

280. *Aliphatic Nitro-compounds. Part I. Preparation of Nitro-olefins by Dehydration of 2-Nitro-alcohols.**

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Nitroethylene and 1- and 2-nitroprop-1-ene are obtained in good yield by heating the appropriate nitro-alcohol with phthalic anhydride. The nitro-olefins are readily polymerised by alkali and decompose on heating; 2-nitroprop-1-ene decomposes rapidly even at room temperature.

ALTHOUGH β -nitrostyrene and its analogues have long been easily accessible, it is only within the last few years that satisfactory preparative methods for the purely aliphatic nitro-olefins have been described.

Four general methods are available all of which involve 2-nitroalkyl esters as intermediates : (a) reaction of olefins with nitrogen peroxide followed by treatment of the product with alkali (Levy and Scaife, *J.*, 1946, 1100), (b) treatment of 2-nitroalkyl esters with mild alkali (Schmidt and Rutz, *Ber.*, 1928, **61**, 2142; Nightingale and Janes, *J. Amer. Chem. Soc.*, 1944, **66**, 352), (c) pyrolysis of 2-nitroalkyl benzoates (Blomquist, Tapp, and Johnson, *J. Amer. Chem. Soc.*, 1945, **67**, 1519), and (d) distillation of the 2-nitroalkyl acetates with a trace of sodium or potassium acetate (U.S.P. 2,257,980). The first two methods are not applicable to the preparation of nitroethylene and the nitropropenes owing to the ready polymerisation of the product.

The direct dehydration of nitro-alcohols to nitro-olefins, though well known in the case of 2-nitro-1-aryl alcohols, has hitherto been effected with only one aliphatic nitro-alcohol, 2-nitroethyl alcohol, which by treatment with potassium hydrogen sulphate gave a 50% yield of nitroethylene; this, however, cannot be used for more than a few grams of material at a time (Wieland and Sakellarios, *Ber.*, 1919, **52**, 898).

Attempts to dehydrate 2-nitro-*n*-propyl alcohol with phosphoric oxide, potassium hydrogen sulphate, sulphuric acid, or zinc chloride failed to give any 2-nitropropene.

When the alcohol was heated with phthalic anhydride at 170° under a short column (to hold back unchanged material) at reduced pressure, a mixture of water and 2-nitroprop-1-ene

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(50—60% yield) distilled. 2-Nitroethyl and 2-nitroisopropyl alcohol under similar conditions gave nitroethylene and 1-nitroprop-1-ene respectively in 65—70% yield. The highest yields were obtained by using equimolecular parts of phthalic anhydride and nitro-alcohol, but, as the water formed distilled from the reactants, it was possible to reduce the anhydride to as little as 10 mol. %. Substituted phthalic anhydrides were equally effective.

Nitroethylene was obtained as a pale yellow lachrymatory oil which was moderately stable to heat and light but darkened slowly on keeping. It polymerised readily on treatment with water (cf. Wieland and Sakellarios, *loc. cit.*) and violently in presence of a trace of alkali. 2-Nitroprop-1-ene (Blomquist *et al.*, *loc. cit.*) was a pale yellow lachrymatory oil which rapidly turned green and decomposed to a black tar on being kept for a few days even in the dark; no means of arresting this decomposition was discovered. It decomposed vigorously on warming to 100° to give a complex mixture of products, and polymerised readily on treatment with alkalis. 1-Nitroprop-1-ene (Levy and Scaife, *loc. cit.*) resembled the two nitro-olefins described above, but was much more stable. It was apparently unchanged after one year's storage, and was unaffected by water, but polymerised vigorously on treatment with alkali, and decomposed on attempted distillation under atmospheric pressure.

EXPERIMENTAL.

Nitroethylene.—2-Nitroethyl alcohol (100 g.) (Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) and phthalic anhydride (180 g.) were mixed in a distillation apparatus fitted with a short fractionating column and heated by means of an oil-bath. The apparatus was evacuated to 80 mm. and the bath temperature maintained at 140—150° until the mixture was homogeneous. The bath temperature was then raised to 175° and held at 175—180° until distillation ceased. The distillate was dried (CaCl₂) and re-distilled, giving nitroethylene (55 g.; 66·5% theory) as a pale yellow oil, b. p. 38—39°/80 mm.

1-Nitroprop-1-ene.—2-Nitroisopropyl alcohol (105 g.) (Levy and Scaife, *loc. cit.*) was brought into reaction with phthalic anhydride (150 g.) at 180°/50 mm. as described above for 2-nitroethyl alcohol. 1-Nitroprop-1-ene was obtained as a pale yellow oil (58·5 g.; 67% theory), b. p. 54°/28 mm.

2-Nitroprop-1-ene.—2-Nitro-*n*-propyl alcohol (105 g.) (Vanderbilt and Hass, *Ind. Eng. Chem.*, 1940, 32, 34) was brought into reaction with phthalic anhydride (150 g.) at 175—180°/80 mm. as described above to give 2-nitroprop-1-ene as a pale yellow oil (48·5 g.; 55·5% theory), b. p. 58°/90 mm.

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