

287. *Aliphatic Nitro-compounds. Part VIII. Addition of Primary and Secondary Nitro-paraffins to α -Nitro-olefins to give 1 : 3-Dinitro-paraffins.**

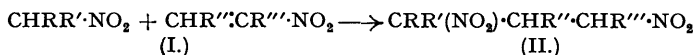
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Interaction of primary or secondary aliphatic nitro-compounds with α -nitro-olefins yields 1 : 3-dinitro-paraffins, which on reduction afford 1 : 3-diamines. The reaction appears to be a general one, but yields are variable. An attempted condensation of 2 : 4-dinitro-2 : 3-dimethylpentane with formaldehyde gave, surprisingly, methyl 2-nitro-1 : 2-dimethylpropyl ketoxime.

* Patent application pending.

MANY authors have described the addition of nitro-paraffins to activated ethylenic systems, including $\alpha\beta$ -unsaturated ketones (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889, and later papers), unsaturated esters (Kohler and Engelbrecht, *ibid.*, 1919, **41**, 764), and nitriles (Bruson, *ibid.*, 1943, **65**, 23), but little attention has been paid to their addition to the α -nitro-olefins. Worrall (*ibid.*, 1935, **57**, 2299; cf. Heim, *Ber.*, 1911, **44**, 2016) recorded the interaction of α -nitrostyrene and phenylnitromethane in the presence of ammonia to give 1 : 3-dinitro-1 : 2 : 3-triphenylpropane, and since the present work was completed, Hass (*Ind. Eng. Chem.*, 1943, **35**, 1151) has mentioned the formation of 1 : 3-dinitro-2 : 3-dimethylpropane from nitromethane and 1-nitro-2-methylpropene, but in neither case was experimental detail presented.

A systematic investigation of the addition of nitro-paraffins to nitro-olefins was undertaken as part of a general exploration of the addition reactions of the nitro-olefins and as a possible route to a wide variety of substituted 1 : 3-diamines of interest in connection with other work in these laboratories. The addition of a primary or secondary nitro-paraffin to a nitro-olefin, although a general reaction, afforded the 1 : 3-dinitro-paraffins in extremely variable yields.



Thus, 2-nitrobut-2-ene (I, $\text{R}' = \text{R}'' = \text{CH}_3$) and 2-nitropropane in presence of sodium ethoxide yielded 47% of 2 : 4-dinitro-2 : 3-dimethylpentane (II, $\text{R} = \text{R}' = \text{R}'' = \text{R}''' = \text{Me}$); in this case the nitro-olefin is not easily polymerised by alkali, the product, containing only one active hydrogen atom, does not easily interact further with unchanged nitro-olefin, and the amount of polymeric by-product was therefore negligible. In the presence of benzyltrimethylammonium hydroxide, nitroethane and 2-nitrobut-2-ene gave the dissecondary nitro-paraffin, 2 : 4-dinitro-3-methylpentane, in 28% yield with a considerable amount of by-product of high molecular weight which decomposed on attempted distillation; with sodium ethoxide or piperidine as catalyst the same product was obtained in lower yield. 2-Nitropropane and 2-nitroprop-1-ene gave (sodium ethoxide catalyst) 2 : 4-dinitro-2-methylpentane in 26% yield, and methyl 2-nitropropyl sulphide and methyl 2-nitropropyl ether (see Parts IV and III in this series) added (sodium methoxide catalyst) to 2-nitroprop-1-ene to give methyl 2 : 4-dinitro-2-methylamyl sulphide and methyl 2 : 4-dinitro-2-methylamyl ether, respectively; the latter was also obtained directly in 52% yield from two molecules of 2-nitroprop-1-ene and one of sodium methoxide without isolation of the intermediate methyl 2-nitropropyl ether. The higher nitro-olefins were less reactive; thus, 2-nitropropane and 1-nitrocyclohexene gave nitro-2-(1-nitroisopropyl)-cyclohexane in only 16% yield.

The properties of the 1 : 3-dinitro-paraffins are parallel to those of the simpler mononitro-compounds; they exhibit none of the instability associated with the 1 : 2-dinitro-paraffins. Hydrogenation in the presence of nickel catalysts affords 1 : 3-diamines; they dissolve in aqueous alkali and treatment of such solutions with bromine gives the α -bromo-derivatives which are useful for characterisation purposes. Surprising results were obtained in an attempt to cause 2 : 4-dinitro-2 : 3-dimethylpentane to interact with paraformaldehyde and sodium hydroxide; instead of the expected 4-hydroxymethyl derivative, methyl 2-nitro-1 : 2-dimethylpropyl ketoxime, m. p. 51°, was formed. This is the only known example of the reduction of a secondary nitro-paraffin by formaldehyde and alkali; the structure of the oxime was confirmed by reduction of the sodium salt of the dinitro-compound with stannous chloride and hydrochloric acid, a method specific for the reduction of primary or secondary nitro-paraffins to oximes (cf. Konowalov, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 960; *Chem. Zentr.*, 1899, I, 597). In addition to the oxime, m. p. 51°, above, the isomeride, m. p. 85–86°, was also formed, which was rearranged with phosphorus pentachloride to an isomeric amide.

The 2-nitroprop-1-ene used in this work was prepared by the method of Buckley and Scaife (this series, Part I).

EXPERIMENTAL.

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

2 : 4-Dinitro-2 : 3-dimethylpentane.—A well-stirred solution of sodium ethoxide (39.6 g.) in alcohol (400 c.c.) was treated with 2-nitropropane (52.5 g.) at 15–20°, followed by 2-nitrobut-2-ene (59.5 g.; this series, Part III), and the whole refluxed. After cooling, the mixture was poured into iced water (1000 c.c.) and neutralised at 0° with 2*N*-hydrochloric acid. The solution was concentrated under reduced pressure and the residue extracted with ether. Distillation gave 2 : 4-dinitro-2 : 3-dimethylpentane (53 g.) as a pale yellow oil, b. p. 90–92°/0.5 mm. (Found : C, 44.9; H, 7.5; N, 14.5. $\text{C}_7\text{H}_{14}\text{O}_4\text{N}_2$ requires C, 44.2; H, 7.4; N, 14.7%). The 2-bromo-derivative, prepared from an aqueous solution of sodium 2 : 4-dinitro-2 : 3-dimethylpentane and the calculated quantity of bromine, formed colourless plates from methyl alcohol, m. p. 40° (Found : C, 30.8; H, 4.7; N, 10.3; Br, 29.7. $\text{C}_7\text{H}_{13}\text{O}_4\text{N}_2\text{Br}$

requires C, 31.2; H, 4.8; N, 10.4; Br, 29.7%). The 2-(*p*-nitrophenylazo)-derivative, prepared from sodium 2:4-dinitro-2:3-dimethylpentane and diazotised *p*-nitroaniline (cf. Feasley and Degering, *J. Org. Chem.*, 1943, **8**, 12), formed orange prisms from alcohol, m. p. 142—143° (Found: C, 46.2; H, 5.1; N, 20.7). $C_{15}H_{17}O_4N_5$ requires C, 46.0; H, 5.0; N, 20.6%).

2:4-Diamino-2:3-dimethylpentane.—2:4-Dinitro-2:3-dimethylpentane (50 g.) in methyl alcohol was hydrogenated at 50–70° and 70 atm. (initial pressure) over Raney nickel. Fractionation of the product gave 2:4-diamino-2:3-dimethylpentane (17 g.) as a colourless liquid, b. p. 66–68°/30 mm., 180°/754 mm. Reduction with iron and hydrochloric acid gave the same diamine in poor yield. The NN'-*dibenzoyl* derivative formed colourless needles from benzene, m. p. 175° (Found: C, 74.5; H, 7.4; N, 8.2). $C_{21}H_{26}O_2N_2$ requires C, 74.6; H, 7.7; N, 8.3%. The *platinichloride* formed orange prisms from aqueous methyl alcohol (Found: Pt, 36.1). $C_7H_{18}N_2H_2PtCl_6$ requires Pt, 36.1%).

Methyl 2-Nitro-1:2-dimethylpropyl Ketoxime.—(a) *By reduction with formaldehyde*. 2:4-Dinitro-2:3-dimethylpentane (10 g.), paraformaldehyde (1.6 g.), 40% aqueous sodium hydroxide (0.5 c.c.), and methyl alcohol (20 c.c.) were stirred at room temperature for 16 hours. After neutralisation with dilute hydrochloric acid, fractionation gave a colourless oil (8.2 g.), b. p. 90–91°/0.5 mm., which slowly deposited crystalline material. *Methyl 2-nitro-1:2-dimethylpropyl ketoxime* separated from light petroleum (b. p. 60–80°) as colourless plates, m. p. 51° (Found: C, 47.9; H, 8.1; N, 15.9). $C_7H_{14}O_3N_2$ requires C, 48.2; H, 8.0; N, 16.1%). The *p*-nitrophenylurethane formed fibrous needles from benzene–light petroleum (b. p. 60–80°), m. p. 109–110° (after being dried at 80° in a vacuum) (Found: C, 49.7; H, 5.2; N, 16.3). $C_{14}H_{18}O_6N_4$ requires C, 49.7; H, 5.3; N, 16.6%).

(b) *By reduction with stannous chloride*. A solution of 2:4-dinitro-2:3-dimethylpentane (30 g.) in aqueous sodium hydroxide (12.6%; 50 c.c.) was added dropwise with stirring to a solution of stannous chloride (35 g.) in concentrated hydrochloric acid (210 c.c.) at 0°. After being stirred for a further ½ hour at 0°, the solution was neutralised with sodium carbonate and extracted with ether. Distillation of the extract gave a viscous pale yellow oil (7 g.), b. p. 80–90°/0.1 mm., which crystallised on standing, m. p. and mixed m. p. with the oxime described above, 51°. The *p*-nitrophenylurethane had m. p. 109–110° alone or mixed with the specimen described above. The product from a second similar experiment was crystallised without distillation, giving an isomeric *oxime*, small needles from light petroleum (b. p. 60–80°), m. p. 85–86° (Found: C, 48.5; H, 8.1; N, 15.8). $C_7H_{14}O_3N_2$ requires C, 48.2; H, 8.0; N, 16.1%). With phosphorus pentachloride in dry ether the latter gave an isomeric *amide* which separated from benzene–light petroleum (b. p. 60–80°) in colourless needles, m. p. 83° (Found: C, 47.8; H, 8.2; N, 15.7). $C_7H_{14}O_3N_2$ requires C, 48.2; H, 8.0; N, 16.1%).

2:4-Dinitro-3-methylpentane.—2-Nitrobut-2-ene (50 g.) was added during 1 hour with stirring at ordinary temperature to a mixture of nitroethane (150 g.), dioxan (150 c.c.), and aqueous benzyltrimethylammonium hydroxide (40%; 6 c.c.). After being stirred for 48 hours at 40°, the mixture was diluted with water (500 c.c.) and neutralised with dilute hydrochloric acid. Extraction with ether, followed by fractionation, gave 2:4-dinitro-3-methylpentane (25 g.) as a pale yellow liquid, b. p. 94–95°/0.5 mm. (Found: N, 15.9). $C_8H_{12}O_4N_2$ requires N, 16.2%). The use of piperidine or sodium ethoxide as catalyst in this reaction gave a smaller yield of the same product. The 2:4-dibromo-derivative, prepared by the method described above from 2-bromo-2:4-dinitro-2:3-dimethylpentane, formed colourless prisms from aqueous methyl alcohol, m. p. 53–54° (Found: C, 21.7; H, 3.3; N, 8.0). $C_8H_{10}O_4N_2Br_2$ requires C, 21.6; H, 3.0; N, 8.3%).

2:4-Dinitro-2-methylpentane.—2-Nitropropane (21 g.) was added to 2-nitroprop-1-ene (20 g.; this series, Part I) as described above for the reaction of 2-nitropropane with 2-nitrobut-2-ene. 2:4-Dinitro-2-methylpentane (10.6 g.) was obtained as a pale yellow oil, b. p. 80°/0.2 mm. (Found: C, 41.3; H, 6.7). $C_8H_{12}O_4N_2$ requires C, 40.9; H, 6.8%). The 2-bromo-derivative formed colourless leaflets from aqueous methyl alcohol, m. p. 76° (Found: C, 27.7; H, 4.5; Br, 31.3). $C_8H_{11}O_4N_2Br$ requires C, 28.2; H, 4.3; Br, 31.4%).

2:4-Diamino-2-methylpentane.—2:4-Dinitro-2-methylpentane (9 g.) in methyl alcohol (100 c.c.) was hydrogenated at 70° and 75 atm. (initial pressure) over Raney nickel. The product was filtered, acidified with hydrochloric acid, evaporated to dryness, treated with excess of 50% aqueous potassium hydroxide, and extracted with ether. After drying over potassium hydroxide, distillation gave 2:4-diamino-2-methylpentane as a colourless liquid which fumed on exposure to air, b. p. 150–155°/756 mm. (Kohn, *Monatsh.*, 1902, **23**, 6, gives b. p. 147–155°). The NN'-*dibenzoyl* derivative formed colourless prisms from aqueous methyl alcohol, m. p. 152° (Found: N, 8.6). $C_{20}H_{24}O_2N_2$ requires N, 8.6%).

Nitro-2-(1-nitroisopropyl)cyclohexane.—2-Nitropropane (8.9 g.) was brought into reaction with nitrocyclohexene (12.7 g.) (Wieland *et al.*, *Annalen*, 1921, **424**, 71) as described above for the addition of 2-nitropropane to 2-nitrobut-2-ene. Fractionation of the product gave a pale yellow oil (3.5 g.), b. p. 95–110°/0.3 mm., which solidified on cooling, and recrystallised from light petroleum (b. p. 60–80°), giving *nitro-2-(1-nitroisopropyl)cyclohexane* in colourless plates, m. p. 103° (Found: C, 49.9; H, 7.3; N, 12.6). $C_9H_{16}O_4N_2$ requires C, 50.0; H, 7.4; N, 13.0%).

Methyl 2:4-Dinitro-2-methylamyl Ether.—(a) *From methyl 2-nitropropyl ether and 2-nitroprop-1-ene*. A well-stirred solution of sodium methoxide (4.1 g.) in methyl alcohol (50 c.c.) was treated with methyl 2-nitropropyl ether (9.1 g.; this series, Part III), followed by 2-nitroprop-1-ene (6.6 g.) at room temperature. After being stirred at 40–50° for ½ hour, the mixture was poured into iced water (100 c.c.) and neutralised with aqueous acetic acid. The alcohol was distilled under reduced pressure and the residue extracted with ether. Distillation of the ethereal solution gave *methyl 2:4-dinitro-2-methylamyl ether* (8.0 g.) as a pale yellow oil, b. p. 92–94°/0.1 mm. (Found: C, 41.2; H, 6.8; N, 13.1). $C_7H_{14}O_5N_2$ requires C, 40.8; H, 6.8; N, 13.6%). The 4-bromo-derivative formed colourless plates from aqueous methyl alcohol, m. p. 64° (Found: C, 29.6; H, 4.8; N, 9.5; Br, 27.9). $C_7H_{13}O_5N_2Br$ requires C, 29.5; H, 4.6; N, 9.8; Br, 28.1%).

(b) *From 2-nitroprop-1-ene and methyl alcohol*. 2-Nitroprop-1-ene (50 g.) was added dropwise with stirring to a solution of sodium methoxide (15.5 g.) in methyl alcohol (200 c.c.) at 0°. After being stirred at room temperature for ½ hour, the mixture was poured into ice-water (500 c.c.), neutralised with aqueous acetic acid, and extracted with ether. Distillation of the ethereal solution gave *methyl*

2 : 4-dinitro-2-methylamyl ether (35 g.), b. p. 94—96°/0.2 mm. The 4-bromo-derivative had m. p. 64°, alone or mixed with the specimen described above.

Methyl 2 : 4-Diamino-2-methylamyl Ether.—The dinitro-ether (above) (41.6 g.) in methyl alcohol (650 c.c.) was hydrogenated at 60—70° and 87 atms. (initial pressure). Fractionation of the product gave *methyl 2 : 4-diamino-2-methylamyl ether* (20 g.) as a colourless liquid, b. p. 77—79°/10 mm. (Found : N, 18.7. $C_7H_{18}ON_8$ requires N, 19.2%). The *bis-2 : 4-dinitrophenylurea* derivative (cf. McVeigh and Rose, *J.*, 1945, 621) had m. p. 190° (Found : C, 44.7; H, 4.5; N, 19.8. $C_{21}H_{24}O_{11}N_8$ requires C, 44.6; H, 4.3; N, 19.9%).

Methyl 2 : 4-Dinitro-2-methylamyl Sulphide.—Methyl 2-nitropropyl sulphide (19.6 g.; this series, Part IV) was brought into reaction with 2-nitroprop-1-ene (12.7 g.) as described above for the addition of 2-nitroprop-1-ene to methyl 2-nitropropyl ether. *Methyl 2 : 4-dinitro-2-methylamyl sulphide* (10 g.) was obtained as a pale yellow oil, b. p. 110—115°/0.05 mm. (Found : N, 12.1; S, 14.3. $C_7H_{14}O_4N_2S$ requires N, 12.6; S, 14.4%).

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