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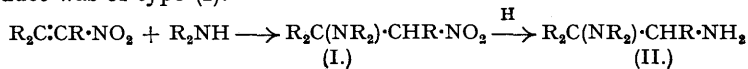
286. *Aliphatic Nitro-compounds. Part VII. Preparation of
2-Nitroalkylamines.*

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Ammonia and primary or secondary amines interact with α -nitro-olefins, giving 2-nitroalkylamines. Those formed from ammonia or aliphatic amines are in general extremely unstable, but can be reduced by nickel and hydrogen to derivatives of ethylenediamine. *N*-2-Nitroalkylarylamines formed from aromatic amines are somewhat more stable, but are best isolated and characterised through their salts. In many cases 2-nitroethyl nitrate can be

used as a convenient laboratory substitute for nitroethylene, and 2-nitroisopropyl acetate or 2-nitroisopropyl nitrate can replace 1-nitroprop-1-ene.

THE addition of ammonia and amines to α -nitro-olefins has hitherto received only scant attention in the literature. The reaction of nitroethylene with aniline (Wieland and Sakellarios, *Ber.*, 1919, **52**, 898) and nuclear substituted anilines (Kodak Ltd., B.P. 539,070; 21.2.40) is known to give *N*-2-nitroethylanilines, but in most cases the products were not characterised and experimental details are lacking. β -Nitrostyrene reacts with hydroxylamine to give $\text{Ph}\cdot\text{CH}(\text{NH}\cdot\text{OH})\cdot\text{CH}_2\cdot\text{NO}_2$ (Posner, *Annalen*, 1912, **389**, 114), but the reaction with other bases is erratic. Worrall (*J. Amer. Chem. Soc.*, 1927, **49**, 1598) attempted to add some forty bases (amines, hydrazines) to β -nitrostyrene and found that only thirteen gave isolatable adducts. Aniline and *p*-toluidine were the only common aromatic bases and piperidine the only secondary amine with which he was able to obtain an adduct, and in each of these three cases the adduct was of type (I).



The addition of ammonia was, however, exceptional, two mols. of β -nitrostyrene being involved to give $\text{NH}(\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}_2)_2$.

Halogen-substituted nitro-olefins have also been reported to react with amines. Thus β -bromo- β -nitrostyrene with ammonia gives 2-bromo-2-nitro-1-phenylethylamine (Loevenich and Gerber, *Ber.*, 1930, **63**, 1707), and 1-bromo-1-nitrobut-1-ene with aliphatic amines gives unstable adducts (Loevenich, Koch, and Pucknat, *Ber.*, 1930, **63**, 636).

A study of the addition of amines to nitro-olefins has now been undertaken as part of a general investigation of the aliphatic nitro-compounds and as a possible route to certain substituted derivatives of ethylenediamine required for other work.

The addition of ammonia and amines to nitro-olefins is a general reaction which in most cases proceeds very readily. The yields are variable, but this is due to the instability of the resulting 2-nitroalkylamine in which the basic group causes rapid decomposition of the primary or secondary nitro-compound. The products from aromatic amines are weaker bases than those from ammonia or aliphatic amines and are therefore more stable, but in both series it was found preferable to isolate the adducts as salts. Hydrogenation of the 2-nitroalkylamines to ethylenediamines was carried out using Raney nickel.

A complication in carrying out these additions was the tendency of the nitro-olefins to polymerise under the influence of the amine. It was found that better yields of some adducts were obtained when esters of the corresponding 2-nitro-alcohols were used in place of the nitro-olefin. Thus 2-nitroethyl nitrate and 2-nitroisopropyl acetate could be used to replace nitroethylene and 1-nitroprop-1-ene, respectively.

Ammonia has been caused to react with 2-nitroethyl nitrate, 1-nitroprop-1-ene, 2-nitrobut-2-ene, and 1-nitro-2-methylprop-1-ene to give the corresponding unstable β -nitro-amines (type I) which were characterised as salts. Hydrogenation of the nitro-amines over Raney nickel gave the 1:2-diamines (type II). Similarly, diethylamine reacted with 2-nitroethyl nitrate and 2-nitrobut-2-ene to give nitro-amines (type I). From 1:2:3:4-tetrahydroquinoline, the *N*-2-nitroethyl derivative was obtained in 75% yield from 2-nitroethyl nitrate, but in only 12.5% yield from nitroethylene itself.

Aniline has been caused to react with nitroethylene, 2-nitroethyl nitrate, 1-nitroprop-1-ene, and 2-nitrobut-2-ene; *N*-methylaniline with nitroethylene, 1-nitroprop-1-ene, and 2-nitroisopropyl acetate; *N*-ethylaniline with nitroethylene, 2-nitroethyl nitrate, and 1-nitroprop-1-ene. All the products were of type I and readily reverted to nitro-olefin and amine on treatment with alkali (which polymerised the nitro-olefin formed), and in some cases dilute acid affected the same fission. A bis-adduct, *di*-(2-nitroethyl)aniline, was isolated as its *hydrochloride* after further reaction of *N*-2-nitroethylaniline with nitroethylene; this salt eliminated nitroethylene on being heated in water. There was evidence that 2-nitroethylaniline reacted with 1-nitroprop-1-ene, but the product was too unstable for isolation.

EXPERIMENTAL.

Analyses are by Mr. E. S. Morton. M. ps. are uncorrected.

2-Nitroethylamine and Ethylenediamine.—2-Nitroethyl nitrate (13.6 g.; Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) was added dropwise with stirring to methyl alcohol (200 c.c.) saturated with dry ammonia at -5° , and stirring continued for 4 hours at -5° to 0° . The mixture was filtered and the filtrate evaporated at 40° under reduced pressure to give a light brown oil (9 g.). The crude 2-nitro-

ethylamine could not be distilled, did not give a crystalline hydrochloride or picrate, and decomposed to a black tar in 1 to 2 hours. The crude product (8 g.) in methyl alcohol (300 c.c.) was shaken with hydrogen and Raney nickel at ordinary temperature and pressure; the hydrogen absorption was almost theoretical. The mixture was filtered, acidified with hydrochloric acid, and evaporated to dryness; the semi-solid crystalline mass was intimately mixed with powdered potassium hydroxide and dry distilled to give an aqueous solution of ethylenediamine (5.4 g.), b. p. 100—110°; the dipicrate, m. p. 232—234° (decomp.), was identical with an authentic specimen.

2-Nitroisopropylamine.—1-Nitroprop-1-ene (30 g.; this series, Part I) was added with stirring to methyl-alcoholic ammonia (200 c.c.) at 0° and stirring continued for 3 hours. The solution was evaporated and distilled, giving 2-nitroisopropylamine, b. p. 50—55°/10 mm. Yield, 55%. 2-Nitroisopropylamine is very unstable and decomposes in 24 hours. The hydrochloride had m. p. 114° (Found: C, 26.0; H, 6.4; Cl, 25.5. $C_3H_7O_2N_2 \cdot HCl$ requires C, 25.6; H, 6.4; Cl, 25.3%).

1: 2-Diaminopropane.—The nitroamine (above) (10 g.) in methyl alcohol (400 c.c.) was shaken with hydrogen in the presence of Raney nickel at ordinary temperature and pressure. The theoretical amount of hydrogen was absorbed. The solution was filtered, acidified with concentrated hydrochloric acid, and evaporated to dryness at 40° under reduced pressure to give 1: 2-diaminopropane dihydrochloride which crystallised in long needles from alcohol-ether, m. p. 221° (Strache, *Ber.*, 1888, **21**, 2359, gives m. p. 220°). Yield, 52%. The dipicrate formed yellow needles from water, m. p. 237° (Windaus, Dorries, and Jensen, *Ber.*, 1921, **54**, 2750, give m. p. 237°).

Di-(2-nitroisopropyl)amine.—Dry ammonia was passed for 1 hour through a solution of 2-nitroisopropyl nitrate (30 g.; Levy and Scaife, *J.*, 1946, 1100) in dry ether (200 c.c.). The solution, filtered from ammonium nitrate (15.7 g.), was fractionated, giving *di*-(2-nitroisopropyl)amine, b. p. 60—62°/0.5 mm. Yield, 12.7 g. (Found: N, 21.6. $C_6H_{13}O_4N_3$ requires N, 22.0%).

2-Nitro-3-aminobutane.—2-Nitrobut-2-ene (20.2 g.; this series, Part III) was added dropwise with stirring to methyl-alcoholic ammonia (250 c.c.) at 0° and stirring continued for 2 hours. The solution was evaporated and distilled, giving 2-nitro-3-aminobutane as an almost colourless liquid, b. p. 75—78°/20 mm., n_D^{20} 1.4720 (60%), which decomposed in 2 days. The hydrochloride, m. p. 115° (decomp.), was also unstable (Found: Cl, 23.4. $C_4H_{10}O_2N_2 \cdot HCl$ requires Cl, 23.0%).

2: 3-Diaminobutane.—2-Nitro-3-aminobutane (6 g.) in methyl alcohol (60 c.c.) was shaken with hydrogen in the presence of Raney nickel. When absorption was complete the solution was filtered, acidified with hydrochloric acid, evaporated to dryness, and the crystalline residue of the dihydrochloride recrystallised from aqueous alcohol to m. p. 312°. Yield, 40% (Found: C, 29.8; H, 8.2; N, 17.4. $C_4H_{12}N_2 \cdot 2HCl$ requires C, 29.8; H, 8.7; N, 17.4%). Angeli (*Ber.*, 1890, **23**, 1357) reports that the dihydrochloride of 2: 3-diaminobutane is crystalline, but gives no m. p. The picrate decomposed at 250—253° (Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, 1924, **43**, 309r, give m. p. 250—252°).

1-Nitro-2-amino-2-methylpropane.—Dry ammonia was passed into a solution of 1-nitro-2-methylprop-1-ene (Levy and Scaife, in the press) in dry benzene (100 c.c.) at 20° for 8 hours, and the solution then distilled giving 1-nitro-2-amino-2-methylpropane as an oil, b. p. 62—65°/11 mm., in 40% yield. The nitroamine was unstable and decomposed in 3—4 days. The hydrochloride, from absolute alcohol, had m. p. 182° (decomp.) (Found: N, 18.1; Cl, 22.9. $C_4H_{10}O_2N_2 \cdot HCl$ requires N, 18.1; Cl, 23.0%). Reduction of the nitroamine with Raney nickel and hydrogen afforded 1: 2-diamino-2-methylpropane isolated in 75% yield as the dihydrochloride, m. p. 302°. Strack and Schwaneberg (*Ber.*, 1933, **66**, 1333) give m. p. 303° (Found: Cl, 44.2. Calc. for $C_4H_{12}N_2 \cdot 2HCl$: Cl, 44.1%).

Diethyl-2-nitroethylamine.—2-Nitroethyl nitrate (6.8 g.) was added dropwise with stirring to diethylamine (7.3 g.) in dry ether (100 c.c.) kept at 0° by external cooling. After the addition was complete, stirring was continued for ½ hour. The solution was filtered and the ether removed at 20° under reduced pressure. An attempt to distil a small portion of the residue at 15 mm. was unsuccessful; the product decomposed violently. The hydrochloride, from alcohol-ether, had m. p. 72—75° (Found: Cl, 19.3. $C_6H_{14}O_2N_2 \cdot HCl$ requires Cl, 19.4%). The picrate formed needles from alcohol, m. p. 88° (Found: C, 38.6; H, 4.8; N, 18.4. $C_6H_{14}O_2N_2 \cdot C_6H_3O_7N_3$ requires C, 38.2; H, 5.0; N, 18.5%).

2-Nitro-3-diethylaminobutane.—2-Nitrobut-2-ene (10.1 g.) in dry ether (10 c.c.) was added dropwise with stirring to diethylamine (7.3 g.) in dry ether (25 c.c.) at 0—10° and the mixture stirred for a further 2 hours. The product was fractionated to give 2-nitro-3-diethylaminobutane, b. p. 90—95°/11 mm., in 65% yield. Much decomposition had occurred after 12 hours. The picrolonate had m. p. 267° (decomp.) (Found: C, 49.4; H, 5.4. $C_{18}H_{26}O_7N_6$ requires C, 49.3; H, 5.9%).

N-(2-Nitroethyl)-1: 2: 3: 4-tetrahydroquinoline.—(a) From 2-nitroethyl nitrate. 2-Nitroethyl nitrate (5.9 g.) was added dropwise with stirring to tetrahydroquinoline (11.8 g.), the temperature being kept below 30°. After 1 hours' stirring the product was dissolved in ether (50 c.c.) and washed with water. Ethereal hydrogen chloride was added to the dried ethereal solution and the precipitated hydrochloride crystallised from absolute alcohol, m. p. 132°. Yield, 75% (Found: N, 11.4; Cl, 14.3. $C_{11}H_{14}O_2N_2 \cdot HCl$ requires N, 11.5; Cl, 14.6%).

(b) From nitroethylene. A mixture of equimolecular amounts of nitroethylene and tetrahydroquinoline stirred at 40° for 1 hour gave the base, isolated as the hydrochloride, m. p. 132°, in 12.5% yield.

2-Nitroethylaniline.—(a) From nitroethylene. The base was prepared according to Wieland and Sakellarios (*Ber.*, 1919, **52**, 898). Yield, 80%; m. p. 37°.

(b) From 2-nitroethyl nitrate. To a well-stirred solution of aniline (37.2 g.) in ether (250 c.c.), 2-nitroethyl nitrate (27.2 g.) was added dropwise at room temperature. After being stirred for 2 hours the ethereal solution was washed with water, dried, and concentrated under reduced pressure below 30°. The resulting syrup crystallised on cooling strongly, and separated from ether-light petroleum in golden plates, m. p. 37° (22 g.); 65%). The hydrochloride formed needles from alcohol-ether, m. p. 109° (Found: N, 13.9. $C_9H_{10}O_2N_2 \cdot HCl$ requires N, 13.8%). The acetyl derivative formed long needles from aqueous alcohol, m. p. 99° (Found: N, 13.2. $C_{10}H_{12}O_3N_2$ requires N, 13.4%).

Di-(2-nitroethyl)aniline.—Nitroethylene (3.7 g.) was added with stirring to 2-nitroethylaniline (8.3 g.) at 0—10°. After 2 hours the product was dissolved in a mixture of acetone (50 c.c.) and ether (50 c.c.), and ethereal hydrogen chloride added. The precipitated hydrochloride separated from dry alcohol

containing hydrogen chloride as prisms, m. p. 128° (7.8 g.; 50%) (Found: Cl, 12.7. $C_{10}H_{13}O_4N_3, HCl$ requires Cl, 12.9%). The free base, m. p. 64°, was obtained by crystallising the hydrochloride from aqueous alcohol (Found: C, 50.0; H, 5.7; N, 17.0. $C_{10}H_{13}O_4N_3$ requires C, 50.2; H, 5.4; N, 17.5%).

Methyl-2-nitroethylaniline.—Nitroethylene (3.6 g.) was added dropwise with stirring to methylaniline (5.3 g.) at 0–10° and the reaction completed by heating at 40° for 1 hour; the product distilled at 110°/0.2 mm. (yield, 4.5 g.; 50%). The hydrochloride had m. p. 82° (Found: N, 12.4; Cl, 16.5. $C_9H_{15}O_2N_2, HCl$ requires N, 12.9; Cl, 16.4%).

Ethyl-2-nitroethylaniline.—(a) From 2-nitroethyl nitrate. The preparation was carried out from ethylaniline and 2-nitroethyl nitrate as described under (b) above for the preparation of 2-nitroethylaniline. The product was isolated in 80% yield as the hydrochloride, m. p. 114° (Found: N, 12.2; Cl, 15.3. $C_{10}H_{14}O_2N_2, HCl$ requires N, 12.2; Cl, 15.4%). The free base was formed by gradual addition of solid sodium carbonate (6.6 g.) to a fine suspension of the hydrochloride (30 g.) in water (100 c.c.) at 0–5°. *Ethyl-2-nitroethylaniline* separated as a pale green oil which was isolated by ether and distilled, b. p. 108°/0.1 mm., n_D^{19} 1.5597. Yield, 70% (Found: C, 61.8; H, 7.2; N, 14.4. $C_{10}H_{14}O_2N_2$ requires C, 61.8; H, 7.2; N, 14.4%). The picrate, from alcohol, had m. p. 106° (Found: C, 45.9; H, 4.5; N, 16.3. $C_{10}H_{14}O_2N_2, C_6H_3O_7N_3$ requires C, 45.4; H, 4.0; N, 16.5%).

(b) From nitroethylene. The preparation was carried out as described above for the preparation of methyl-2-nitroethylaniline, and the hydrochloride, m. p. 114°, isolated in 75% yield.

2-Nitroisopropylaniline.—This was prepared from 1-nitroprop-1-ene (8.7 g.) and aniline (9.3 g.) in ether (100 c.c.) at room temperature for 2 hours. Removal of the ether under reduced pressure gave a yellow oil which solidified on cooling to –50°, and was crystallised from alcohol, giving yellow needles of 2-nitroisopropylaniline, m. p. 33° (Found: C, 60.05; H, 6.45; N, 15.2. $C_9H_{12}O_2N_2$ requires C, 60.0; H, 6.6; N, 15.5%). The hydrochloride, from 2N-hydrochloric acid, had m. p. 148° (Found: N, 12.8; Cl, 16.6. Calc. for $C_9H_{12}O_2N_2, HCl$: N, 12.9; Cl, 16.4%). Fournéau (*Bull. Soc. chim.*, 1944, 11, 143) gives m. p. 141°.

Methyl-2-nitroisopropylaniline.—(a) From 1-nitroprop-1-ene. Methylaniline (53.5 g.) was added dropwise to well stirred 1-nitroprop-1-ene (43 g.), the temperature being kept below 30° by external cooling. The crude product was dissolved in ether (500 c.c.) and added slowly with stirring to cool ethereal hydrogen chloride (500 c.c. containing 20 g. of hydrogen chloride). The separated solid was triturated twice with methyl alcohol–ether (1:2), giving the pure hydrochloride (106 g.; 92%), m. p. 126° (Found: Cl, 15.5. $C_{10}H_{14}O_2N_2, HCl$ requires Cl, 15.3%). The hydrochloride, which is largely hydrolysed in aqueous solution, was treated in water with sodium carbonate, giving a pale green oil, which was isolated with ether and distilled, yielding methyl-2-nitroisopropylaniline, b. p. 112–115°/0.5 mm., in 80% yield (Found: C, 62.3; H, 7.2. $C_{10}H_{14}O_2N_2$ requires C, 61.8; H, 7.2%). The picrate had m. p. 116° (Found: C, 45.3; H, 4.3; N, 16.8. $C_{10}H_{14}O_2N_2, C_6H_3O_7N_3$ requires C, 45.4; H, 4.0; N, 16.6%). The perchlorate formed colourless prisms from alcohol–ether, m. p. 116° (Found: C, 40.3; H, 5.1; N, 9.4. $C_{10}H_{14}O_2N_2, HClO_4$ requires C, 40.7; H, 5.1; N, 9.5%). The hydrochloride of the p-nitrosoderivative, prepared by nitrosation of the hydrochloride, formed dark green crystals from methyl alcohol, and decomposed at 160° (Found: C, 46.4; H, 5.2. $C_{10}H_{13}O_3N_2, HCl$ requires C, 46.2; H, 5.4%).

(b) From 2-nitroisopropyl acetate. A mixture of methylaniline (5.3 g.) and 2-nitroisopropyl acetate (7.4 g.; Schmidt and Rutz, *Ber.*, 1928, 61, 2142) was heated at 50° for 8 hours. The crude product was converted into the hydrochloride, m. p. 126°, which was obtained in 50% yield.

Ethyl-2-nitroisopropylaniline.—This was prepared from 1-nitroprop-1-ene and ethylaniline as described for methyl 2-nitroethylaniline above. The hydrochloride, from alcohol, had m. p. 123°. Yield, 90% (Found: C, 54.1; H, 6.7; N, 11.3. $C_{11}H_{16}O_2N_2, HCl$ requires C, 53.9; H, 6.9; N, 11.4%).

Ethyl-2-nitro-n-propylaniline.—This was prepared from 2-nitroprop-1-ene (58 g.) and ethylaniline (80 g.) in ether (250 c.c.) as described for the isomeride above. It was isolated as the hydrochloride, m. p. 126°, in 50% yield (Found: C, 54.1; H, 6.9; N, 11.3. $C_{11}H_{16}O_2N_2, HCl$ requires C, 53.9; H, 6.9; N, 11.4%).

2-Nitro-1-methyl-n-propylaniline.—2-Nitrobut-2-ene (24 g.) was added dropwise with stirring to aniline (18.6 g.) at 20°, the mixture maintained at 30° for 3 hours, and distilled, giving the base, b. p. 86°/0.5 mm., n_D^{17} 1.5570, in 72% yield. The hydrochloride, from methyl alcohol–ether, had m. p. 122° (Found: C, 52.4; H, 6.5; N, 12.0. $C_{10}H_{14}O_2N_2, HCl$ requires C, 52.1; H, 6.5; N, 12.1%). The perchlorate explodes on warming (Found: C, 41.1; H, 5.2; N, 9.4. $C_{10}H_{14}O_2N_2, HClO_4$ requires C, 40.7; H, 5.1; N, 9.5%).

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