

chloride (0.12 mole of hydrogen chloride) and 0.5 ml. of distilled water. The flask was placed under a hydrogen pressure of 60 p.s.i. and shaken for one hour at room temperature. The flask was then heated to 70° and at the end of the second hour an almost quantitative amount of hydrogen had been taken up. Water was added to the cooled reduction mixture, dissolving the precipitate in the reduction vessel. The catalyst was filtered off, and the filtrate of alcohol, water and spermidine trihydrochloride was evaporated to dryness on a steam-bath. The residue was triturated three times with 30-ml. portions of absolute ethanol, then recrystallized from a solution of 2 ml. of concentrated hydro-

chloric acid in 65 ml. of absolute ethanol, yielding 2.1 g. (28.7%) of spermidine trihydrochloride melting at 256–258°.

Anal. Calcd. for $C_7H_{22}N_3Cl_3$: N, 16.5. Found: N, 16.4, 16.3.

The chloroaurate and the picrate derivatives were prepared and found to melt at 219.5–220.5° and 210–212°, respectively. Dudley, Rosenheim and Starling⁷ reported a melting point of 220–222° for spermidine chloroaurate and a melting point of 210–212° for spermidine picrate.

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Reverse Addition of Lithium Aluminum Hydride to Nitroolefins

BY R. T. GILSDORF¹ AND F. F. NORD

The reverse addition of lithium aluminum hydride to 1-phenyl-2-nitropropene-1 was studied in detail in order to correlate this method with those previously recorded in the literature for the reduction of nitroolefins. A variety of products was isolated by varying the reaction temperature and the ratio of reactants. Among them was 1-phenyl-2-nitropropane, arising from the selective reduction of the double bond. By employing acidic hydrolysis of the intermediate organometallic complex, phenylacetone was obtained *via* a modified Nef reaction. Several other α -aryl ketones were similarly prepared. A study on the reverse addition of lithium aluminum hydride to ω -nitrostyrene, led to the development of a novel method of converting benzaldehyde to its next higher homolog.

A. Reduction of 1-Phenyl-2-Nitropropene-1 Introduction

It has been shown^{2,3} that when compounds of the type $ArCH=CRX$, where X is a polar group such as CHO, COOH or NO₂, are treated with lithium aluminum hydride *via* normal addition, the double bond, as well as the functional group, is reduced. However experiments⁴ on the reverse addition of the above reagent to cinnamaldehyde demonstrated that the carbonyl function could be selectively reduced by such a method. In view of the above findings and of the fact that nitroolefins prepared from aromatic aldehydes conform to the type, $ArCH=CRX$, where X is NO₂, the reverse addition of lithium aluminum hydride to nitroolefins was studied, as a continuation of our earlier investigation,³ to correlate this method with those previously reported⁵ for the reduction of nitroolefins. In these latter cases a wide variety of products has been obtained but at no time has any uncondensed⁶ β -aryl nitroalkane been isolated.

The nitroolefin chosen for study was 1-phenyl-2-nitropropene-1.

Experimental

Reduction of 1-Phenyl-2-nitropropene-1 to β -Phenylisopropylamine and N-(β -Phenylisopropyl)-hydroxylamine.—

(1) Condensed from a part of the dissertation submitted to the Graduate Faculty of Fordham University in partial fulfillment for the degree of Doctor of Philosophy.

(2) (a) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1197 (1947); (b) **69**, 2548 (1947); (c) **70**, 3738 (1948).

(3) R. T. Gilsdorf and F. F. Nord, *J. Org. Chem.*, **15**, 807 (1950).

(4) F. A. Hochstein and W. G. Brown, *THIS JOURNAL*, **70**, 3484 (1948).

(5) (a) G. Alles, *ibid.*, **54**, 271 (1942); (b) O. Schales, *Ber.*, **68**, 1579 (1935); (c) J. Kindler, E. Brandt and B. Geglhaar, *Ann.*, **511**, 209 (1934); (d) B. Reichert and W. Koch, *Arch. der Pharm.*, **273**, 265 (1935); (e) L. Beauvauit and A. Wahl; *Compt. rend.*, **134**, 1145 (1902); (f) A. Sonn and A. Schellenberg, *Ber.*, **50**, 1513 (1917); (g) H. Cerf de Mauney, *Bull. soc. chim.*, [5] **7**, 133 (1940); (h) E. P. Kohler and N. L. Drake, *THIS JOURNAL*, **45**, 1281 (1923).

(6) The reduction of ω -nitrostyrene to 2,3-diphenyl-1,4-dinitrobutane has been reported.^{5f}

In a three-necked two-liter flask equipped with a mechanical stirrer, dropping funnel and a condenser through which was suspended a low temperature thermometer (openings protected with calcium chloride tubes), a solution of 12.2 g. (0.075 mole) of 1-phenyl-2-nitropropene-1 in 300 ml. of absolute ether was cooled to below –30° with an acetone-Dry Ice-bath. During rapid stirring, a solution of 4.25 g. (0.112 mole, the calculated amount for the reduction of the nitro group) of lithium aluminum hydride in 100 ml. of absolute ether, was added at such a rate that the temperature of the reaction mixture was maintained between –30 and –40°. Exothermic reaction progressed during the addition and the color of the nitroolefin was discharged. The temperature in the reaction flask was then allowed to fall below –40°, the freezing bath was removed and the temperature allowed to rise to 15°. Hydrolysis was carried out with 400 ml. of 20% aqueous sodium potassium tartrate. The addition of the first few drops of this solution caused slight reaction indicating that the hydride had not been completely utilized. The aqueous layer was extracted with two additional 50-ml. portions of ether and the combined ethereal extracts, after drying over Drierite, yielded, on rectification, 4.4 g. (44%) of β -phenylisopropylamine, b.p. 72–74° (4.0 mm.) and 2.6 g. (23%) of N-(β -phenylisopropyl)-hydroxylamine, b.p. 116–118° (4.0 mm.). The latter substance readily solidified. Recrystallization from light petroleum ether afforded a white crystalline solid, m.p. 63–64°.

Anal. Calcd. for $C_9H_{13}NO$: C, 71.42; H, 8.66. Found: C, 71.69; H, 8.42.

The β -phenylisopropylamine isolated was characterized as its hydrochloride and phenylthioureide: The hygroscopic hydrochloride, prepared by bubbling anhydrous hydrogen chloride through a solution of the amine in absolute ether, after recrystallization from an absolute alcohol-ether combination, had a m.p. of 147–148°. In the literature,⁷ the m.p. is listed as 145–147°.

Anal. Calcd. for $C_9H_{14}ClN$: N, 8.15. Found: N, 8.30. The phenylthioureide, prepared in the usual way,⁸ had a m.p. of 131.5–132.5° after recrystallization from alcohol.

Anal. Calcd. for $C_{14}H_{18}N_2S$: C, 71.07; H, 6.71. Found: C, 71.30; H, 6.38.

The previously unreported N-(β -phenylisopropyl)-hydroxylamine readily reduced Tollens reagent at room temperature. It had the same melting point as, and did not depress the melting point of, N-(β -phenylisopropyl)-hy-

(7) D. H. Dey, *J. Chem. Soc.*, 18 (1930).

(8) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 206.

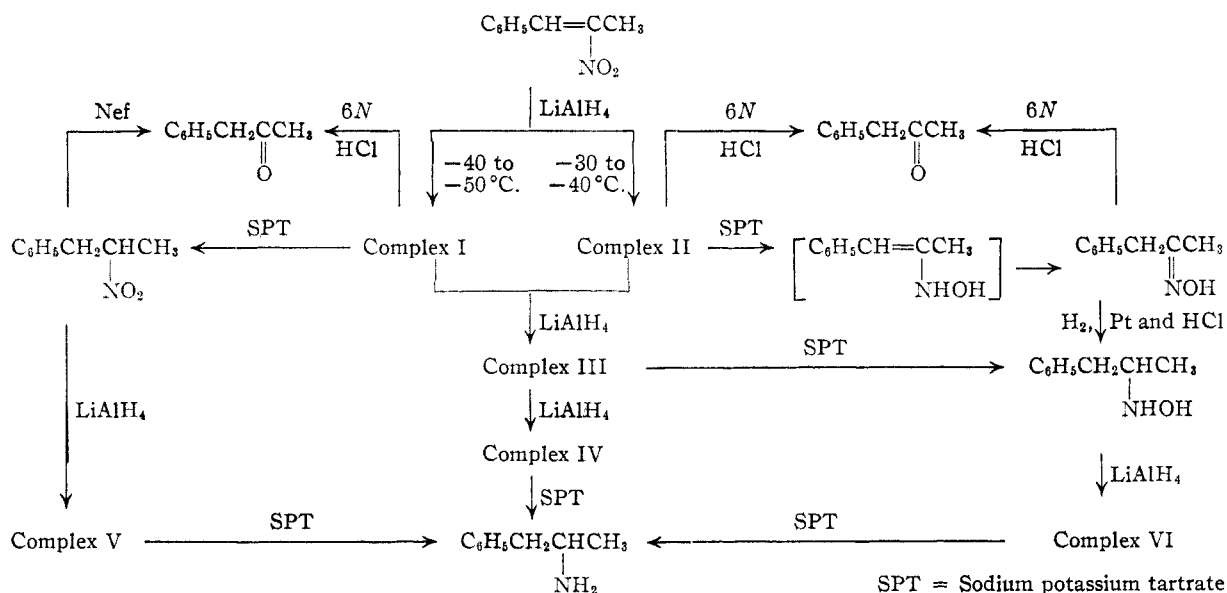


Fig. 1.

droxylamine synthesized according to an earlier method⁹: A mixture of 1.5 g. (0.01 mole) of phenylacetoxime dissolved in 25 ml. of 70% alcohol containing 0.365 g. of hydrogen chloride and 0.1 g. of platinum black was shaken under hydrogen until 0.01 mole was taken up. The catalyst was removed by filtration. The volume of the filtrate was increased to 75 ml. with water and extracted with ether. The aqueous portion was then neutralized with aqueous sodium bicarbonate and the precipitate was collected. On recrystallization from light petroleum ether, there was obtained 0.64 g. (42%) of *N*-(β -phenylisopropyl)-hydroxylamine, m.p. 63–64°, which was not depressed when mixed with the sample obtained from the reverse addition of lithium aluminum hydride to 1-phenyl-2-nitropropene-1.

***N*-(β -Phenylisopropyl)-hydroxylamine Oxalate.**—When 0.18 g. (0.02 mole) of oxalic acid dissolved in 10 ml. of absolute ether, was added, with stirring, to a solution of 0.6 g. (0.04 mole) of *N*-(β -phenylisopropyl)-hydroxylamine in 10 ml. of absolute ether, there was obtained a white precipitate of the neutral oxalate which, on recrystallization from an absolute methanol-ether mixture, melted at 175–176°.

Anal. Calcd. for $C_{20}H_{28}N_2O_6$: C, 61.21; H, 7.19. Found: C, 61.30; H, 6.99.

***N*-(β -Phenylisopropyl)-*p*-nitrophenylnitron.**—The procedure employed here was essentially reported previously.¹⁰ There were mixed together 0.3 g. (0.02 mole) of *N*-(β -phenylisopropyl)-hydroxylamine dissolved in 6 ml. of absolute alcohol and 0.3 g. (0.02 mole) *p*-nitrobenzaldehyde in 10 ml. of absolute alcohol. After standing 24 hours, the alcohol was removed under reduced pressure and the residue was recrystallized from absolute ether (freezer). There was thus obtained a light yellow crystalline product, m.p. 119–120°.

Anal. Calcd. for $C_{18}H_{18}N_2O_5$: C, 67.59; H, 5.67. Found: C, 67.45; H, 5.50.

β -Phenylisopropylamine.—A solution of 6.0 g. (0.04 mole) of *N*-(β -phenylisopropyl)-hydroxylamine in 80 ml. of absolute ether was treated with 1.9 g. (0.05 mole) of lithium aluminum hydride dissolved in 150 ml. of absolute ether in the usual manner and refluxed for an additional hour. After cooling, a sample of the reaction mixture gave a positive Gilman-Schulz color test²⁰ indicating an excess of the hydride. Hydrolysis was carried out with 400 ml. of 20% aqueous sodium potassium tartrate and after separation of the layers, the aqueous portion was extracted with two additional 75-ml. volumes of ether. Rectification afforded 2.0 g. (37%) of β -phenylisopropylamine, b.p. 72–74° (4.0 mm.), identified by its phenylthioureide.

***N*-(β -Phenylisopropyl)-hydroxylamine and Phenylacetoxime.**—When 2.13 g. (0.056 mole, half the amount necessary

for the reduction of the nitro group) dissolved in 100 ml. of absolute ether, was added to 12.2 g. (0.075 mole) of 1-phenyl-2-nitropropene-1 in 300 ml. of absolute ether at –30 to –40°, as before, and after hydrolysis with 20% aqueous sodium potassium tartrate, there were obtained 1.1 g. (8%) of β -phenylisopropylamine, b.p. 72–74° (4.0 mm.), and 5.6 g. of a fraction,¹¹ b.p. 116–118° (4.0 mm.), which failed to reach rigid solidity after 2 days in a vacuum desiccator over sulfuric acid. A portion of this material was treated with warm petroleum ether (b.p. 30–60°). After decantation the petroleum ether, on cooling, yielded crystalline *N*-(β -phenylisopropyl)-hydroxylamine.

Another aliquot of the higher boiling fraction was dissolved in ether and shaken with an excess of cold 1 *N* hydrochloric acid to remove the hydroxylamine derivative. The ether layer was then washed well with water and dried over Drierite. Removal of the ether on the steam-bath afforded an oil which on chilling and scraping, solidified. Recrystallization from petroleum ether (b.p. 60–75°) yielded phenylacetoxime of m.p. 68.5–70°. In the literature¹² the m.p. is recorded as 68–70°.

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43. Found: C, 72.40; H, 7.24.

A third aliquot of the higher boiling fraction was weighed (2.0 g.) and dissolved in 100 ml. of 6 *N* hydrochloric acid. Steam was passed through the solution until phenylacetone (identified as its semicarbazone) ceased to be distilled. The clear acidic hydrolytic solution was made basic with 4 *N* sodium hydroxide, affording 1.36 g. of *N*-(β -phenylisopropyl)-hydroxylamine. Assuming that the ketone was quantitatively hydrolyzed and that there was no loss of the hydroxylamine in handling, this experiment allows the estimation of the ketoxime content of the mixture as being 32%. This corresponds to over-all yields of 8% β -phenylisopropylamine, 16% phenylacetoxime and 34% *N*-(β -phenylisopropyl)-hydroxylamine.

Action of 2,4-Dinitrophenylhydrazine Sulfate on Phenylacetoxime.—When phenylacetoxime was treated with 2,4-dinitrophenylhydrazine sulfate in the usual manner,¹³ precipitation occurred immediately. Recrystallization from

(11) (a) This fraction was incorrectly described as benzyl methyl ketimine in our preliminary communication, *THIS JOURNAL*, **72**, 4327 (1950). The hydrated trimer of the imine mentioned, actually was the hydroxylamine derivative; (b) similarly, a mixture of phenylacetaldoxime and *N*-(β -phenylethyl)-hydroxylamine was mistaken for phenylacetalimine and the compound erroneously described as the hydrated trimer of the aldimine, was actually the hydroxylamine derivative.

(12) P. W. Neber and A. von Friedolsheim, *Ann.*, **449**, 109 (1926).

(13) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(9) G. Vavon and Crajinovic, *Bull. soc. chim.*, [4] **43**, 231 (1928).

(10) G. W. Watt and C. M. Knowles, *J. Org. Chem.*, **8**, 540 (1943).

an ethyl acetate-alcohol mixture afforded orange crystals of m.p. 152.5–153.5° which was not depressed when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of phenylacetone. This m.p. was originally reported as 155.5–156.5°.¹⁴

Anal. Calcd. for C₁₅H₁₄N₄O₄: N, 17.83. Found: N, 17.70.

Phenylacetone (via Phenylacetoxime).—A solution of 2.13 g. (0.056 mole, half the amount necessary for the reduction of the nitro group) of lithium aluminum hydride in 100 ml. of absolute ether, was added to 12.2 g. (0.075 mole) of 1-phenyl-2-nitropropene-1 in 300 ml. of absolute ether, at –30 to –40°, as above. After the temperature of the reaction mixture had been allowed to rise to 15°, 300 ml. of 6 *N* hydrochloric acid was introduced to hydrolyze the intermediate organometallic complex. The layers were separated and the ethereal layer was successively washed with two 100-ml. volumes of 6 *N* hydrochloric acid. The combined aqueous acidic portions were steam distilled. The distillate was extracted with the original ether layer and two additional 50-ml. portions of ether. Rectification afforded 2.9 g. (29%) of phenylacetone, b.p. 73–74° (4.0 mm.).

The 2,4-dinitrophenylhydrazone was prepared and recrystallized as previously indicated. Its m.p. was 152.5–153.5°.

The semicarbazone was prepared according to the usual procedure.¹⁵ Recrystallization from 75% alcohol afforded a white crystalline product of m.p. 186–187°. This m.p. was previously reported¹⁵ as 187°.

Anal. Calcd. for C₁₀H₁₃N₃O: C, 62.80; H, 6.85. Found: C, 63.25; H, 6.61.

1-Phenyl-2-nitropropane. A.—Lithium aluminum hydride (0.855 g., 0.0225 mole, a 20% excess of the amount required for the reduction of the double bond) in 100 ml. of absolute ether, was added to 12.2 g. (0.075 mole) of 1-phenyl-2-nitropropene-1 in 300 ml. of absolute ether at –40 to –50° as described above. The organometallic complex was hydrolyzed with 20% aqueous sodium potassium tartrate. On rectification, there was obtained 4.7 g. (38%) of 1-phenyl-2-nitropropane, b.p. 103–104° (4.0 mm.).

Anal. Calcd. for C₉H₁₁O₂: C, 65.43; H, 6.71. Found: C, 65.99; H, 6.69.

B.—When the above experiment was repeated using as the hydrolytic agent the calculated amount of 1 *N* hydrochloric acid which was introduced dropwise over the course of three quarters of an hour, 1.5 g. (15%) of phenylacetone and 6.9 g. (56%) of 1-phenyl-2-nitropropane were obtained.

1-Phenyl-2-nitropropane gave a definite blue-green coloration characteristic of the pseudo-nitroles produced by secondary nitro compounds when treated according to the conditions of the nitrous acid test.¹⁷ The coloration was chloroform extractable. A similar test performed omitting the sodium nitrite, gave only a very faint green color.

β -Phenylisopropylamine.—By the normal addition, 1.65 g. (0.01 mole) of 1-phenyl-2-nitropropane in 50 ml. of absolute ether, was treated with 0.68 g. (0.018 mole, a 20% excess) of lithium aluminum hydride in 70 ml. of absolute ether. Hydrolysis was brought about by means of 150 ml. of 20% aqueous sodium potassium tartrate. Upon distillation of the ethereal layer, there was obtained a small amount of oil which gave a phenylthioureide of m.p. 131.5–132.5° which was not depressed when mixed with an analyzed sample of the phenylthioureide of β -phenylisopropylamine.

Nef Reaction¹⁸ on 1-Phenyl-2-nitropropane.—One-half of a gram of 1-phenyl-2-nitropropane was dissolved in 10 ml. of aqueous solution containing 0.5 g. of sodium hydroxide. This solution was added dropwise to a solution of 2.5 ml. of concd. sulfuric acid and 16 ml. of water during rapid stirring and cooling with an ice-bath. An oil separated with the characteristic odor of phenylacetone. It was extracted with ether and after the removal of the ether, was treated with semicarbazide hydrochloride and sodium acetate in

the usual manner for the preparation of a semicarbazone.¹⁵ In this way, there was obtained a white crystalline product which, after recrystallization from 80% alcohol, had the same m.p. as, and did not depress the m.p. of, an authentic sample of the semicarbazone of phenylacetone (186–187°).

Absorption Data.—The infrared curves (Figs. 2, 3, 4) were obtained on a Perkin-Elmer 21-Double beam spectrophotometer using Nujol mulls of the samples.

Discussion

The experiments carried out on 1-phenyl-2-nitropropene-1 and its reductive derivatives are outlined in Fig. 1. These reactions demonstrated that the reduction was stepwise and capable of regulation so as to afford the amine, hydroxylamine derivative, oxime or nitroparaffin in various mixtures. While the formation of Complex I was undoubtedly the favored reaction at –40 to –50° since the nitroparaffin, 1-phenyl-2-nitropropane, was obtained in 56% yields, and while some of Complex II must have been formed at –30 to –40° to account for the phenylacetoxime isolated, neither reaction has been proven as being mutually exclusive of each other at the temperatures involved.

The preparation of its hydrochloride and phenylthioureide served to characterize the β -phenylisopropylamine formed. The identity of the *N*-(β -phenylisopropyl)-hydroxylamine was proven by its ready reduction of Tollens reagent, the preparation of its oxalate, the nitron formation and by the fact that it did not depress the melting point of an authentic sample prepared according to the method of Vavon and Crajinovic.⁹ The phenylacetoxime was characterized by virtue of its melting point, hydrolysis to phenylacetone and conversion to the 2,4-dinitrophenylhydrazone. The blue-green coloration, manifested by pseudonitroles which are formed by secondary nitro compounds under the conditions of the V. Meyer nitrous acid test,¹⁷ its reduction to β -phenylisopropylamine with lithium aluminum hydride and conversion to phenylacetone when treated according to the conditions of the Nef reaction, established the structure of 1-phenyl-2-nitropropane.

The reduction of *N*-(β -phenylisopropyl)-hydroxylamine to β -phenylisopropylamine with lithium aluminum hydride is novel since we have been able to find no report in the literature on the reduction of a hydroxylamine derivative with this reagent.

It is noteworthy that the phenylacetoxime and *N*-(β -phenylisopropyl)-hydroxylamine distilled together in the fraction obtained at 116–118° (4.0 mm.). The fact that the distillate failed to crystallize readily, led to the assumption that it might be a mixture. This contention was verified by the chemical separation of the components and supported by the infrared absorption data. Curve H was obtained for *N*-(β -phenylisopropyl)-hydroxylamine. It is noticed that there is a strong absorption band at 1108 cm.⁻¹ which is absent in curve O. Curve O, that of phenylacetoxime, demonstrates absorption at 1666 cm.⁻¹ assignable to the C=N bond of the oxime group. Curve D, that of the reaction distillate, shows absorption at both the above frequencies and, in general, has all the peaks present in curves H and O.

The major portion of the phenylacetone formed

(14) W. D. McPhee and E. Klingsberg, *THIS JOURNAL*, **66**, 1132 (1944).

(15) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 170.

(16) P. A. Levene and A. Walti, *J. Biol. Chem.*, **90**, 81 (1931).

(17) V. Meyer, *Ann.*, **175**, 120 (1875).

(18) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 399 (1943).

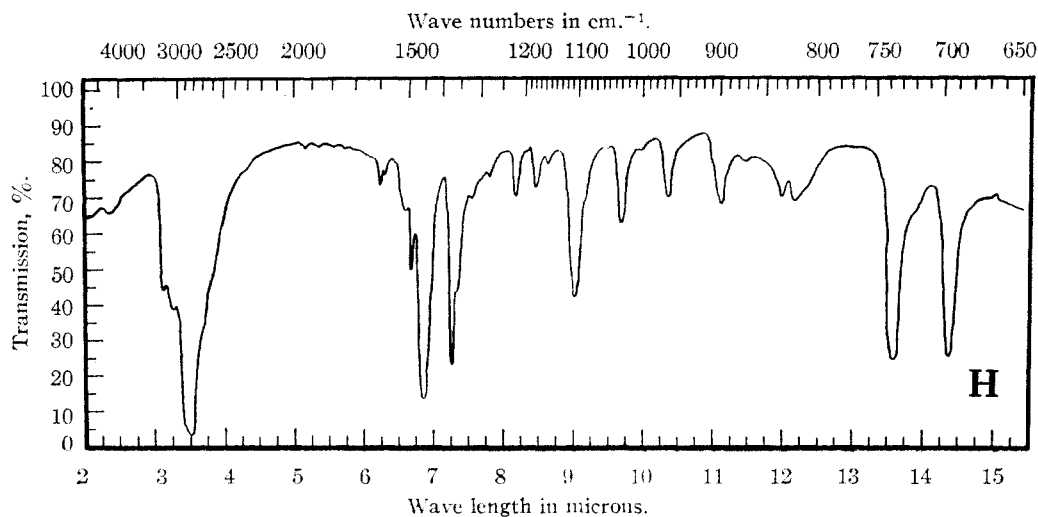


Fig. 2.

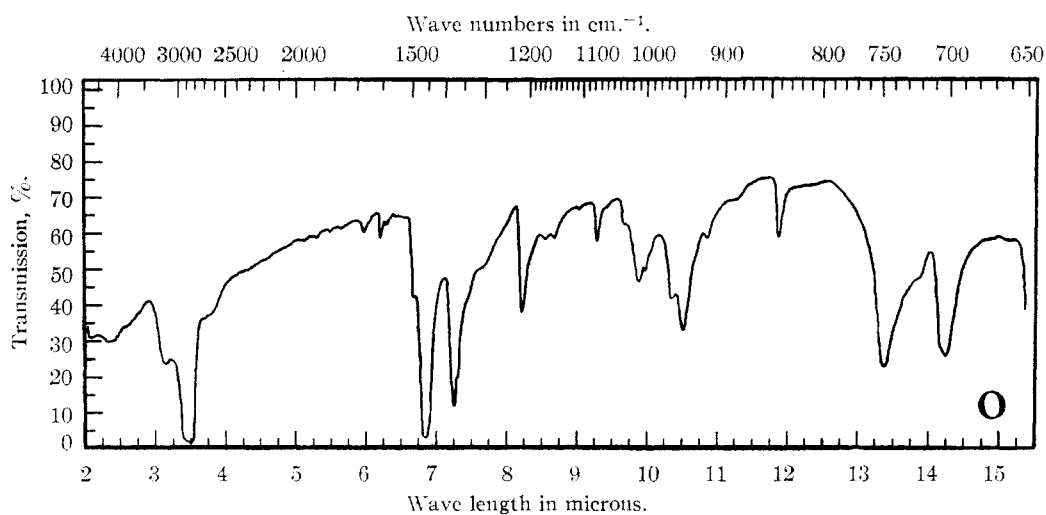


Fig. 3.

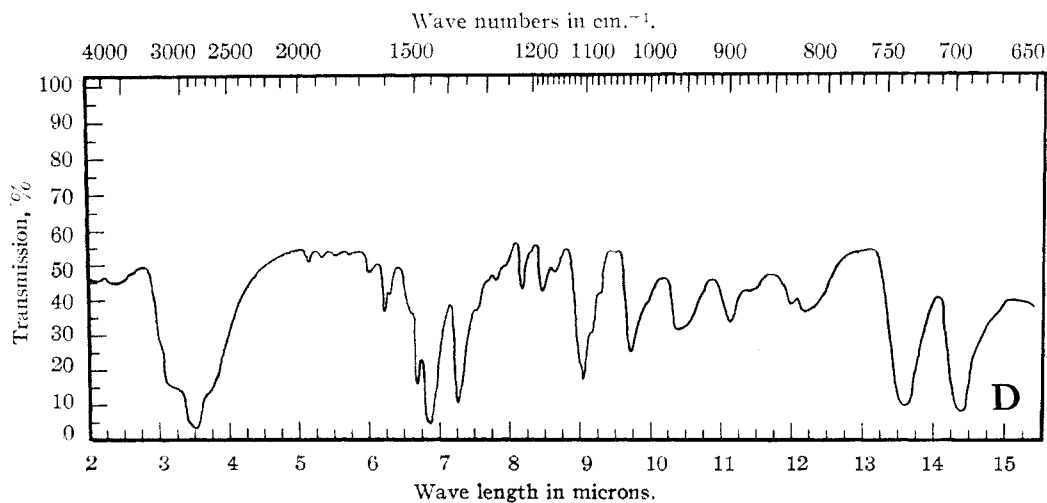


Fig. 4.

when one half the amount of lithium aluminum hydride was added at -30 to -40° , probably arose from the acidic hydrolysis of the oxime which, it-

self, was isolated by applying hydrolysis with 20% aqueous sodium potassium tartrate.

The conversion of the nitroolefin to the corre-

TABLE I

Starting material	1-Phenyl-2-nitrobutene-1	1-Phenyl-2-nitropentene-1	1- <i>o</i> -Chlorophenyl-2-nitropropene-1	1-(2-Thienyl)-2-nitropropene-1			
Products	Ketone	1-Phenyl-2-butanone	1-Phenyl-2-pentanone	<i>o</i> -Chlorophenylacetone	2-Thienylacetone		
	B.p. ^a { °C. Mm.	83-85 5.0	96-97 5.0	103-104 6.0	75-77 5.5		
	Yield, %	62	52	62	43		
	Hydroxylamine	N-(1-Phenyl-2-butyl)-	N-1-(Phenyl-2-amy)-	N-(β- <i>o</i> -Chlorophenylisopropyl)-	*		
Derivatives of Ketone	M.p., °C.	77-78	58.5-60	88-89			
	Carbon {	Calcd.	72.69	73.70	58.22		
		Found	72.90	73.37	58.35		
	Hydrogen {	Calcd.	9.15	9.56	6.52		
		Found	8.67	9.06	6.25		
	Semicarbazones	M.p., °C.	148-149 ^b	97-98 ^d	174-176	179-180 ^f	
		Carbon {	Calcd.	64.37	66.18	53.22	48.71
			Found	64.15	66.20	53.46	48.53
		Hydrogen {	Calcd.	7.37	7.82	5.04	5.72
	Found		7.10	7.66	4.92	5.56	
2,4-Dinitrophenylhydrazones	M.p., °C.	140-141 ^c	129.5-130.5	92-93	116-117		
	Nitrogen {	Calcd.	17.04	16.34	16.06	17.49	
		Found	17.05	16.40	16.20	17.48	

^a All m.p.s. and b.p.s. are uncorrected. ^b M. Montagne and M. Roch, *Compt. rend.*, **218**, 679 (1944), list the m.p. as 148-150°. ^c T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 2607 (1932), report the same m.p. ^d D. Ivanov, *Bull. soc. chim.*, [5] **4**, 682 (1937), records the m.p. as 82°. ^e Decomposition occurred during the steam distillation and no hydroxylamine derivative was isolated. ^f P. Cagniant, *Bull. soc. chim.*, [5] **16**, 847 (1949), lists the m.p. as 194-195°.

sponding nitroparaffin, 1-phenyl-2-nitropropane, is novel since no similar reduction, *i.e.*, the selective reduction of the double bond, has been reported in the aryl series without condensation.⁶

The fact that either 1-phenyl-2-nitropropane or phenylacetone can be isolated from the same reaction mixture depending on the type of hydrolysis, indicates that the mechanism of the ketone formation when the lower concentration of hydride was used, is a modified Nef reaction. The transitory blue color which is characteristic of the Nef reaction, and which was observed during the hydrolysis, supports this contention.

In view of the findings by Hochstein and Brown⁴ on the reduction of cinnamyl alcohol to hydrocinnamyl alcohol, it is possible that the reduction of 1-phenyl-2-nitropropene-1 to 1-phenyl-2-nitropropane involves only the double bond¹⁹ and is effected by 0.25 mole of lithium aluminum hydride per mole of nitroolefin.

B. Synthesis of Other α-Aryl Ketones

Experimental

Preparation of Other α-Aryl Ketones and N-(β-Aralkyl)-hydroxylamines.—By treating the corresponding nitroolefins with a 20% excess of the amount of lithium aluminum hydride necessary for the reduction of the double bond *via* reverse addition at -40 to -50°, followed by hydrolysis by means of the rapid introduction of 400 ml. of 6 *N* hydrochloric acid, and steam distillation of the aqueous phase, the ketones, listed in Table I, were prepared. The corresponding N-(β-aralkyl)-hydroxylamines were isolated in low yields by making the aqueous acidic solution through

(19) It is also quite possible that the reduction may occur *via* a 1,4-addition especially in view of the polarity of the nitro group and of the fact that the reduction takes place at -40 to -50°. It was reported⁴ that the reduction of the double bond of cinnamyl alcohol proceeds slowly at room temperature after the rapid interaction of the polar alcoholic group with the hydride.

which the steam had been passed, alkaline and extracting with ether.

1-*o*-Chlorophenyl-2-nitropropene-1. A. **Modified Knoevenagel-Walter Synthesis.**²⁰—There were refluxed together for 8 hours, 28.1 g. (0.2 mole) of *o*-chlorobenzaldehyde, 15.0 g. (0.2 mole) of nitroethane, 1.74 g. (0.02 mole) of *n*-amylamine and 30 ml. of absolute alcohol. On cooling, the mixture was stored in the refrigerator until the precipitation was complete. The mixture was filtered and the precipitate washed with a few ml. of absolute alcohol. There were thus obtained 20.0 g. of 1-*o*-chlorophenyl-2-nitropropene-1. An additional amount of 2.0 g. was obtained by concentration of the filtrate and washings, bringing the total yield to 56%.

B. **Knoevenagel-Walter Synthesis.**²¹—When the same quantities of the above reagents were mixed and allowed to stand at room temperature for 2 weeks, and the product was isolated in the same manner, there was obtained a total yield of 24.1 g. (61%) of 1-*o*-chlorophenyl-2-nitropropene-1. Recrystallization from absolute ethanol produced bright yellow crystals, m.p. 40°.

Anal. Calcd. for C₉H₈ClNO: C, 55.00; H, 4.08. Found: C, 54.98; H, 3.88.

2-Thienylacetoxime.—When 2-thienylacetone was treated in the usual manner²² for the preparation of an oxime there was obtained, on recrystallization from petroleum ether (b.p. 60-75°), a white crystalline product, m.p. 91-92°, which was not depressed when mixed with a sample prepared according to the method of Bouveault and Wahl²⁰ by the action of aluminum amalgam on 1-(2-thienyl)-2-nitropropene-1.

Discussion

The preparation of the ketones listed in Table I demonstrated the general applicability of this method of synthesizing carbonyl compounds from β-arylnitroolefins. In general, the yields were good, the lowest (43%) being obtained from the

(20) H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

(21) E. Knoevenagel and L. Walter, *Ber.*, **37**, 4502 (1904).

(22) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 202.

relatively unstable 1-(2-thienyl)-2-nitropropene-1. The ketones are assumed to arise *via* the same mechanism as did phenylacetone in the previous experiment, *i.e.*, by a modified Nef reaction after the selective reduction of the double bond of the nitroalkene.

The substituted hydroxylamines listed in Table I all readily reduced Tollens reagent at room temperature.

The experiments on the synthesis of the previously unreported 1-*o*-chlorophenyl-2-nitropropene-1 showed a slightly higher yield for the Knoevenagel-Walter synthesis (61% *vs.* 56%) as compared to the much shorter reaction time of the modified Knoevenagel-Walter synthesis (8 hours *vs.* 14 days).

The authenticity of the oxime prepared from 2-thienylacetone was proven by means of the mixed melting point determination with the sample obtained by the reduction of 1-(2-thienyl) 2-nitropropene-1 with aluminum amalgam.

C. Reduction of ω -Nitrostyrene

Experimental

Reduction of ω -Nitrostyrene to β -Phenylethylamine, N-(β -Phenylethyl)-hydroxylamine and Phenylacetaldoxime.—When 2.13 g. (0.056 mole, half the amount necessary for the reduction of the nitro group) of lithium aluminum hydride dissolved in 100 ml. of absolute ether, was added to 11.2 g. (0.075 mole) of ω -nitrostyrene at -30 to -40° as before and after hydrolysis with 20% aqueous sodium potassium tartrate, a mixture of products was obtained. Upon distillation, there was isolated 0.5 g. (6%) of β -phenylethylamine, b.p. $72-77^\circ$ (6.0 mm.). The residue^{11b} in the distilling flask was dissolved in ether and extracted with an excess of 1 *N* hydrochloric acid. After removal of the ether by distillation there was obtained 1.6 g. (16%) of phenylacetaldoxime which melted at $97-98^\circ$ after recrystallization from petroleum ether (b.p. $60-75^\circ$). The recorded²³ m.p. is $97-99^\circ$.

Anal. Calcd. for C_8H_9NO : C, 71.09; H, 6.71. Found: C, 71.03; H, 6.45.

Neutralization of the acidic washings with dilute aqueous sodium carbonate afforded 3.4 g. (33%) of N-(β -phenylethyl)-hydroxylamine. After recrystallization from light petroleum ether, it melted at $83-84^\circ$.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08. Found: C, 70.12; H, 7.93.

Phenylthioureide of β -Phenylethylamine.—This white crystalline substance was synthesized according to the previously utilized procedure.⁴ Its m.p. was $110-110.5^\circ$. The m.p. was previously reported²⁴ as 111° .

Anal. Calcd. for $C_{13}H_{16}N_2S$: C, 70.27; H, 6.29. Found: C, 70.38; H, 6.10.

β -Phenylethylamine Hydrochloride.—This compound was prepared by the previously described procedure. It was recrystallized from an absolute alcohol-ether combination. Its m.p. was $215-217^\circ$. Literature²⁵ records the m.p. as 217° .

Action of 2,4-Dinitrophenylhydrazine Sulfate on Phenylacetaldoxime.—When 0.5 g. of phenylacetaldoxime was treated according to the previously utilized procedure for the preparation of a 2,4-dinitrophenylhydrazone, there was obtained an orange crystalline solid, m.p. $121-121.5^\circ$, which did not depress the m.p. of an authentic sample of the 2,4-dinitrophenylhydrazone of phenylacetaldehyde.

N-(β -Phenylethyl)-*p*-nitrophenyltrone.—When 2.7 g. (0.02 mole) of N-(β -phenylethyl)-hydroxylamine dissolved in 6 ml. of absolute alcohol, and 0.3 g. (0.02 mole) of *p*-nitrobenzaldehyde dissolved in 10 ml. of absolute alcohol, had been mixed together, the solution started to deposit yellow crystals after 2 hours standing at room temperature.

After 24 hours the precipitate was filtered and recrystallized from absolute alcohol. In this way there was obtained a yellow crystalline solid, m.p. $157-158^\circ$.

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22. Found: C, 66.75; H, 5.29.

N-(β -Phenylethyl)-hydroxylamine Oxalate.—The neutral oxalate was prepared as previously described and recrystallized from a methanol-ether combination. Its m.p. was $165.5-167^\circ$ with decomposition.

Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 59.30; H, 6.59. Found: C, 59.85; H, 6.49.

Phenylacetaldehyde.—When 0.855 g. (0.0225 mole, a 20% excess for the reduction of the double bond) of lithium aluminum hydride was treated with 11.2 g. (0.075 mole) of ω -nitrostyrene *via* reverse addition at -40 to -50° and hydrolysis was brought about by 400 ml. of 6 *N* hydrochloric acid introduced rapidly, there was obtained after steam distillation of the acidic hydrolytic mixture and rectification, 0 to 0.46 g. (0-5%) of phenylacetaldehyde, b.p. $61-65^\circ$ (5.0 mm.).

When hydrolysis of the intermediate organometallic complex was effected with the calculated amount of 1 *N* hydrochloric acid, added slowly, the ether layer afforded a crude yellow oil which, when treated according to the nitrous acid test, gave an orange-red coloration comparable in shade and intensity to that given by 1-nitrobutane when similarly treated.

The crude oil was then triturated with a solution of 4.0 g. of sodium hydroxide in 75 ml. of water to yield a dispersion which, when added to an ice cold solution of 12.5 ml. of sulfuric acid in 80 ml. of water during rapid stirring (Nef reaction), allowed the separation of 0.92 g. (10%) of phenylacetaldehyde, b.p. $63-64^\circ$ (5.0 mm.).

The methone derivative of phenylacetaldehyde was prepared by the usual method.²⁶ Its m.p. was $164-165^\circ$, the same as reported previously.²⁷

The 2,4-dinitrophenylhydrazone of phenylacetaldehyde was prepared as before. Its m.p. was $121-121.5^\circ$ which was not depressed when mixed with an authentic sample.

Discussion

In general, the experiments on the reduction of ω -nitrostyrene *via* the reverse addition of lithium aluminum hydride indicated that it behaved similarly to 1-phenyl-2-nitropropene-1. In most cases, the same derivatives were prepared to characterize the various products.

However, a dissimilarity showed itself in the synthesis of the carbonyl derivative insofar as the yield of phenylacetaldehyde was very low. It is believed that here the mechanism of the reduction is still comparable while the ease of hydrolysis differs. The facts that a positive nitrous acid test was obtained for a primary nitro compound and that the yield of phenylacetaldehyde was improved when the conditions of the Nef reaction were more strictly imposed, support this contention.

The preparation of phenylacetaldehyde marks the first reliable synthesis of the next higher homolog of benzaldehyde *via* ω -nitrostyrene, since the reported reduction of ω -nitrostyrene to the aldoxime followed by hydrolysis to the aldehyde,²⁸ has been described as being incapable of repetition.²⁹

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(26) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(27) K. H. Lin and R. Robinson, *J. Chem. Soc.*, 2005 (1938).

(28) L. Bouveault and A. Wahl, *Bull. soc. chim.*, [3] **29**, 518 (1903).

(29) H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 399 (1943).

(23) W. Dollfus, *Ber.*, **25**, 1917 (1892).

(24) J. von Braun and H. Deutsch, *ibid.*, **45**, 2188 (1912).

(25) K. Kindler, German Patent 562,714 (1931).

interpretation. The analyses were performed by A. A. Sirotenko of this Department. The platinum black catalyst was placed at our disposal by

Baker and Co., Inc., Newark 5, N. J., and the nitroparaffins by Commercial Solvents Corp. NEW YORK 58, N. Y. RECEIVED OCTOBER 17, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW HAMPSHIRE]

The System Ammonium Fluoride-Sodium Fluoride-Water at 25°¹

BY HELMUT M. HAENDLER AND AVIS CLOW

The system ammonium fluoride-sodium fluoride-water has been studied at 25°. The system is simple; the solid phases are ammonium fluoride and sodium fluoride. No hydrate of sodium fluoride was found.

In a previous article² a study of the system ammonium fluoride-potassium fluoride-water was reported. Similar measurements have been made on the corresponding system involving sodium fluoride in place of potassium fluoride. The system is a simple one; no double salts are formed, the solid phases being only ammonium fluoride and sodium fluoride. No evidence was found for the existence of hydrated sodium fluoride in the equilibrium mixture.³

TABLE I

ANALYSES OF SOLUTIONS AND WET RESIDUES

Solutions, weight %			Wet residues, weight %		
NH ₄ F	NaF	H ₂ O	NH ₄ F	NaF	H ₂ O
0.90	4.43	94.67	0.60	45.66	53.74
2.45	4.01	93.54	1.33	40.16	58.51
4.80	2.99	92.21	3.22	43.61	53.17
5.02	3.24	91.74	3.22	43.61	53.17
6.90	3.25	89.85	4.75	37.98	57.27
7.26	2.60	90.14	4.97	37.98	57.05
10.18	2.33	87.49	5.55	46.32	48.13
12.08	2.24	85.68	7.49	42.91	49.60
15.10	3.07	81.83	8.06	44.07	47.87
19.26	2.39	78.35
20.31	2.57	77.12	12.12	38.29	49.59
24.45	2.48	73.07
29.45	3.25	67.30	... ^a
33.26	3.15	63.59	12.76 ^a	61.99	25.25
34.37	3.49	62.14	20.28	41.05	38.67
35.97	4.22	59.81	21.76	43.61	34.63
41.57	2.88	55.55	14.87	62.83	22.30
44.32	0.08	55.60	... ^b
44.49	.16	55.35	88.40	0.00	11.60
44.85	.23	54.92	... ^b
45.50	.00	54.50

^a X-Ray analysis showed NaF as solid phase. ^b X-Ray analysis showed NH₄F as solid phase.

(1) This work is part of a program of research on inorganic fluorides supported by the Research Corporation and the Atomic Energy Commission.

(2) H. M. Haendler and A. W. Jache, *THIS JOURNAL*, **72**, 4137 (1950).

(3) Compare N. V. Sidgwick, "The Chemical Elements and their Compounds," Vol. I, The Clarendon Press, Oxford, 1950, p. 94, and H. J. Emeléus in J. H. Simons, ed., "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 27.

Experimental

As in the previous work, the Schreinemakers wet residue method was used. The apparatus was the same, with polyethylene cups fitted with motor-driven lucite stirrers. All chemicals were C.P. grade.

The solutions and wet residues were analyzed for ammonium ion and sodium ion. Ammonia was determined by distillation from alkaline solution into boric acid and titration with standard acid. Sodium was weighed as sulfate after ignition with sulfuric acid and heating with ammonium carbonate. The low concentration of sodium fluoride in the equilibrium mixture made satisfactory analysis more difficult than with the potassium fluoride system. The solutions were slow in attaining equilibrium.

In several cases the identity of the solid phase was checked by X-ray diffraction, using copper radiation with a nickel filter and a Philips 114.59 mm. powder camera.

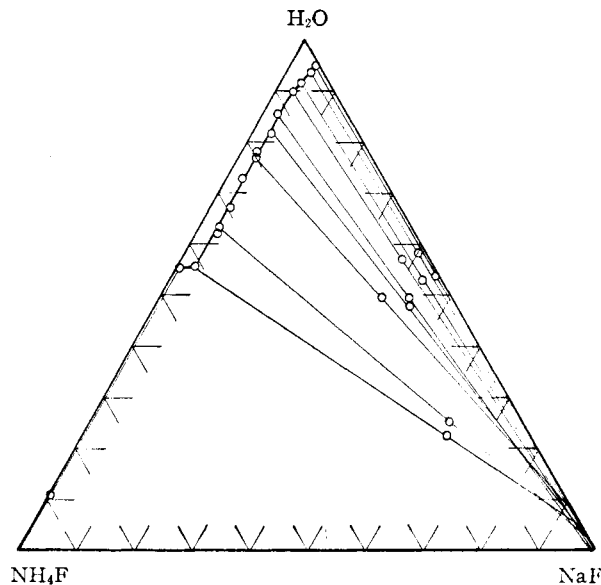


Fig. 1.—The system ammonium fluoride-sodium fluoride-water at 25°.

Results

The results of the analyses of the solutions and wet residues are given in Table I and representative points have been plotted in Fig. 1.

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