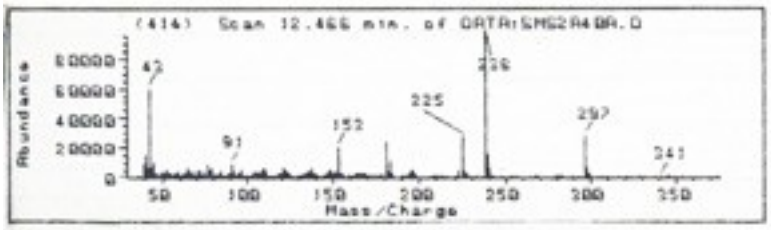
Nov 18, 1990.  —> mono
or
di acetate ?

A little of
the 2.68 g yellow solid - into pyridine + ~~Ho~~ Ac_2O
Δ SB ~ 1/2 hr. - + H_2O, HCl, xtrt CH_2Cl_2 -> yellow oil
that slowly xtallizes.



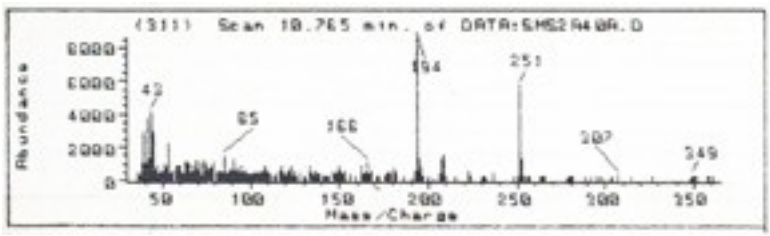
A 

355



B 

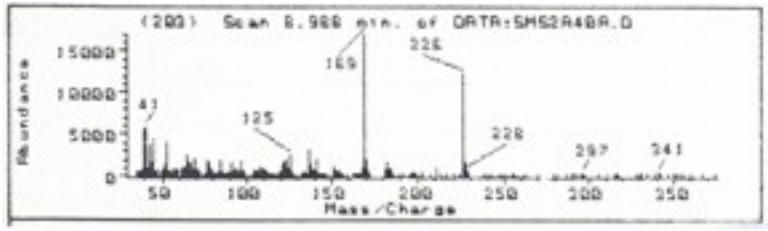
297



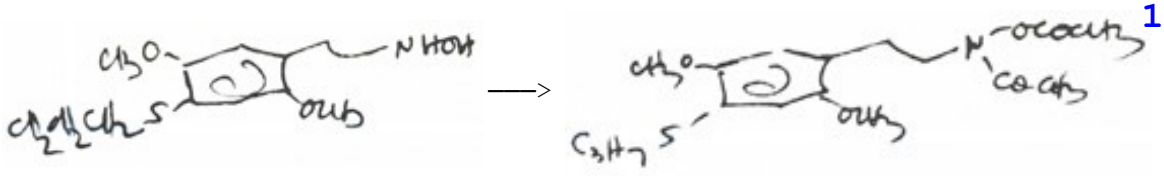
C 

251

D



diacetate OK, + mom acetate -> WE [with] Δ



0.26 g amine .HCl page 158. dissolve in:

1.0 g pyridine - add.

3.0 g Ac_2O. on SB. 10:30.

[Editor's Note: Pages 161 & 162 are missing from the original document]

1/27/91. Characterization of 2C-T-2· aldehyde., 2C-T-2 itself.

Aldehyde:

original sample: 87-88°. ex EtOH. ← already analyzed. C, H·

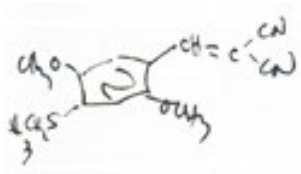
remelt. 1/27/91 72°sint., 76-77°
rextal. MeOH - 70°sint 83-84°.
→ for Microanalysis:

$C_{11}H_{14}O_3S$

C_{11}	58.38
H_{14}	6.24
O_3	21.21
S_1	14.17·

Nitrostyrene mp 151-152° $C_{12}H_{15}NO_4S$; C,H

Malononitrile:



malononitrile MW 66 -> 33mg
AcCHO MW 226 -> 133mg
combine- add ~ 0.2ml. EtOH
Δ -> sol.
+ 1 drop Et_3N.
immediate xtals

6:163A

C_{14}
H_{14}
N_2
O_2
S

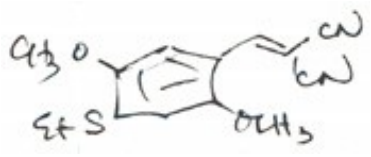
press on plate -> orange xtals sint 129°
rextal f. 3 mL MeOH sint·135°
mp 136-138°
→ orange xtals
mp 138-138.5°

2C-T-2 $C_{12}H_{20}ClNO_2S$ 37/37

6:163B

Next page

Microanalyses.

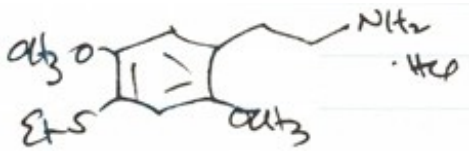


6:163A
Sample from
previous page

6:163A

C	14	= 61.29159	C 60.70 / 61.17
H	14	= 5.144207	H 5.10 / 5.22
N	2	= 10.21259	
O	2	= 11.66487	
S	1	= 11.68674	

MW IS 274.328



6:163B
Sample from
5:59A
(see 5:152)
(get mp)

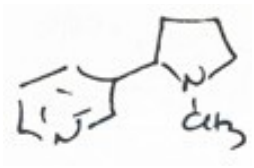
6:163B found.

C	12	= 51.87812	C 51.91
H	20	= 7.256889	H 7.21
N	1	= 5.042386	N 5.04
O	2	= 11.51887	
C1	1	= 12.76327	
S	1	= 11.54047	

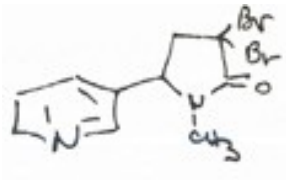
Nicholas 6:163B
P-7376

MW IS 277.805

April 24, 1991



Br_2 ——> hexane



? ++

0.5 g nicotine in 20 mL hexanes. add
0.5 g Br_2 in 20 ml hexane (there was some (+Br ^ ex just hexane
is there some hexane there?)
stirring - immediate decoloration, -> clear, pale yellow.
add:
2.5 g Br_2 in 20 ml hexane. At 1/2 way point, color finally persists. Stir -> deposition of yellow-brown gum.
Stir ~ 1 hr.

decant

gum - hints of xtals.

hexane

dissolve in 5 ml boiling EtOH abs cook on S.B. a while off. ∇ -> looks almost xtals coming out. scratch most promising.

let evap a bit outside ->light oil dropout. trivial- discard

~ colorless evap on Rotary. ->1.1 g clear oil sharp smell

decant

EtOH

let stand a week or so - evap to small puddle with blue - colored stuff up out of the RB. fumes a bit. Bromo hexane? some colorless condensate at top 24/40. 0.39 black fluid

165 A

evap

-> yellow oil. 1.75 g clear oil acetone insol! H_2O sol. another ·HBr

165 C

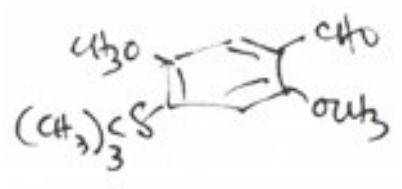
almost solid residue - let stand a few days -> yellow oil.

165 B

0.54g - not Sol. in acetone! Sol H_2O something ·HBr. make basic before GCMS this, to page 180

To Page 167

Microanalysis.



May 26, 1991

5:98, 0.56g. reference sample.

mp.(retainer sample) 55-57°
rextal f. MeOH -> pale cream. 59-60°

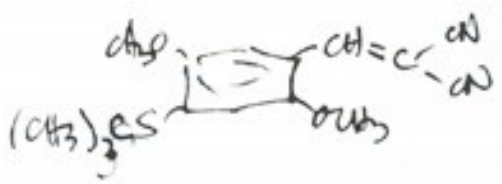
6:166 A $C_{13}H_{18}O_3S$

C
H

10mg Malononitrile + } into ~ 200 ml EtOH, Δ -> sol -
40mg aldehyde } add 1 drop Et_3N -> ROD

scratch -> yellow-red xtals- onto plate - wash [with] MeOH

-> orange xtals, mp 112-113.



6:166 B. $C_{16}H_{18}N_2O_2S$ 39/39

2C-T-9 NS see MB V-29 analysed—mp 93-94° $C_{14}H_{19}NO_4S$

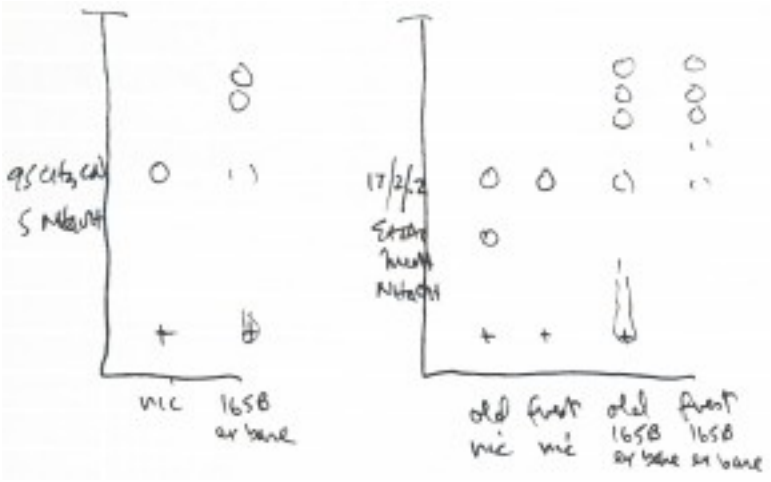
	theo	found
C	56.54	56.50
H	6.44	6.51

May 27, 1991

from page 165

165 C - decantings - looks pretty much nicotine out
165 A - a forest of Brominated hexanes. some di bromo out
165 B - largely 2 things by GCMS - more by TLC.

TLC April TLC May 17.

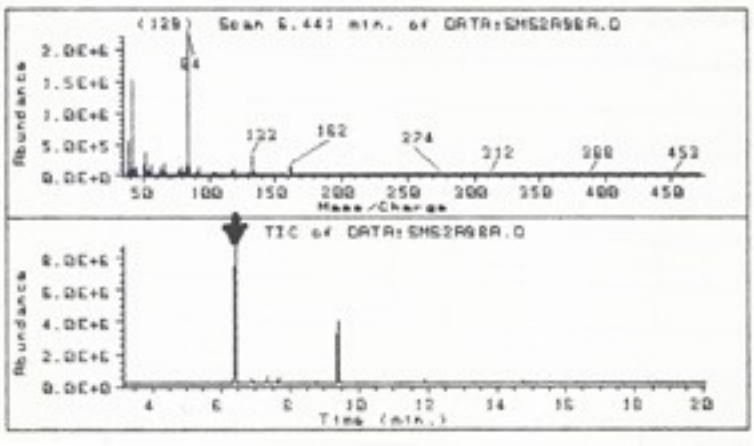


the old 165B (as base) sat in air (in light) a month.

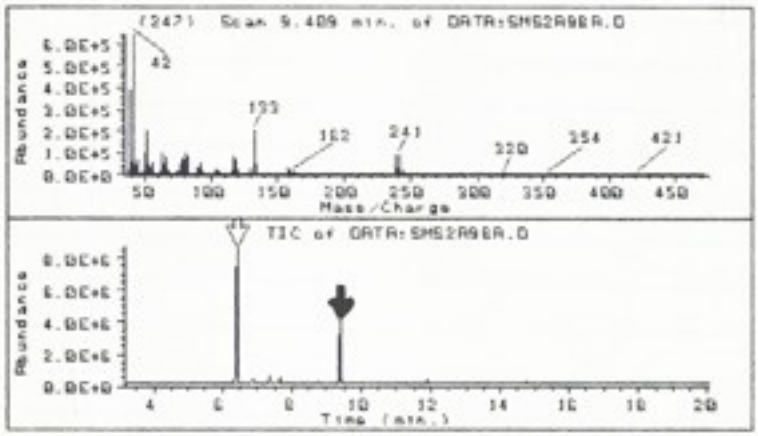
It is the sample used then fresh then, fresh in the GCMS
see next few pages.

GCMS of 165B ex base .

APRIL 1991

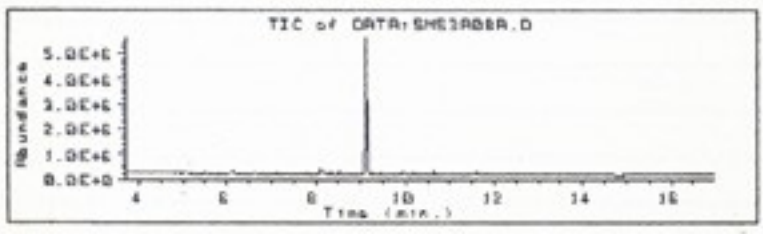


nicotine
SMS2 - A98A

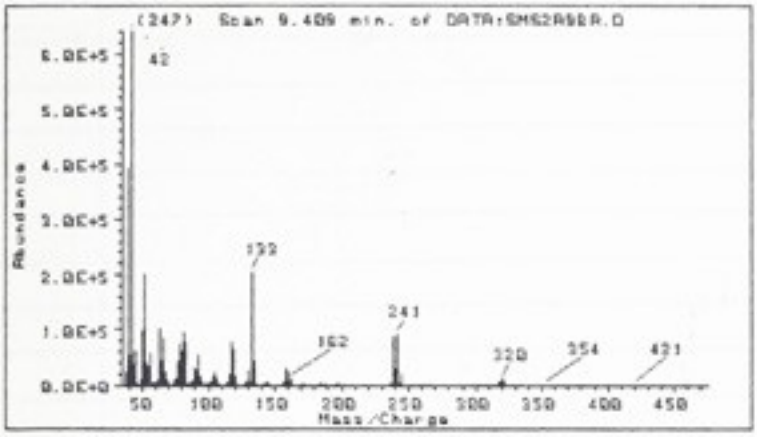


dibromo
nicotine
SMS2 - A98A

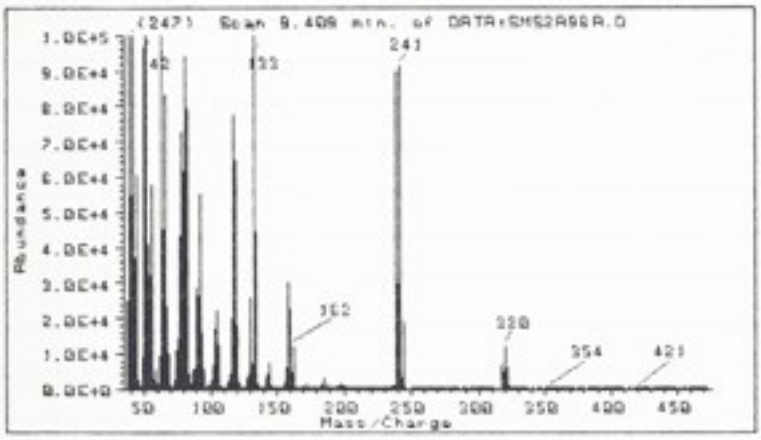
MAY 1991



only dibromo
nicotine
SMS3 ~~A06A~~
~~5?~~
A08A

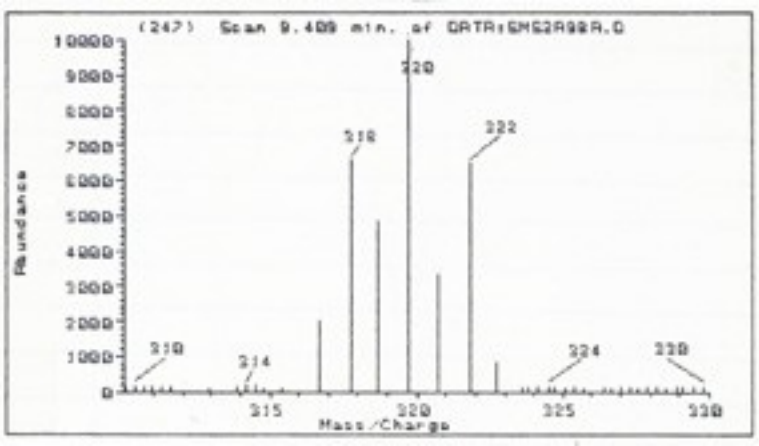


Blow-up of Dibromo nicotine spectrum.



		see page
for analysis of	~320	170
	~241	171
	~186	172
	~159	172
	133	172

Dibromonicotine 320 cluster



314.80	109.00
315.40	118.00
316.70	2015.00
317.80	6583.00
318.70	4822.00
319.70	12324.00
320.70	3324.00
321.80	6476.00
322.70	823.00
323.60	135.00

assume 110-120 background

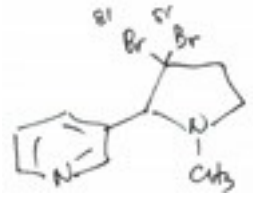
M+1/M = ~~8.96%~~ ~~6360/710~~ 710/6360 = 11.2%

323 710
322 6360
321
320 12210
319
318 6470
317

3210-1363 = 1847

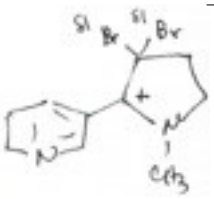
4710-710 = 4000

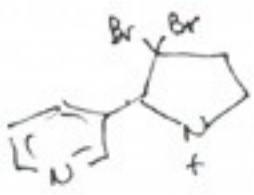
1900-0 = 1900



Parent
+ 322
320
318

parent - 1
321
319
317

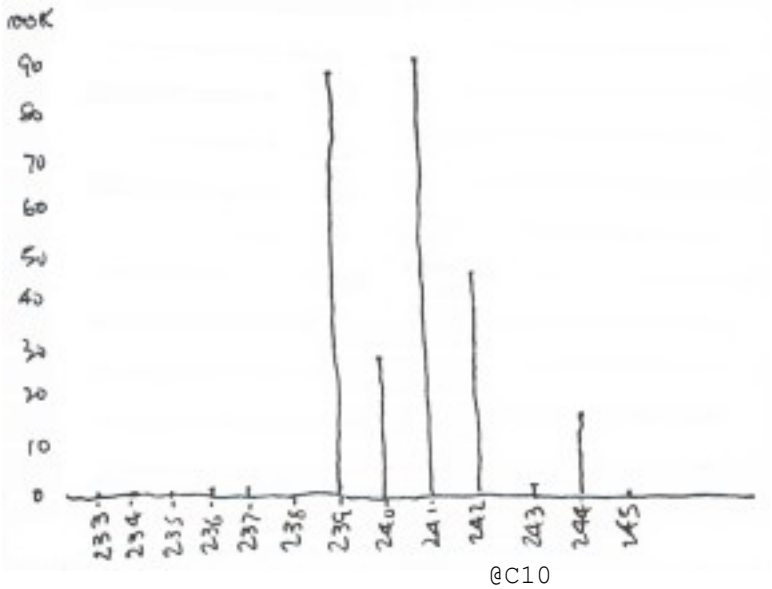




307
305
303

-140	301.95		143.00
190	302.65	303	329.00
	303.25		144.00
	303.55		145.00
	303.85		106.00
290	304.75	305	427.00
	305.55		159.00
	305.85		150.00
170	306.85	307	313.00
	307.55		133.00
	307.85		157.00

Dibromonicotine 241 cluster.



231.45	169.00
231.75	170.00
232.85	272.00
233.85	354.00
234.85	347.00
235.85	1192.00
236.85	1181.00
238.85	89576.00
239.85	29848.00
240.85	91536.00
241.75	47488.00
242.85	2998.00
243.75	18904.00
244.75	1130.00
245.55	120.00
245.95	127.00
246.15	140.00

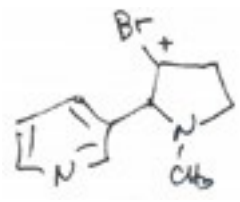
@C10

assume M+1/M = 11.2% background, 100-200 noise

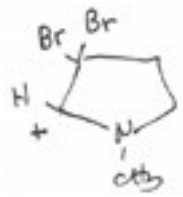
5%@C5

```
244
243
242            5% 29700
241     91400 -   1485   89900
240
239     89400       ---->  89400

18800           ---->  18800
       91400x112
47300-   10200 ---->  36900
       87400x.112
29700-   9800  ---->  19900
```

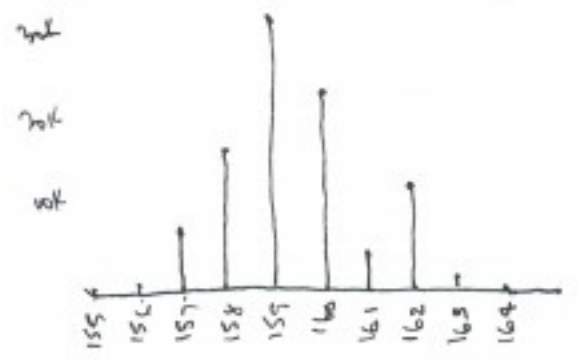


241
239



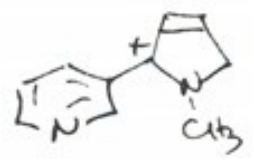
244
242
240

Dibromonicotine 159 cluster , 186 cluster, 133

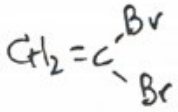


	154.30	195.00
	155.00	715.00
	156.00	1772.00
	157.00	6440.00
	158.00	15582.00
→	159.00	30256.00
	159.90	22560.00
	161.00	4848.00
	161.90	12224.00
	162.90	2043.00
	163.80	515.00
	164.65	146.00

159

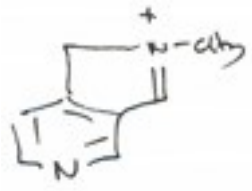


188
186
184



	182.25	219.00
	182.55	175.00
	183.75	1659.00<—184
	185.75	3048.00<—186
	186.65	251.00
	187.75	1407.00<—188
	188.65	201.00

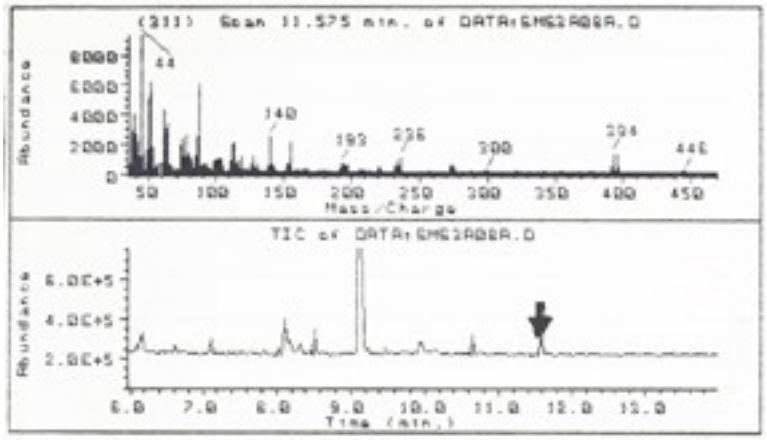
133



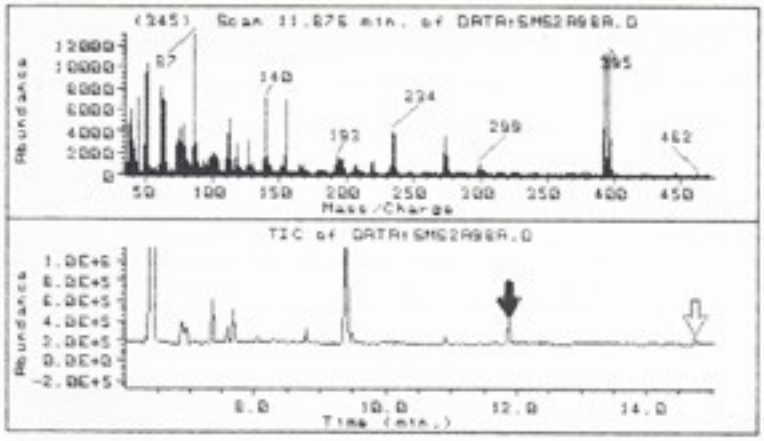
	124.35	195.00
	124.65	187.00
	124.95	174.00
	125.65	212.00
	125.95	211.00
	126.65	413.00
	126.95	434.00
	127.95	2923.00
	129.05	4341.00
	129.95	25984.00
133	131.05	7328.00
→	132.95	205248.00
	134.05	44496.00
	134.90	3736.00
	135.80	1727.00
	136.60	199.00

Small stuff from dibromonicotine - page 167-on.

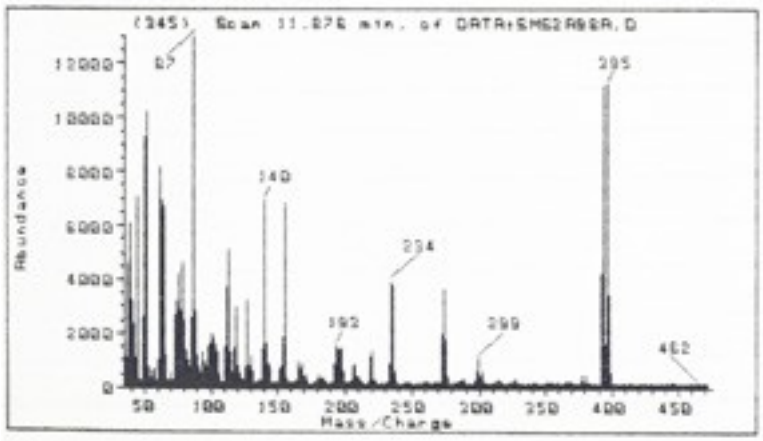
TRIBROMONICOTYRINE



SMS3 A08A

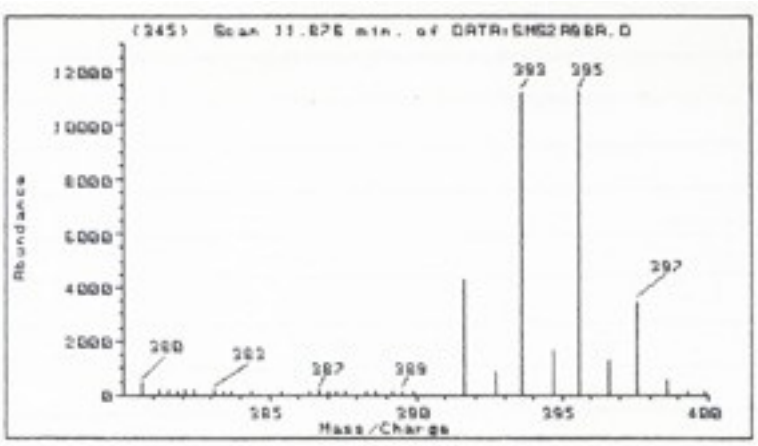


SMS2 A98A



SMS2 A98A

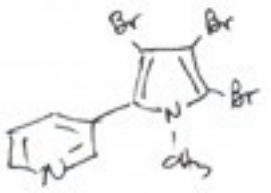
~395 cluster pm~~m~~174
300 cluster 175
274 cluster 175
234 cluster 175



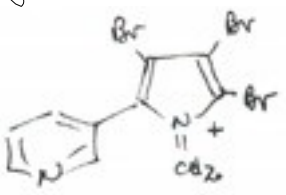
-100 to 200

398	400	3300
397		
396	1100	11100
395		
394	1500	11100
393		
392	700	4100
391		

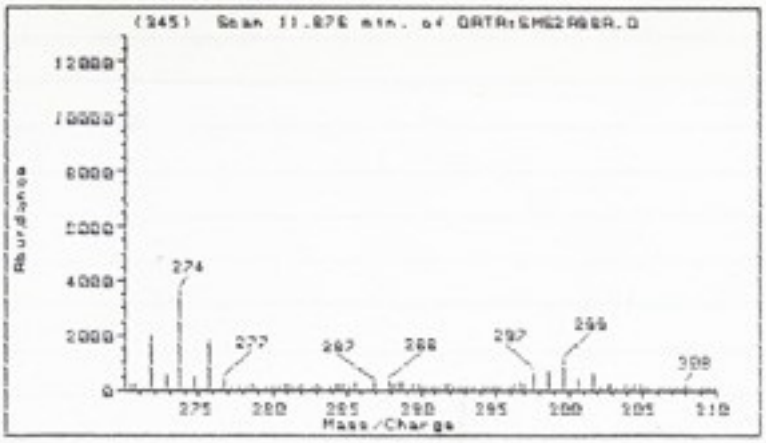
389.90	105.00	
391.60	4269.00	
392.70	864.00	
393.60	11201.00	
394.70	1617.00	
395.60	11232.00	
396.60	1294.00	
397.60	3456.00	
398.60	553.00	398
399.30	108.00	



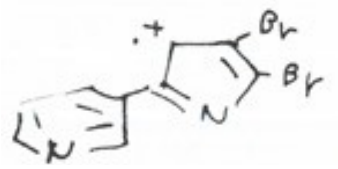
+ 398
396
394
392

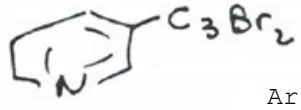


397
395
393
391



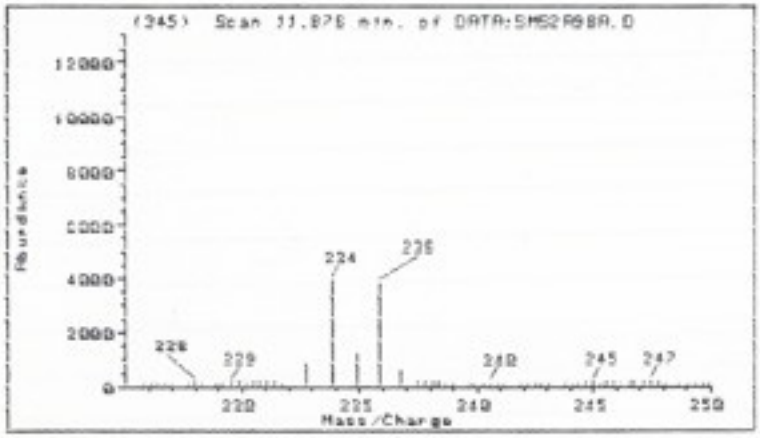
296.95	192.00		270.60	191.00	
297.65	632.00	298	271.70	1986.00	272
298.65	644.00		272.80	553.00	
299.65	1069.00	300	273.70	3644.00	274
300.65	397.00		274.70	500.00	
301.65	620.00	302	275.70	1787.00	276
302.25	149.00		276.70	395.00	
302.65	189.00				

$C_9H_4N_2Br_2$  ?

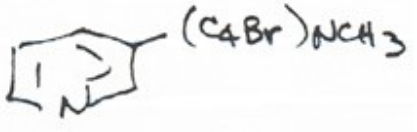


276
274
272

Br
Ar C-C≡C Br
+
Br Br
Ar C = C:=C
+

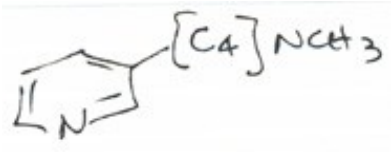


231.65	119.00				
232.75	857.00				
233.85	3939.00	234			
234.85	1245.00				
235.85	3821.00	236			
236.75	626.00				
237.45	179.00				

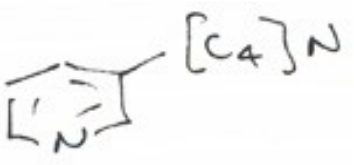


236
234

peaks of triBromonicotyrene.

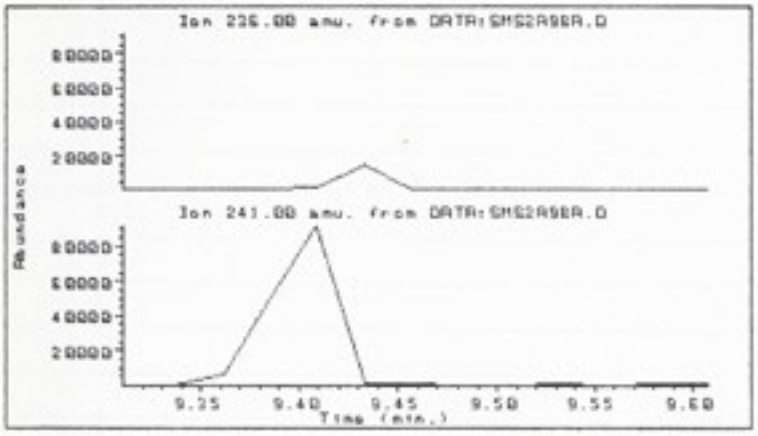
"155" 

+ 155

"140" 

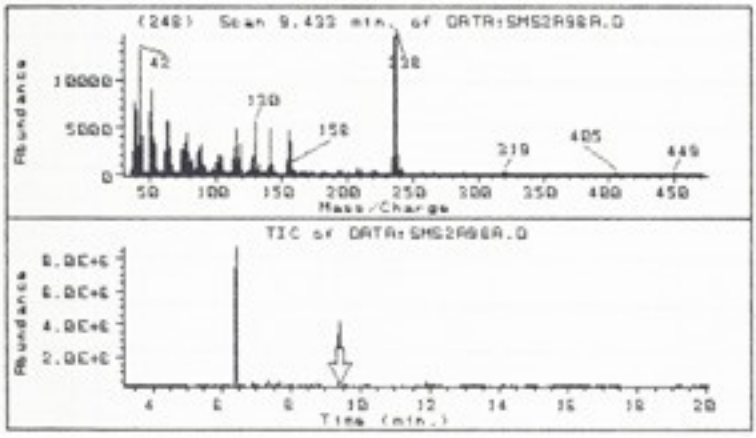
+ 140

Search for DIBROMONICOTYRINE
(right alongside DIBROMONICOTINE)

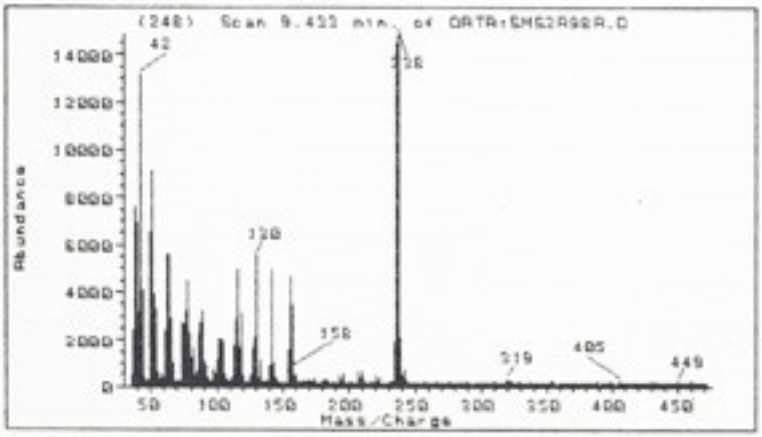


236 - major peak (fragment) of dibromonicotyrene

241 - major peak of dibromonicotine



See mass data next page.



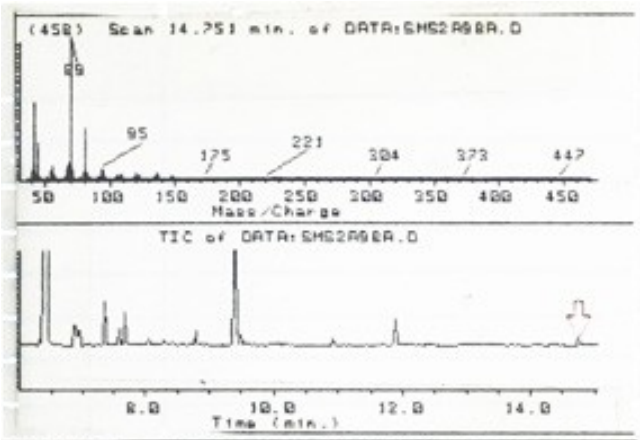
Scan 9.433 min. of DATA:SMS2A98A.D

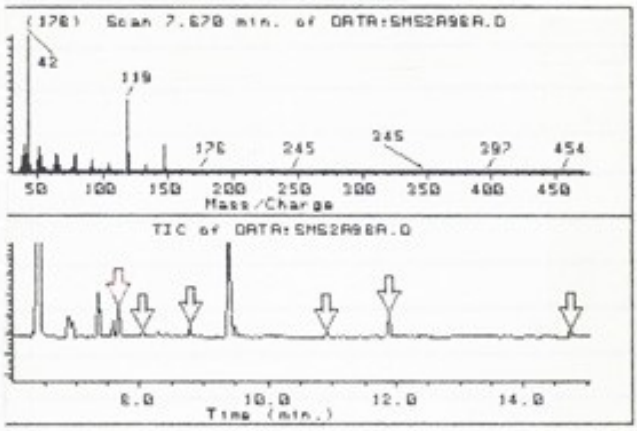
AMU.	Abundance	AMU.	Abundance	AMU.	Abundance
306.15	148.00	312.05	130.00	318.60	214.00
306.45	176.00	312.35	139.00	318.90	152.00
306.75	134.00	312.60	116.00	319.60	302.00
307.05	136.00	313.30	128.00	320.20	139.00
307.35	152.00	313.50	136.00	320.50	142.00
307.65	133.00	313.90	104.00	320.80	109.00
307.95	131.00	314.20	138.00	321.20	131.00
308.25	134.00	314.50	146.00	351.50	175.00
308.55	129.00	314.80	104.00	321.80	191.00
308.95	133.00	315.40	126.00	322.10	186.00
309.25	134.00	315.80	150.00	322.40	134.00
309.55	181.00	316.10	143.00	322.70	113.00
309.85	157.00	316.40	118.00	323.30	118.00
310.15	148.00	316.70	152.00	323.70	129.00
310.45	144.00	317.00	144.00	324.00	159.00
310.75	125.00	317.30	99.00	324.30	113.00
311.45	125.00	317.90	224.00	324.60	125.00
311.75	151.00	318.30	169.00	324.90	137.00

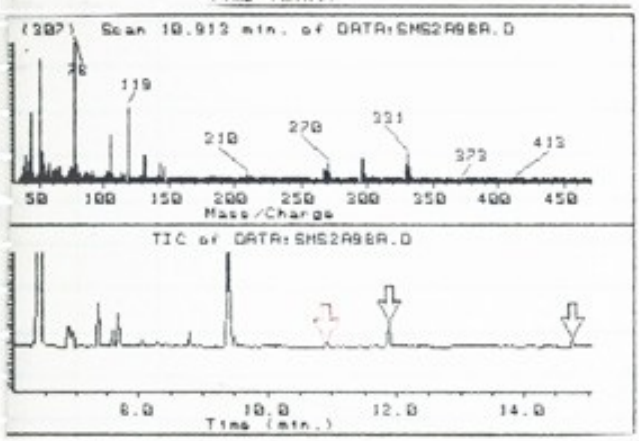
Scan 9.433 min. of DATA:SMS2A98A.D

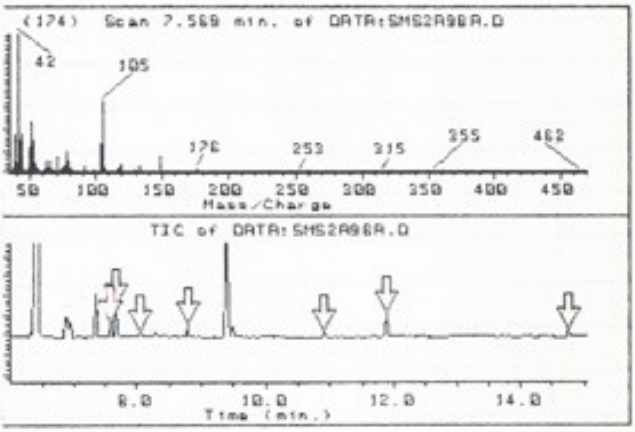
AMU.	Abundance	AMU.	Abundance	AMU.	Abundance
217.60	187.00	225.65	113.00	232.95	178.00
218.00	154.00	225.95	119.00	233.25	161.00
218.30	172.00	226.25	148.00	233.55	128.00
218.60	144.00	227.65	116.00	234.95	1942.00
218.90	159.00	227.95	146.00	235.85	14516.00
219.20	158.00	228.25	122.00	236.85	3604.00
219.50	130.00	228.95	120.00	237.85	14835.00
219.90	139.00	229.15	145.00	238.85	2084.00
220.10	144.00	229.55	125.00	239.95	429.00
220.90	416.00	229.85	128.00	240.85	724.00
221.80	204.00	230.05	116.00	241.75	356.00
222.90	360.00	230.45	122.00	242.35	129.00
223.75	140.00	230.75	177.00	242.65	166.00
224.05	135.00	231.05	146.00	242.95	118.00
224.45	131.00	231.75	189.00	243.65	266.00
224.65	149.00	232.05	138.00	244.25	167.00
225.05	141.00	232.35	181.00	244.55	156.00
225.35	157.00	232.65	181.00	244.85	140.00

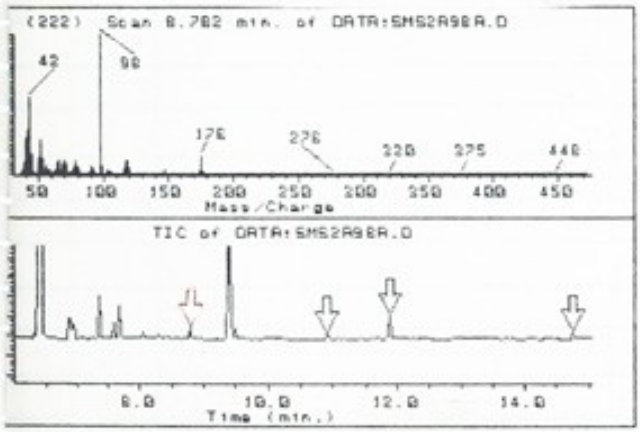
Minor peaks from
SMS3A98A
first dibromonicotine

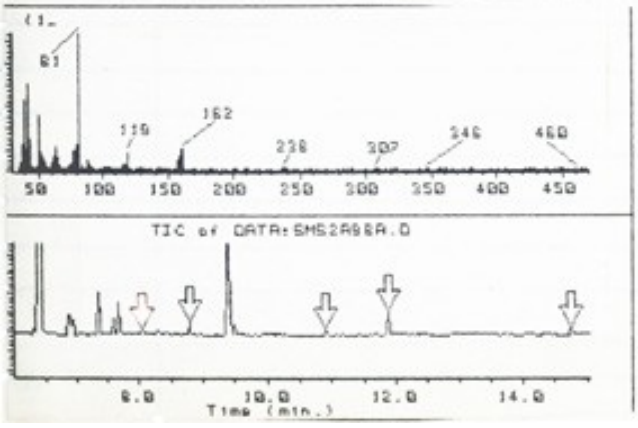


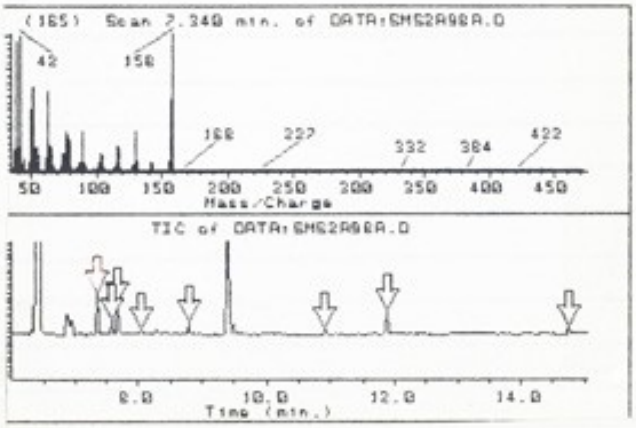








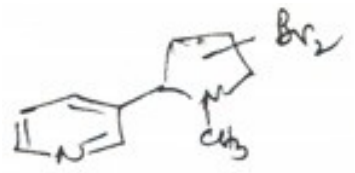




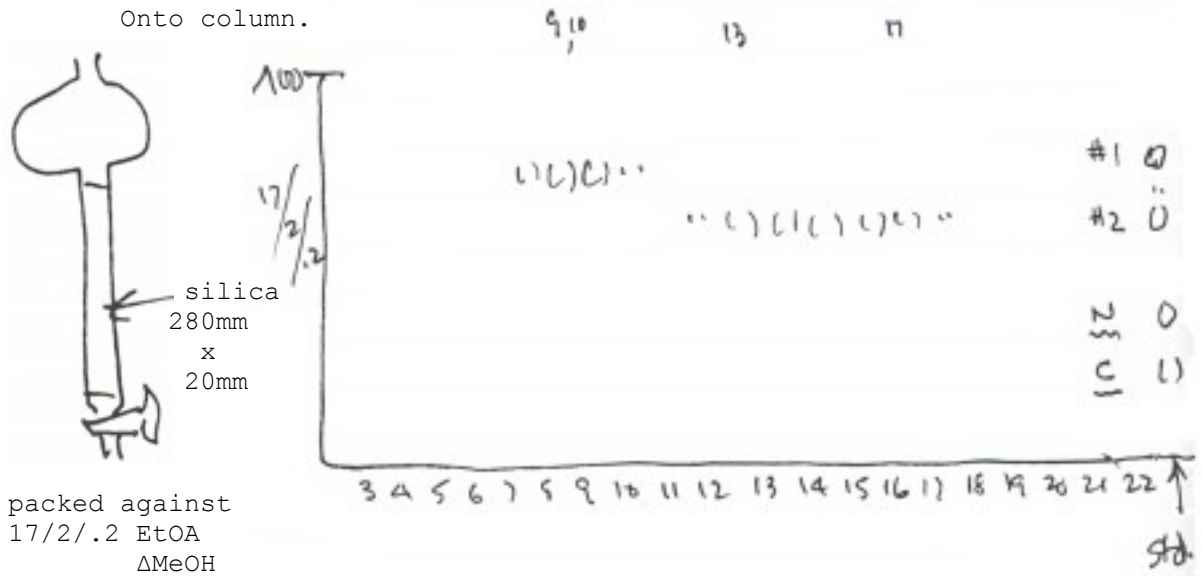
June 3, 1991

Chromatography of dibromonicotine

All remaining HBr salt 165B.
0.46 g.

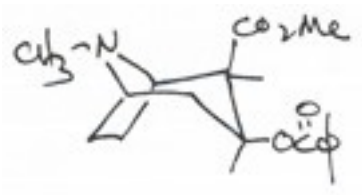


Onto column.



June 4, 1991

Convert.



conc. HCl.

Ref. Zir/cle et al. JOL

27 1269 (1962)

10 g (10.06 g) Sigma Cocaine HCl. into 80 ml conc. HCl - onto relfux 9 PM

See repeat page 191

Also MB 12/22/87 p128 SFGH notes

off 7PM = 22h. Even at reflux, xtals apparent. ∇ to RT over ~12 hrs.

→ heavy, glistening xtals. filter, wash [with] 4 x 5 ml H_2O

1.2g ->.6 mp 240-242

aq. ML.

Solids spectacular needles air dry. 3.18 g VI-181B

benzoic acid

(Ecq·HCl= 229-231°)

Extract [with] 2 x 50 ml Et_2O

all [with] ???? & dark

aq →to dryness on R.E. at full H_2O pump @ 70°bath

Et_2O → let evap. 0.19 g pale yellow xtals VI-181C

theo. 3.59g

> 6.66 g white xtals- several drops of water still there. Grind under 75 ml Ether (anh)

wet feel. decant → decant

MW C 303 ·HCl 339.5

another 75 ml ether - grind -> much looser solids → decant

MW E 185 ·HCl 221.5

evap -> 30 mg pale yellow film OUT

MW AE 167 ·HCl 203.5

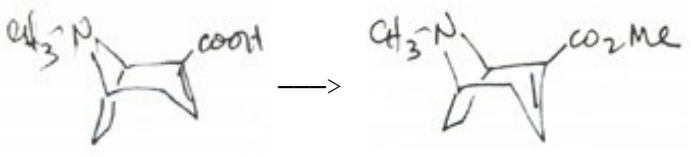
6.46 g sint 85°- darken ~ 220 melt ~ 238° broadly.

slight HCl smell

VI-181A

crude anhydroecgonine HCl theo. 5.97

June 8, 1991



6.45 crude AE (181A) [with] some smell of HCl - into 150 ml jug MeOH. sat [with] anh. HCl. stand a few hrs - then 2 hr on SB.

Strip -> a few mL of almost white oil.
Stand O.N. ⟶ a few beautiful rosettes- ester -HCl?

into 150 ml MeOH. Sat [with] anh. HCl
wait a couple hrs. (RT) resaturate
stand a few more hrs. onto SB. ~2 hr. off -stand ON
strip to dryness on R.E. stand ON. viscous almost white oil again to rosettes.

Dissolve in ~60 ml H_2O - clear solu -
xtrt 2 x 10 ml CH_2Cl_2 ⤷ let evap.
Make basic [with] sat aq. K_2CO_3 -> cloudy.
xtrt [with] 3 x 20 ml CH_2Cl_2 ⤷ evap -> ~2-3
to KR - 0.5mm over 100-110° as white oil. clear oil
3.55g VI-182 give to Maurice R.

June 10, 1991
Small scale diddle

Br_2
——> ?
various solvents

Heptane. 2 ml Heptane, 1 drop N 2 drops Br_2 (3 moles~) onto S.B. -> pearly orange globs. ∇ -> colorless overhead. decant solvent. suspend in dil HCl very little sol. decolorize [with] sat $NaHSO_3$ OH^- [with] dil NaOH - xtrt [with] 90 ΦCH_3/BuOH spin
——> SMS 3A11A.
VI-183A

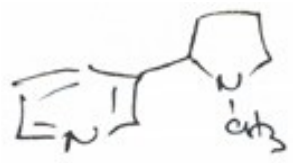
Methylchloroform. 2 ml CCl_3CH_3, 1 drop N 2 drops Br_2 - much cleaner. Δ a while - decant - add H_2O to orange residue + drop HCl + several drops $NaHSO_3$ never completely in. decant - OH [with] aq. NaOH extract [with] 90/10. SMS 3A12A VI-183B

cyclohexane. 2ml CH 1 drop N 6 drops Br - Δ a few minutes on SB. -> orange residue stand, decant, + H_2O + HCl - ~~amp~~ + $NaHSO_3$ - rub until all in & colorless. + NaOH - xtrt [with] 90/10. SMS 3A13A VI-183C

CH_2Cl_2 ~ 2 ml dichlor - add 2 drops N - then spatula full (~ 100ml NBS) -> solution. Add ~ 200mg $FeCl_3$ - some color goes in ~~a~~ globs on wall - + squirt 35% H_2O_2 -> deep aq. layer on top - bubbles & gets warm - vigorously stir. Now quiet. add more water, $NaHSO_3$ (not much good) + HCl -shake- remove

Aq. layer, OH^- [with] 4 N -> black sup. xtrt [with] 1 ml 90/10 - spin - dilute 1 -> 4 [with] fresh 90/10 GCMS [with] SMS3 A14A VI-183D

June 17, 1991
Attempt:



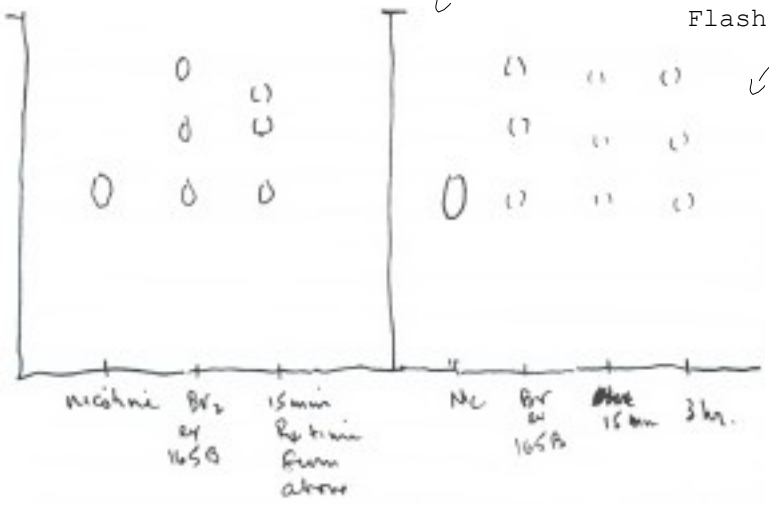
NBS
——> ?
RT.

0.162 g nicotine in ~ 5 ml CH_2Cl_2
0.356 g NBS (2 x theo for now) in 5 ml CH_2Cl_2 (most dissolves)

~1PM Add. ——> blush of yellow, then fades to ~ white.
add another 5 ml CH_2Cl_2 of remaining NBS
add another 10 ml CH_2Cl_2 [with] remaining NBS - all dissolved

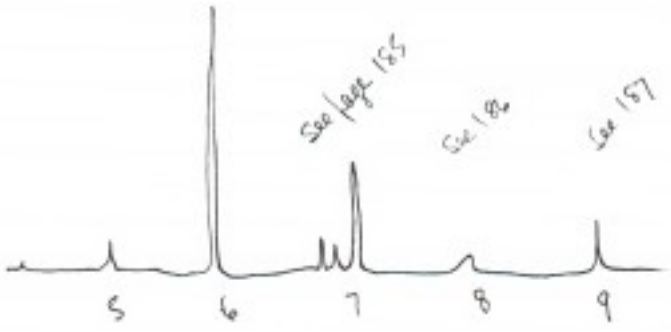
color darkenes (is this exothermic?)
no heating. 15 min. TLC. 3hrs ~~HC~~ work up drop [with] B.carb
2 x 5ml 1 N NaOH
Flash
TLC

17/2/12
EtOAc
MeOH
NH_4OH

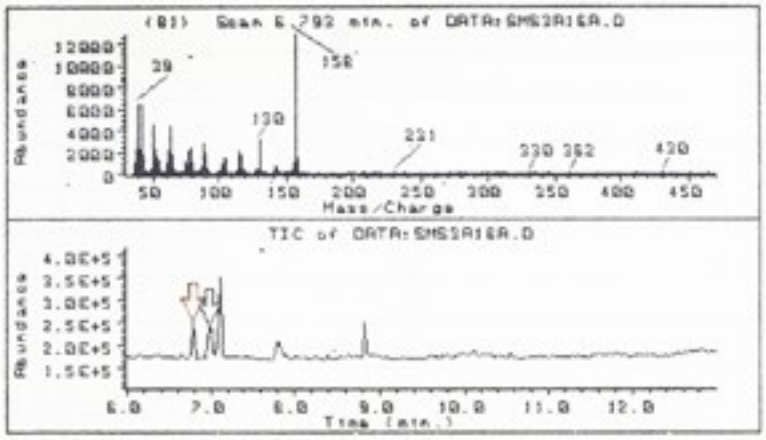


now the 2 faster peaks are both different from 165B

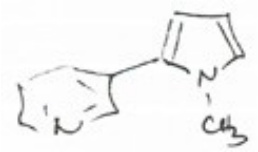
GCMS
SMS3A16A
S450



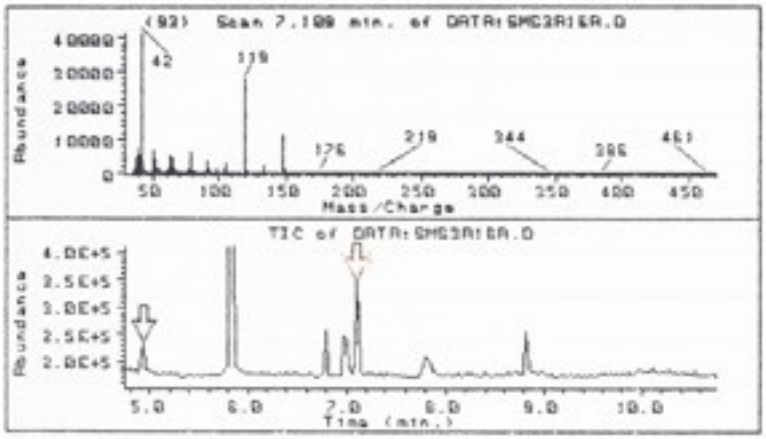
7 min peaks

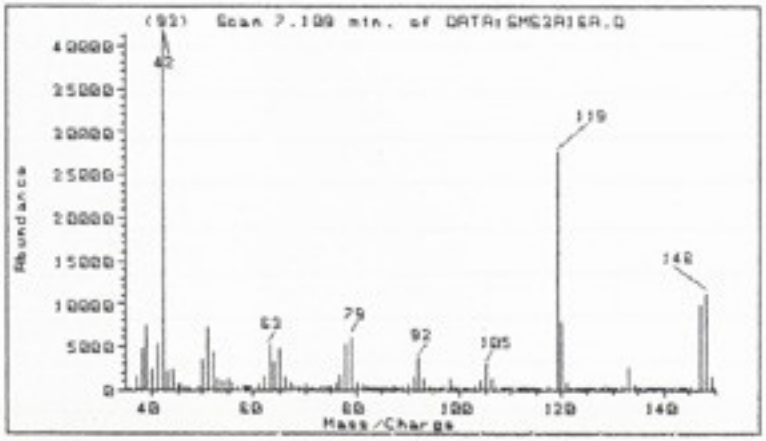


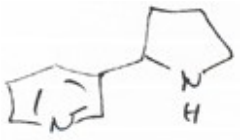
See spectra on rerun - (p189) in comparison with these.



=158



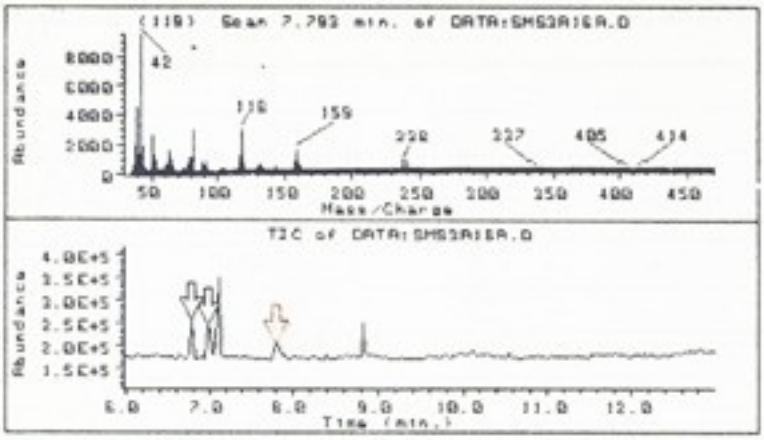


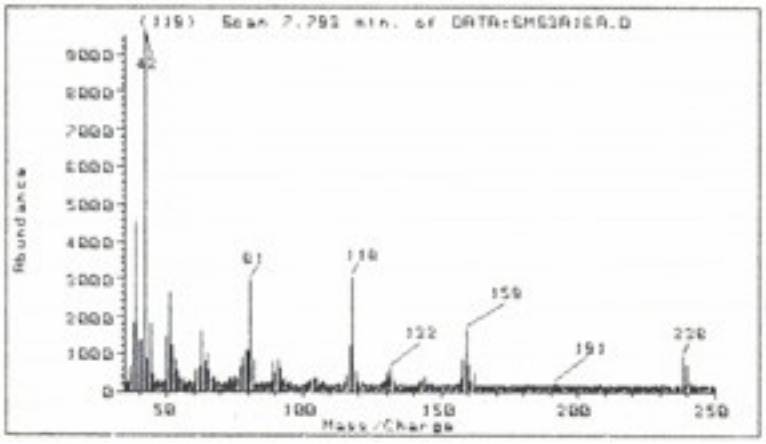


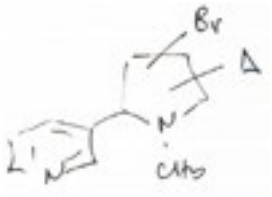
= 148

See changes with time. page 189

8 min peak. 238/240 = N+Br-H_2



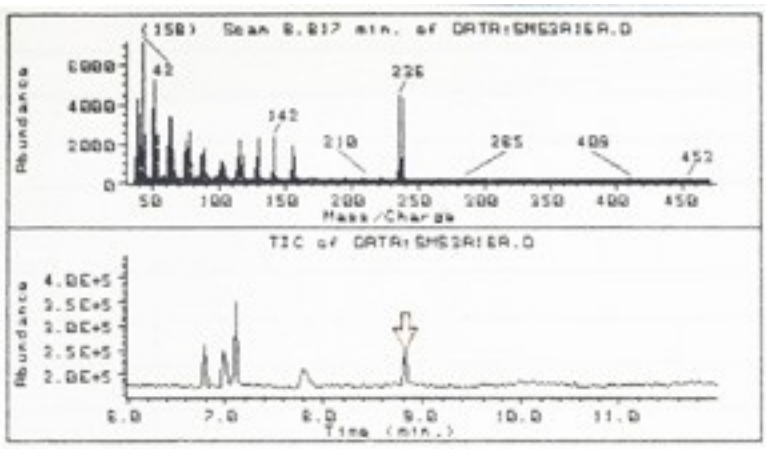


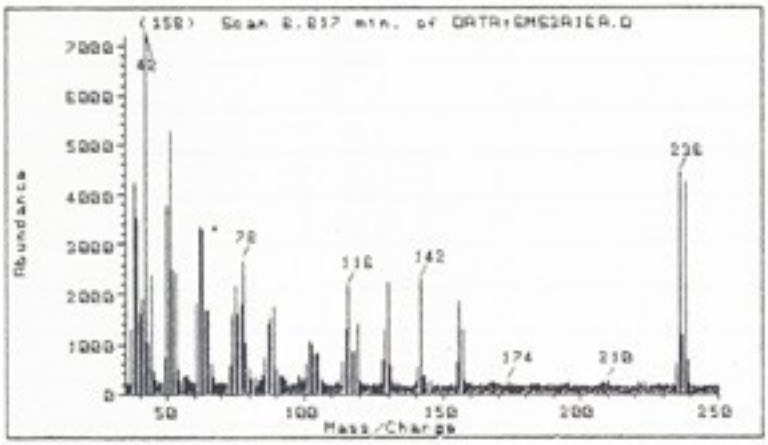


=240/238

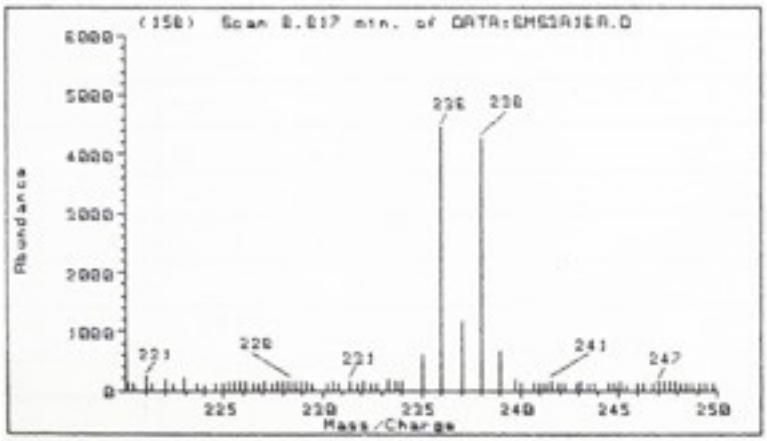
disappeared over the week - see page 190

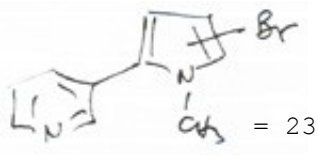
9 min peak.





See changes [with] time
p 190





= 238/236

June 23, 1991 nicotine $\xrightarrow[\Phi COOOOCO\Phi]{NBS}$?

A solution of 3.24 g nicotine in 20 g CH_2Cl_2, add

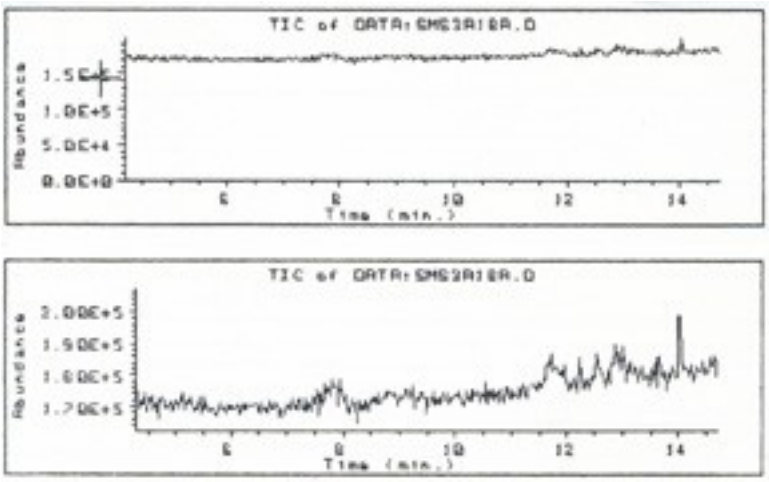
~.7 g benzoylperoxide as solid. (~1/6 equivalent?)
sputter, some gas ↑, some darkening

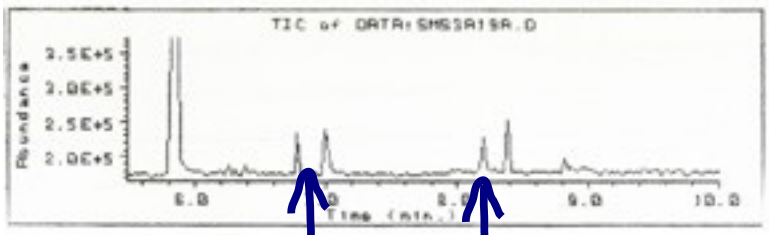
Then add a suspension (almost a solution) of
14.2 g (x4 equiv) NBS in 100 ml CH_2Cl_2 - exotherm
~~st~~ flash loss of color [with] each early addition.

stir - 1 hr -> oily deposit.
ON -> extensive oily deposit

dig out a 20 mg glob - suspend in 2 ml ^ dil HCl -> lots of insoluble gums, + pale yellow color.
decant, make basic [with] N NaOH , deeper color.
xtrt [with] 2 ml CH_2Cl_2 - color stays in aq.
1 droplet in 1 ml 90/10 ΦCH_3/BuOH
└──> nothing by GCMS

continue on page 192





re-run of 6:184 after standing a week (see page 185)

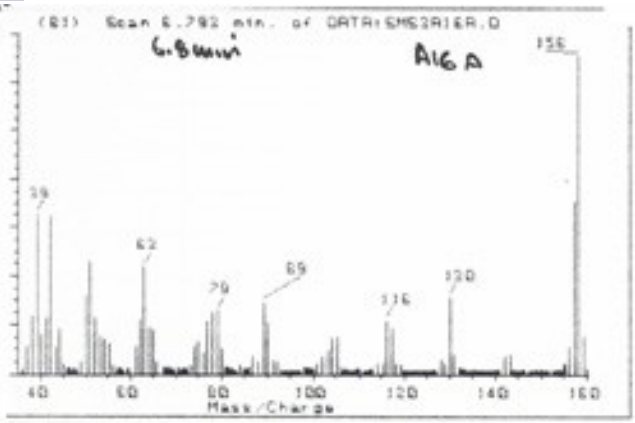
6/17/91

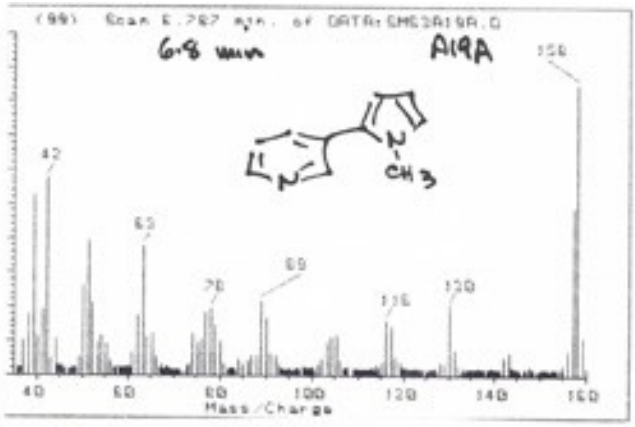
6/24/91

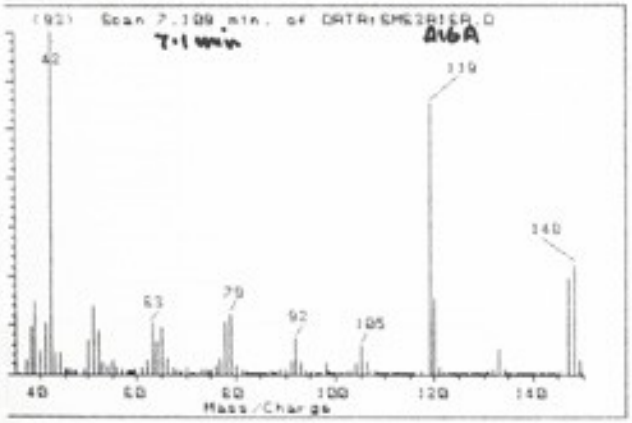
see page 185

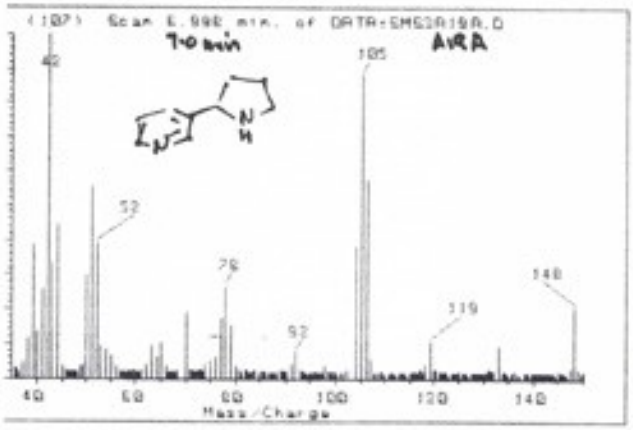
gone

new =cotinine





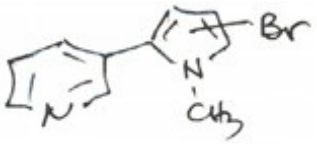


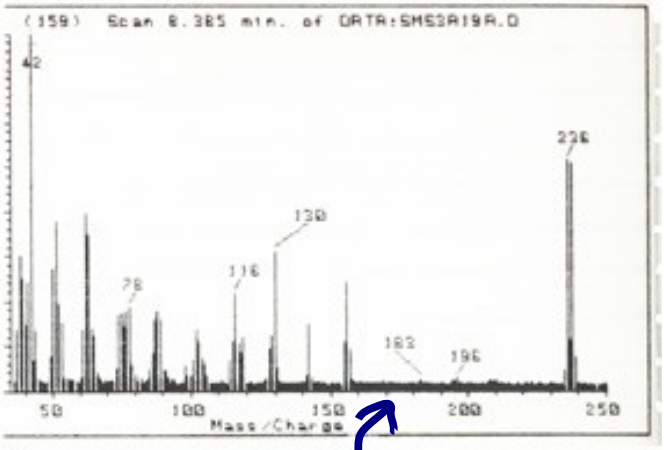


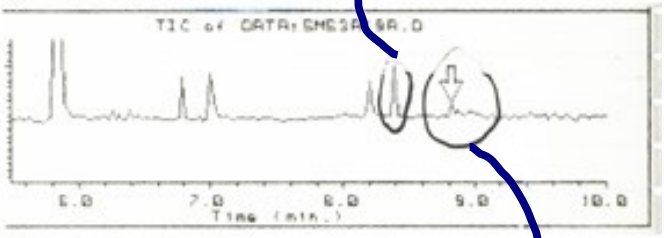
6/24/91

8·4 min A19A

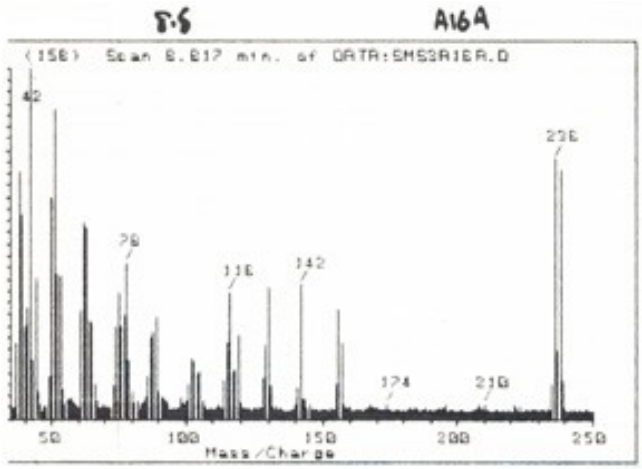
The two isomers of

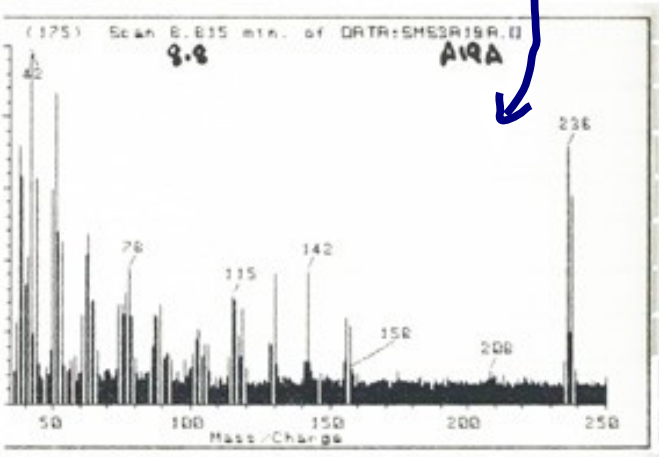


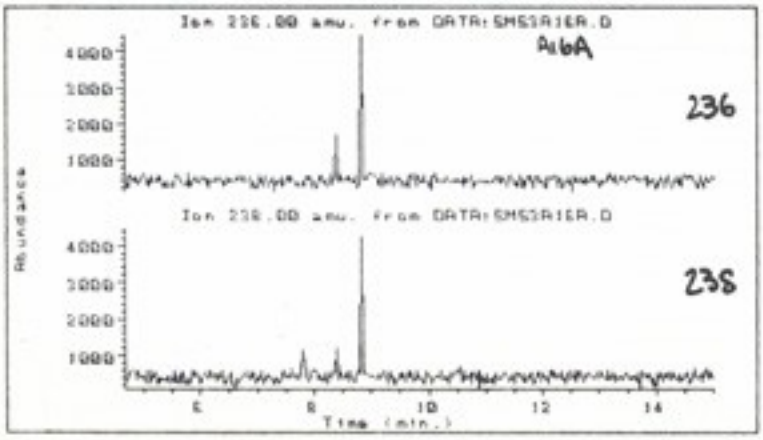




6/17/91







in the 6/17/91 run

ONLY the late isomer is Wockle. The 8.8 minute isomer

in the 6/24/91 run (one week later, above

it is the early isomer that is seen (largely)

June 29, 1991

Repeat page 181 x4 6:191A

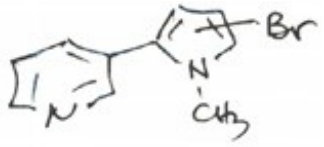
40 g cocaine from Sigma (39.97 g actual minus 0.2 g as retainer for quality control - anal ref), add 320 ml conc HCl - to reflux. 4PM -> 11PM 6/30 = 31 hrs. ∇ RTON Filter off ΦCOOH, water wash = evap on R.E. at 85°. finally, to wet-looking white xtals. off, ∇, +320 mL ether. scrape out, air-dry, ⟶ 26.61 g white xtals [with] strong HCl smell. Put 1.00g aside for eventual Et-ester. 6:191B

July 5 All into 600 jug MeOH - sat [with] HCl. Stand 24 hr. work up || to p.182

⟶ 14.05 g white oil - to Maurice.

[Editor's Note: The following is carry over from the previous page]

And, the 8 minute



has disappeared over the week.

July 1, 1991 Continue nicotine —NBS—> ?

ex page 188

All evaporated to residue on standing a week or so.
Solids from white (on sides) to light brown (in oil on bottom of beaker).

heads out [with] CH_2Cl_2 (color stays largely into gummy insolubles.

3 x 20 ml CH_2Cl_2

granular pasty brown
dissolved in ~~4~~ 3 x 40 ml H_2O

pale yellow
solu.
evap.

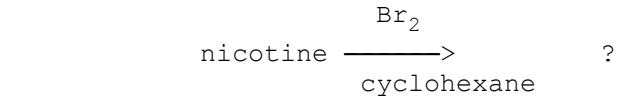
A

aqueous
yellow-clear
wash once [with]
20 ml CH_2Cl_2

combine [with] A

residue
a couple hundred
milligrams of a
deep brown oil,
not sol in CH_2Cl_2
ether.

OH^- [with] sat. K_2CO_3 -> heavy cloudy -
xtrt 3 x 25 ml CH_2Cl_2
combine flash -> deep red-brown oil -
to KR. 0.5mm -> froth & foam
slow heating, pumping. . finally
can heat [with] full vacuum
0.4mm 85 - white solid? film.
110° - lots of tarring in pot



2 g nicotine (used 2.07 g) in 80 mL cyclohexane

12 g Br_2 (used ~15g) in 50 ml cyclohexane.

Add, [with] stirring B to A. initially ⟶ color loss and immediate cloudy
1/2 ⟶ some red remains.

3/4 ⟶ oily lower phase, I think . v.dark.
all (at 2 min point) slightly exotherm (~30°)

3 PM. stir amb, temp.
3 hrs - color fading - looks very good.
decant reddish overhead
from oily (dark) residue

decant

residue - Δ on SB [with] ~15mL abs EtOH ⟶ gone to dryness
After dinner. Back up [with] EtOH somehow - (I forget) into

strip on R.E. ⟶ 6.7 g of clear, pungent oil (white)

?

EtOH soluble HBr salts, + EtOH insoluble HBr salts

into water, carbonate (or OH)
CH_2Cl_2
dryness

~ 2 g oil turns brown

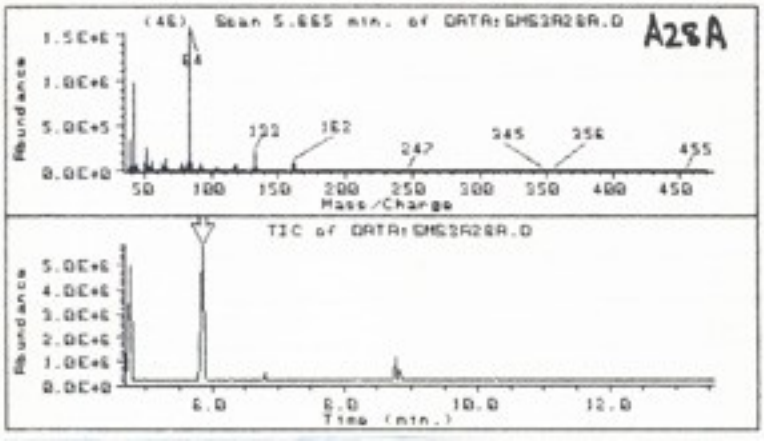
into water, carbonate (or OH)
CH_2Cl_2
dryness.

2.1 g oil that turns brown

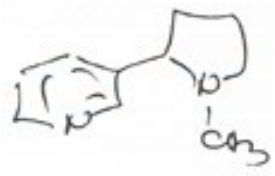
this is 193 A <- (see page 194) ⟶ this is 193 B

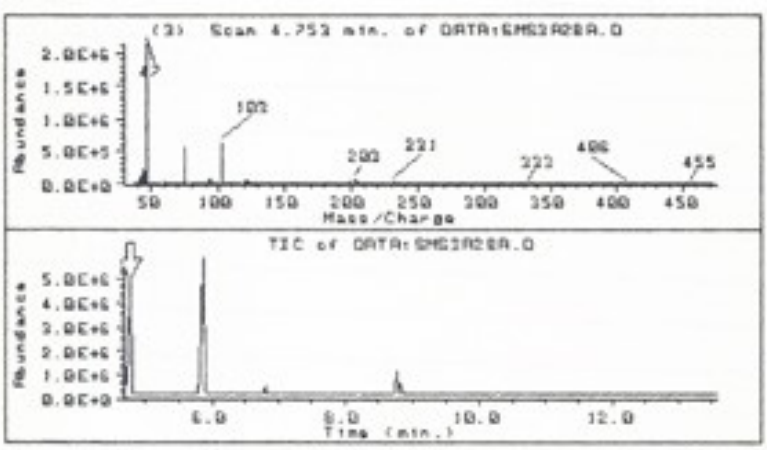
⟶this KR'ed (to ~200°->filter⟶ 193 C

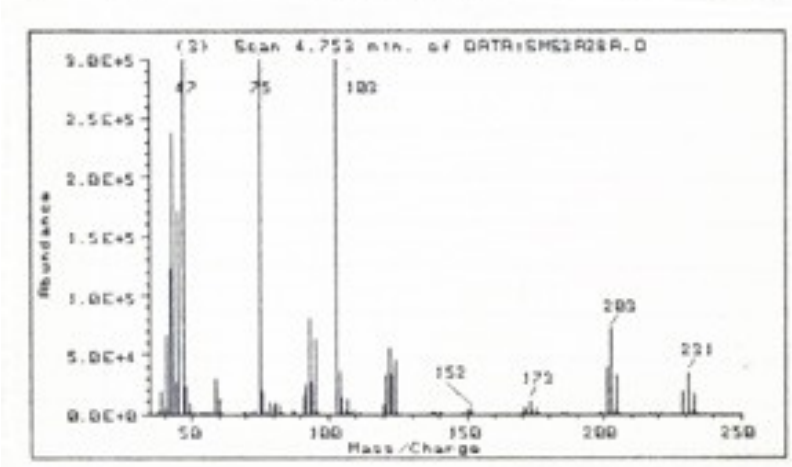
193A. EtOH soluble HBr salts.



nicotine

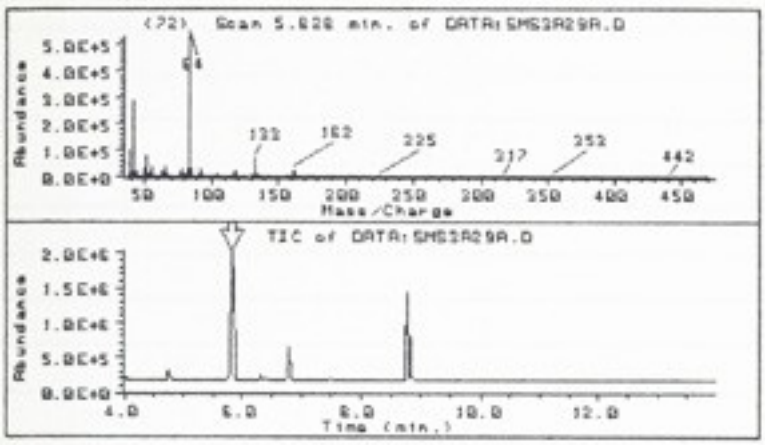




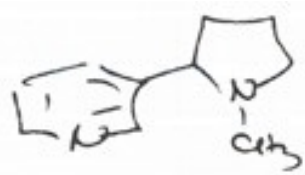


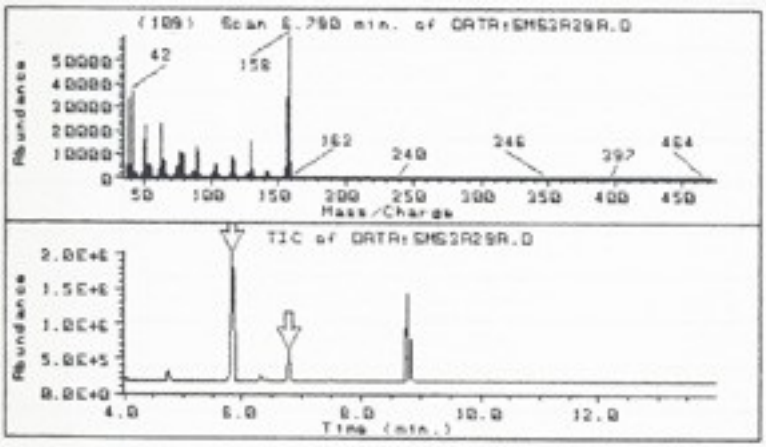
?
~~22kcC, H, Br_2~~!
233=
61 + Br_2

193 B. EtOH. insoluble HBr Salts.

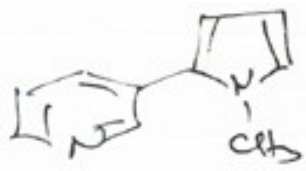


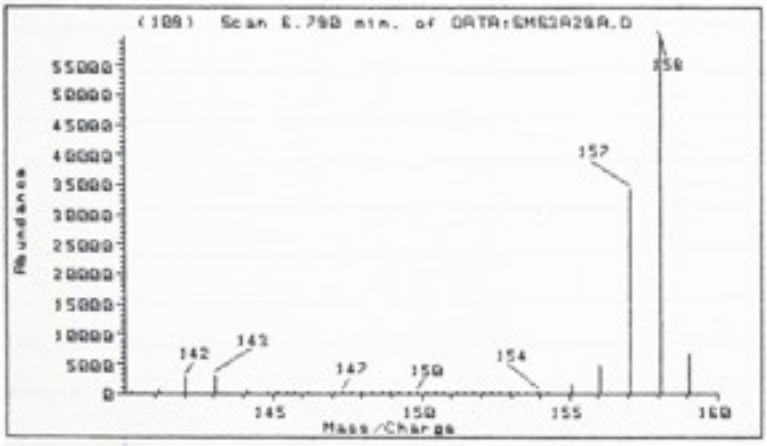
nicotine





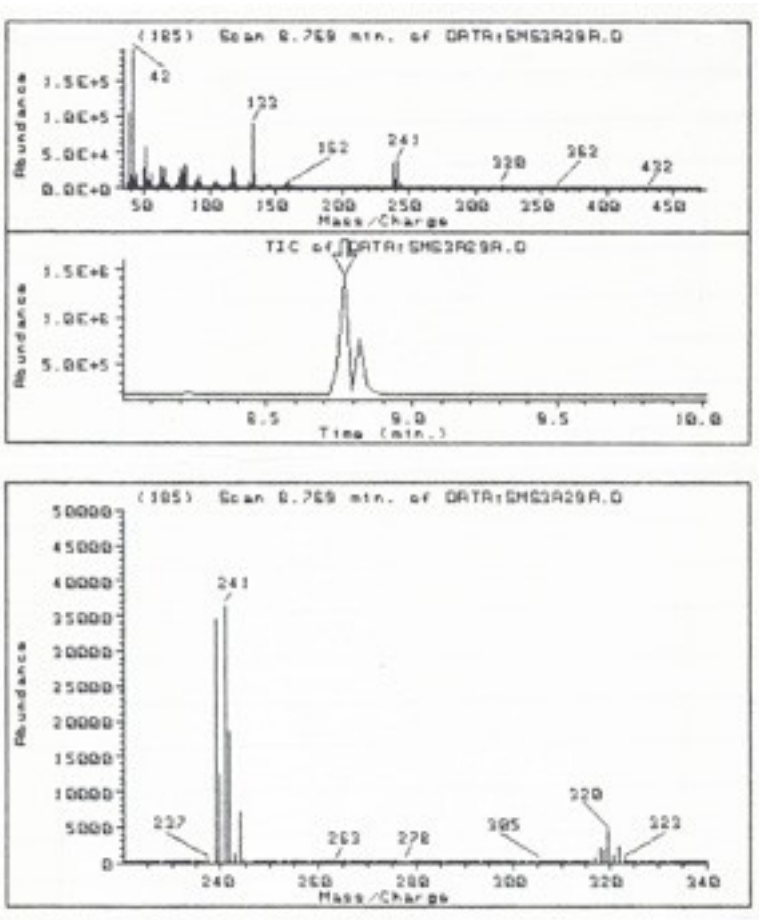
nicotyrine

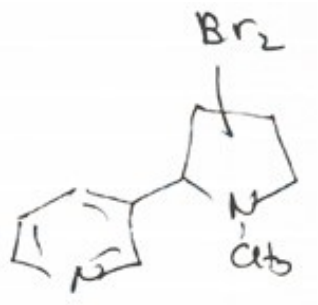




Continued —>

193 B. EtOH insol HBr Salts.



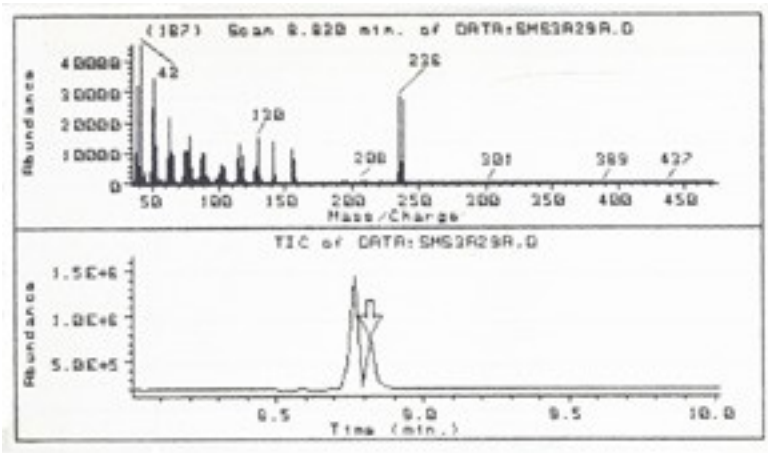


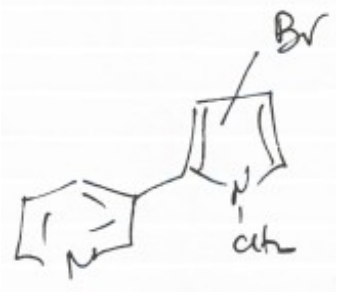
(in carbons 3 and or 4)

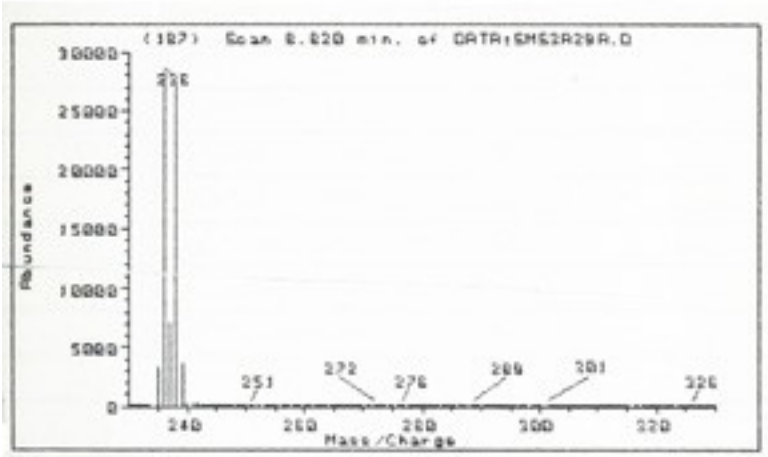
			315.30		138.00
			315.60		155.00
235.70		247.00	315.90		142.00
236.00		309.00	317.00		775.00
236.30		287.00	318.00	318 -	2073.00
237.00		371.00	318.85		1702.00
239.00	239-	34568.00	319.85	320 -	4462.00
239.90		12324.00	320.95		1075.00
241.00	241-	36392.00	321.95	322 -	2225.00
242.90		1231.00	322.95		363.00
243.90		7188.00	323.55		131.00
244.80		519.00	323.95		142.00
245.80		141.00	324.25		157.00
246.10		103.00	324.55		130.00
246.70		120.00	324.85		128.00
			325.15		136.00
			325.45		109.00

See analysis of cracking patterns -

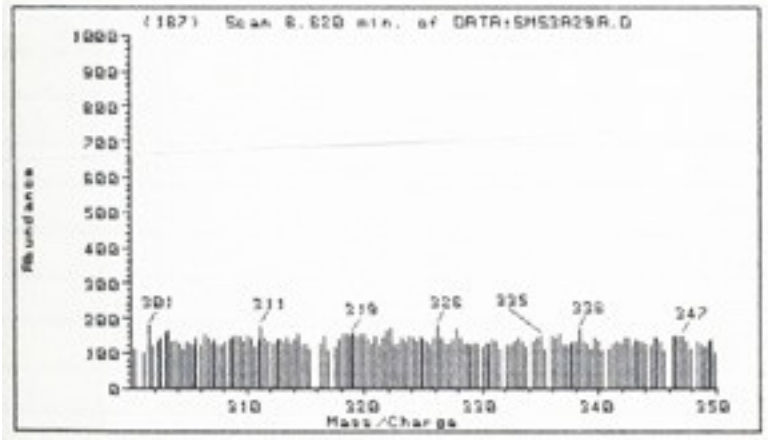
page 170-171





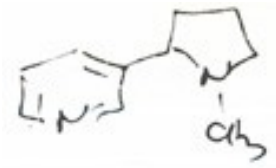


See page 190
for two isomers.



232.70	191.00
233.00	171.00
233.30	178.00
235.00	3333.00
236.00	28192.00
237.00	7149.00
238.00	27216.00
239.00	3685.00
239.90	347.00
241.00	302.00
241.80	245.00

August 12, 1991



CCl_3Br ?
——→

168 mg nicotine (MW 162) (10 drops)

in 3 ml dry CCl_4 - add

24.4 mg ΦCOOOCOΦ (~10% of an equiv)
then

461 mg CCl_3Br (2.2 equiv). ~35 drops.

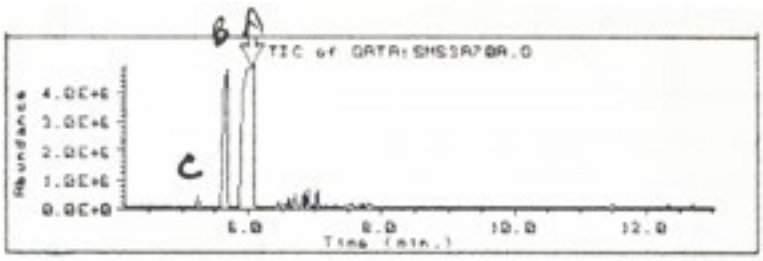
Almost clear solu. (slight opalescence) into beaker of hot water on SB at 3:35 (colorless) 3:40 almost black. shake -> gradual loss of color [with] dep of black insol oil on walls. Finally colorless again. Δ another 30 min - no further change.
add H_2O, $KHCO_3$ to basic. 2 drops to
1 ml [with] 90/10
A40A

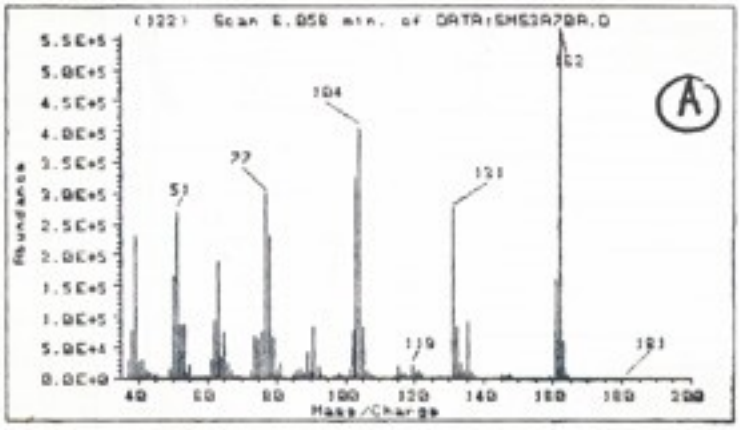
Another 10 drops nicotine
3 ml CCl_4
35 drops CCl_3Br· sunlight ~ 3 min
1 drop [with] 90/10 A41A

Same sample - + 25 mg (about) of 2,2'azobis(2-methylpropionitrile)
onto SB (hot water beaker) $N\text{-}C(CH_3)_2CN$
~5 min blue "
~15 min deep blue - $N\text{-}C(CH_3)_2CN$
throw out insol, now solvent looks lighter?
~30 min + = vol H_2O, $KHCO_3$ to basic shake
1 drop 90/10
↳→ A42A

Index for MDMA Clan lab study:

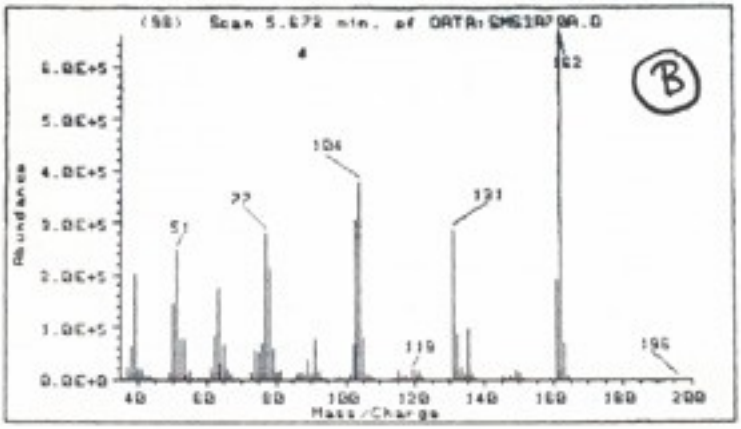
Isosafrole
PFALTZ & BAUER
SMS3 A70A





162

isosafrole



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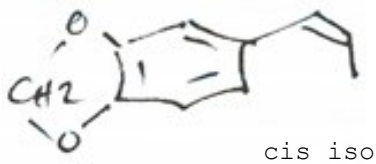
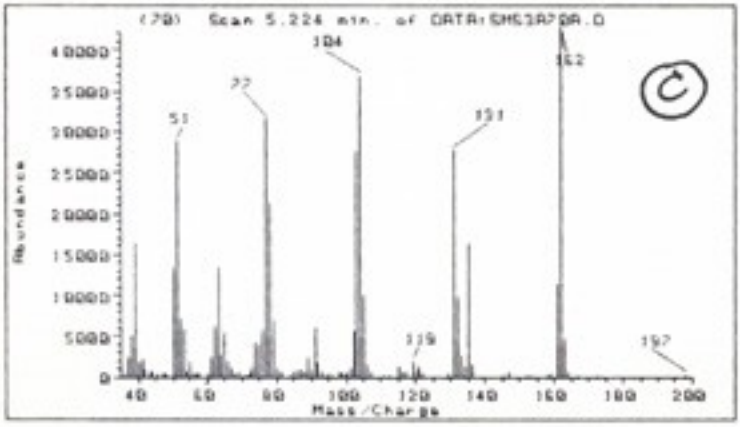


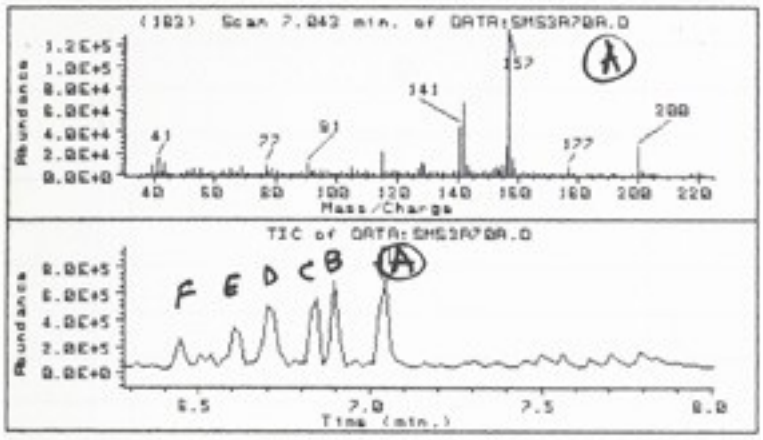
cis isosafrole



162

safrole

Small stuff from isosafrole



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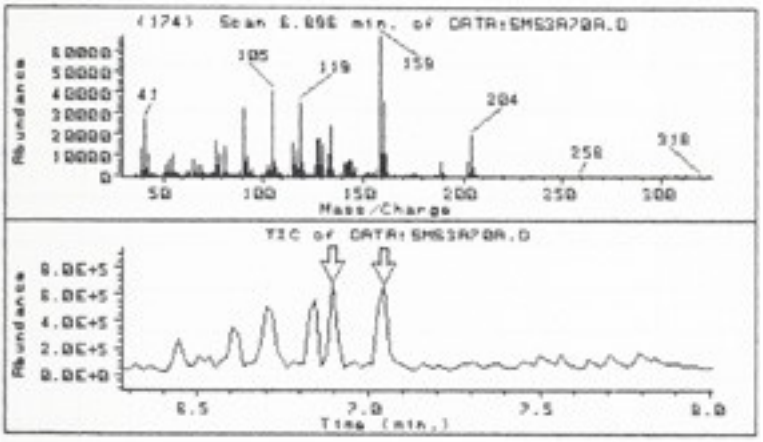

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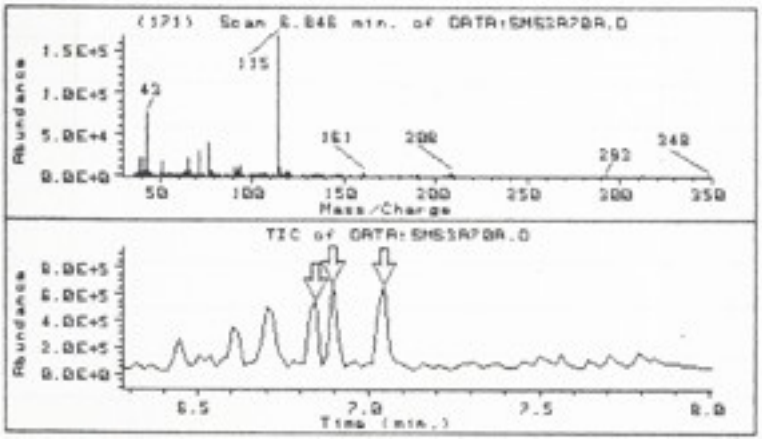
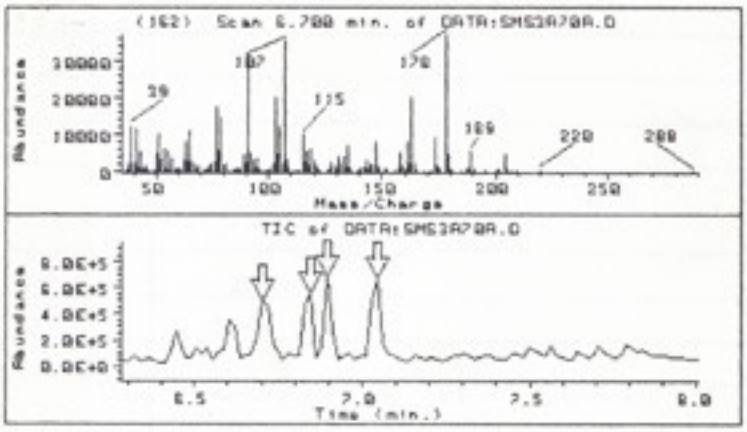
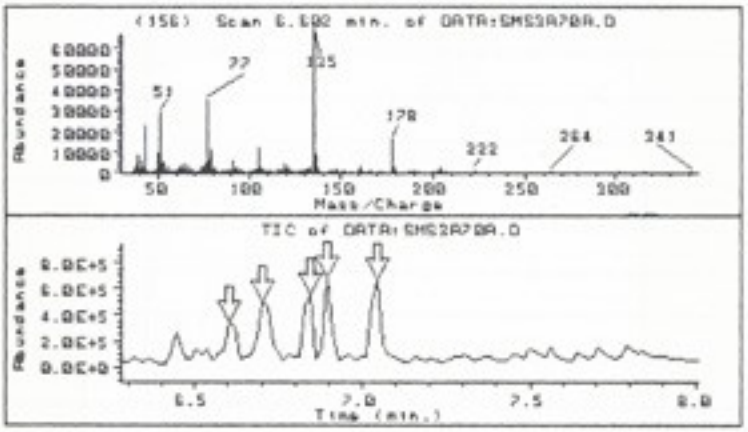
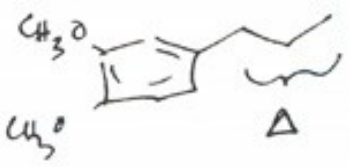


more small stuff from isosafrole



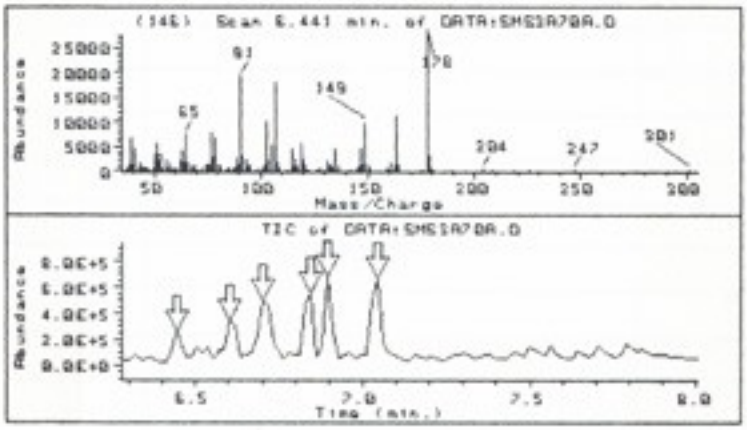
178





?

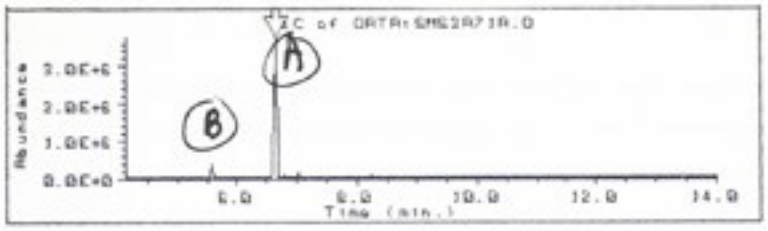
178

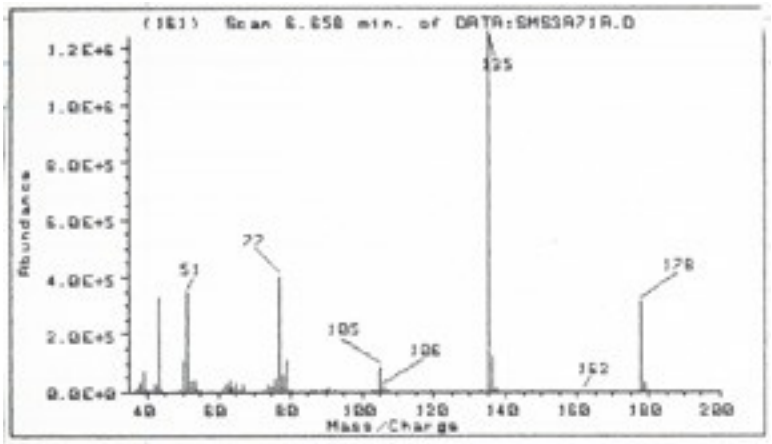


Piperonylacetone

Commercial -
origin unknown.

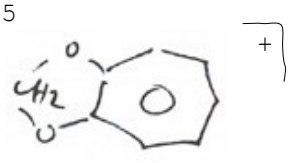
SMS3 A71A.

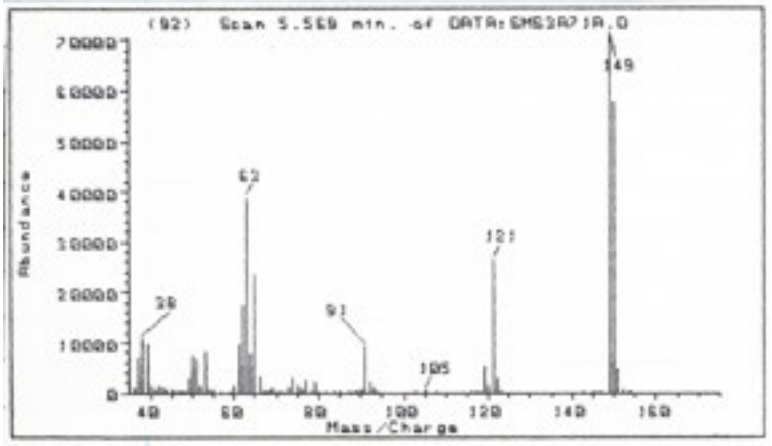




178

135

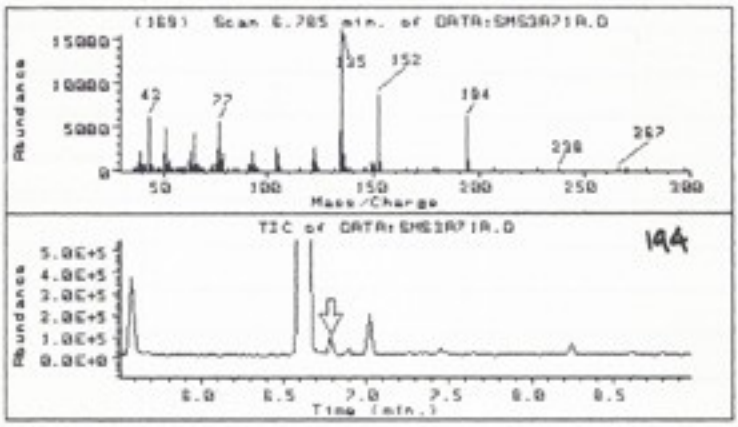


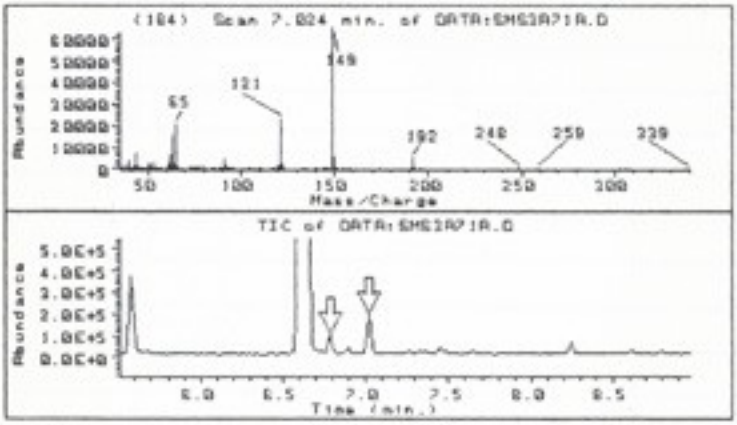


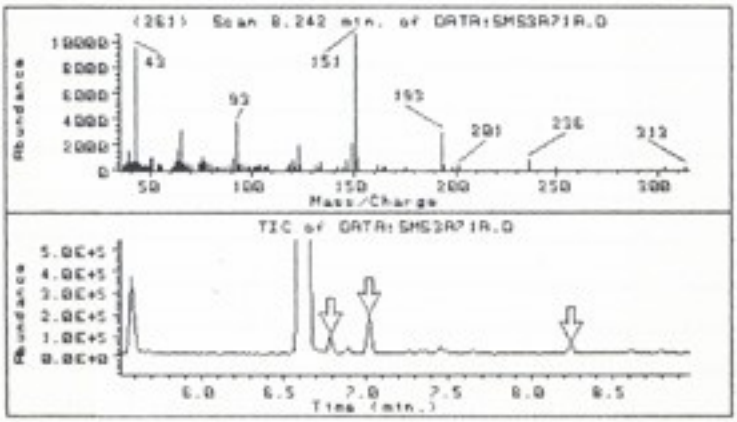
150

Small stuff from piperonylacetone

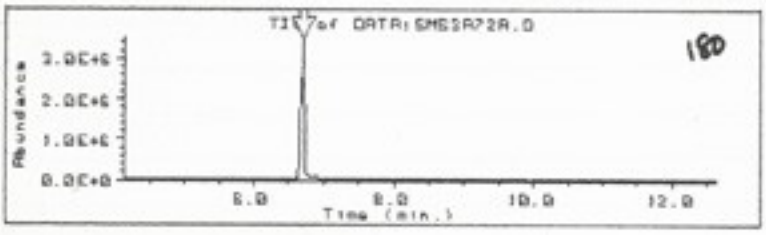
194

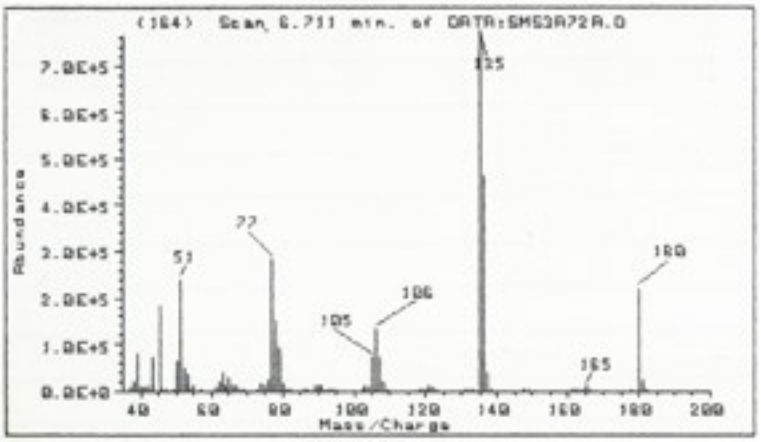




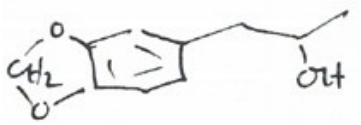


Piperonyl Isopropanol.
ATS synthesized.
SMS3 A72A

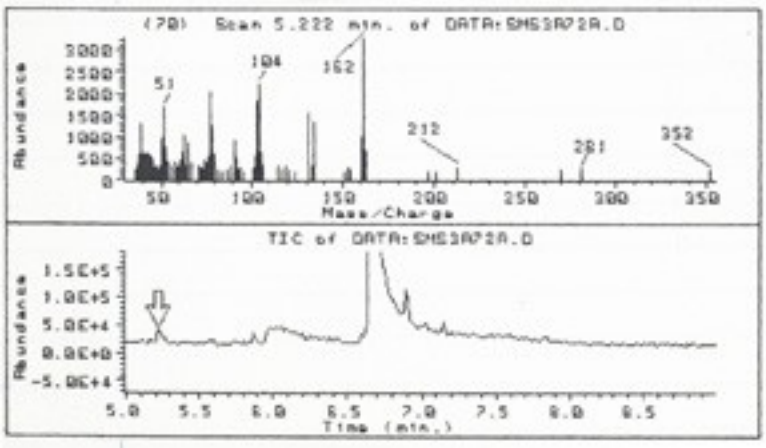




180

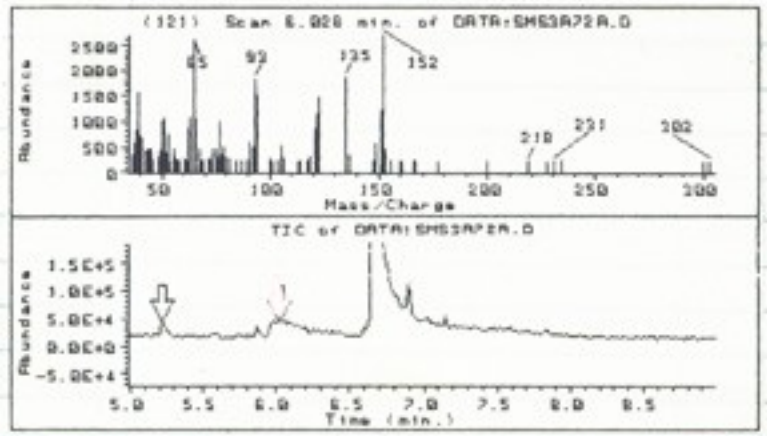


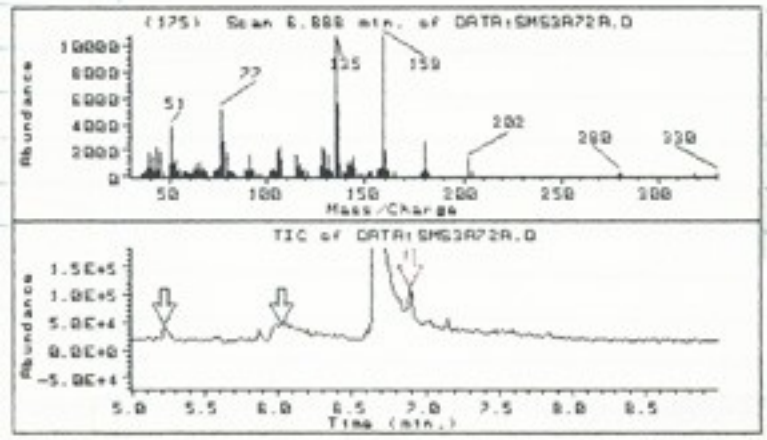
Small stuff from piperonyl isopropanol.

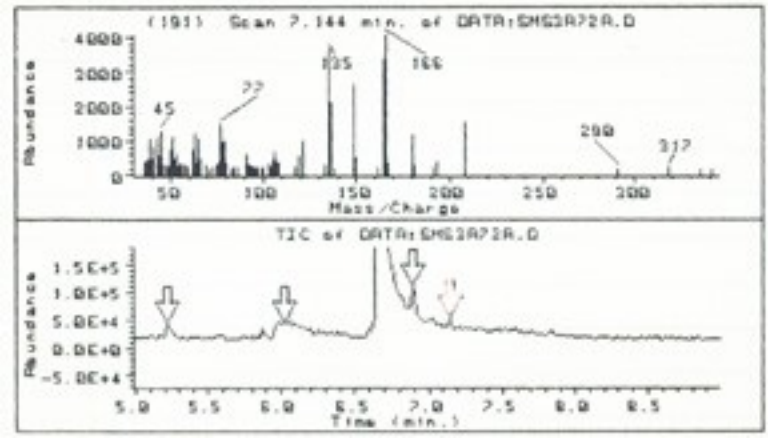


162

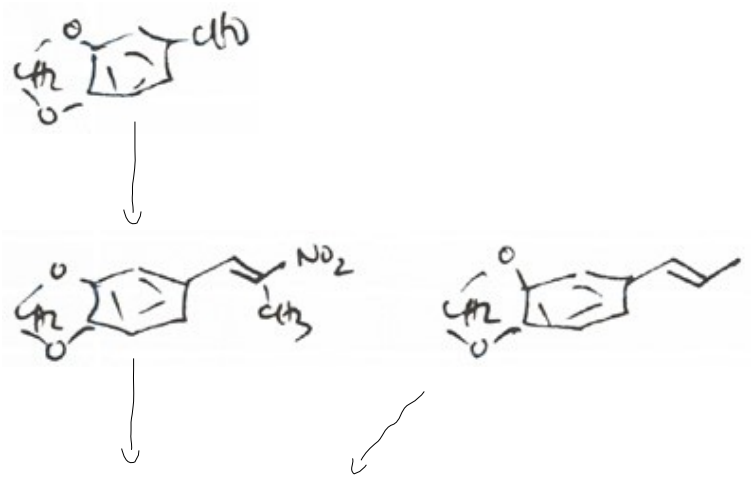
Small stuff from piperonyl isopropanol





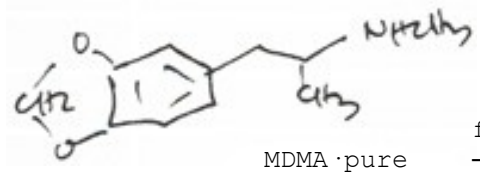


flow sheet - MDMA flow diagrams



MDMA crude

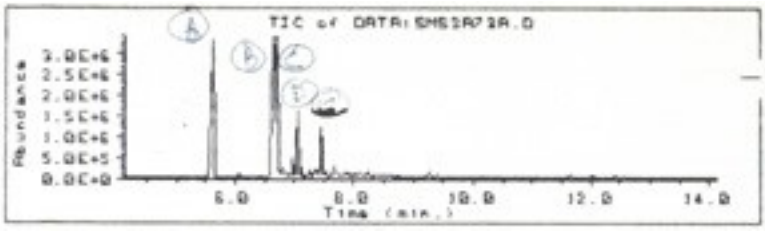
acid, base ——> neutral + acidic washes — VI-207A

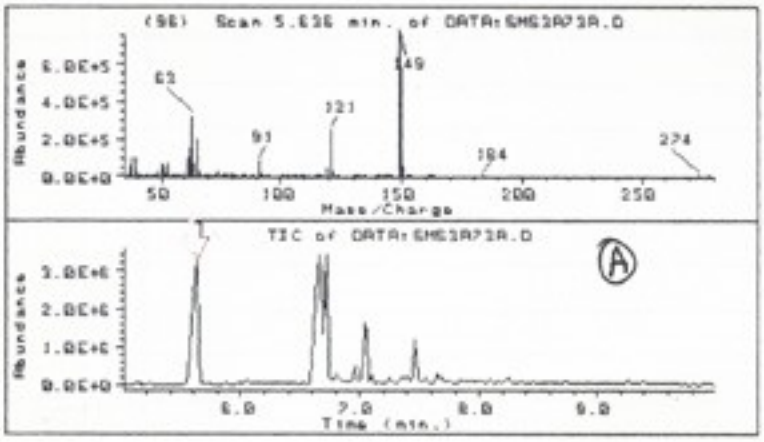


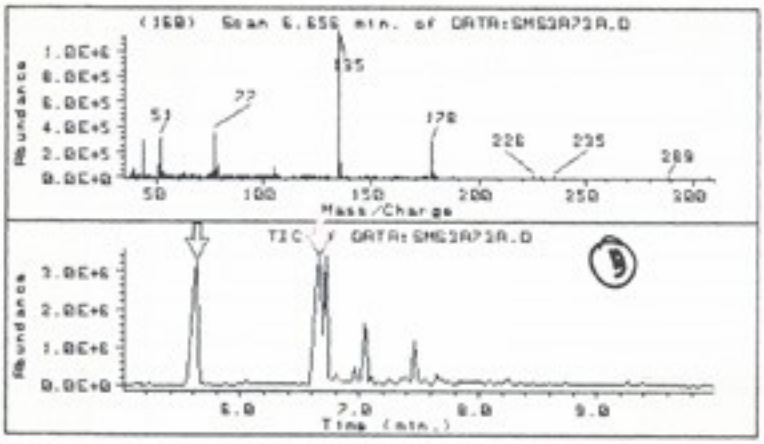
MDMA·pure

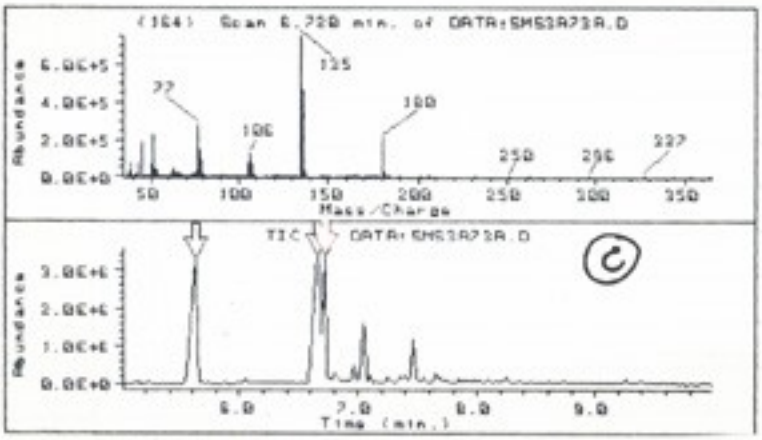
filter. ——> ML's- evaporate — VI-211

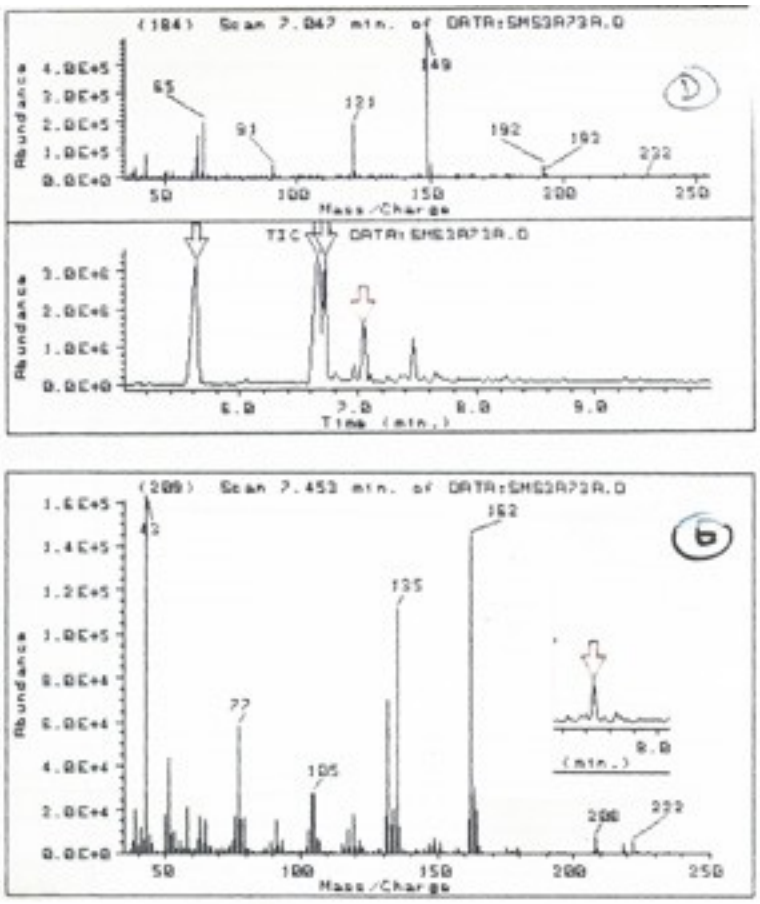
acid extracts
+ neutrals
VI-207A.
SMS3 A73A.



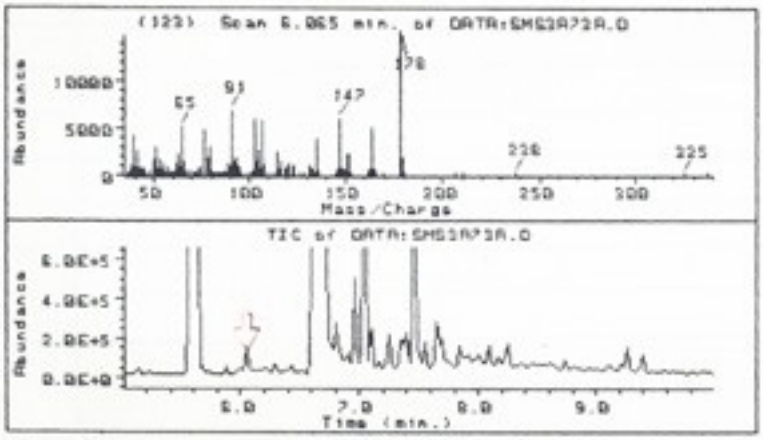




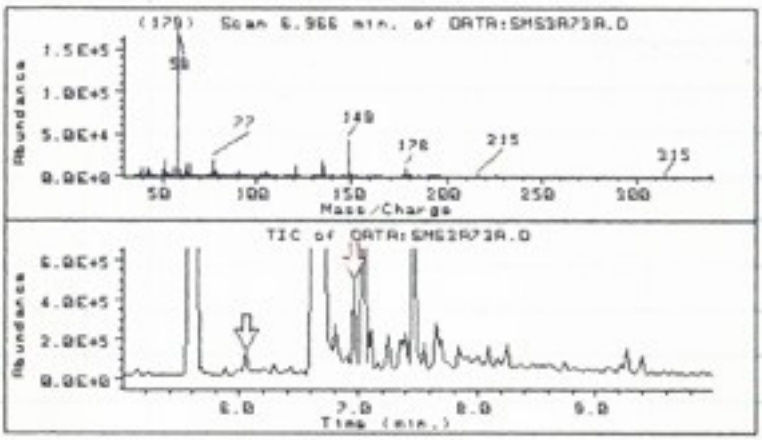


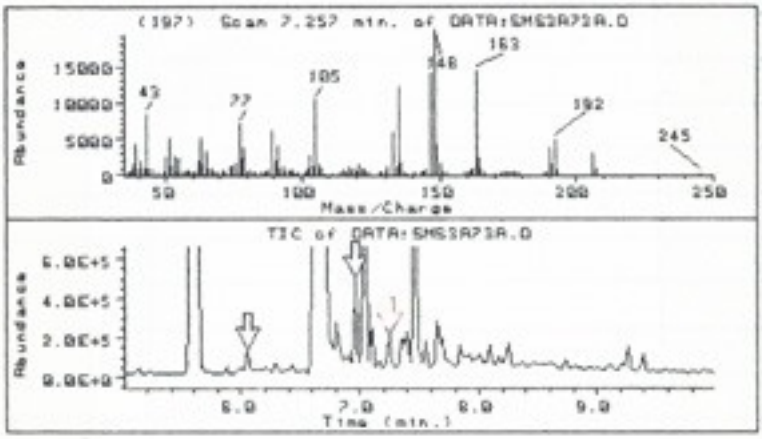


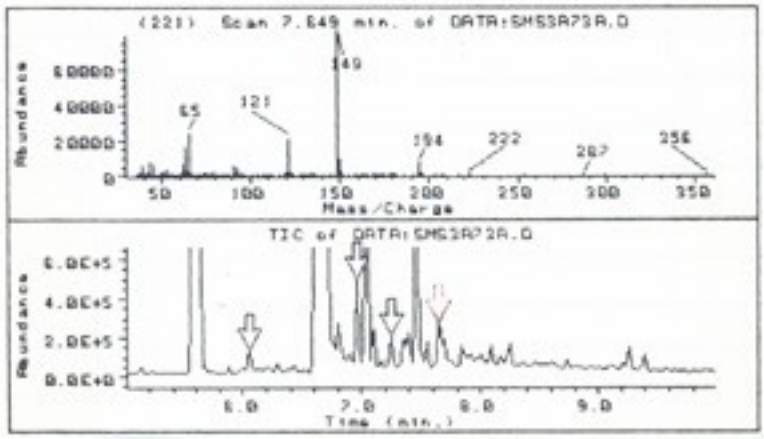
Small stuff out of neutral/acids



more small stuff - acid/neutrals.

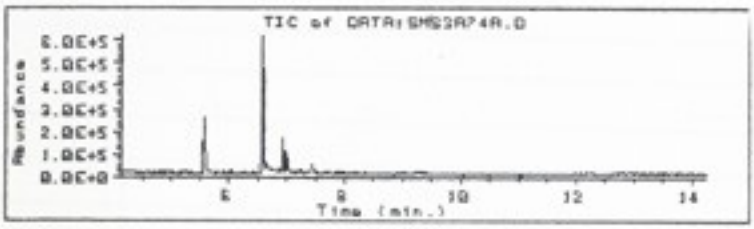


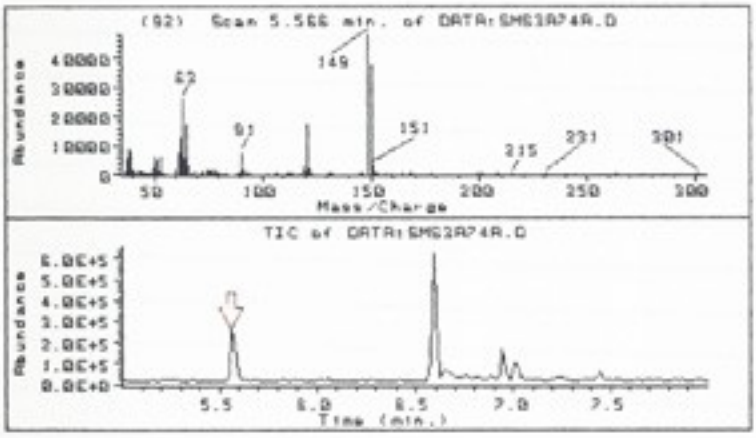


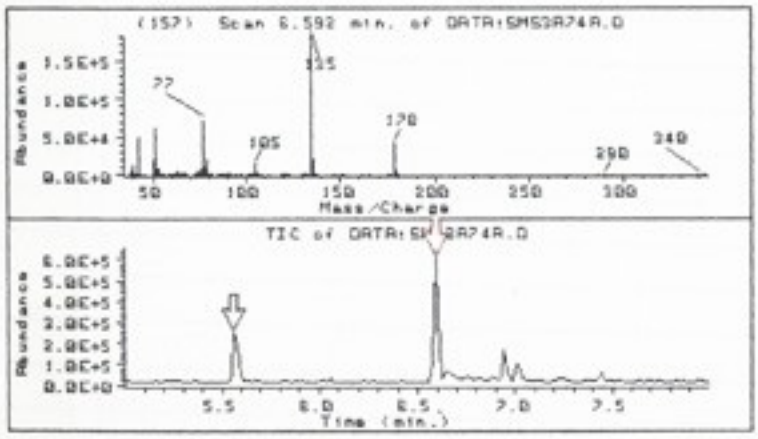


HCl extracts · ML's evaporate

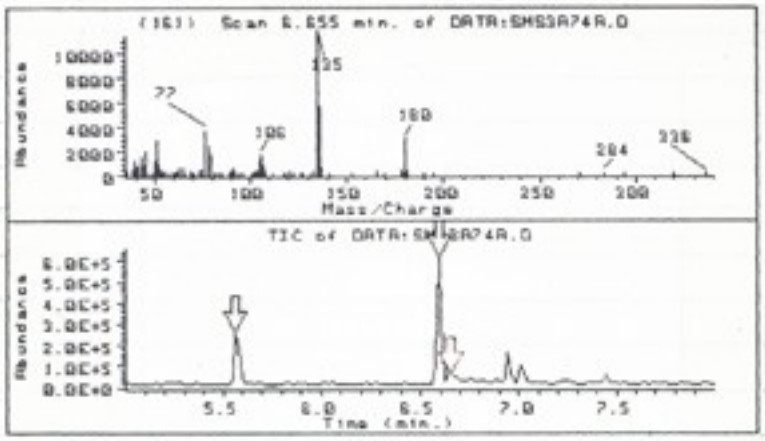
SMS3 A74A.

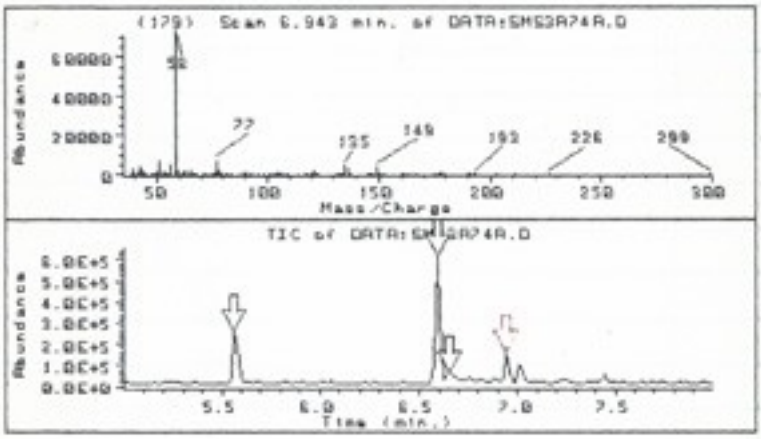


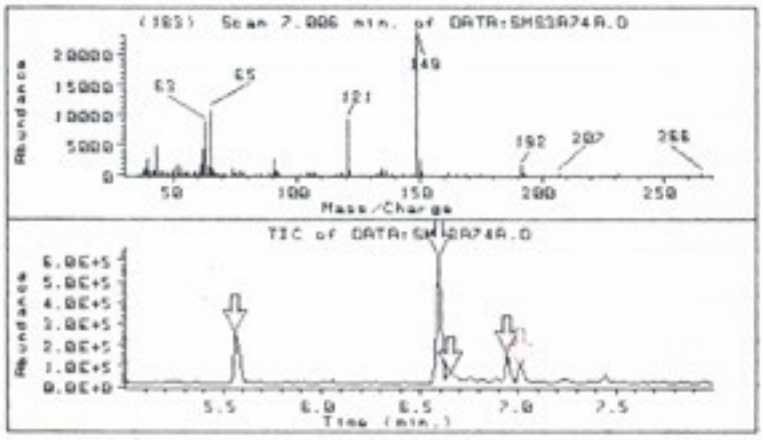




small stuff - HCl ML's residue

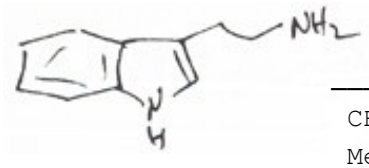






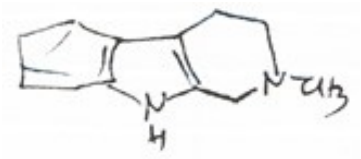
Attempt:

12/19/91



CH_2O
MeOH
(HOAc)
BH_4^-

+/or

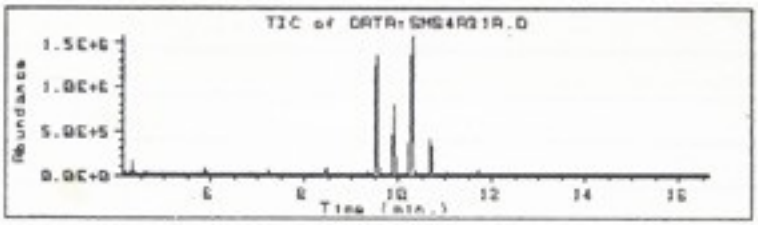


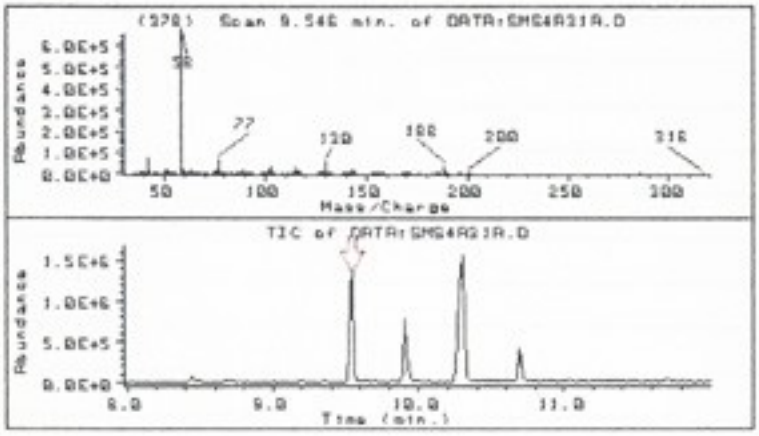
~10 mg tryptamine, in
MeOH add.
37% H_2CO add HOAc ∇ to ~ 0° -
~30 mg $NaBH_4$

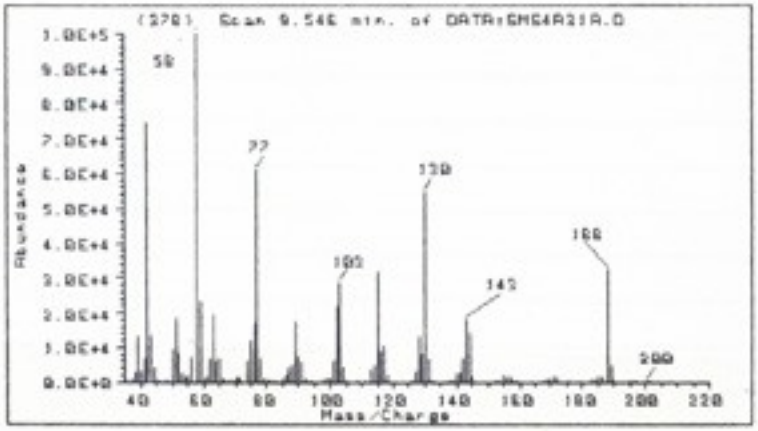
It got a bit warm - add ~2 ml H_2O - then a few drops of 1 N NaOH -
xtrt [with] CH_2Cl_2 - spin, pipette out - evap -
add more CH_2Cl_2 - evap again -> film.

to GCMS.
four major peaks. see 214 on. ⟶

fractions of formylation of DMT- p.213

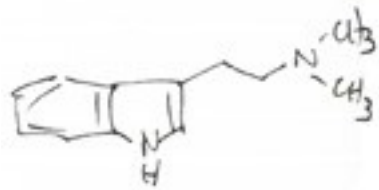


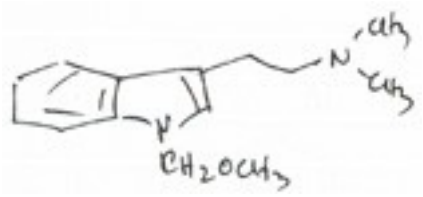




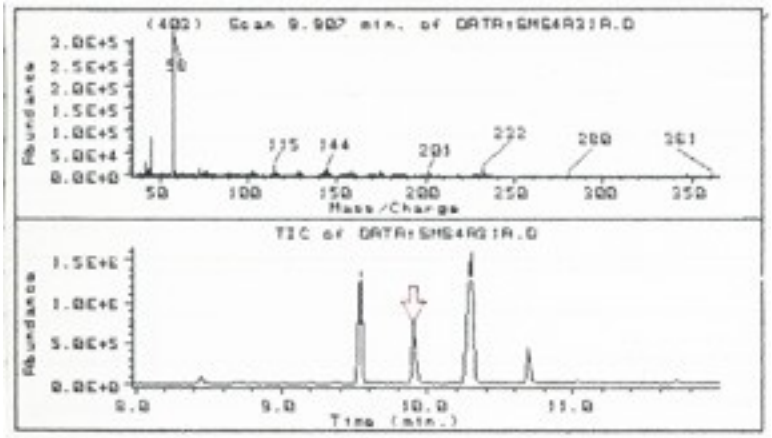
188

DMT




N
CH2OCH3

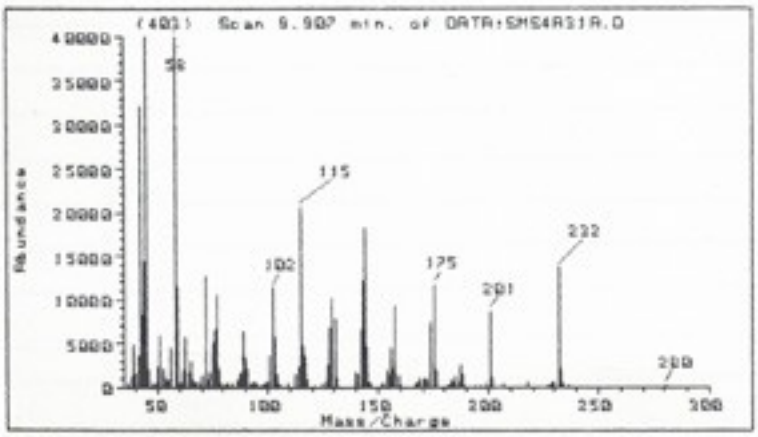
31


(402) Scan 9.907 min. of DATA:SMS4AQ1A.D
Abundance
Mass/Charge
TIC of DATA:SMS4AQ1A.D
Time (min.)

232

-31

201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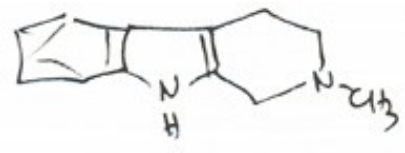
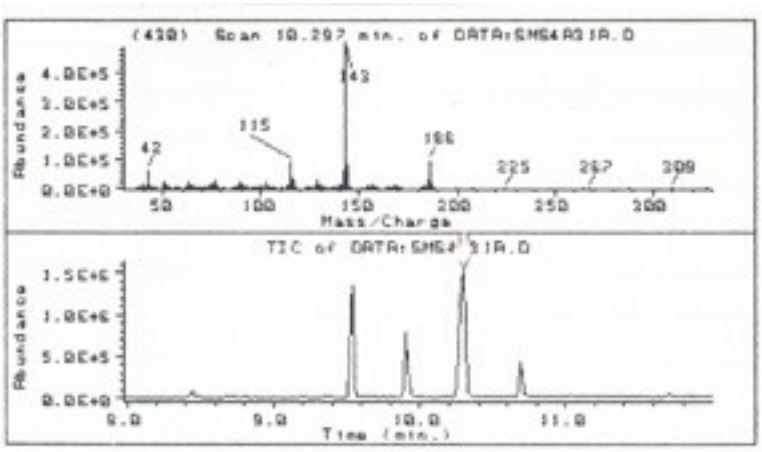
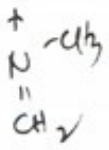
Abundance
Mass/Charge
58
115
102
175
201
222
200





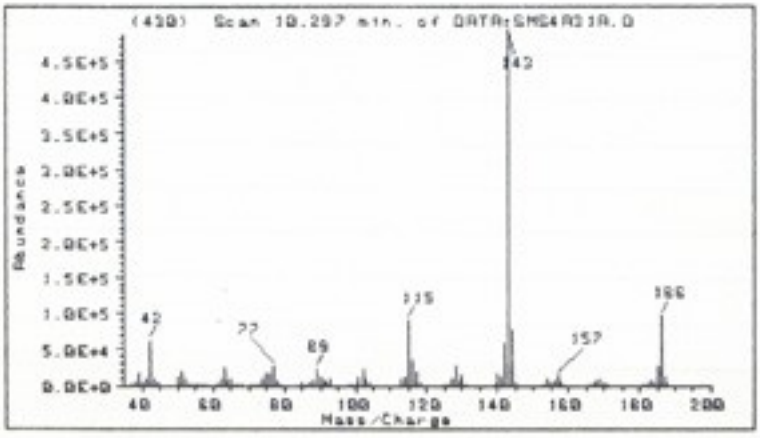
186

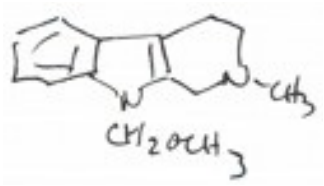
-minus

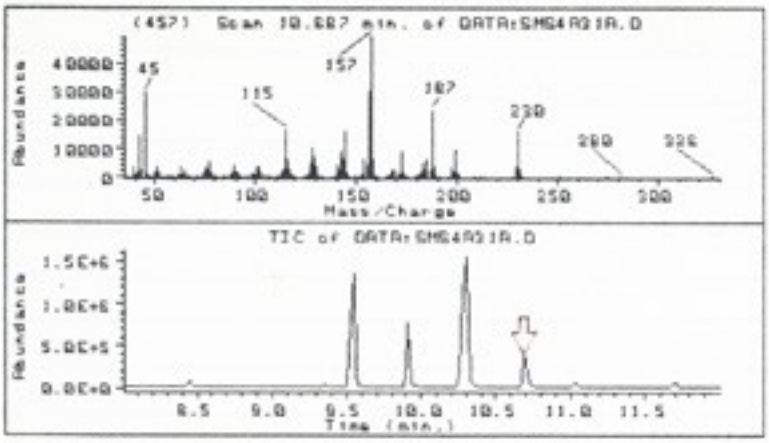


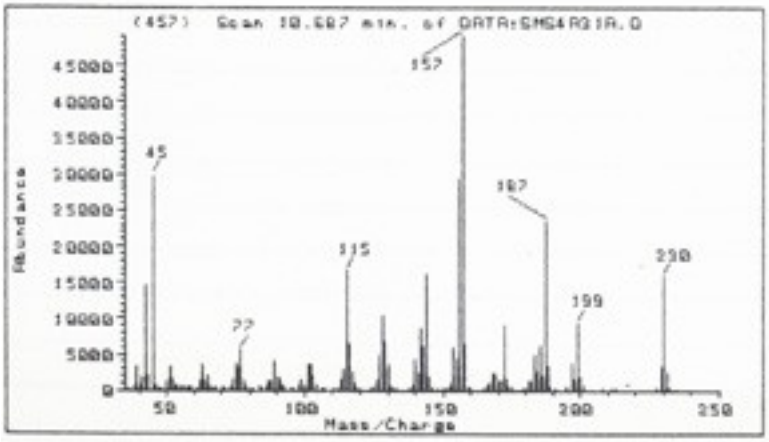
43

143







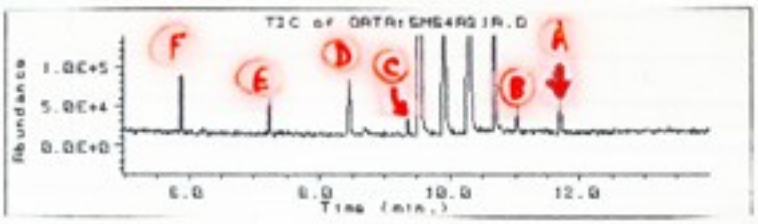


230

| $-OCH_3$ (31)

V

199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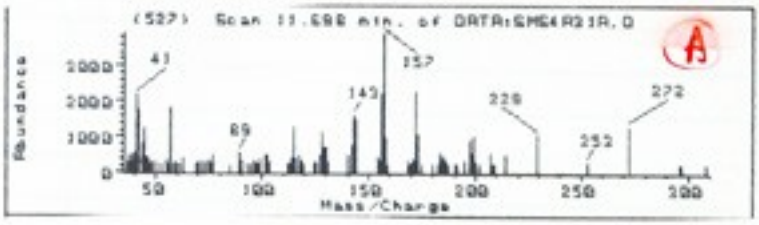
Abundance
1.0E+5
5.0E+4
0.0E+0
6.0
8.0
10.0
12.0
Time (min.)
F
E
D
C
B
A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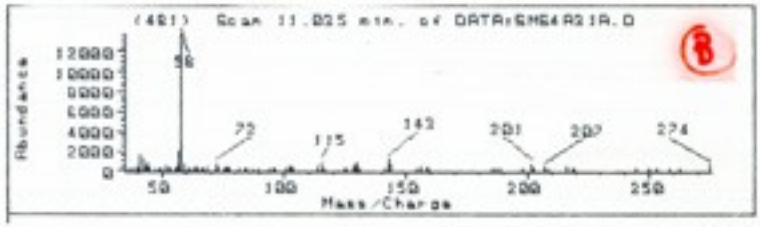
A
Abundance
Mass/Charge
41
89
143
157
228
252
272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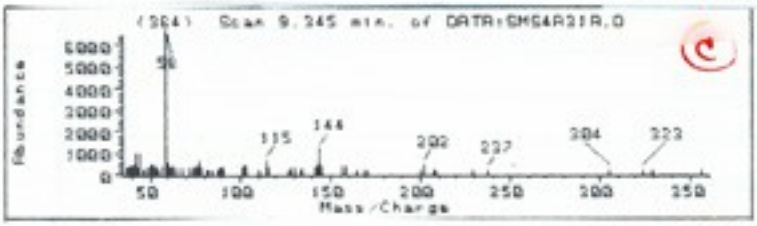
B
Abundance
Mass/Charge
56
77
115
143
201
207
274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C
Abundance
Mass/Charge
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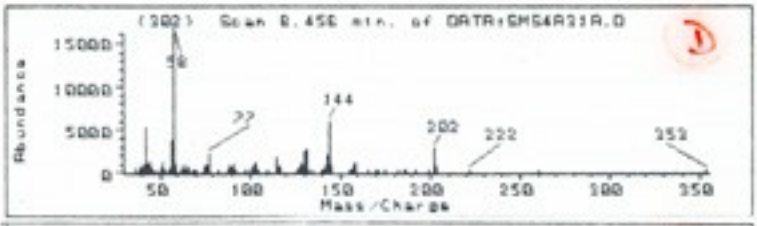
115
144
202
237
304
323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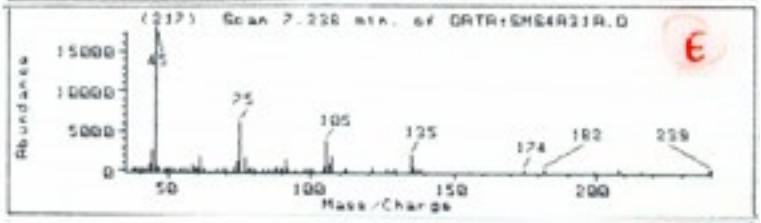
D
Abundance
Mass/Charge
56
77
144
202
222
253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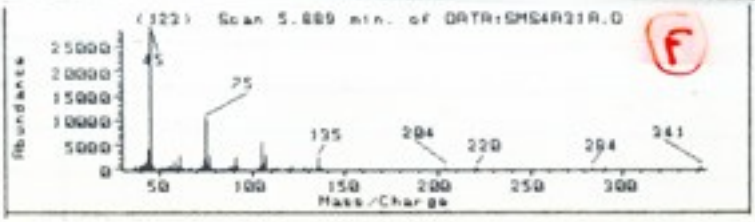
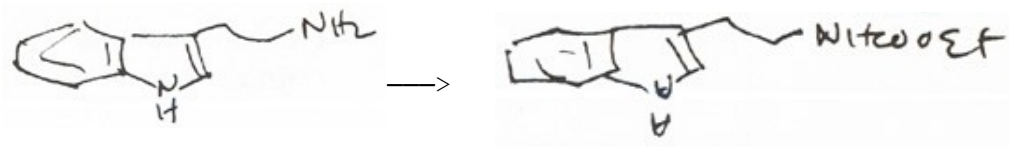
E
Abundance
Mass/Charge
41
55
105
135
174
182
239


(123) Scan 5.889 min. of DATA:SMS4R21A.D
F
Abundance
Mass/Charge
45
75
135
204
220
284
341

Jan 5, 1992



A solution of 3.36 g (21mM) tryptamine in 40 ml CH_2Cl_2
-> almost complete solution. a few turds. decant new flask. add:

A solution of 5.52 g K_2CO_3 in 40 mL H_2O

Stir [with] vigor - to the froth, add.

2.0 mL EtOCOCl (2.28 g, density 1.135)
becomes cloudy - cottage cheese. stir vigorously - in 20 min -clear. - stir 2 h. - separate - ~~wash [with]~~ org to dryness -> 5.1 g crude oil - quite dark.

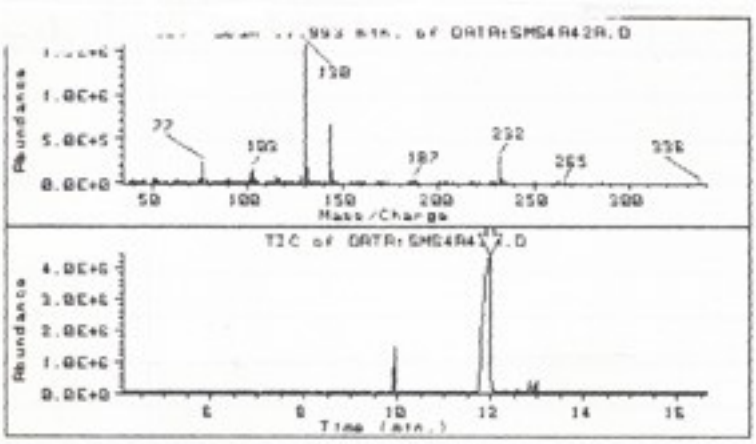
Distill. 0.3 mm 70°/ nothing.
0.4 mm 110° nothing.
0.3 mm 120° no
0.3 mm 150° no
0.25 mm 170° no
0.25 mm 185° all over -> 3.74 g pale amber oil.

See MS- next page.
6:219

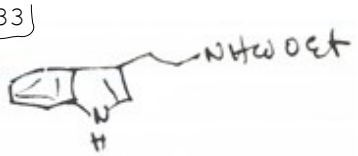
GCMS of the ~~methane~~ of tryptamine.
Urethane

6:219

SMS4 A42A

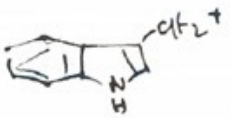


233



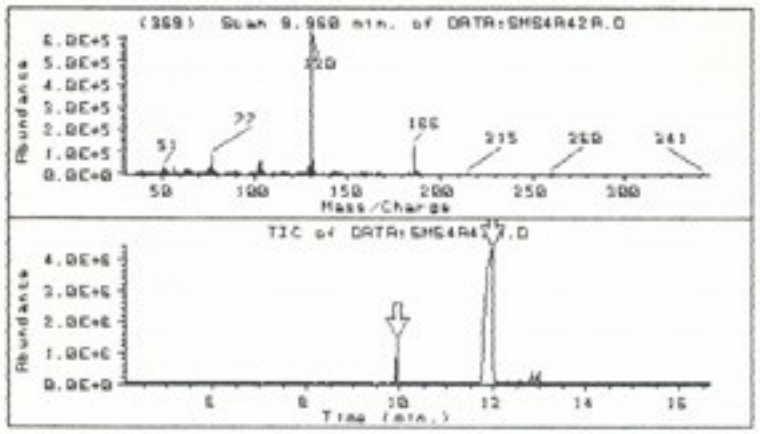
MW 232

130

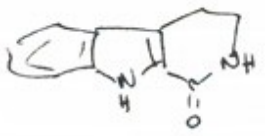


CH2 = NH CO_2Et 102

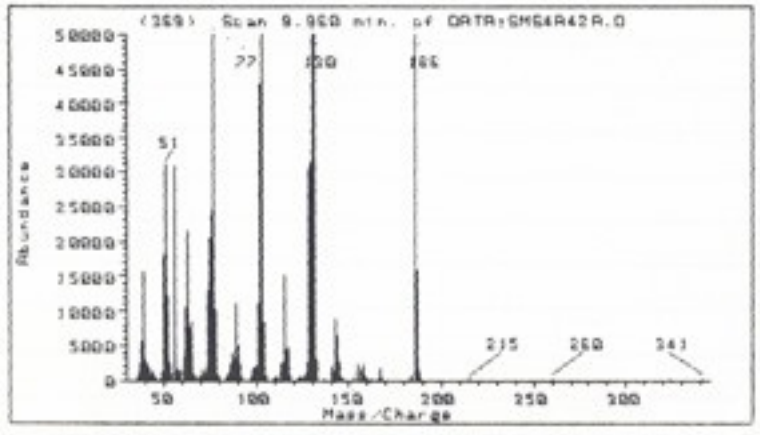
+



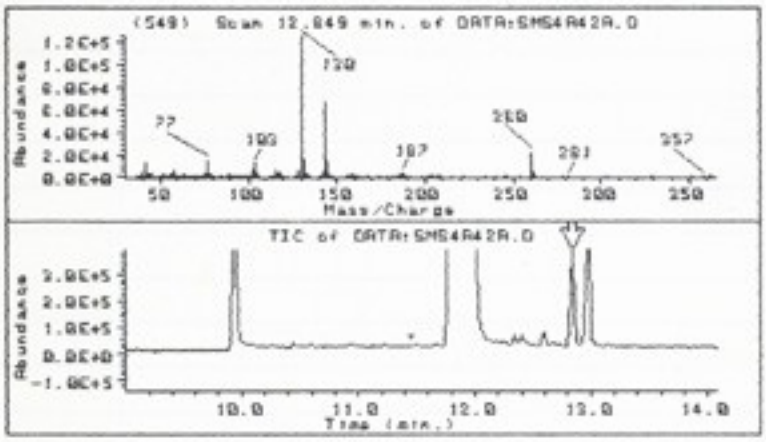
186



130 see above!

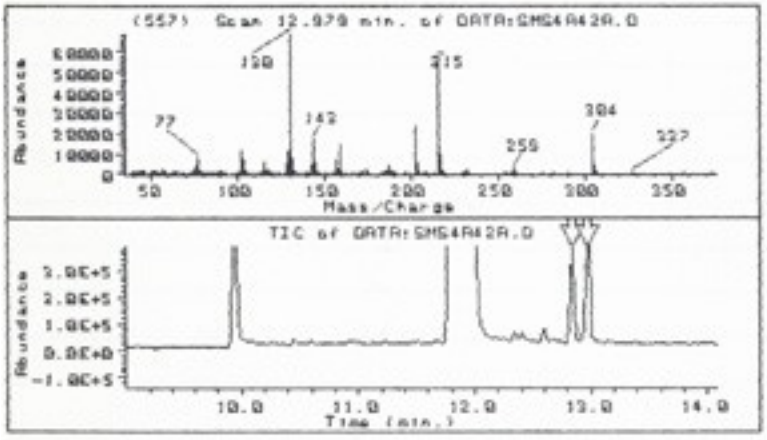


two high-movers from · 6:219

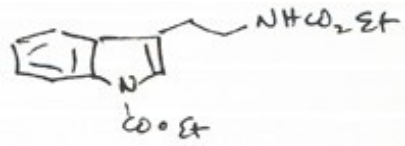


260

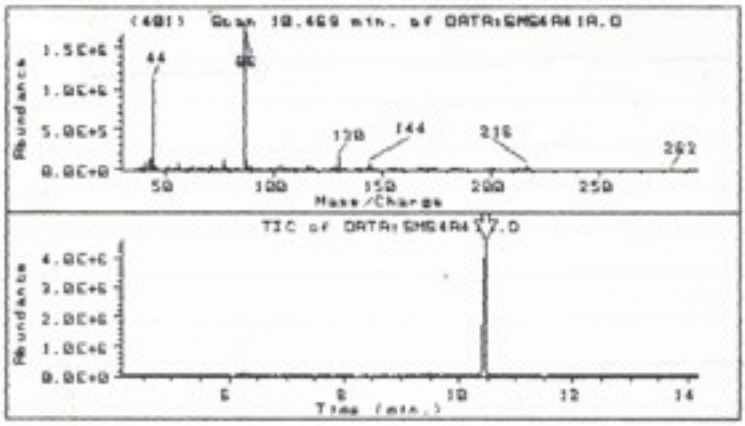
?

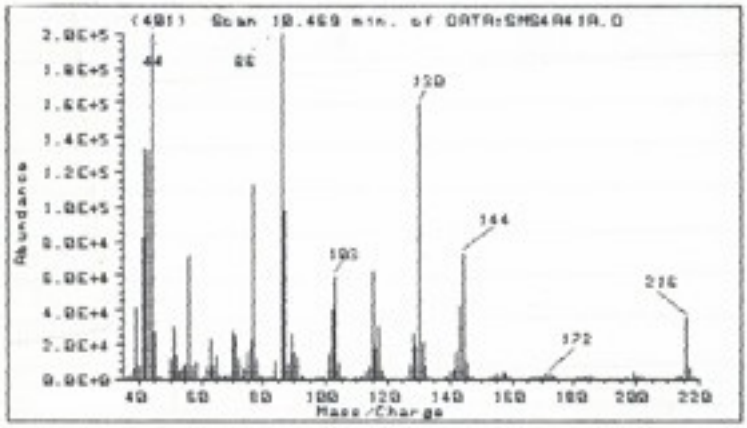


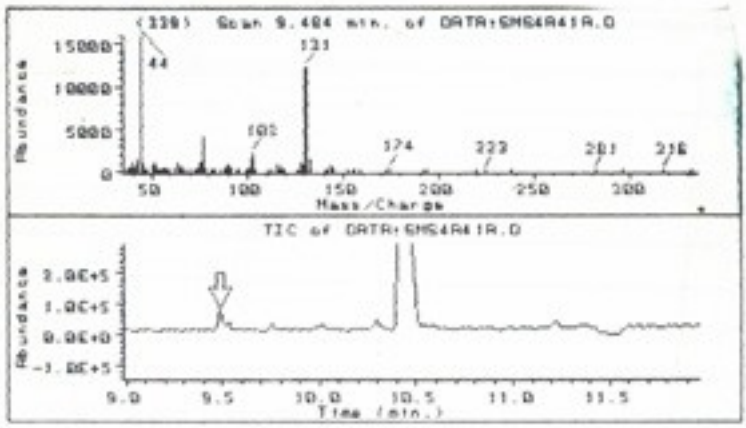
304



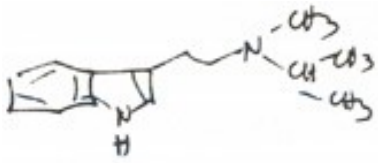
Danny's MIPT SMS4A41A



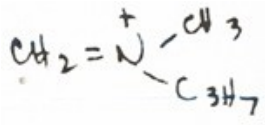




216



(ß-carboline is 214)



86

174

86

CH_2=NH CH_3

+

ß-carboline 214

[Editor's Note: Pages 223 & 224 are missing from the original document]

Same Rx  [H] ——>

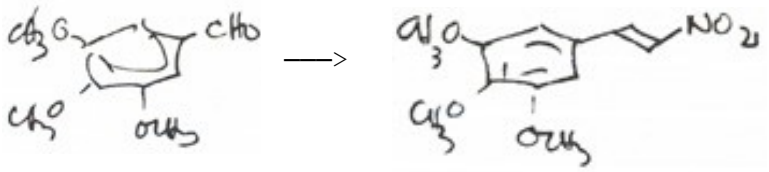
6.0 g Mescaline NS. 6:156A. - good, xtalling metered
into
60 mL conc HCl. ——> virtually complete solu.
add.
12.6 g powdered Zn. onto SB 4 hrs. ∇ to RT. stand 1 week
filter ——> inorganics - OUT.
add ~ 250 ml H_2O - stand -> dark solids.

filter ——————————————————> solids - acetone soluble ! 6:225A.

aq:-add sat K_2CO_3->ph~10
~ 40 g K_2CO_3.

——> aq. [with] lots of white solids.

MS
233-234

Repeat: 

See page 63.

x2. Add 200 ml HOAc to
20 g 3,4,5-trimethoxyΦCHO. Δ SB-> solu. add:
40 g NO_2CH_3 - swirl. add:
20 mL cyclohexylamine. - Δ SB 11:00PM. slowly -> yellow. then gold.
Off - let cool - reheat - total time on SB = 3 1/2 hrs- add, to well stirred solu, 250 ml 55° H_2O - clear, then slightly turbid, then [with] seed -> xtals. Stand at cool RT ON.
filter. air dry 19.6 g -> 15.7 when only a trace of HOAc smell remains.

use 7.8 g p.235

2/19/92 Repeat above. the rest - p236

21.6 g wet -> 19.17 somewhat dry.

recrystallize from = wt CH_3CN

Air dry ⟶ 15.35 g spectacular yellow xtals.

3.40 g 11.95 g

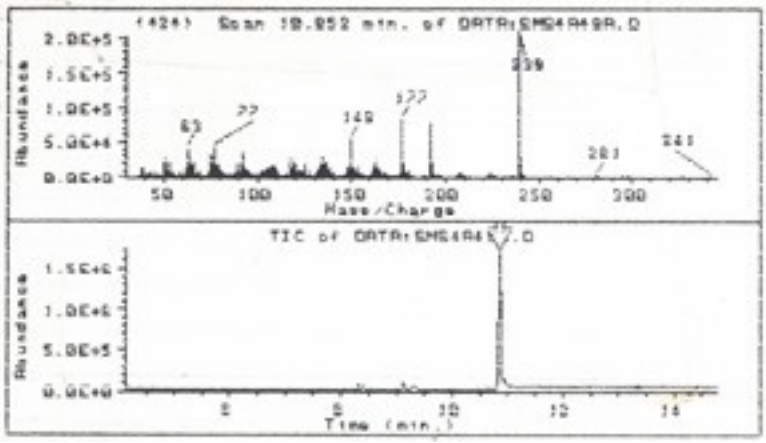
hold. to reverse addition

~~NaHB~~ $NaBH_4$

Susan repeat 20 g -> 18.2 g crude (wet) -> 13.94 ex CH_3CN

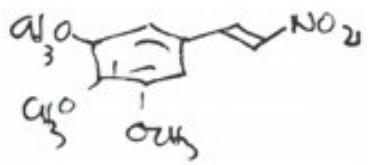
ATS repeat 40 g -> 47.7 g very wet -> 32.49 ex CH_3CN
46.43 g dry
226:C

ATS repeat 5/13/92 40 g -> 46 g -> somewhat wet -> 33.74 g ex CH_3CN
226:D



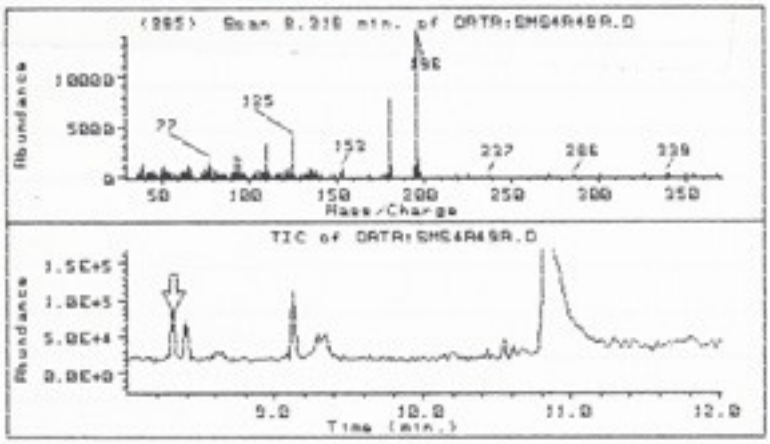
239)

Page 224

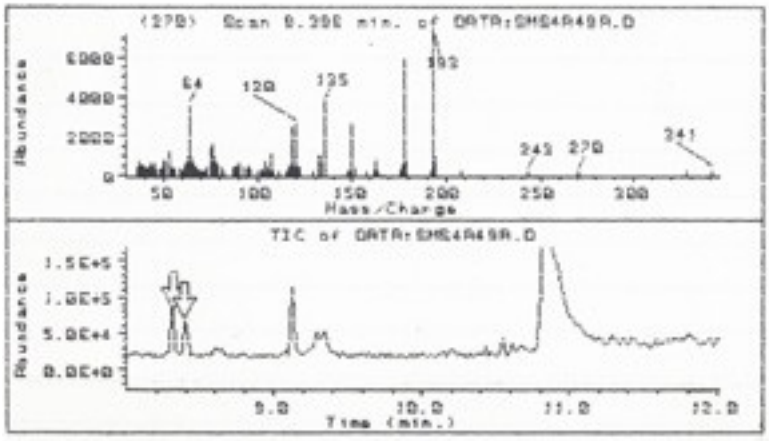


+ trace impurities #1,#2 & #3.

Small # 1

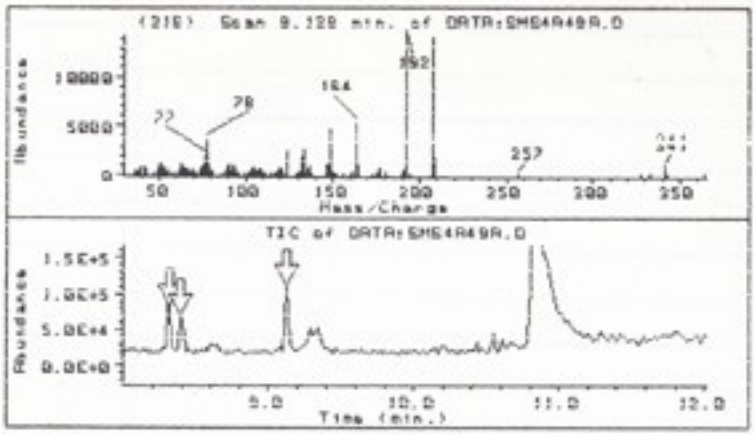


Small # 2

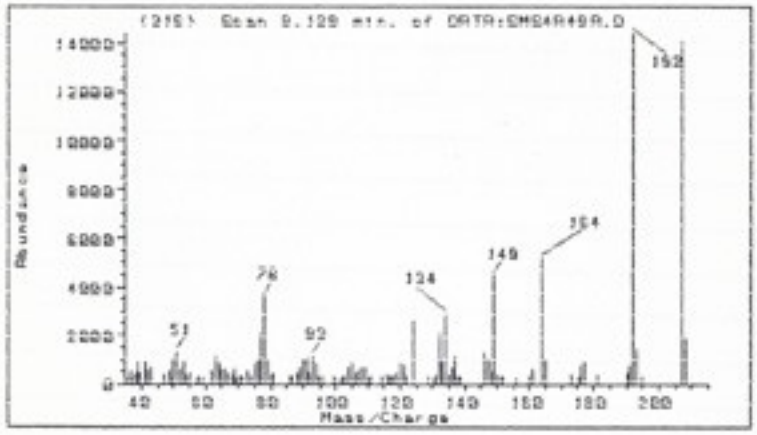


Over

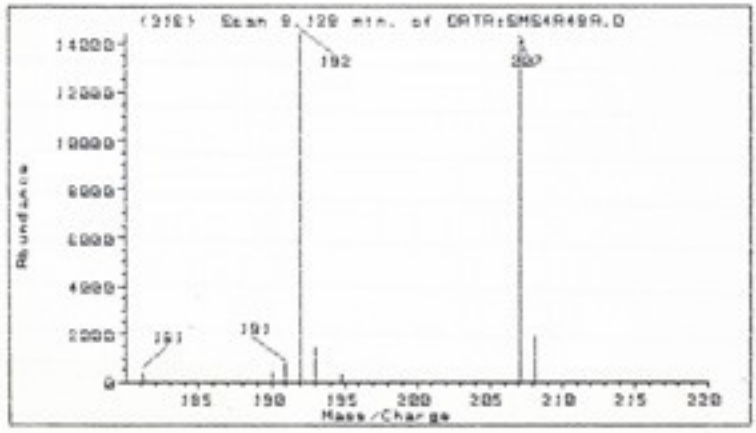
impurities in mescaline nitrostyrene



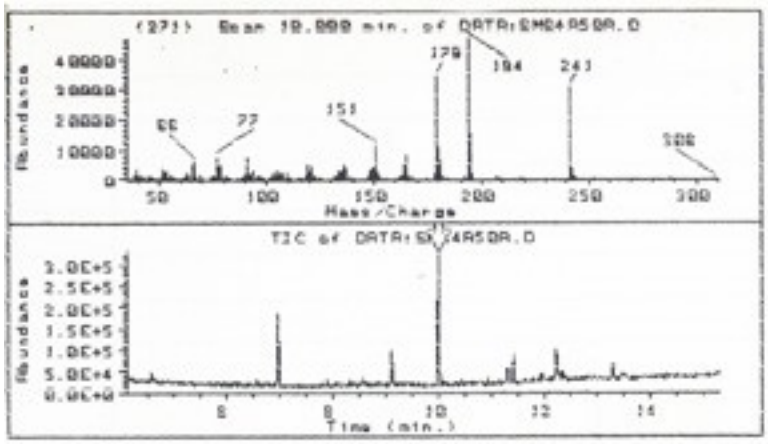
trace #3



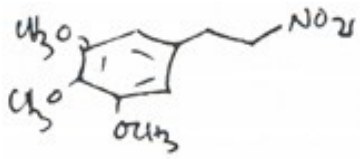
expanded



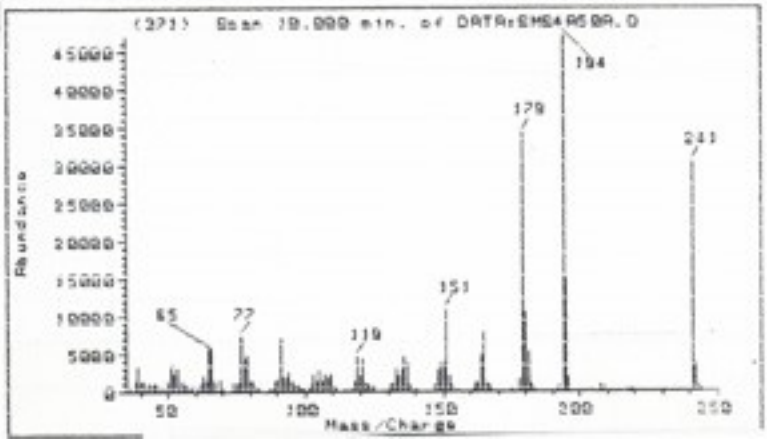
more yet!



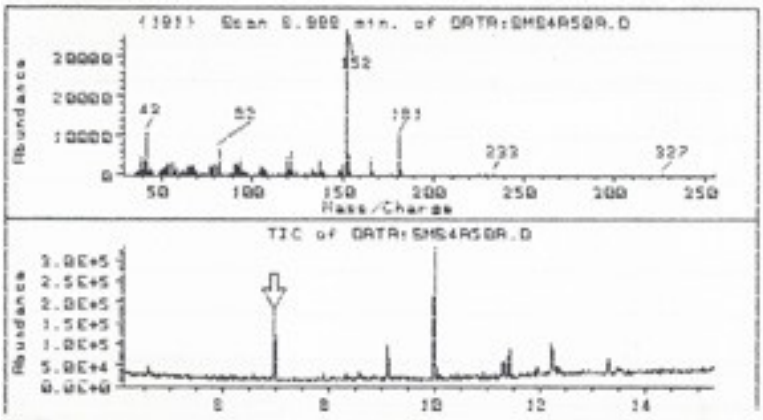
241



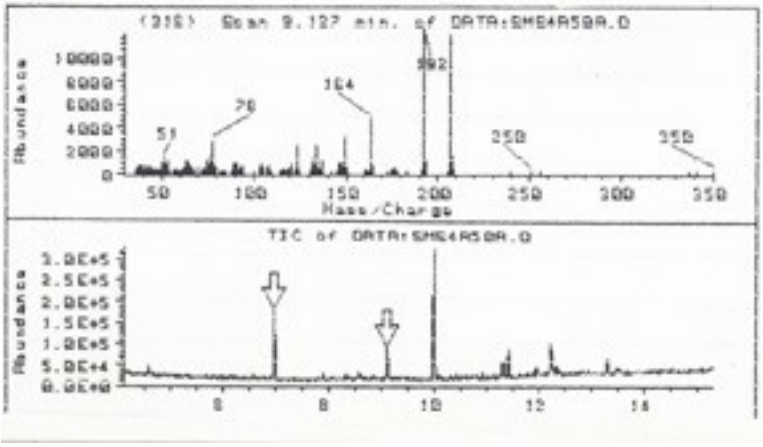
to 230



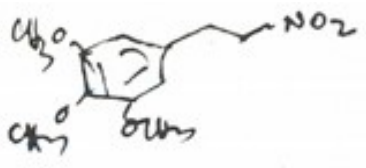
full spectrum.



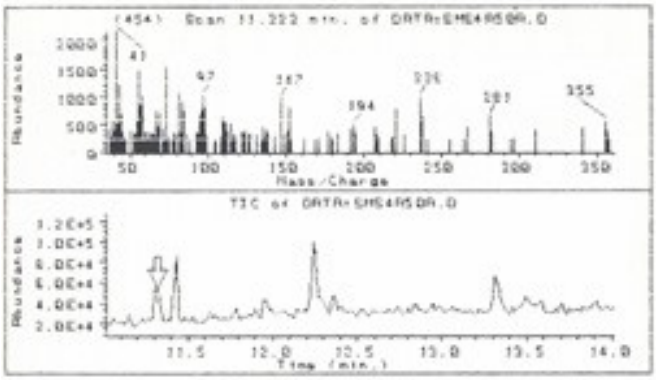
major #1

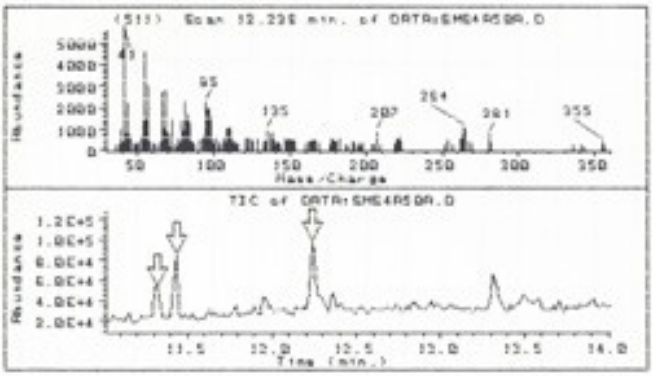


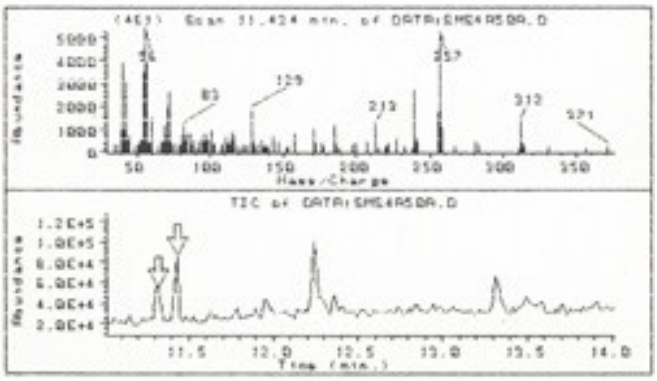
major #2.

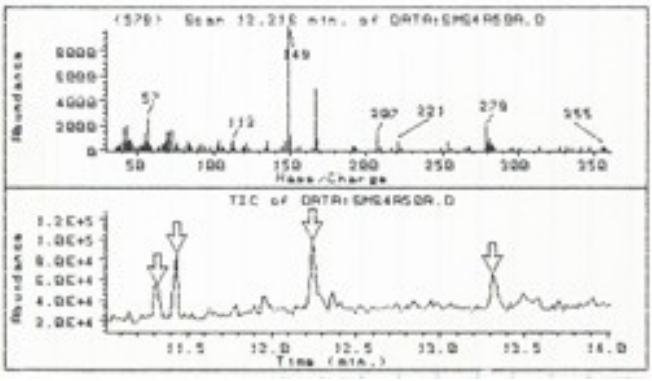
minors #1,2,3,4- from 

Page 229





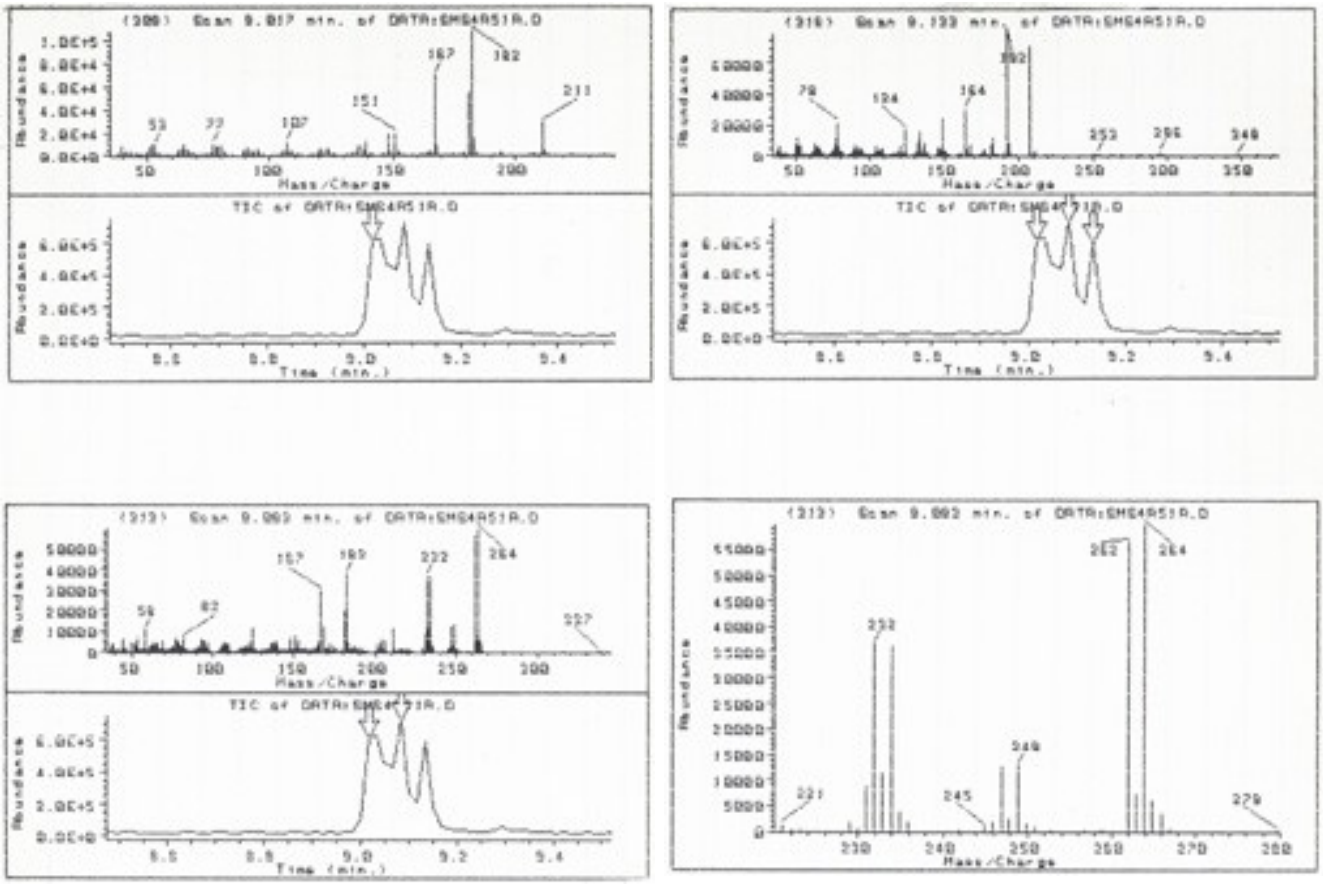




[Editor's Note: The preceding graphs were originally vertical on the page]

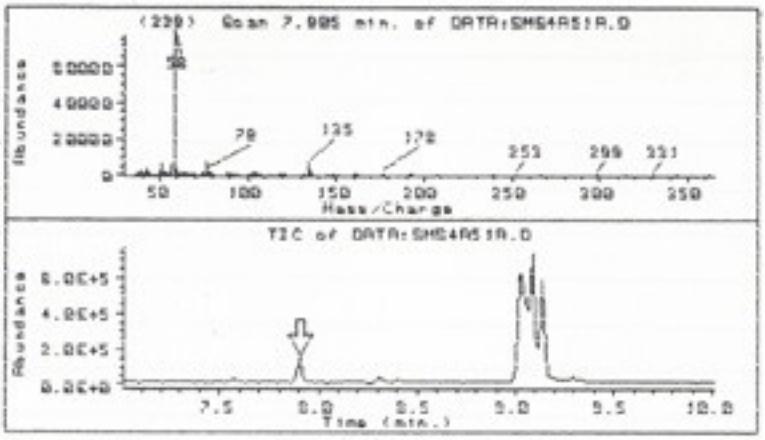
Reduction of nitro-ane [with] Fe.

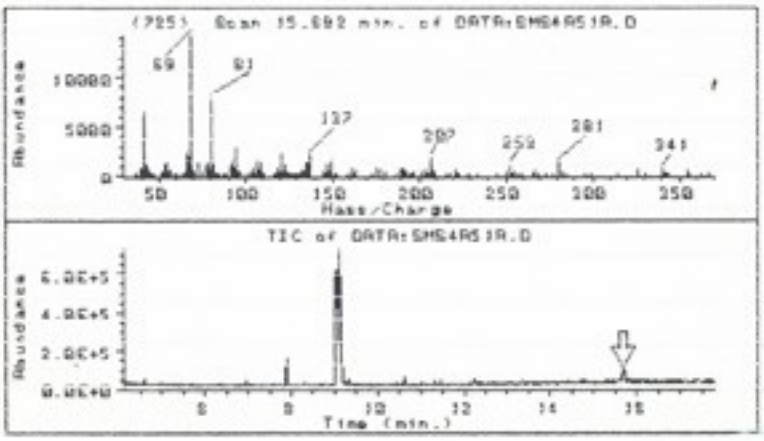
Three
major
peaks.



[Editor's Note: The preceding graphs were originally vertical on the page]

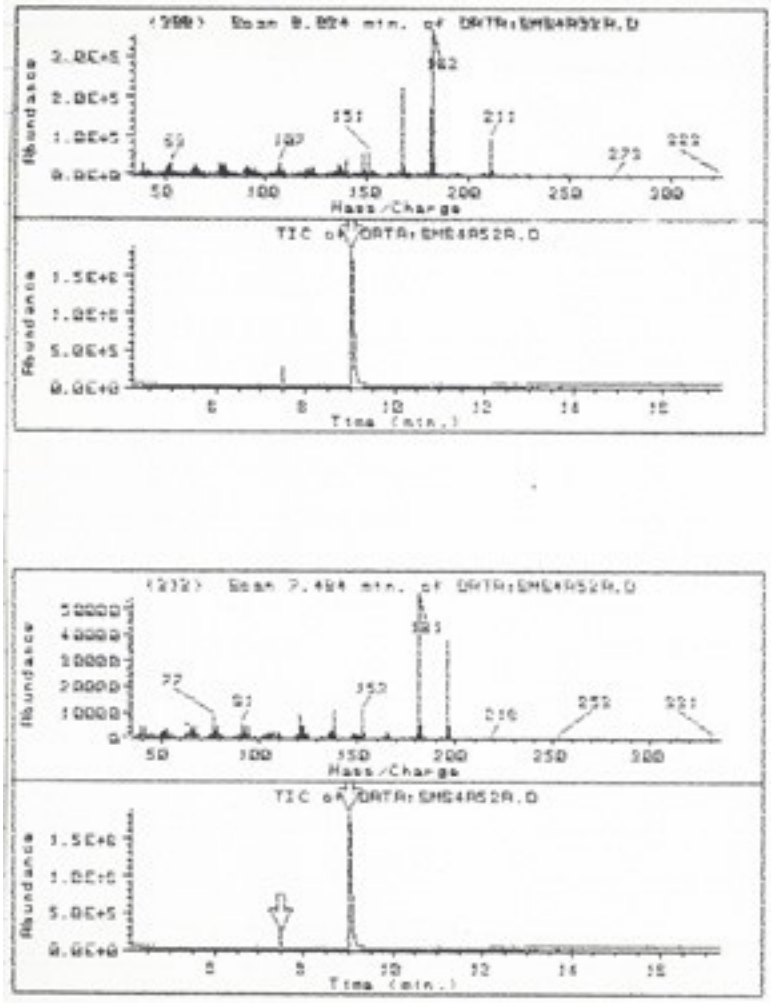
intermediate stuff from Fe reductions



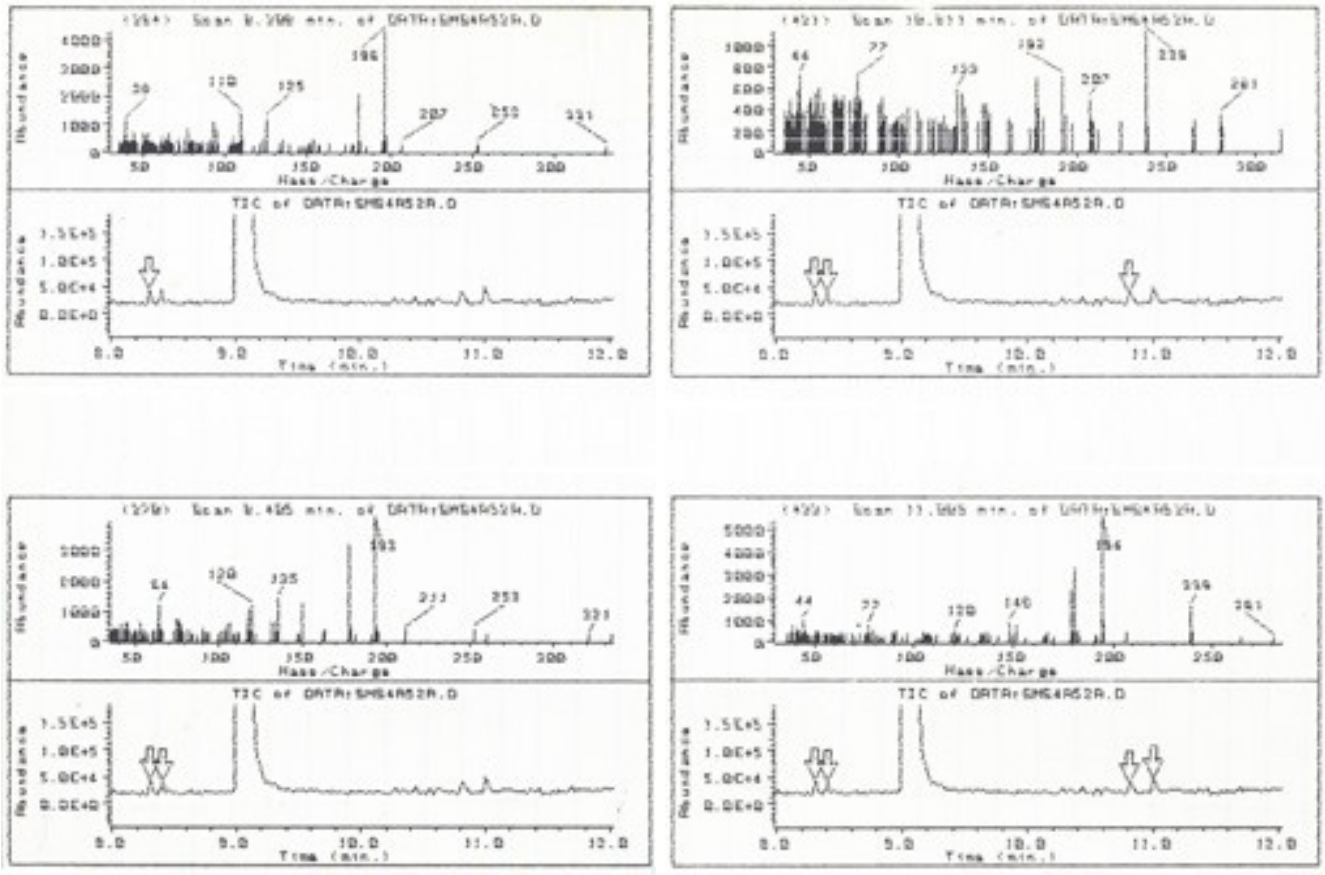


page 224- Small scale Rx [with] mescaline NS & zinc
direct reduction (at ~55°). to the N.S.

page 224- bottom



trace stuff from mescaline NS + Zn on steambath p.225



[Editor's Note: The preceding graphs were originally vertical on the page]

[Editor's Note: Pages 235 & 236 are missing from the original document]

Feb 23 1992.

—> $ArCH_2CH_2NO_2$

Reverse Addn

Method of hal & Castagnoli, via MBII p14
4/16/75.

A suspension of 4.2 g $NaBH_4$ in 100 ml denatured EtOH was put under Ar, and magnetically stirred, and cooled to 0° [with] external ice bath. to this; add, dropwise (under Ar)

11.95 g mescaline nitrostyrene in 50 mL EtOH + 100 ml THF.

As addition goes on , immediate discoloring of the yellow NS, but with a residual pink that takes 5x as long to discolor. Total addn - 3 hrs.

Killed with 12g wea
25 ml HOAc
40 ml H_2O
} add dropwise to the still cold solution.

Extraction [with] CH_2Cl_2 (3 x 75 ml) , wash [with] saturated $NaHCO_3$, then water, then flash.

—> 12.34 g crude product

Small amt saved ex MeOH->white xtals

KR ~ 0.5mm
as I remember,
quite high Temp.
150° ?

↓

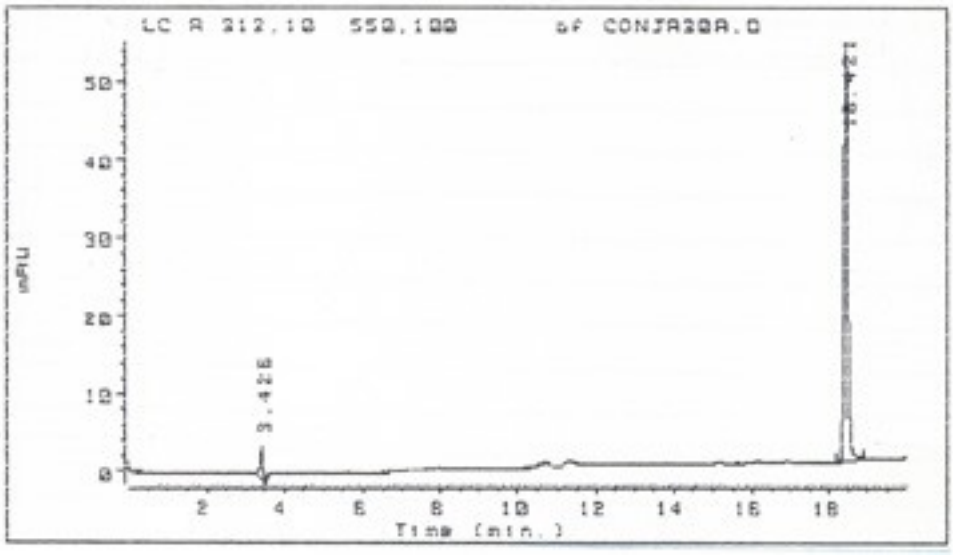
7.27 on to Fe reduction

p. ~~246~~ 247, lousy, OUT

7.30 g fused white xtals (brown color last over)

Analysis. 3/4/92

Samples of possible LSD from Atty Lash via Cross & Associates. Total of 16 samples - ranging from mouldy pot to possible mushrooms to tablets to various tabs to got knows what. Three samples were of particular interest to Cross 25A, 25B, 26B - and those I will run. from here on in the book, until everything is posted.



C-18 Reverse phase. Program (A) H_2O 0.1% pH 7.1 buffer CH_3O $CH_2CH_2NH_2$ ·HOAc

10 µg ATSref. LSD tartrate into 1 ml 2% buffer. 10 µl inject at 1.0 ml/min

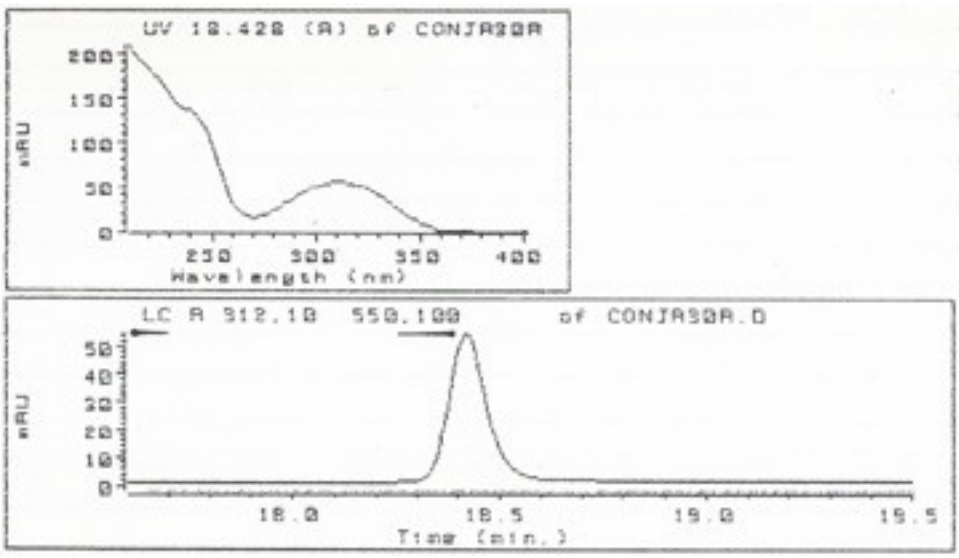
(B) 95% MeOH 0.1% pH 7.1 buffer, as above

DAD at 312 mµ. HP-1090M.

Conj A 30 A

0-2 min A 100%
2-18 min to B 100%
18-20 100% B

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	3.426	BV	0.074	21.17	3.260	3.525
2	18.421	BBA	0.102	353.32	18.183	18.881



Assay . LSD concentration 10 µg/ml pH 7.1

10µl injection ⟶ 18.421 peak [with] OD 54 mAU
min.

standardize 10 µl of 1 ml -> 54 mAU
[with] 10µg

1 µg/ml -> 5.4 mAU

UV sean excellent
(312 max)
(240 bump.)

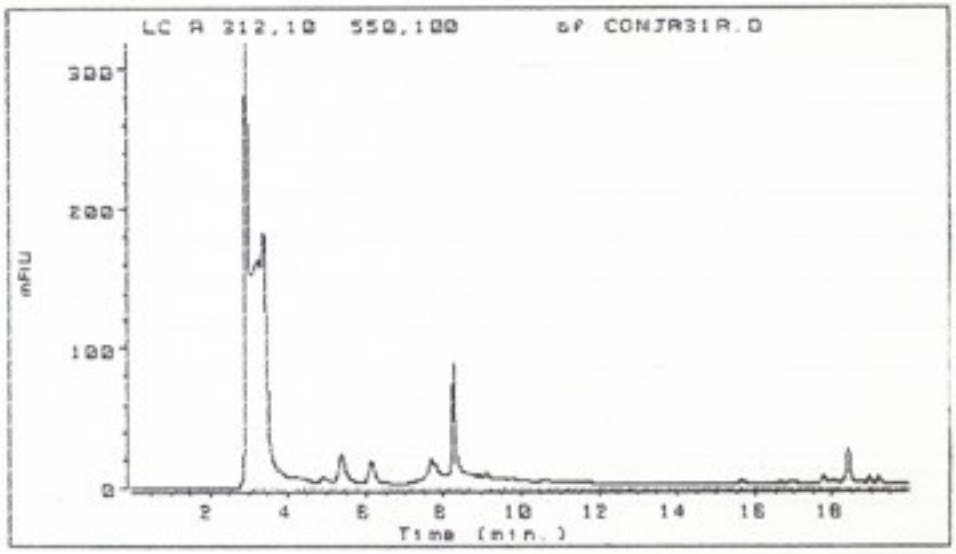
Sample 25A. conj A31A

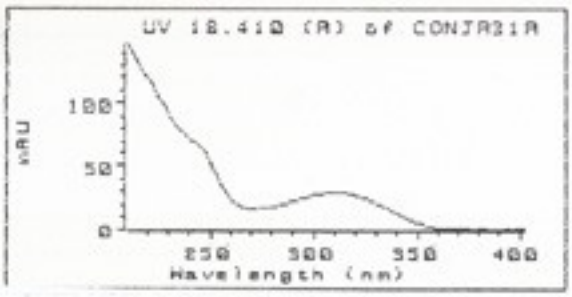
Amt insuf.
to quantitate

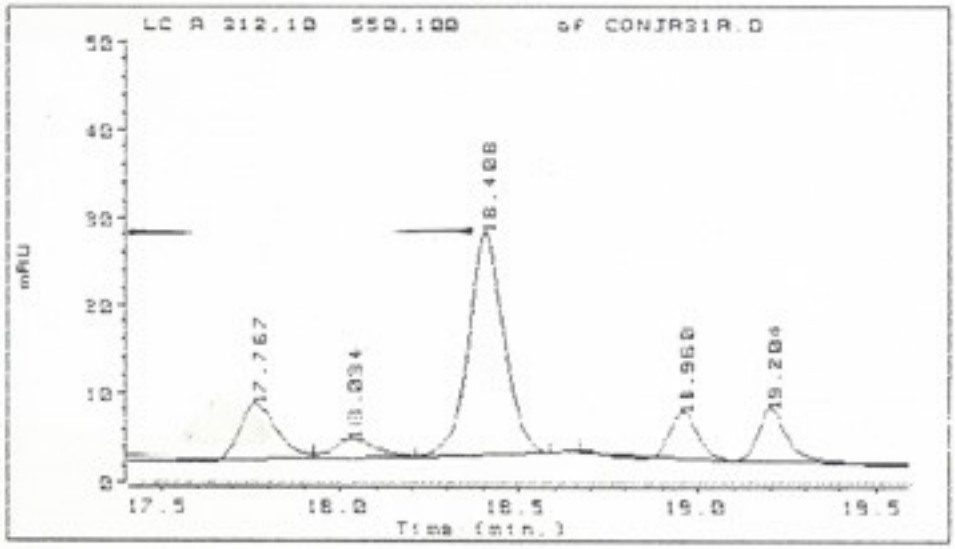
Given: Report says (DEA) Color test, GC-MS, IRD,
TLC, LC ——> ~20 µg / tab
Gerald Pinder's report: LSD /MDMA* 18.9 µg / tab
tabs 115 g 13.4g reserve (68 tabs)
original 175 tabs - total -> 3.308 mg.
I was allowed up to 12 tabs (of the 68) and
took 11 of them.

I am asked: Verify presence of LSD - qualitative
ball-park quan. (which can wait
if need-be)

I did:
Dissolved 1 tab in 1 ml 7.1pH 2%
buffer - yellow solu [with] lots of insolubles - add
1.0 ml H_2O - spin - pipet to first tube - spin
again - assay 10 µl as [with] standard







Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.962	BV	0.106	2324	2.605	3.096
2	3.263	VV	0.184	2199	3.096	3.330
3	3.402	VV	0.153	1922	3.330	4.115
4	4.931	BV	0.158	32.96	4.760	5.176
5	5.381	VV	0.185	242.46	5.176	5.901
6	6.130	PV	0.180	177.85	5.901	6.797
7	7.680	PV	0.248	297.85	6.797	7.992
8	8.260	VV	0.116	690.44	7.992	9.048
9	9.125	VV	0.101	38.28	9.048	9.410
10	15.645	BV	0.119	17.26	15.373	15.874
11	17.767	BV	0.111	39.09	17.400	17.927
12	18.034	VBA	0.129	15.71	17.927	18.210
13	18.408	BBA	0.105	168.81	18.210	18.589
14	18.960	BV	0.086	21.95	18.669	19.094
15	19.204	PV	0.098	30.17	19.094	19.750

OD (10µl) 25 mAU ————> 9.2µg LSD / tab - say - as ball park - ~~a little~~ less than the DEA finding, but I am content.

U.V. perfect-
∴ it <u>is</u> LSD
very heavy H_2O-sol stuff at zero volume.

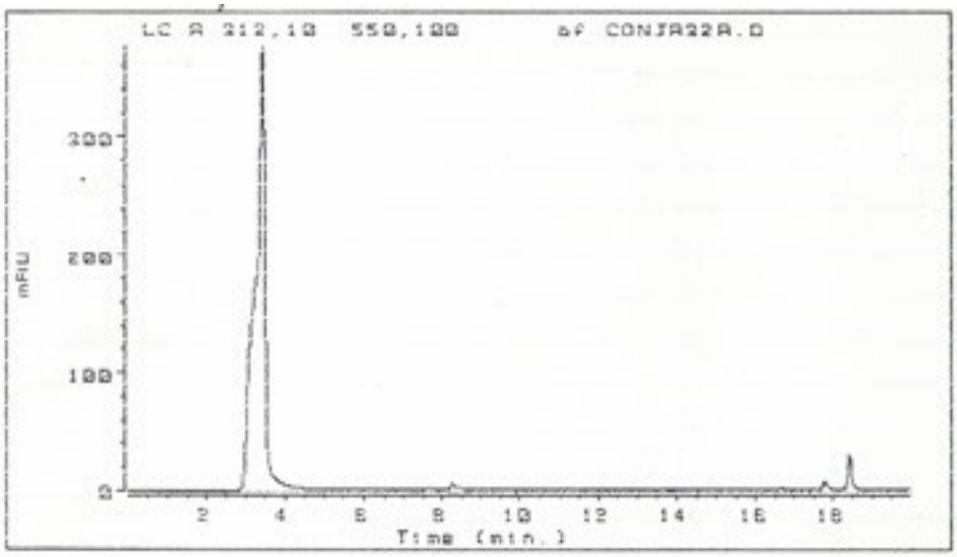
(note-several surrounding peaks not seen on normal phase of DEA

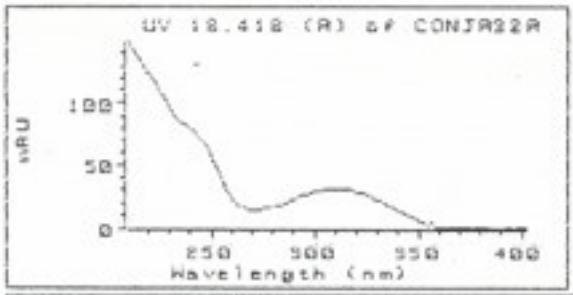
Sample 26B (conj A32A)

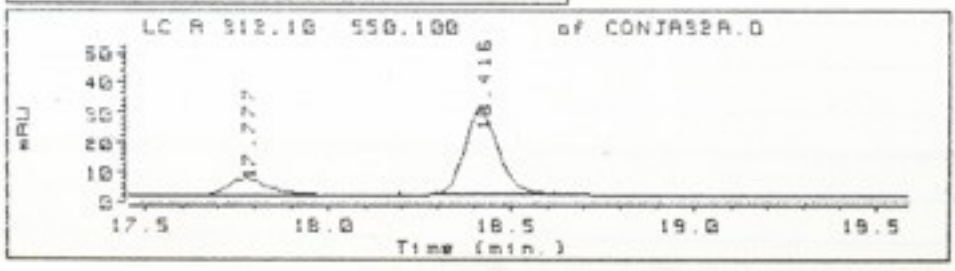
Given: Report (DEA) says LSD 0.02% in a white/yellow powder 267 g -reserve 102.8 g. I can have up to 15 g - I take 4 g. They used TLC IRD, IR.

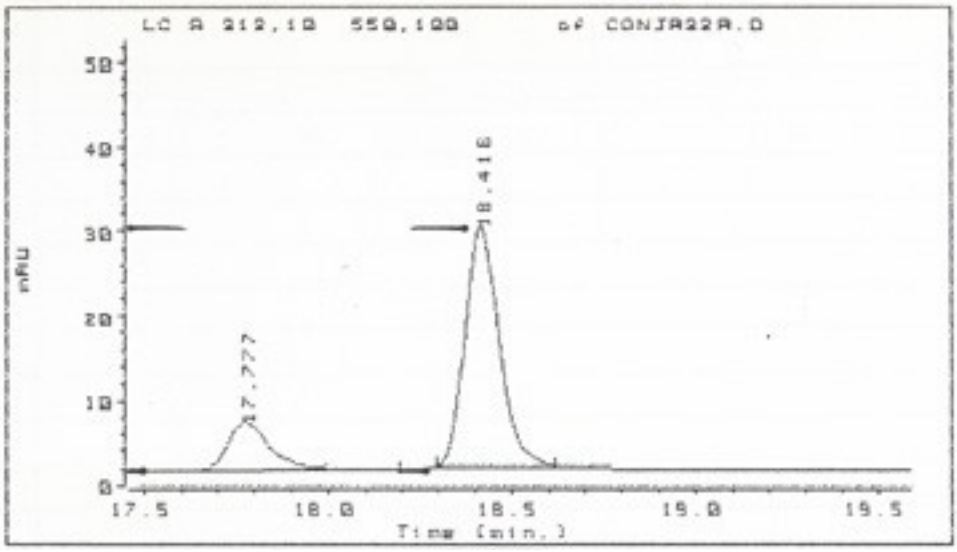
I am asked: Verify LSD is there, quantity, what is excipient? By product? or Cut?

I did: dissolved 50 mg / 1 ml 2% 7.1 buffer - completely clear solution. Assay 10 µl.









Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	3.428	BB	0.244	6724	2.645	4.853
2	8.270	BB	0.148	55.68	7.242	8.640
3	17.777	BV	0.123	47.07	17.450	18.194
4	18.416	BBA	0.102	185.74	18.293	18.618

I have 0.028 OD 28 mAU.

since 5.4 mAU = 1 µg/ml

28 mAU = 5.2 µg/ml

50 mg ⟶ 5.2 µg - quan is 0.01% LSD.

sample is heterogeneous. I am happy.
much polar coloring material

IR of 26B ⟶ clean spectrum of Ascorbic A.
not by-product, but clearly an excipient.

∴ ~ 1/2 g to give a single dose.

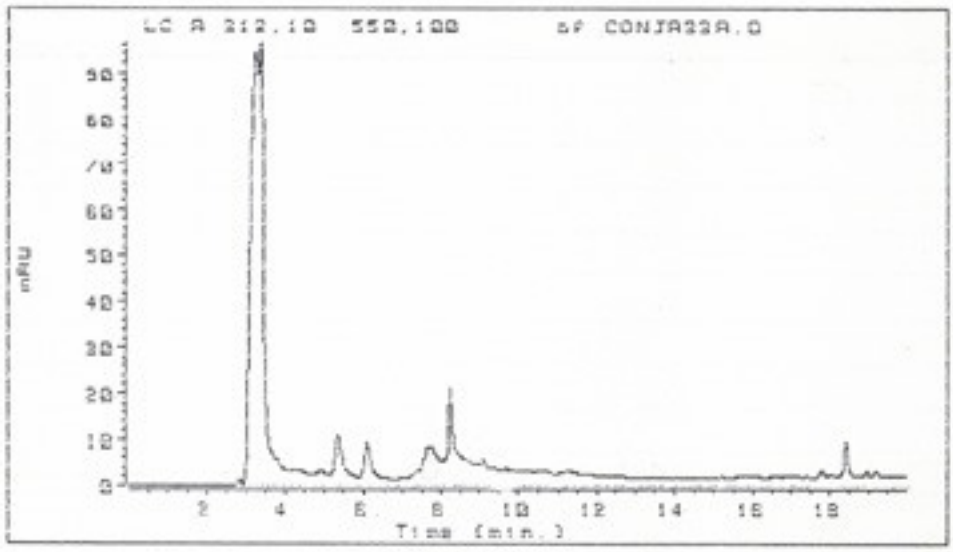
at 50 µg = 280 doses in 145 g original seizure

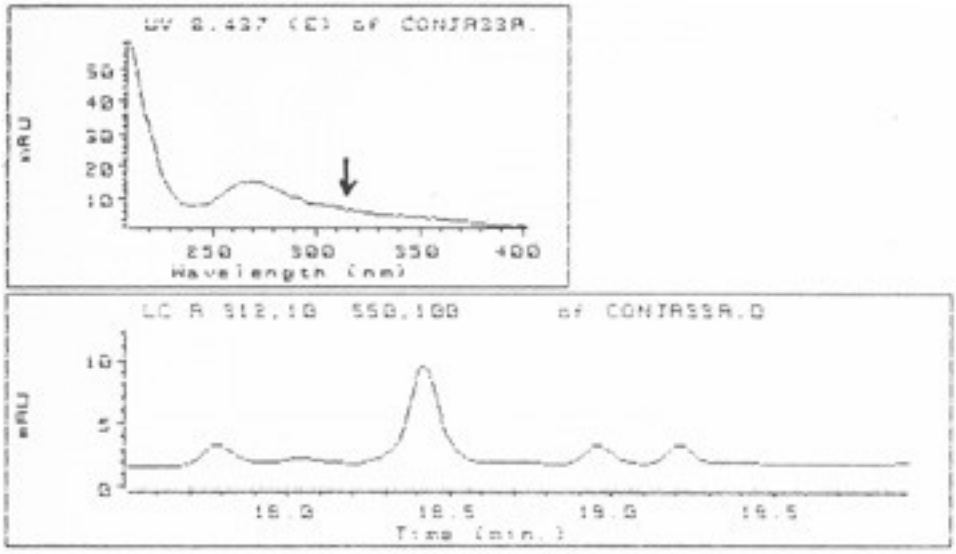
Sample 25B (conj A33A)

Given: Report (DEA) IR TLC GC-MS 20 tablets
LSD found - amt ~~too~~ insufficient to quantitate
Reserve 12 tablets 2.43 g - I take .39 g
all is in powder form.

I am asked: verify LSD, ball park quan.

I did . Dissolved (not all sol) 50 mg / 1 ml 7.1 buffer - dilute another 1 ml H_2O - spin - pipet out respin - inject 10 µl





There is a peak at 18.4 min, recorded at 312 mμ-
that, had it been LSD, would have been (8 mAU,
= ~ 1 1/2 μg/ml @ 2 ml = less than 1 μg.).

BUT. UV absolutely wrong - peak is
at ~270 mμ and the 312 is part of the tail.
The absence of a swelling at 312 (< 1 mAU)
says less than 0.1 μg/50 mg

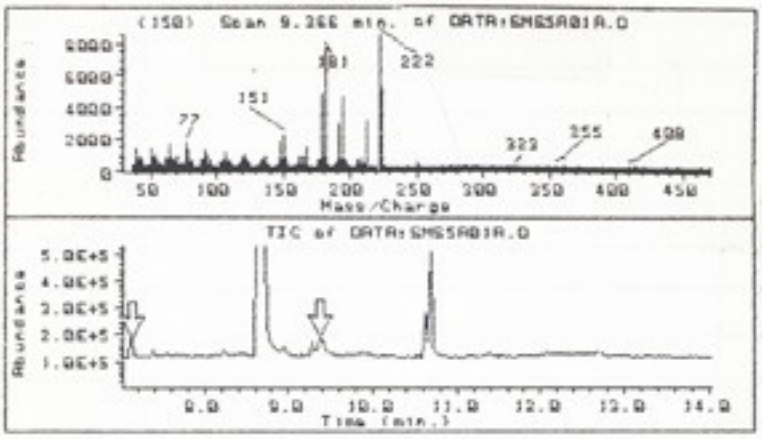
= < 0.0002 % LSD (limit of
detectability.

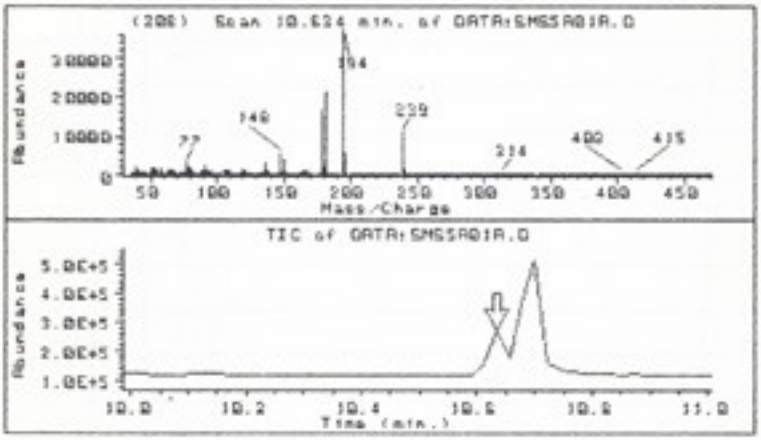
<u>There is no detectable LSD present.</u>

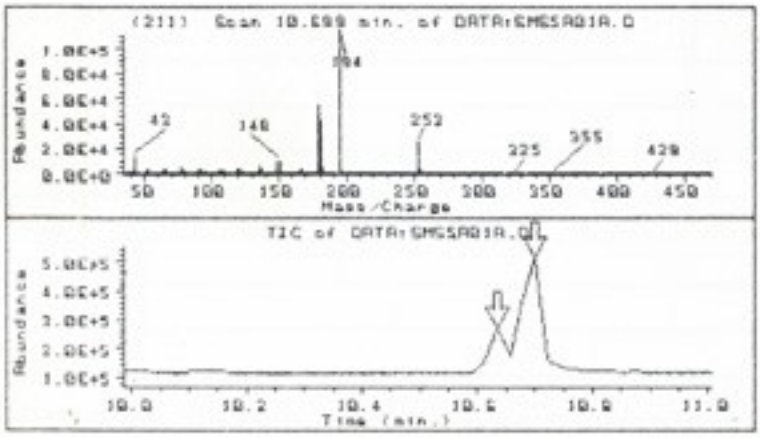
If I were to consume all 20 tablets,
~ 4 g,
I would take in less than
10 μg LSD.

[Editor's Note: Pages 246 & 247 are missing from the original document]

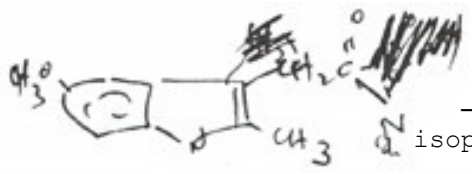
ex page 246

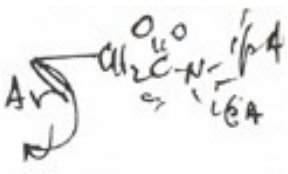






[Editor's Note: Pages 249 to 256 are missing from the original document]

Prep. for  ——> isopropyl)



from 254. saved most -see 273 Trial: sent a ranifile

combine 2c-T-7 -try clemmenson condition -light water wash
ML's <——> solids looks like nitrostyrene

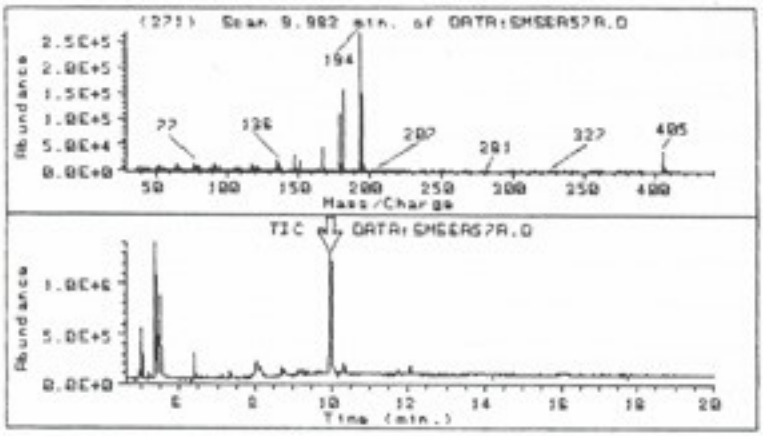
[Editor's Note: The following has been photocopied and pasted onto the page]

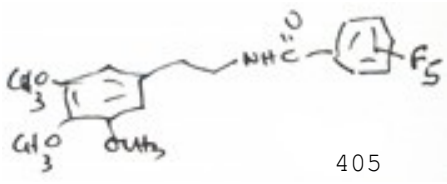
amt by R.E., into 1.5 L
H_2O -> light yellow solid.
filter -> fair amt of solid
(yellow, a little lime) and [with]
water washing, redissolves! -
put back in, xtrt [with] 3 x 50 ml
CH_2Cl_2 - removes most of the color ——> CH_2Cl flash.
aq.
basic [with] conc NH_4OH, then add
goodly amt. of 25% Base. face
the oxide! Looks like it might settle.
filter - pretty good! wash [with] 3 x 50 ml
H_2O ML's solid mat - wash [with] 3 x 150 ml
MeOH - pool ——> flash combine
xtrt [with] 3 x 75 ml
CH_2Cl_2 - No Color.
Pool.

into 1 L. H_2O [with] acid - extract [with] CH_2Cl_2 pool -
take xtrt, bait xtrt [with] dil HCl
combine·
OH [with] 25% base
extract [with] CH_2Cl_2 - separate
flash ——> 2.36 crude - Ch_2Cl_2 transfer
to small RB. 2.14 g- RK distil at 0.4mm @ 120°
——> 1.78 g colorless xtals.
into IPA (10ml ?), HCl, ether
——> 2.23 g 2C-T-7. IR perfect.

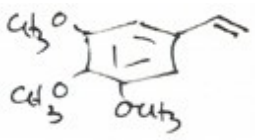
Mescaline as pentafluorobenzoyl derivative

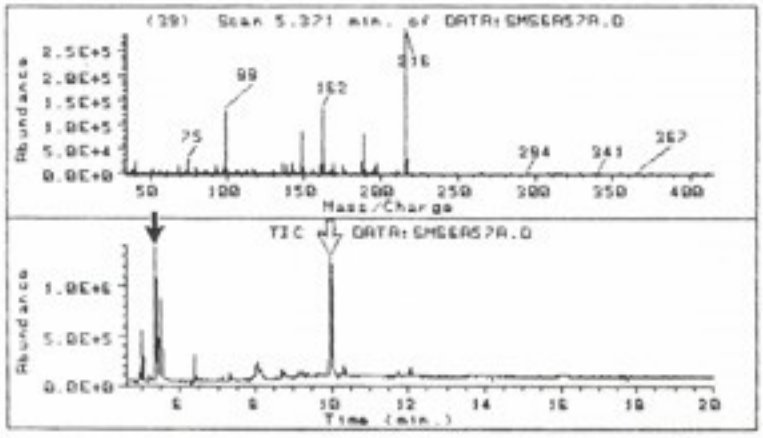
1 mg (or less each mescaline or lophophine)
100 µl 10% 'penta'fluorobenzylimidazole in DMA
Δ 75° 15mm
∇ RT add 1 ml 10% K_2CO_3, vortex, 1 ml 90/10
vortex, spin, GCMS. tol BuOH



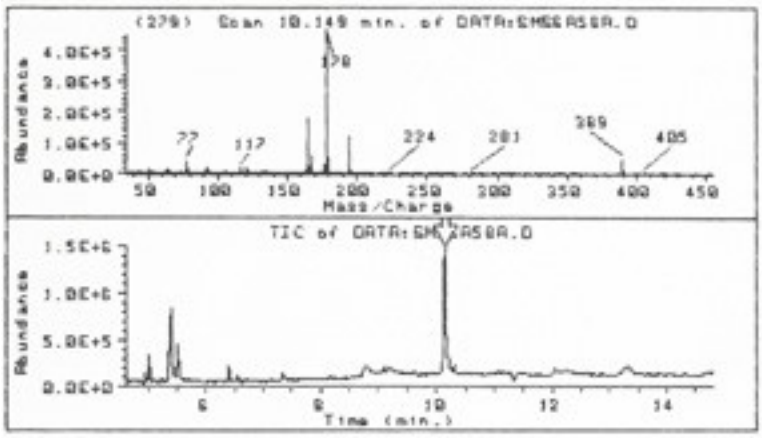

405

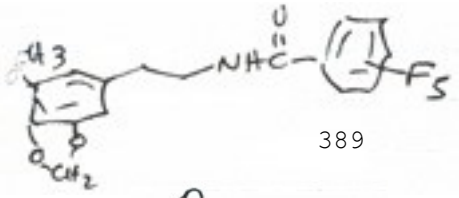

195


194



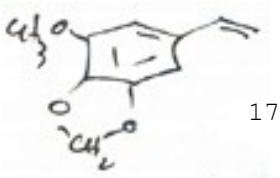
With Lophophine



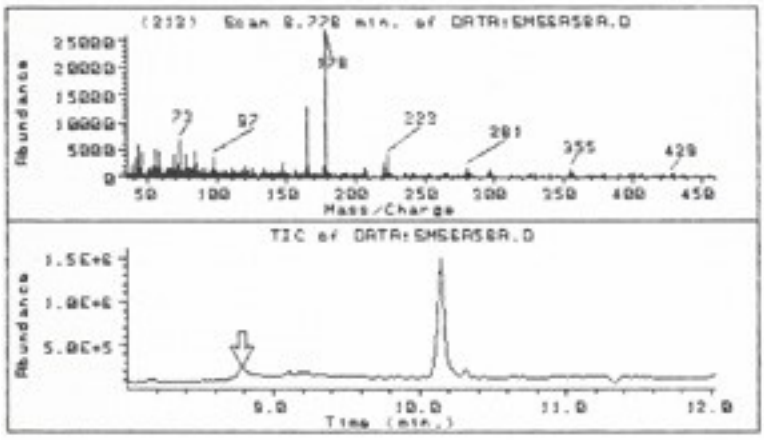


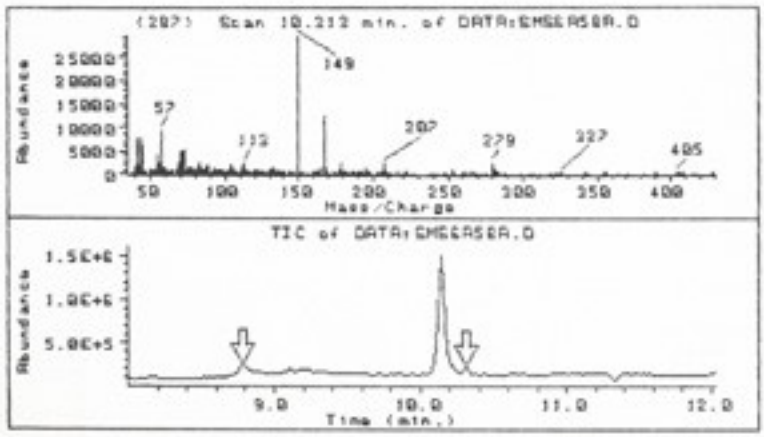
389

195

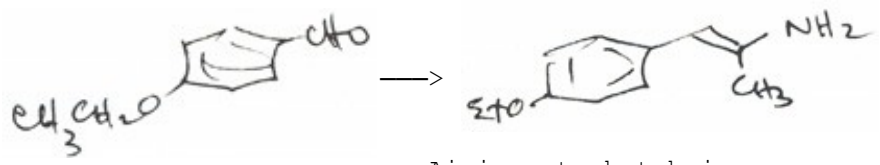


178





November 3 1992



Aiming at what beige might be!

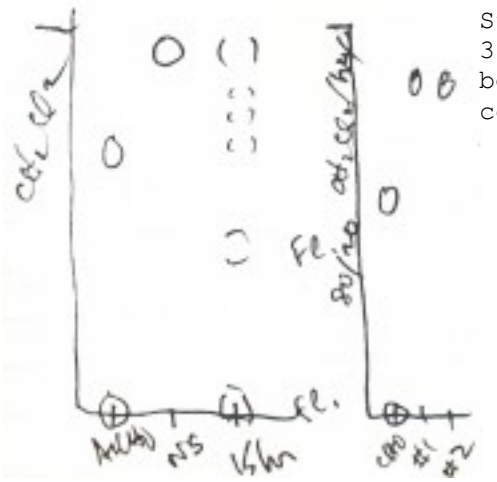
See page 6:226

Dissolve
15 g p-ethoxybenzaldehyde to
200 mL HOAc, add
50 g NO_2Et and then
20 ml cyclohexylamine.

Δ. SB. assay TLC (silica CH_2Cl_2) 12:45
1 hr. 1/2 : 1/2 1:45
4 hrs. 4:45
5 hrs. off.
While hot, add 125 ml 55° H_2O - ∇ until seed does not redissolve - ∇ to RT [with] stirring, scratching -> fine xtals - to ~10°. stand a few hrs. ~~filter air dry~~ 15.1g wet air dry.
11:30 dry. one spot TLC. good! IR ≡ [with] below - save trace rest ·Fe°

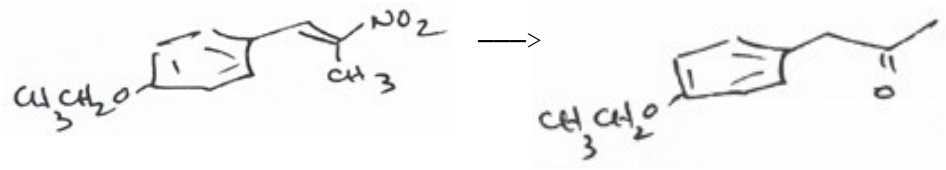
Try ~neat.

9:20PM. 15 g ArCHO in 50 g NO_2Et + 1 g NH_4OAc - on SB 9:20PM
1.5 hrs. product seeable, largely ArCHO.
15 hrs. largely done, [with] ~ 3 in betweens.



Strip on R.E. —> deep red oil - add 30 ml boiling MeOH , dissolves - out into beaker. cool to RT. filter, wash heavy color out [with] 20 ml RT MeOH.

→ yellow granular xtals 14.80 g dry
TLC identical to the above
IR's identical



Ref-page 734 Pihkal

A solution of 26.1 g NS is made in 200 ml sl. warm HOAc

On the steam bath, add, in a 3 L beaker:
78 g electrolytic Fe° and
350 ml HOAc. Δ until some burpees and evidence of Rx. (at ~ 50°) add NS in HOAc over 20 min. let get hotter & hotter - never any foam or froth, just a steady urge to swell, and to form a real crust on the surface. Knock back in every 1/2 hr. Δ 4 hrs..

Dilute [with] water to 2500 ml, filter through paper to get particulate stuff out, wash stuff [with] H_2O, then CH_2Cl_2 . Xtrt 3 x 75 ml CH_2Cl_2 - pool, wash 1x xtrted one [with] 20ml CH_2Cl_2.

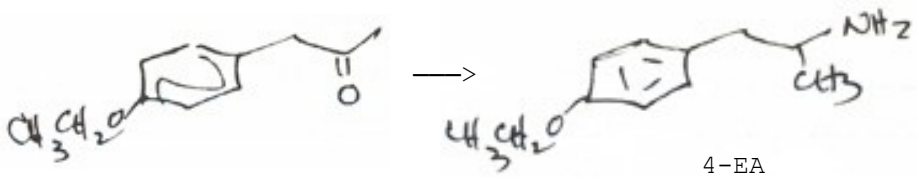
Pool - roto to deep amber oil - onto KR at 0.3mm

16.56
0.3mm
125°

White oil over at ~125°@0.3mm 16.56 g beautiful -

use - next two pages 262 263

Nov 7,1992



4-EA

4.0 g stripped Al foil into
140 ml H_2O [with] 100 mg $HgCl_2$ - stand 15 min.

drain - wash thoroughly [with] 2 x 150 ml H_2O - drain
add:

7 g ammonium acetate in 6 ml warm water
18 ml IPA
15 ml 25% NaOH
5.3 g 4-ethoxyphenylacetone in 35 ml IPA.

Immediate purple color, which fades, then
green, which fades, then grey.

12:15 PM

4hrs- quiet & done. filter, wash [with] MeOH flash
filtrates - acid-base

-> strip
yellow oil -
KR -> 0.15 g white oil
0.3mm/140mm.
terrible.

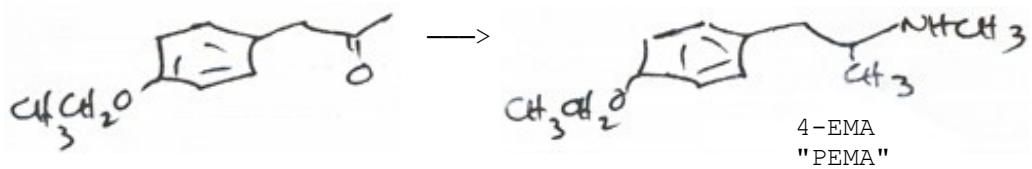
neutrals ?

Into 0.75 IPA - one drop HCl -> pH red.
add ether -no xtals- let stand. -still no xtals. -no yield

Based on MDE - Pihkal

Flash -> 5.1g. into 100 ml MeOH, add 30 g $NH_4{}^{+O}Ac^-$ - add
3.4 g Na^+ $CNBH_3^-$ - stir (ph green) add squirt 50:50
HCl MeOH,.
All goes solid. Into CH_2Cl_2 + H_2O + HCl ——> color in org
separate - xtrt 1x [with] dil HCl - pool HCl, OH [with] 5% NaOH->cloudy
xtrt 3 x 25 ml CH_2Cl - strip ——> 2.07 g white oil - KR ——>
~~xtrt~~ 0.5 mg 110-120mm white oil , 1.95g into 5 IPA-
+ HCl to pH red (xtals) + 10 ml ether ——> xtals .
2.25g.

Nov 7,1992



4-EMA
"PEMA"
(not good, as it suggests that 4-MA could be PMA, and that has been used)

4.0 g stripped Al foil into
140 ml H_2O [with] 100 mg $HgCl_2$. stand 15 min
drain - wash 2 x 150 ml H_2O, drain
add:

6 g NH_2CH_3 - HCl in 6 ml Warm H_2O
18 ml IPA
15 ml 25% NaOH
5.3 g 4-ethoxyphenylacetone in 35 ml IPA

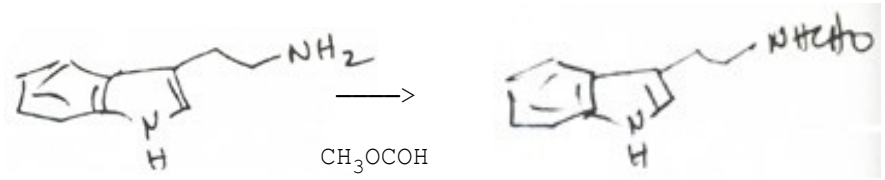
12:20 PM 4hr - done - stand rest of the day.

Found - on bench Jan 31, 1993 - a 500 ml E.Flask [with]
~ 80 ml yellow cloudy liquid marked "to be stripped".
Into | 1 RB leaved long white xtals behind - those on
in with water (MeOH insoluble) strip on RE.

Into 400 ml H_2O, H^+ [with] HCl. xtrt 3 x 50 ml CH_2Cl_2 -
almost all color out. OH [with] 25% - cloudy, to blue,
4.2 extract [with] 3 x 50 ml CH_2Cl_2 - flash -> 4.2 g,
pipet into KR flask 4.0g .
.15 micron KR 0.15mm 85-95° -> 3.1 g white oil.
85° . into 10 ml IPA.
+ 45 drops HCl (acid)
3.0g ,3.1 dry. + ether to 100ml. sudden xtals
drain filter - wash [with] ether -
air dry to constant wt.
10g IPA 3.28g 6:263.
ML
30
40 base
45 acid·

to 100 ml ether,
3.28 dry.

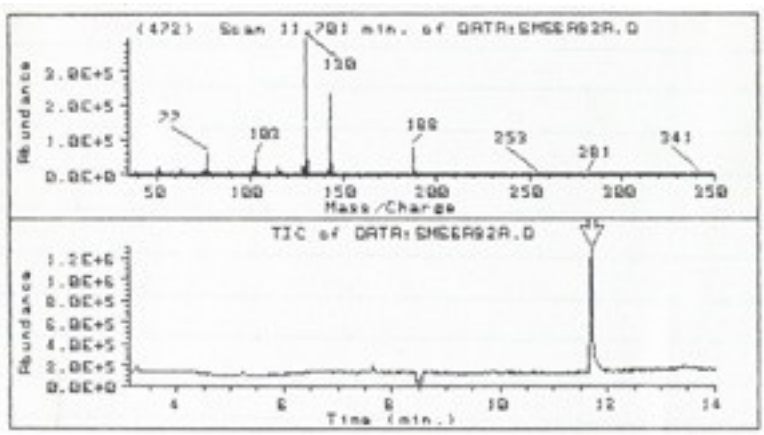
Jan 24, 1993



CH_3OCOH
HC=O
OMe

10 g tryptamine base (light purple, ex Aldrich) in
25 g sweet-smelling methylacetate. - on S.B.
reflux.
2 1/2 hrs - finally into solution - strip -> deep amber oil.

into 75 ml CH_2Cl_2 - wash 2x 1N HCl ⟶ little color.
but oils.
wash 1 x 75 ml 5% NaOH ⟶ little color.
flash
⟶ red-amber oil (~10g?)-

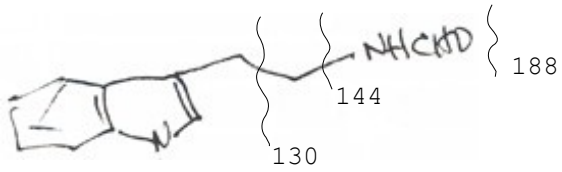


188

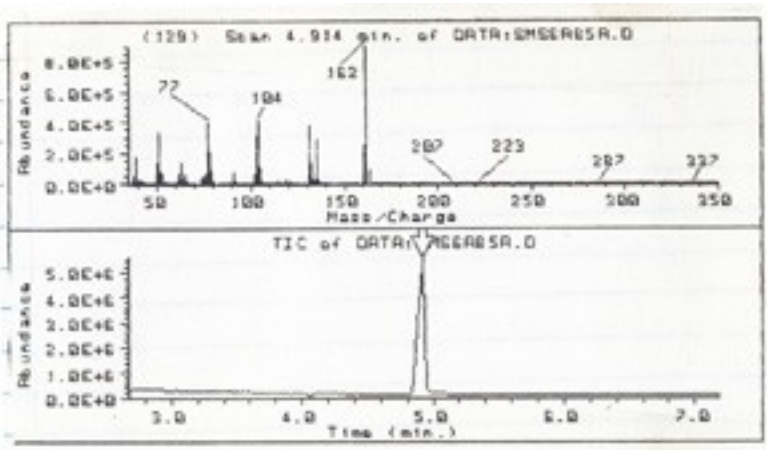
21.0

12.0 57%

3.9 19%

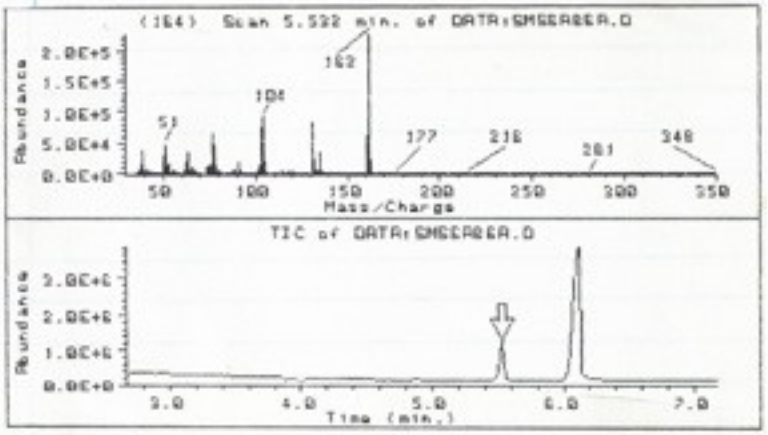


[Editor's Note: Page 265 is blank]

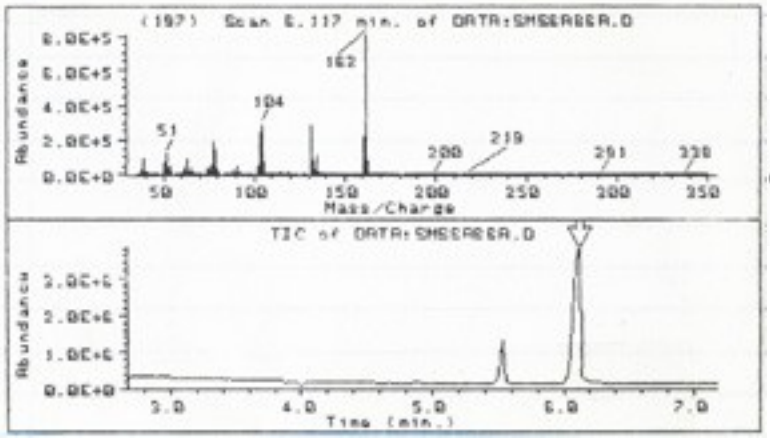


162

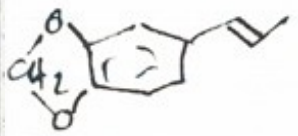
Safrole

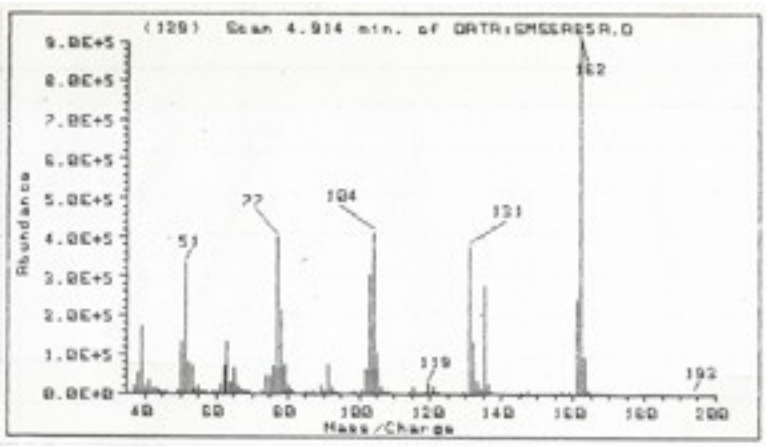


162 cis-isosafrole

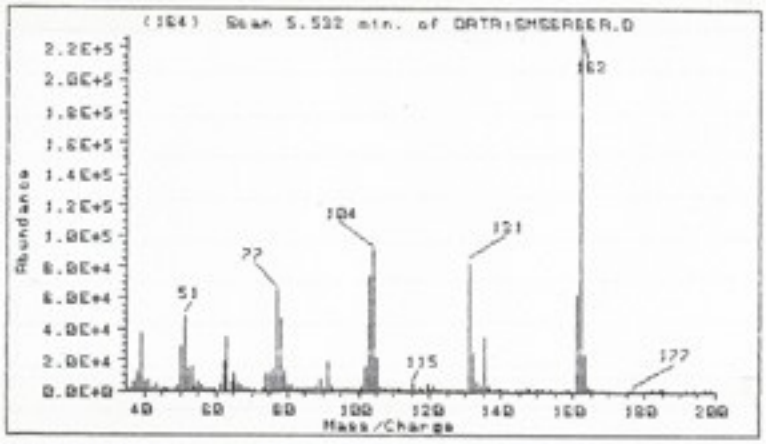


162 trans isosafrole

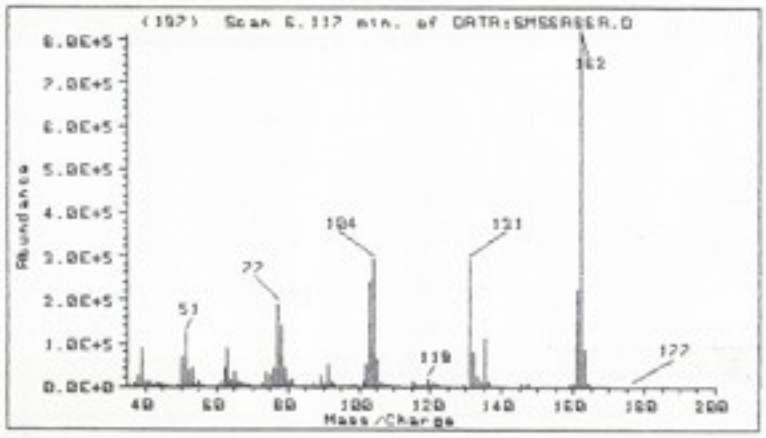




Safrole

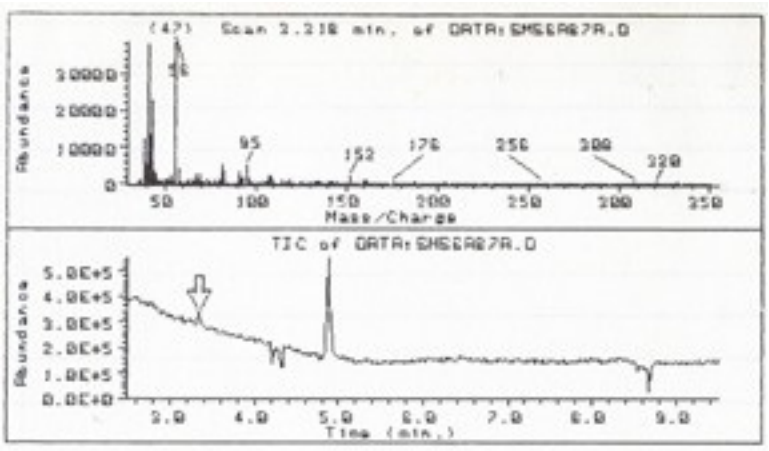


cis
isosafrole

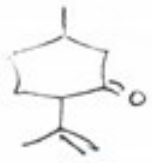


trans
isosafrole

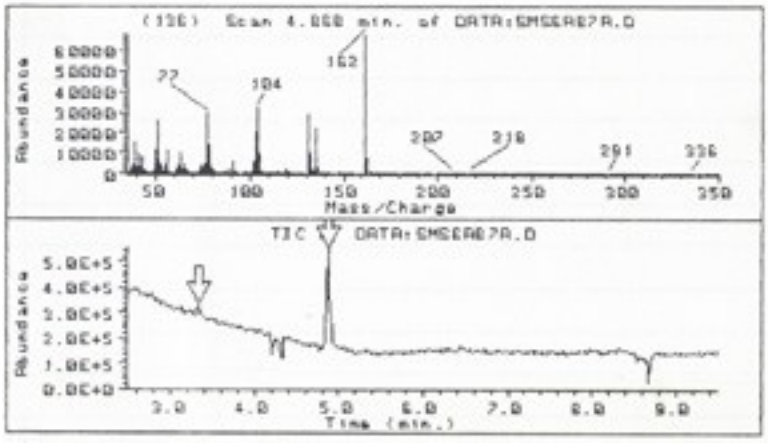
Sassafras extract!



152 = $C_{10}H_{16}O$

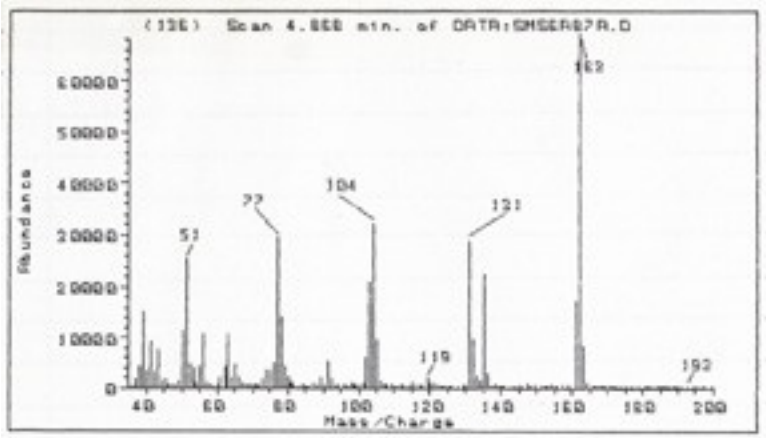


or isomer

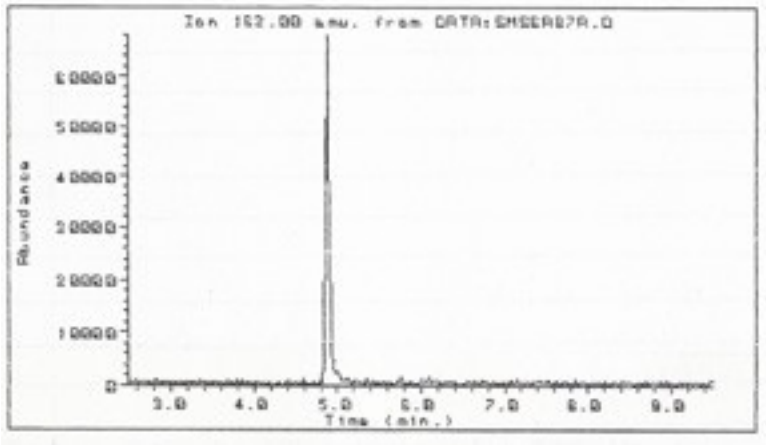


162

Safrole



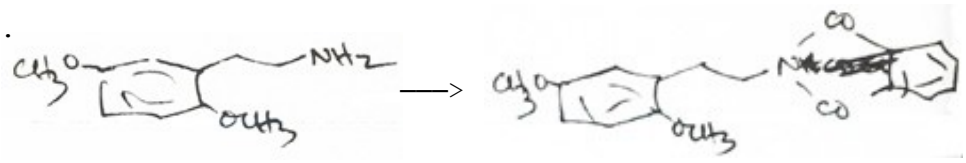
Safrole
blow-up



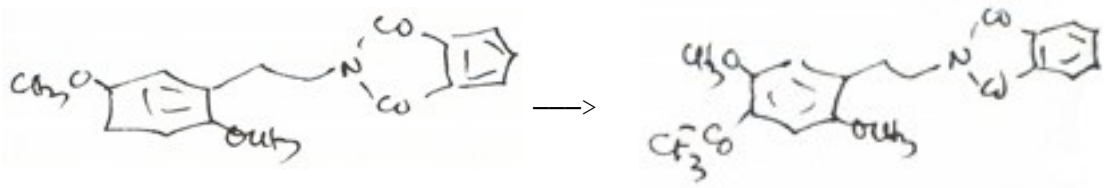
single ion-
look for
either isosafrole

Repeat.

February 14, 1993



2.23 g DMPEA - free base - aldrich commercial in 1 g bottles
1.83 g phthalic anhydride-
Δ [with] flame -> clear solu, H_2O ↑ then hot & quiet. yield "4.06-.22" = 3.84 found 3.83.
∇ - stir [with] spatula, seed -> start solid.
+ 3 ml IPA - scratch around -> white solids.
add total of 10 ml IPA- grind as best possible.
filter - wash 2 x 2 ml IPS -> off white xtals- (slightly yellow).
put out to air-dry.



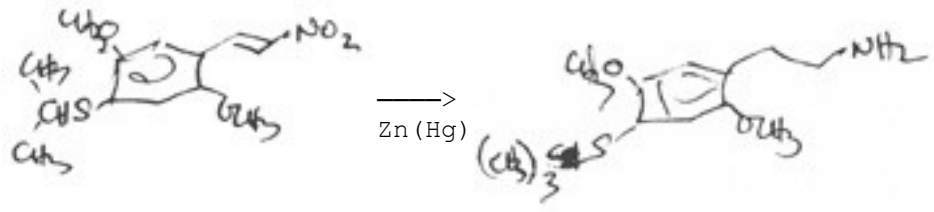
To 7.5 g polyphosphoric acid (1/2 liq., 1/2 dry-out solid) and all of the phthalide (3.39 g , slightly damp [with] IPA) and 3 ml CF_3CO_3H. . onto SB

Mass spec. - only phthalimide starting material. - into water wash -(CH_2Cl_2). wash [with] 2 x 50 ml 5% NaOH 0 strip -> 2.48 g off-white solid. starting phthalide.

[Editor's Note: Pages 271 & 272 are missing from the original document]

[Editor's Note: The following has been photocopied and pasted onto the page]

5/10/29
Attempt:



|| page 252

A suspension of

13.80 g 2C-T-7 NS (See 6:5)(some used at 6:158)
in
190 ml warm MeOH (not in sol) +
90 ml conc HCl -> gets warm - not in sol.
stir vigorously - back to RT.

prepare 5% HgCl
1.9 g/38ml hot H_2O
let cool

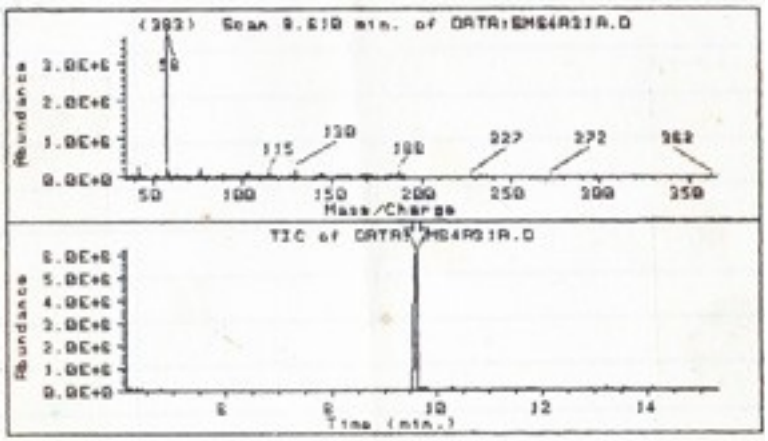
Add 19 g Zn powdered
NR- 15 min
Add 1.5 ml conc HCl.
Immediate clobber -
15 min - wash 2 x H_2O by
decantation - drain

Add a small amt Zn(Hg) [with] silver spoon.
1/2 in (10 min) up to 35 only. No color going,
all at (15 min) to 37°,
add a shot HCl. prepare more HgCl 1.9g
40 ml H_2O
19 g Zn

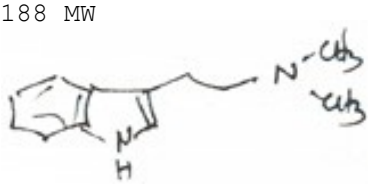
Add new amalgam - (very warm, no HCl)
temp to 45°,
add 20 ml HCl —— to 50° - cool [with] ice let stir
11:30PM.

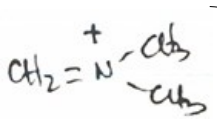
overnight - AM - some orange solids as chapeau-
Knock in - another shot of HCl - stir the day.

GCMS DMT

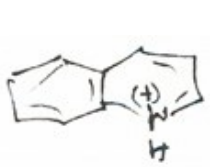


188 MW

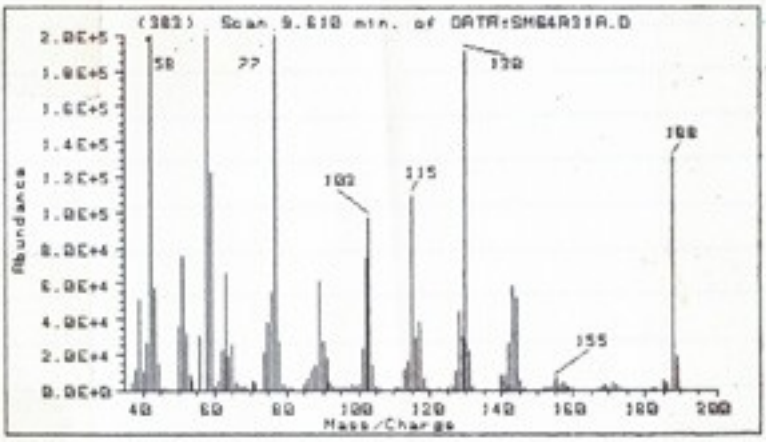


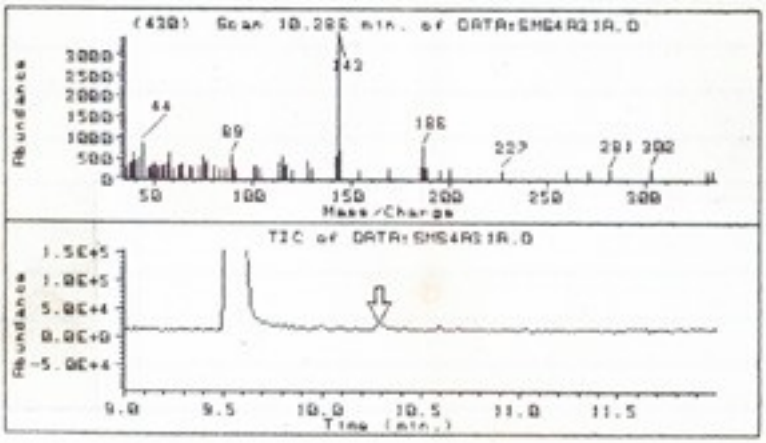


58

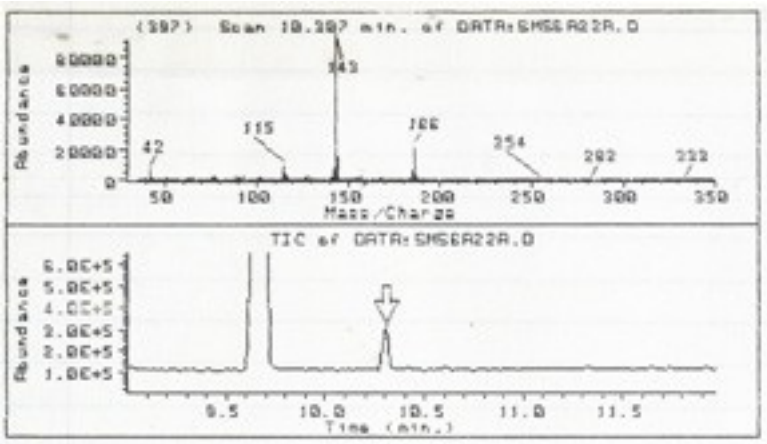


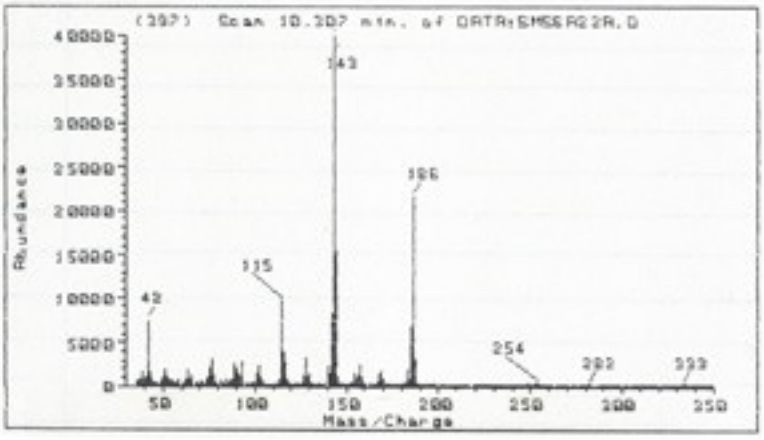
130



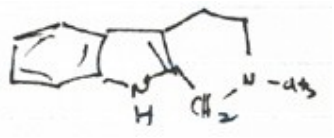


DMT contaminant - carboline

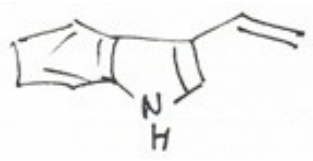




186



143



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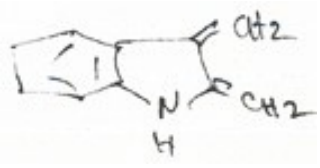

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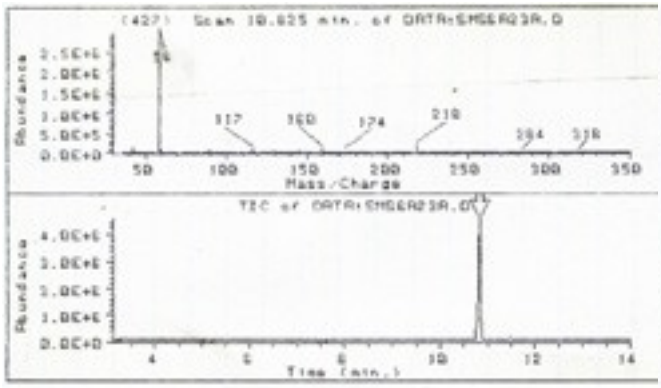
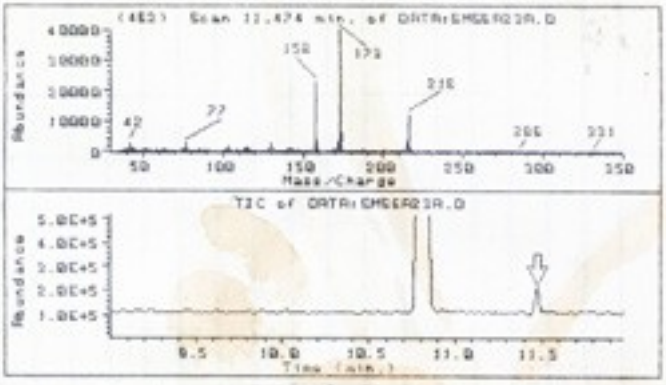
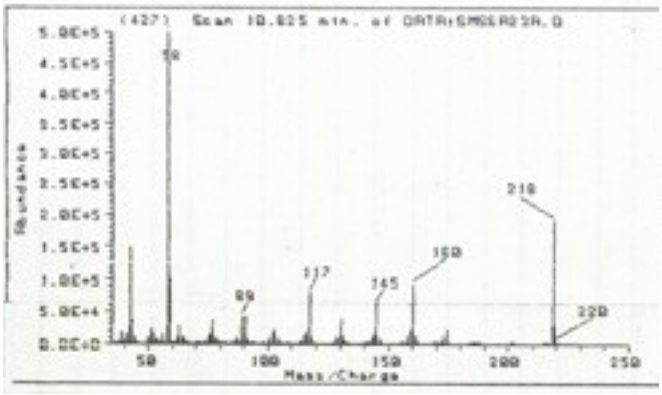
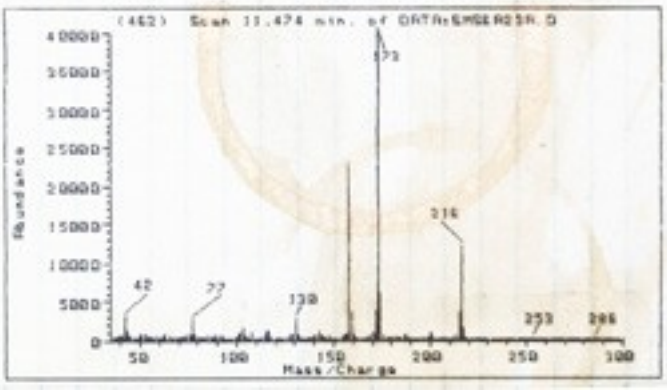
5-Methoxy DMT

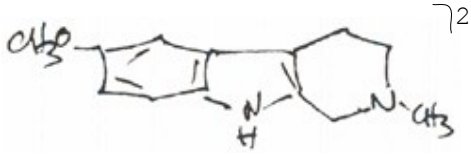




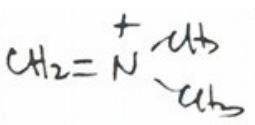




218



216



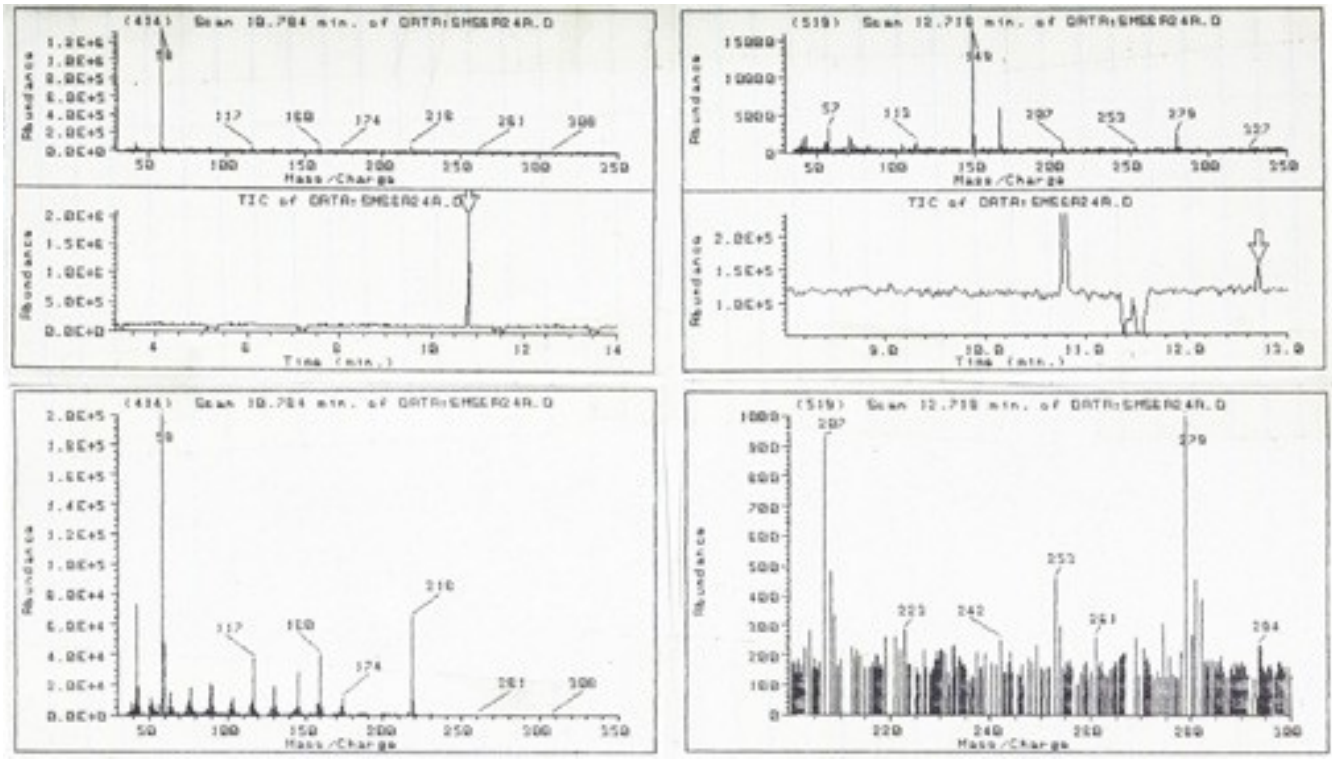
58

or

173

[Editor's Note: This page was originally orientated vertically]

Bufo Alvarius



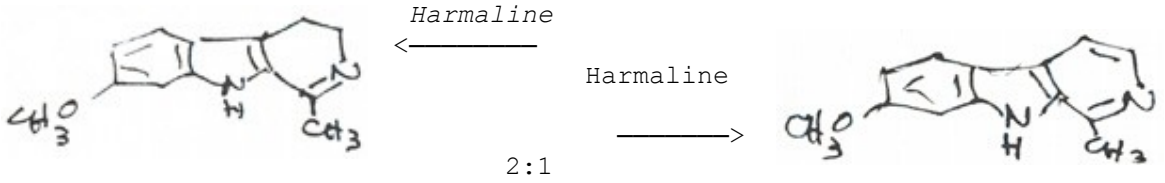
218
58
major ≡ 5-MeODMT
160
small retention times
off 10.825
10.784
———— 2 1/2 seconds
.041

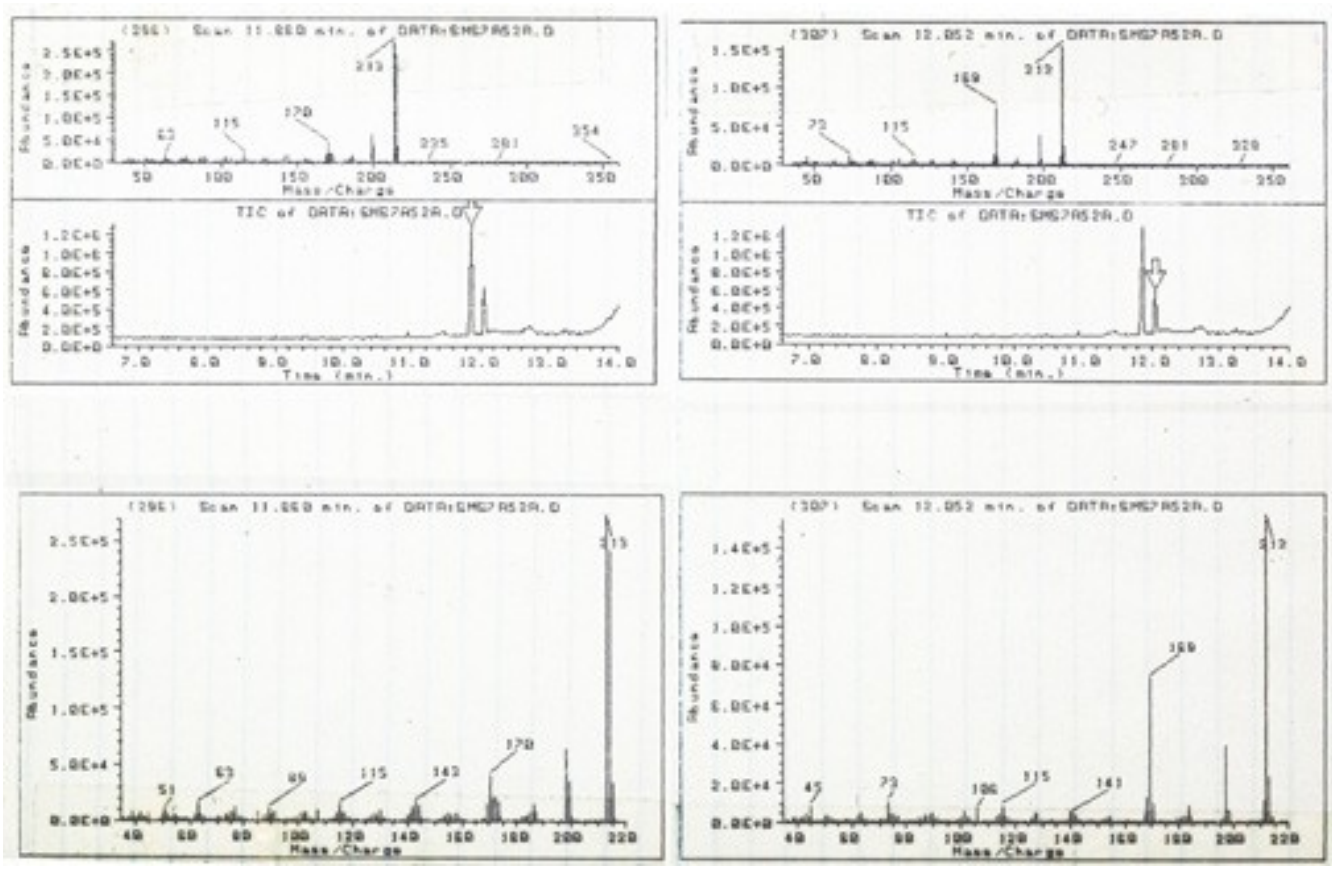
1 25mg pellet, into
1 mL anh. DMF
grind until nearly
all gum is dissovled

0.1ml + 0.9ml sat
$NaHCO_3$
+ 1ml 50% KOH in
0.2 NH_4O_3
1ml 90/10 $\Phi OCH_3 \cdot BuOH$
shake, spin.

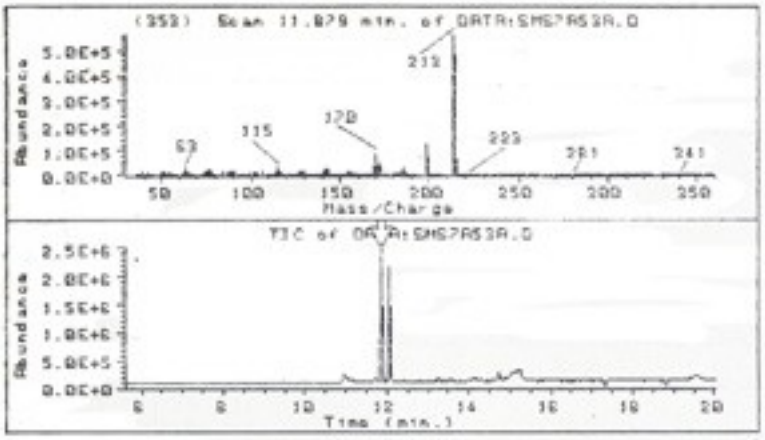
[Editor's Note: This page was originally orientated vertically]

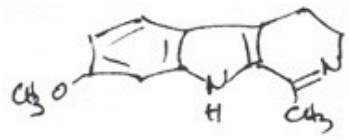
HARMALINE ·HCl ex MERCK A.G. Lot 602572
4/12/93 DARMSTADT Control 62473H



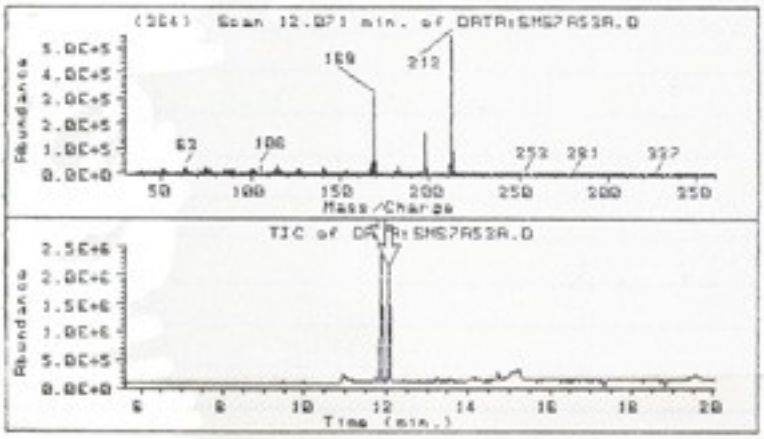


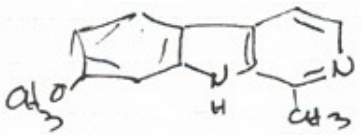
Major alkaloids of Syrian Rue Seeds
Peganum harmala 4/12/93



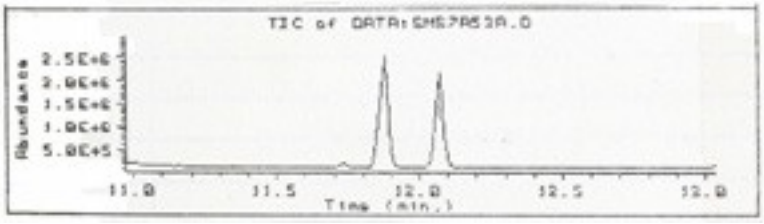


harmaline





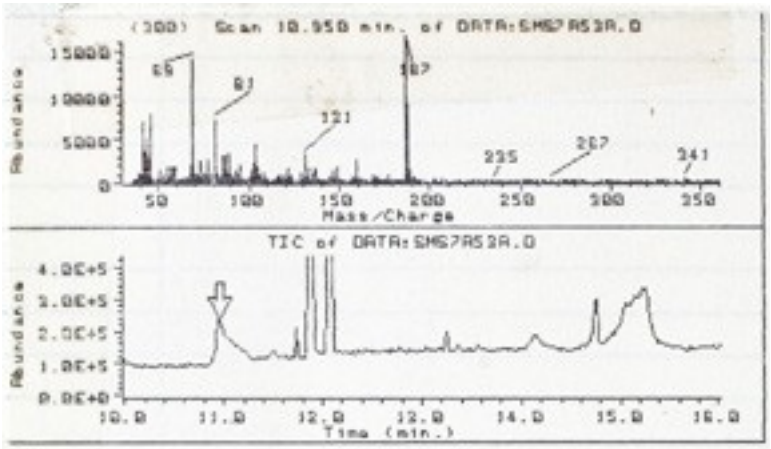
harmine



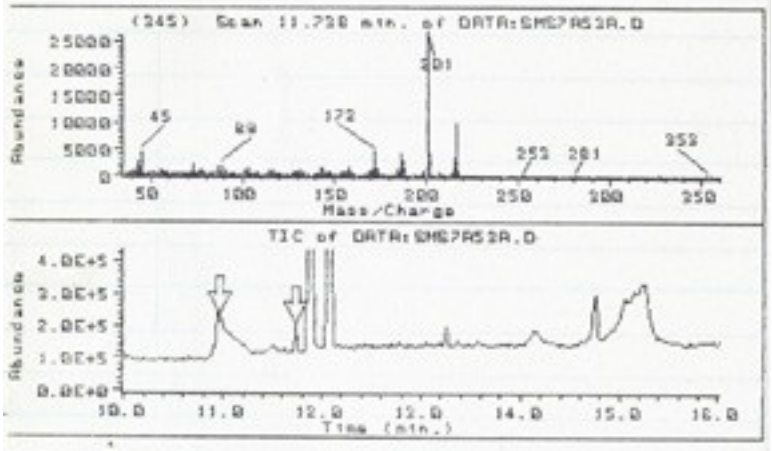
about 1:1

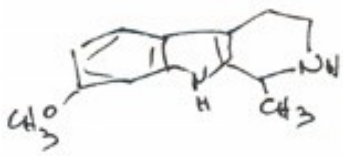
Minor Components, Syrian Rue

188

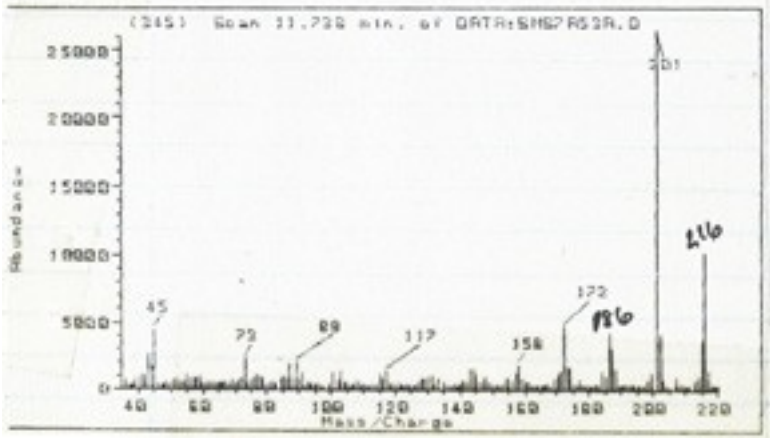


216





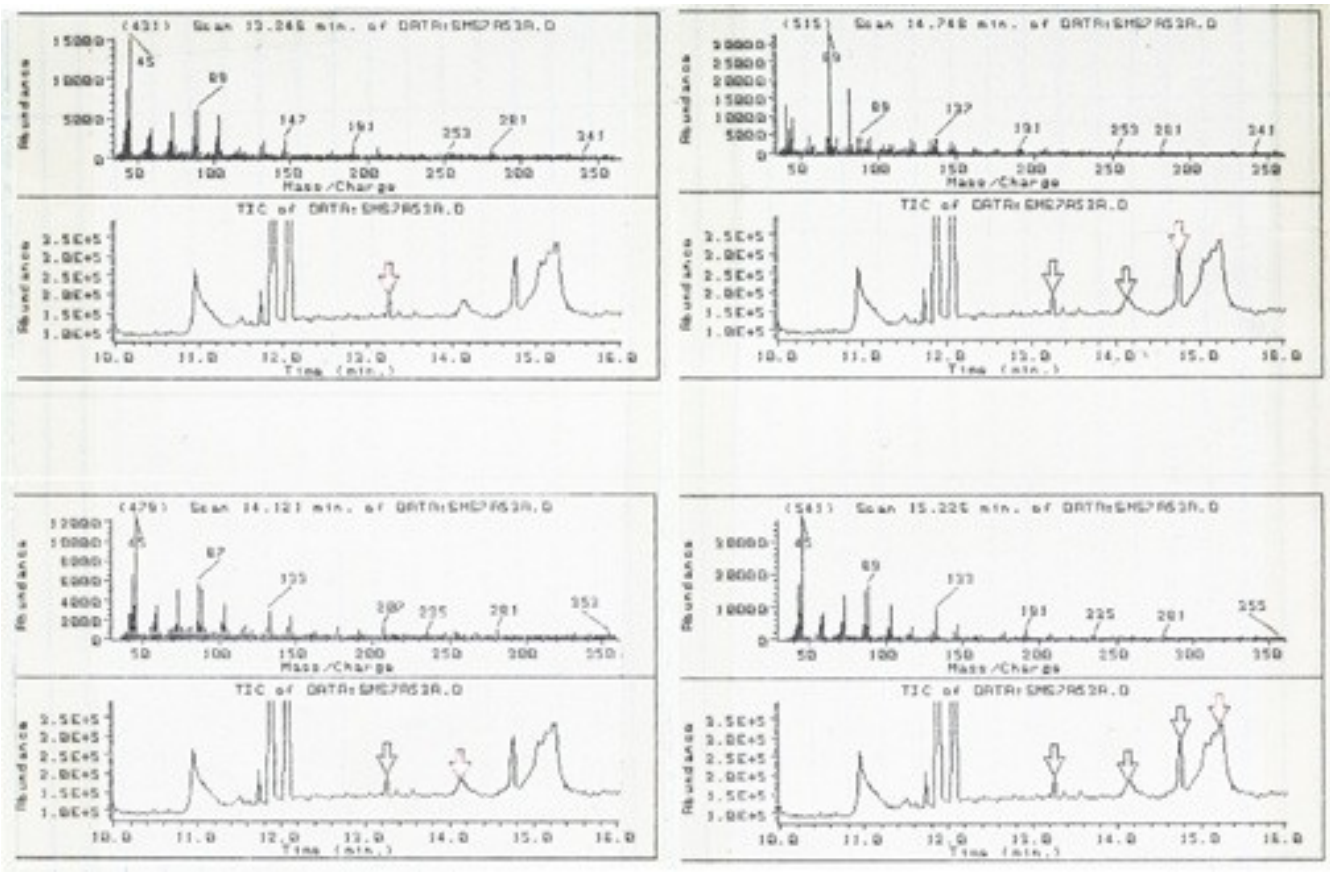
or



211.30	193.00
213.10	666.00
214.10	891.00
215.10	3664.00
216.10	10014.00
217.10	1367.00
218.00	255.00
218.30	241.00

[Editor's Note: This page was originally orientated vertically]

more minor components

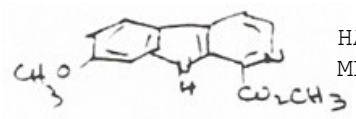


Alkaloids of
Banisteriopsis

harmaine - related

reduced harmine - related

260

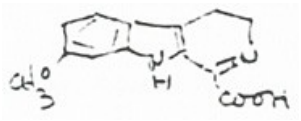


HARMIC ACID METHYL ESTER 256

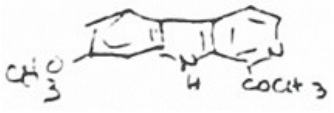
250

HARMIC AMIDE 244

HARMALINIC ACID

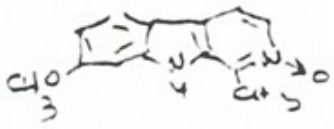


240



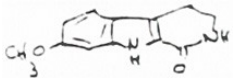
ACETYL NORHARMINE 240

228 230

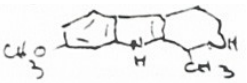


HARMINE N-OXIDE

KETO TETRA-HYDRO NOR-HARMINE



TETRAHYDRO HARMINE



220

216

212

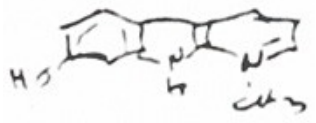
HARMINE

214

HARMALINE

210

198 200



HARMOL

190

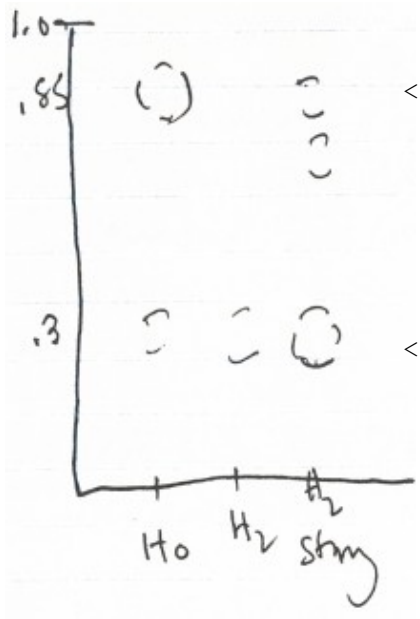
182

HARMAN P.incarnata

180

TLC of harmine / harmaline

Ho H_2



95% CH_3CN
5% NH_4OH

	short wave	long wave
<- purple fluoresce	deep purple	dark blue
<- pale blue fluoresce	light blue	blue-white

Attempt:
May 14, 1993

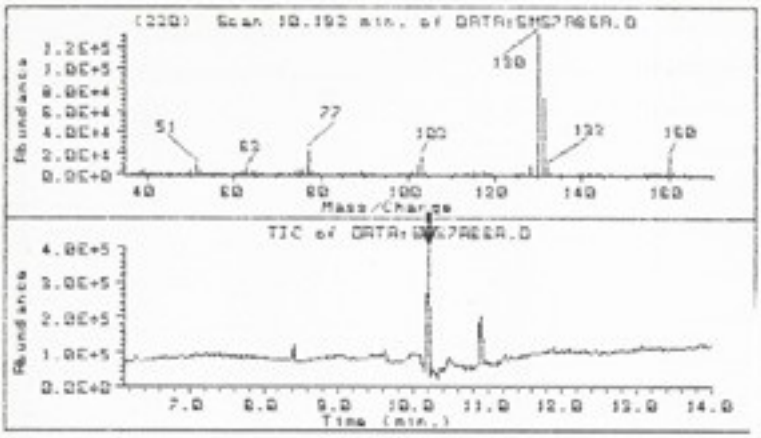
CH_3 CHBr CH_3 ——> ? (K_2CO_3)

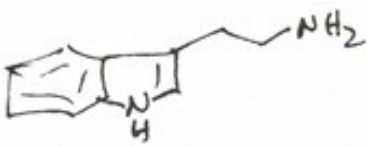
iPrBr
——>
Tryptamine 4.8 g (MW 160 30 mM)
Isopropylbromide 37 g (MW 123 300 mM)
powdered anh. K_2CO_3 41.4 g (MW 138, 300mM)
MeOH 100 mL.
at reflux 4 hrs.
filter, wash carbonate [with] MeOH
strip, into CH_2Cl_2, xtrt 2 x 75 ml dil H_2SO_4
aq. OH^-, xtrt [with] 2 x 75 ml CH_2Cl_2- flash
—> pale yellow-orange xtals, 4.73 g (28% conversion)

iPrI
——>
repeat
ReDissolve in 100 ml MeOH , add
20.4 g Isopropyliodide , add 120 mM
16.6 g powdered K_2CO_3 anh. 120 mM
reflux 10 hrs. work up as above - more tarry stuff
—> 4.19 g pale oil -AM- some xtals and yellow oil around it (75% conversion)

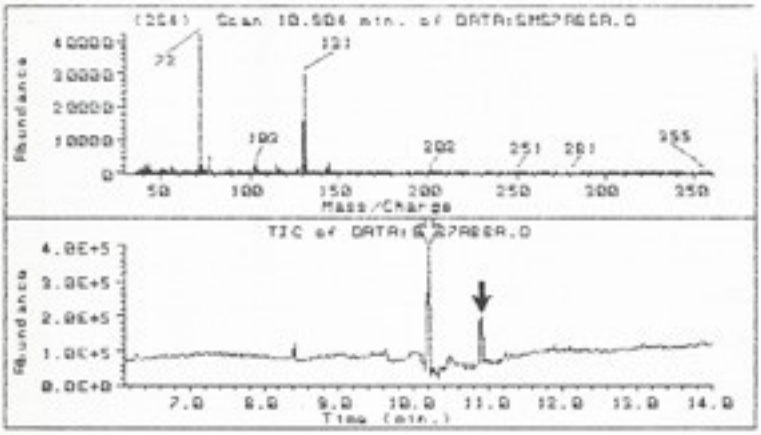
iPRI
——>
repeat
Redissolve in 100 ml MeOH. exactly as above iPrI- one more cycle - on at 4 PM Tuesday 5/18/93
off Wed AM 12 hrs. heavy bumping. lost some -
don't strip off MeOH. - lotsa water - xtrt into CH_2Cl_2 -
xtrt org [with] 2 x 100 ml dil H_2SO_4- back after OH^- [with] 25% base into CH_2Cl_2
—> pale amber oil 2.65g
140°/.5mm. am- fine rosettes!!
-> 1.97g oil GCMS completely propylated
that xtallizes.
page 286 (100%)
Scrape out 1.92 g white solid

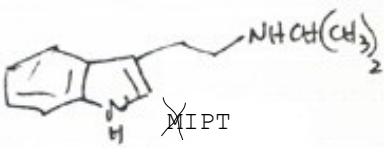
See 7:22



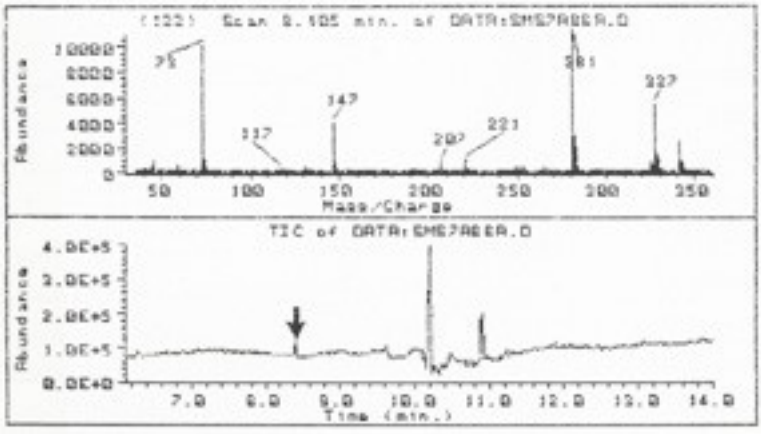


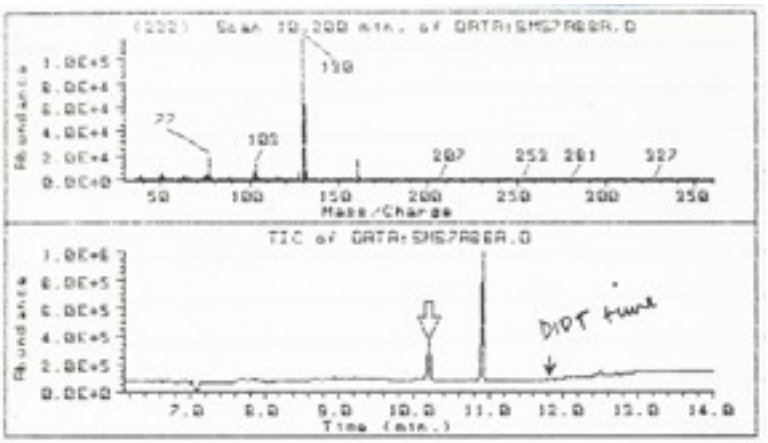
tryptamine



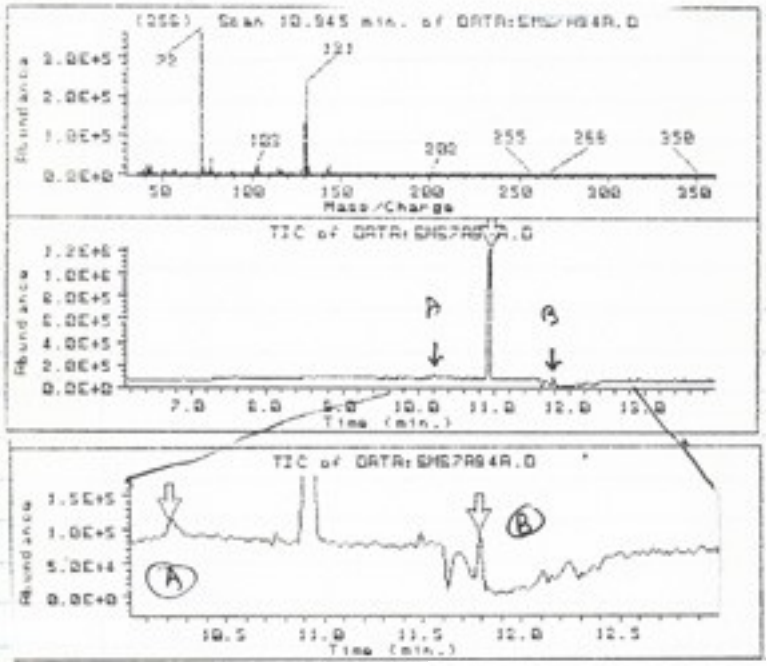


28% conversion
4 hrs, IP bromide
10 fold excess.



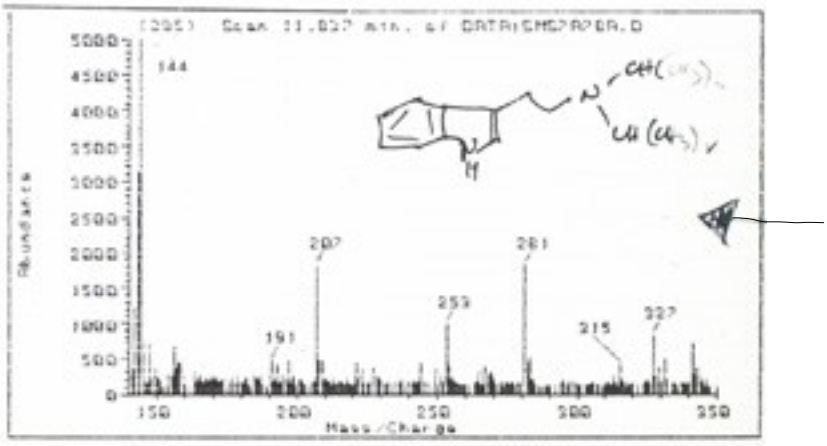


Isopropyl iodide
K_2CO_3 4x excess
10 hrs
75%
conversion

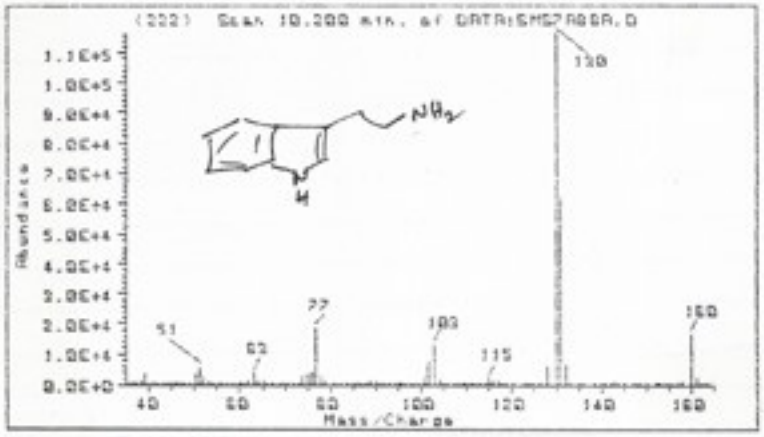


third pase
page 284
100%
conversion

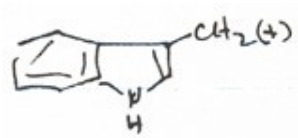
A is tryptamine
B is di-i-pro. T.

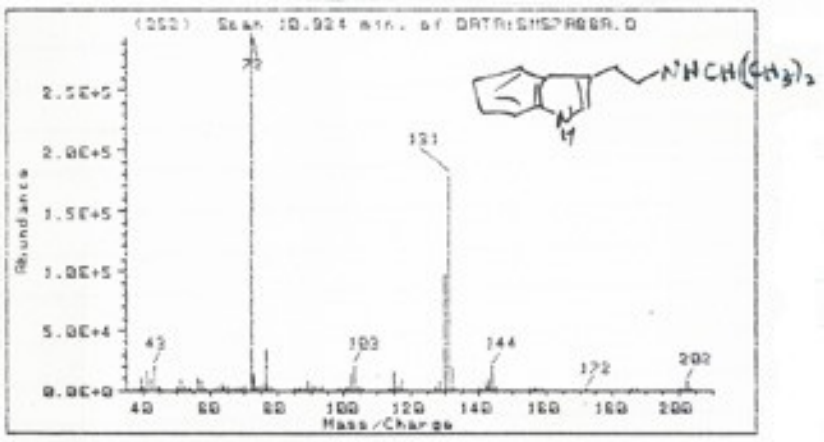


Reference Spectra



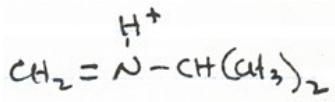
160 parent peak

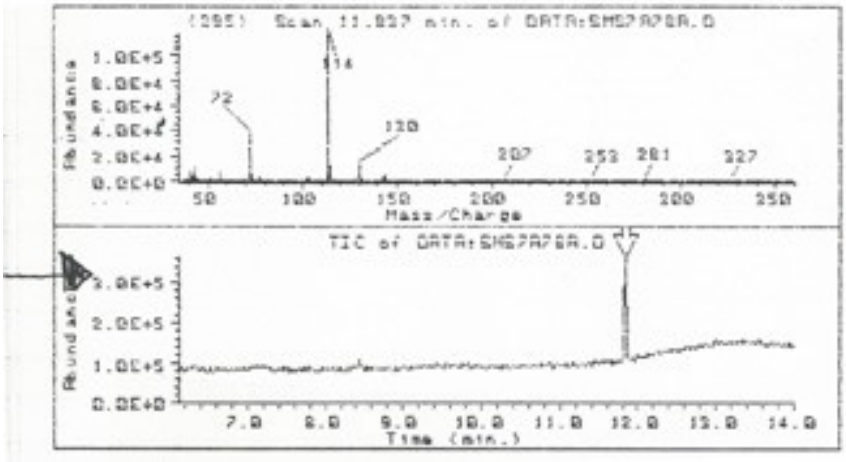
130 



202 parent peak

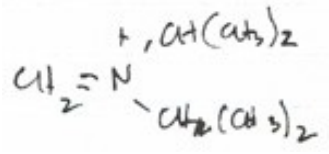
130 see above

72 



244 parent peak

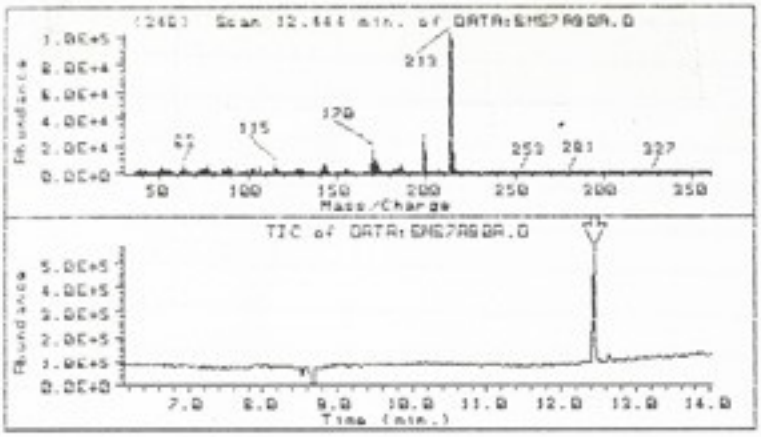
230 see above

114 

72 see above

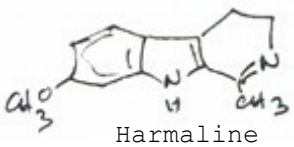
Aldrich reference Harmaline

Sigma is extremely Similar

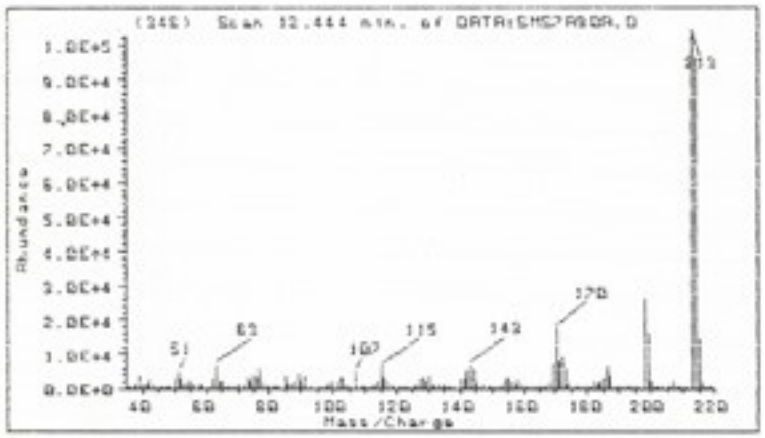


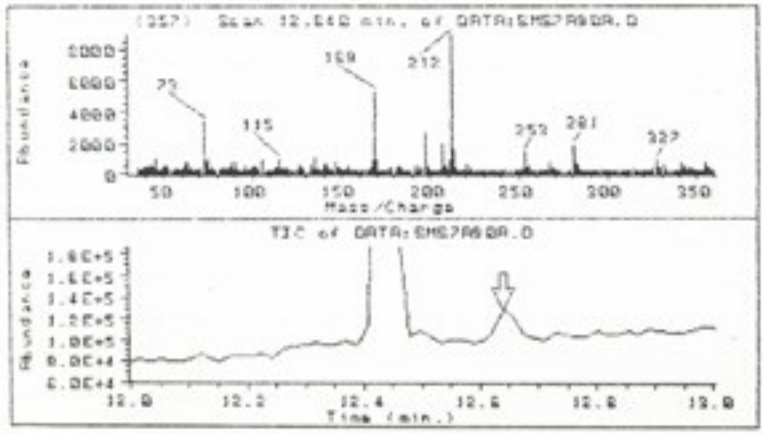
214 parent

K&K ~10% harmine in harmaline



Harmaline

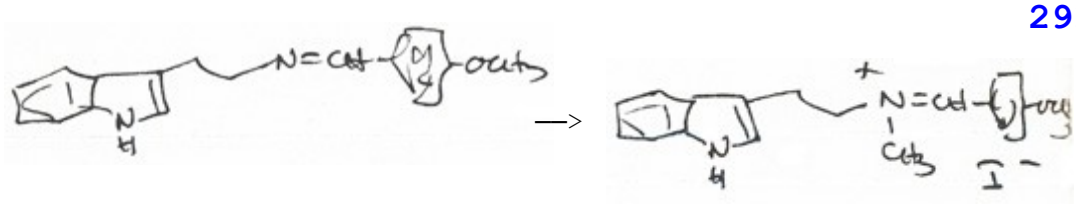




212 parent

Harmine

[Editor's Note: Pages 289 & 290 are missing from the original document]

Attempt. 

4.9 g schiff's base - see recovered 289. add.
15 g CH_3I - not sol. onto SB. reflux immediately -
looks as if changing - into some sol, then solids
not at all sure. —— add
20 ml IPA - much looser - almost in sol. some deep
yellow gobs at bottom. -add
13 g CH_3I - now goes into solution - soft S.B. &,
glass barrier between steam & flask.
keep on S.B. - some white solids 1/2 hr- then they
redissolve. on at 5:30PM.
darker & darker . by 10:30 deep red.
off 11PM.
It didn't feel to be up to a real boil.

May 22 1993 (p 289)

tryptamine ——> p.methoxybenzylidine ——> quat [with]
propyl I ——> PT H_2O↑
4.80 g +4.14 anisaldehyde Δ -> oil - touch [with]
MeOH -> white solids everywhere.
1 g NaI 8.37 g PrBr 8.4 g anh. K_2CO_3
steambath 2 1/2 hrs. Strip RE -> solids everywhere.

Suspend in H_2O (200 ml) 100 ml ether - color to organic
insol's at interface -filter, wash, xtrt etc etc.

ether	aqueous	insoluble
flash -ivory-colored Solids 7.20 g	a bit of acid red. acid to 1N SB 4 hrs. dark ∇ OH → sl.cloudy	wash air-dry 1.17g 1 g [with] 1N Hcl 100° 1hr.
full air-dry 4.95g	xtrt CH_2Cl_2 → 0.1g.	not much here.

Isolate minor alkaloids.

June 27 28? 1993

3 x 6 oz TOP Cigarette Tobacco.
TOP tobacco company.
distributed by Republic Tobacco Co.
Chicago, IL 60640.
bought at Thirfty's Drugstore
5100 N. Ravenswood.
chi . 60640

171 g 6 oz into 1 L. 1N HCl 5-7 PM
x g 6 oz " 7-
173 g 6 oz "

each - Δ 55° 2 hrs.
stand 1-2 months.
filter - wash 2x N HCl
→ 1800! ml dark extract.
wash [with] 2 x 100 ml CH_2Cl_2 (900) x 2

→ CH_2Cl_2 pale yellow
flash -> 0.77g
yellow oil.
Acids/Neutrals

residue on
bottom of flask -
~ dark green HCl in-
soluble - out [with] acetone

aq.
make basic
[with] NaOH to
blue -
xtrt 3 x 100 ml
CH_2Cl_2 - centrifuge
as needed

CH_2Cl_2

in aqueous - deep brown
→ OUT.

flash -> 5.05g
thin amber fluid -k
steam distil - take over about 250 ml condensate -

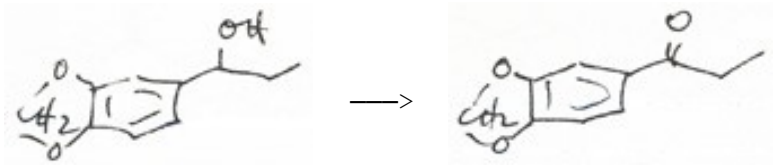
extract non-volatiles
→ 0.63 g brown oil
GCMS at SFGH

o

extract condensate
→ 2.48 g yellow oil
nicotine

.63g
amber oil
2.48 recovery
nic
-

[Editor's Note: Pages 293 & 294 were discarded by Shulgin due to acid spill]

9/29/93  ——>

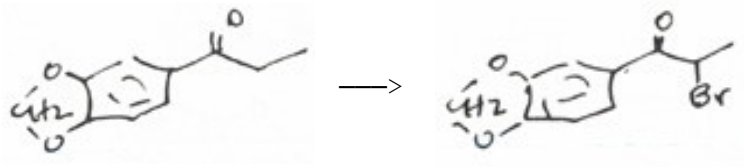
To a solution of 10 g potassium dichromate in
65 ml H_2O +
7 ml cold. H_2SO_4 There was added, with stirring,

11.7 g carbinol added neat. With 1/2 in - very hot spontaneously, ∇ in running water - add rest dropwise over 1/2 hr ⌄ Let stir to RT - stand a week.
Δ 1 hr on SB

dark ??? acid is the native compound.
into
13.6g The entire Rx was poured into 2 L H_2O,
made distinctly acid [with] a little
0.4mm 50° HCl- extract 3 x 75ml, no 100 ml CH_2Cl_2 - combine -
separate out once the slash is localized,
~20° name by separation - and wash slash [with] 3 x 75 ml
120°/.3 CH_2Cl_2
over —> ~ 400 ml yellow CH_2Cl_2 solution - wash [with]
~ 100 ml sat. $NaHCO_3$ (still basic) and flash —> 13.6 g amber oil.
KR. 120-130°.0.3mm —> 7.66 g white oil -
TLC against starting carbonol. - maybe 4:1 Ketone/ alcohol. - Hit again
7.66 g. into 6.6 g K dichromate in
42 ml H_2O
+4.5 ml H_2SO_4

4PM-SB. very exothermic - turns dark, short temp to ~ 60° - stir to RT. 2 1/2 hrs on SB. - into 1 L H2O, H+ [with] HCl (10 ml) - xtrt [with] 3 x 100 ml CH_2Cl_2 - not too much sludge this time - fairly
0.5mm clean. wash sludge [with] CH_2Cl_2 combine, wash [with] 100 ml sat $NaHCO_3$
.3 (still basic.) strip. 6.32g crude over 135° @ 0.3 —> 5.10 g
.25 120° water white. TLC excellent. >95% right stuff.
5.10 g

<———— 293,4 - acid spill - discard.

10/10/93 

There
1.8 Ketone
+ 2.2g Br 1hr> 50:50
+ 1 g Br 1hr> 70:30
+ 2 g Br 1hr> complete

Based on MB same Rx 2/20/82 Book III

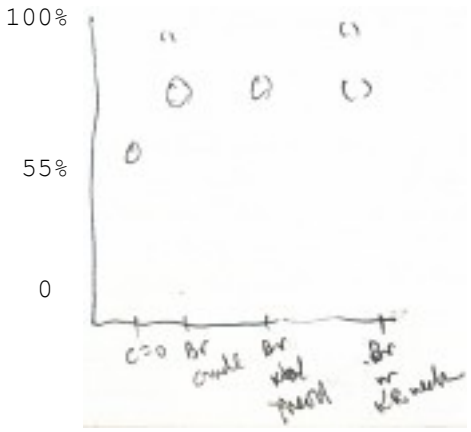
To a mixture of 60 ml $CHCl_3$ & 60 ml EtOAc - add
12.6 g anh. granular $CuBr_2$ (should I have ground 'it' up?)
add:
5.10 g Ketone from p 295 - onto SB reflux 11:45
TLC at [12:15] - no sign of Br [with] 85/15 CH_2Cl_2/hexane.
add . 12.6 g anh. finely powdered $CuBr_2$ - let go ON. - AM.
mostly white solids - stand a week - filter through paper - wash Cu salts [with] CH_2Cl_2 - flash all solvents on R.E. . into 150 ml H_2O xtrt 3 x 75 ml CH_2Cl_2 - wash pooled extracts [with] 100 ml H_2O flash CH_2Cl_2 phase. —> 7.44 g of a fairly deep colored oil - fluid.

7.44g

Try 1.05 g distilling at the KR. —> 1.00 g white oil +
off white late oil
(1.00g total)

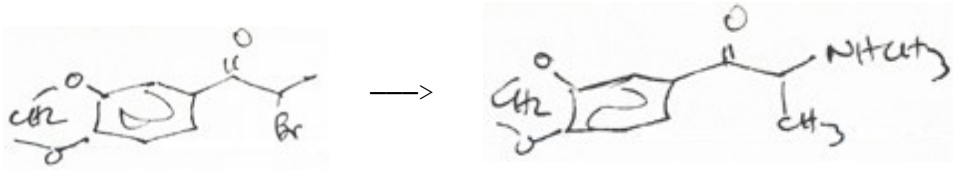
120° 0.1 mm — distill the rest
150-155° 0.1 (85v) —> 6.13 (total 7.13 g ex 7.44 g crude) white oil- [with] seed sets to slightly moist xtals. - on plate [with] MeOH →fine ☆xtals

Use all in animation - save a bit fine xtals for MS, seed
save a bit of late oil for MS.



to GCMS see page 299

Oct 17, 1993



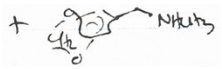
~6.5 g bromo - all crude (+ dichromo's) from page 296 into 15 ml IPA
heat until dissolved, add a small squirt at a time to

25 ml aq. 40% NH_2CH_3 -first addition -> cloudy & quite yellow swirl - more - cloudy and to orange. - more - no more cloudy, and ends up amber . Addn over 5 minutes. Slight warming, put on SB 10:30 PM.

6.5 g Bromo
15 ml IPA

25 ml 40% aq. NH_2CH_3
wt 1:3
mole 10x ex es

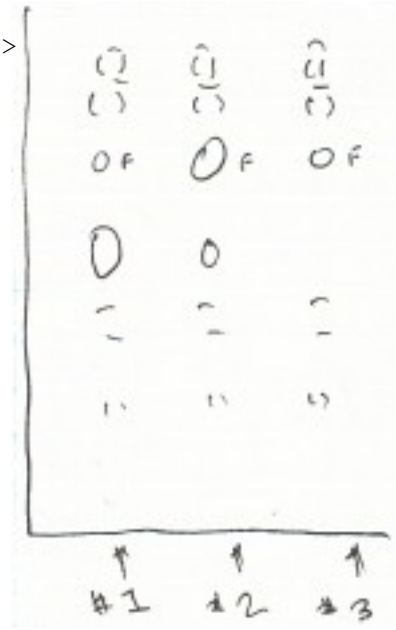
MW Br 257
MW NH_2CH_3 31
1:3 @ 40% HO
77.5
x10 ex es
775

Off in AM. clear amber- strip to amber oil. Into 500 ml H_2O + CH_2Cl_2 + Hcl to strong acid - xtrt 3 x 75 CH_2Cl_2 - lots of color in organic - make basic [with] 25% NaOH- some cloudiness xtrt 3 x 75 ml CH_2Cl_2 ,
pool - flash solvent -> 1.53 g (?) of amber oil. GCMS; contains product +  !
KR at ~~1.0 → 0.7 microns~~
0.1mm -> 0.07mm 70°-160°
3 cuts & pot !

flash
2.35 g red oil
save a sample
p 297:2.35

Cut 1	Cut 2	Cut 3	pot
70-90°	onto ~110°	onto 160°	red glass
130 mg drained in 2 ml IPA - +HCl to red - spont xtas - wash dry -> 157 mg	280 mg drained rinse [with] 2ml IPA H↑ to acid pH. + >8 less 10 drops HCl- ↑ether to turbid. Scratch- filter,wash->.174g off white	~0.1 g . +2ml IPA + HCl to acid + ether-> xtals filter, wash -> 92 mg	out TLC next page

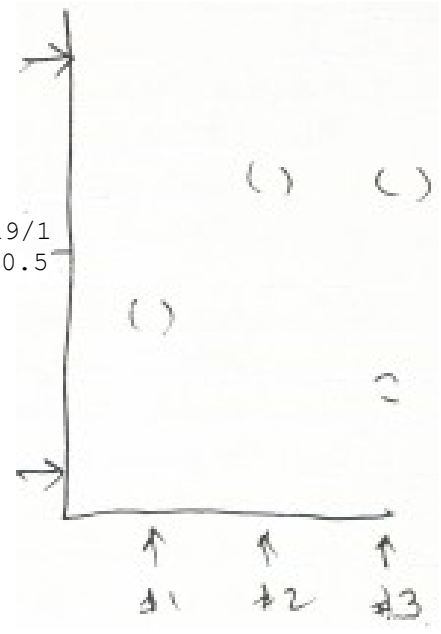
TLC KRed
bases page 297



<— MDM·ONE

<— Benzyl?

TLC ·HCl Salts.

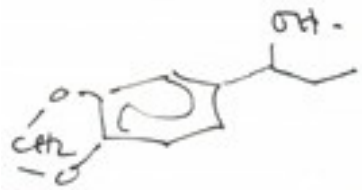


Piperonal —> carbonol

9/29/93

Et MgCl.

——>

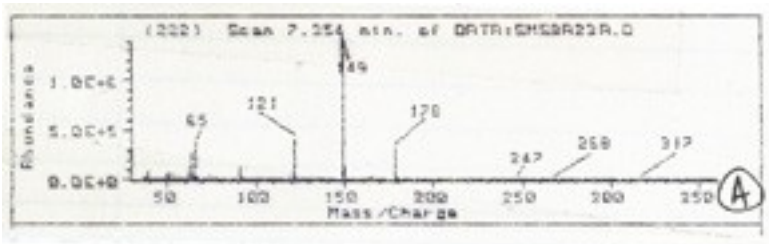


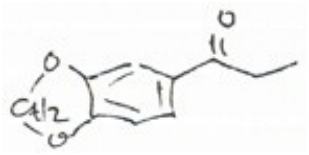
To a solution of 10.6 g piperonal (0.1 Mole) dissolved in 90g anh. ether, under Ag, good stirring - add 30 mL 2.0 M Et MgCl (+5 ml extra) in ether Aldrich. Cool immediately [with] external ice bath -> cottage cheese. 5 ml more Grignard. Quiet - add rest Total 30+5+30 Had to use new syringe.

Dump into 60 g ice [with] 3 ml H_2SO_4 - xtrt [with] CH_2Cl_2 -> pool flash —> 13.03 g amber oil,

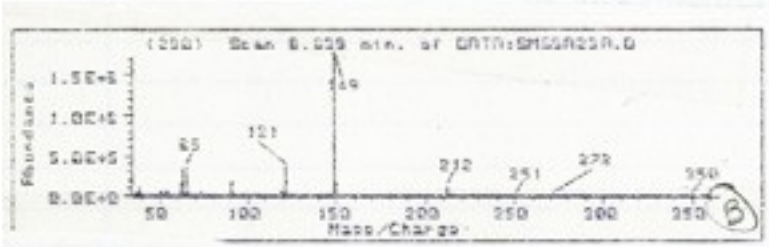
100-
KR @ 110 / 0.3mm —> 11.73 g white oil - save some rest to Ketone.

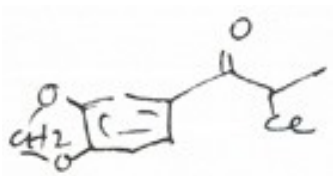
This is the "pure" bromo ketone
from page 296



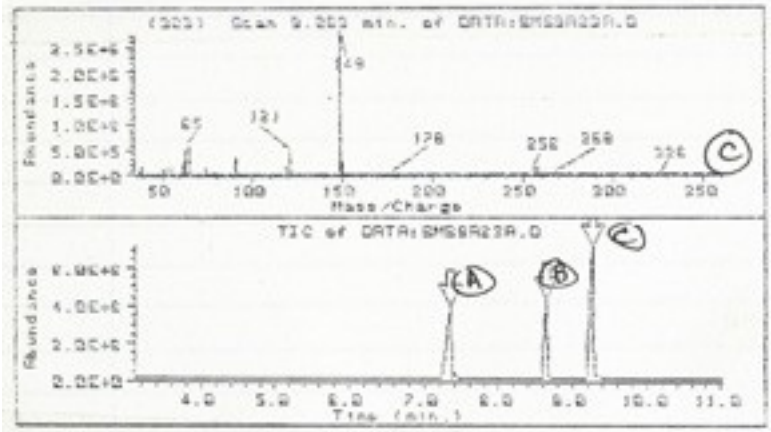


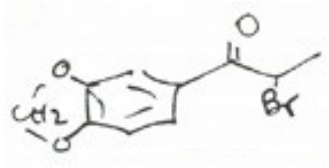
178





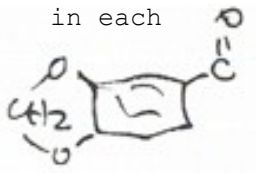
212
/214



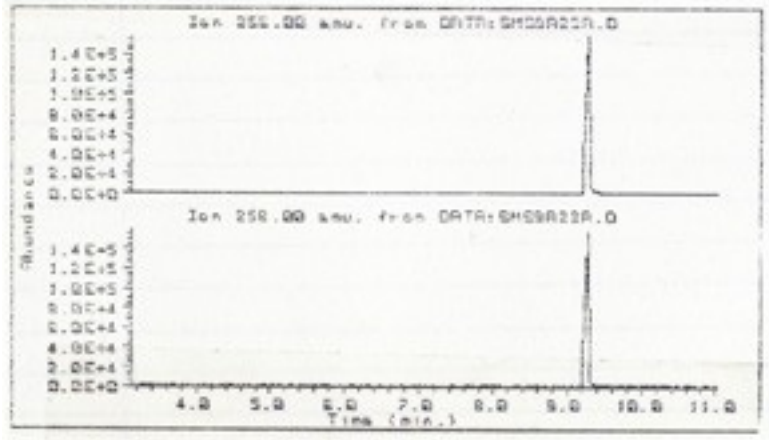


256
/258

in each

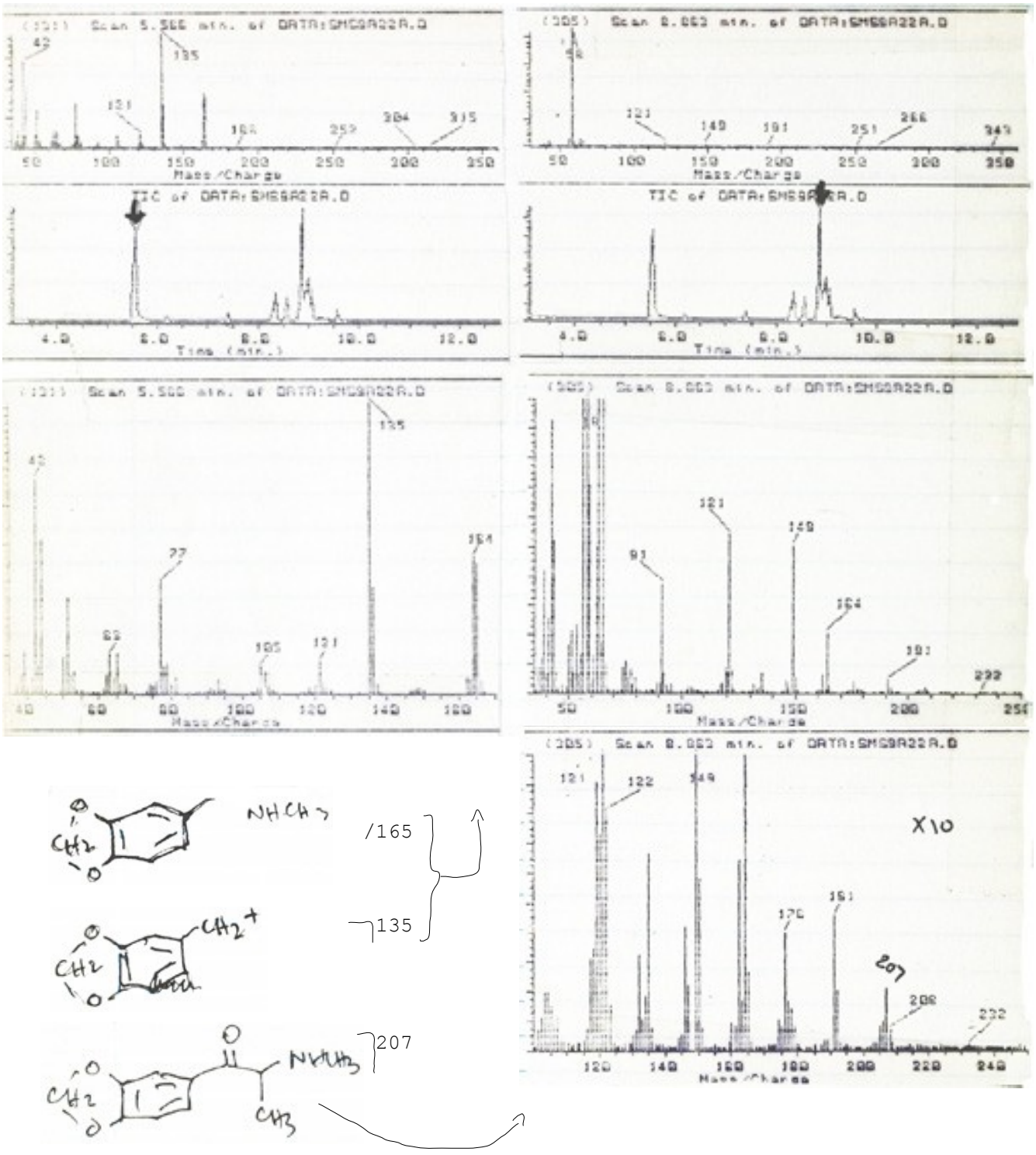


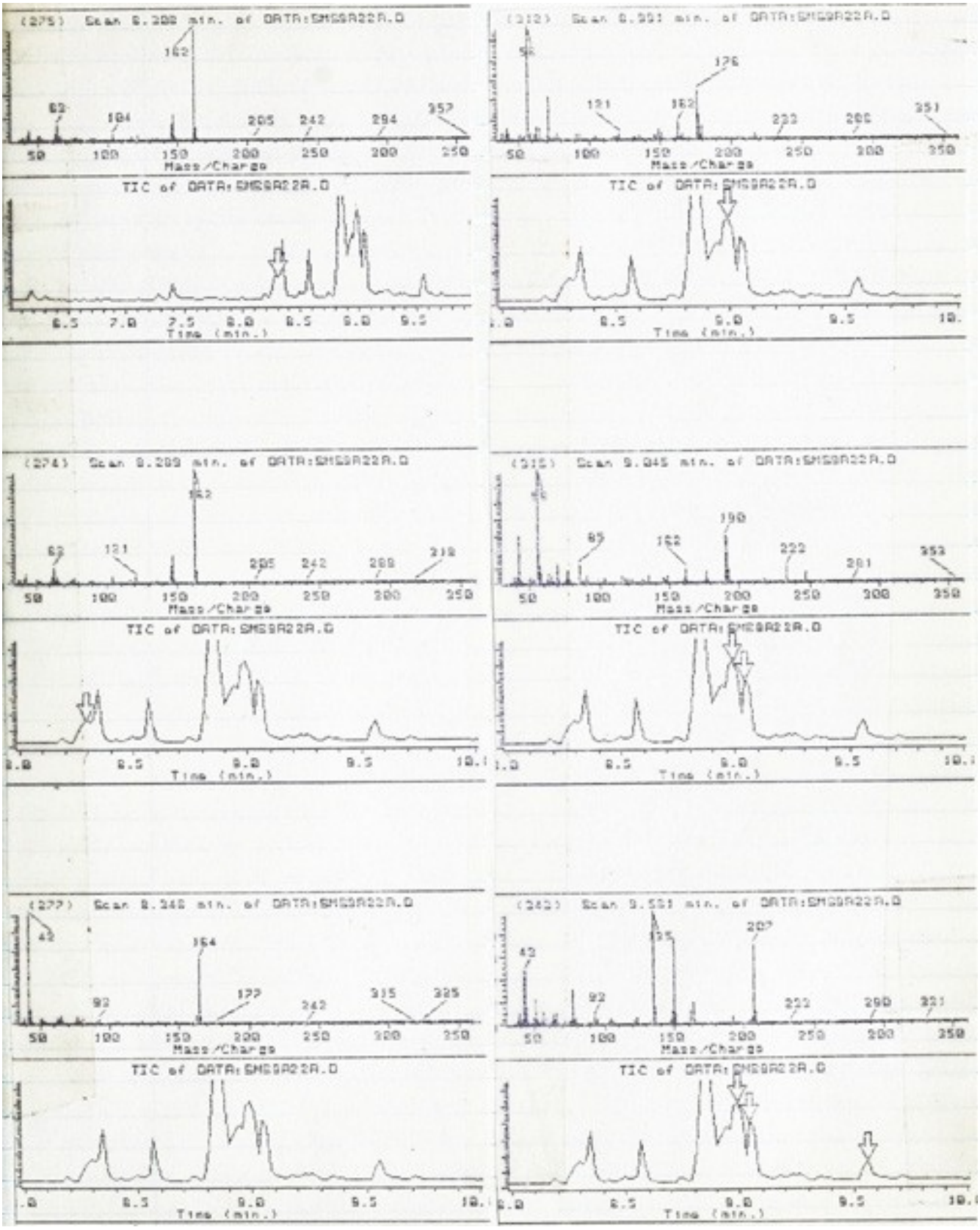
is 149



ion extraction for
256/258

Spectra of MDM-one





[Editor's Note: Pages 302 & 303 are blank]

their #	my #	CODE	1989 sent	red'd	ELEMENT ∨ T	% theo	% found	Empirical formulae
F-6540	6:60	3C-4-4 NS 6:20	5/8	6/20	C	63.86	63.84	$C_{14}H_{17}NO_4$
					H	6.51	6:50	
F-6541	6:61	G-4 NS 6:20	6/8	6/20	C	64.96	65.02	$C_{15}H_{19}NO_4$
					H	6.91	6:90	
F-6542	MB:6:75	2C-T-4(S) NS 6:70	6/8	6/20	C	55.10	55.35	$C_{13}H_{17}NO_4S$
					H	6.05	6:06	
F-6543	MB:6:78	2C-T-4(S) anie 6:70	6/8	6/20	C	66.06	66.03	$C_{19}H_{23}NO_3S$
					H	6.71	6:68	
I-9945	6:89B	HOT-E	12/1	12/26	C	63.97	64.33	$C_{12}H_{19}NO$
					H	8.50	8.73	
					N	6.22	6.22	
I-9946	MBVI-86	ΨT4ether	12/1	12/26	C	46.25	[44.58	44.45]
					H	4.34	[4.20	4.19]
					N	9.52	9.46	
I-9947	MBVI-85	ΨTbzether	12/1	12/26	C	51.53	51.21	
					H	3.92	3.89	
					N	8.59	8.43	
I-9948	MBVI-84	ΨT1ether	12/1	12/26	C	43.58	43.48	
					H	3.66	3.63	
			1990		N	10.17	10.04	
	MBVI100	ΨT1 NS	1/15					See page 6:107
	MBVI96	ΨT1 CHO	1/15					
	6:104	ΨT1CHO MN	1/15					
	6:130 D	ΨT1·HCl	12/8/91		C			$C_{11}H_{18}ClNO_2S$
					H			
	6:129 A	ΨT2·CHO	12/8/91		C			$C_{11}H_{14}O_3S$
					H			
	6:129 B	ΨT29(CN)$_2$	12/8/91		C			$C_{14}H_4N_2O_2S$
			(1991)		H			
P-7375	6:163 A	2CT2(CN)$_2$	2/13	3/1	C	61.29		$C_{14}H_{14}N_2O_2S$
					H	5.14		
P-7376	6:163 B	2C-T-2	2/13	3/1	C	51.88	51.97	$C_{12}H_{20}NOClS$
					H	7.26	7.21	
					N	5.04	5.04	
	6:129C	Ψ-T2NS	12/8/91		C			
					H