513. *Molecular Rearrangements. Part VI.* The Thermal Rearrangement of* N-*Methyl*-N-p-*nitrophenylnitramine.*

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N-Methyl-*N*-*p*-nitrophenylnitramine, when heated at its melting point or in an indifferent solvent, rearranges to *N*-methyl-2,4-dinitroaniline; also formed are nitric oxide, formaldehyde, *N*-methyl-*p*-nitroaniline, and 2,4-dinitroaniline.

The rearrangement is prevented if the nitramine is heated with 2,6-dimethyl- or 2,6-di-isopropyl-phenol; good yields of *N*-methyl-*p*-nitro-aniline and of the appropriate 2,6-dialkyl-*p*-nitrophenols are obtained. With 2,6-di-t-butylphenol, the formation of the nitrophenol is accompanied by the production of nitric oxide, 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone, and some 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butylbiphenyl.

It is evident that the nitro-group of the nitramine can be transferred in good yield to the nucleus of a suitable phenol. Evidence on the course of this nitration has been obtained from the behaviour of the nitramine in *NN*-diethylaniline and in alkylbenzenes.

The significance of these observations is discussed in relation to the course of the rearrangement.

IN contrast to the volume of work on the acid-catalysed rearrangement of arylnitramines to nitroanilines,[1] the only recorded observation on the thermal rearrangement is by Bamberger and Landsteiner.[2] They found that heating phenylnitramine gave mainly *o*-nitroaniline with some *p*-nitroaniline, *o*- and *p*-nitrophenol, nitrosobenzene, carbon dioxide, nitrogen, and nitrous fumes. The present work is a further study of the thermal iso-merisation of arylnitramines. For this purpose *N*-methyl-*N*-*p*-nitrophenylnitramine seemed suitable: it can give only one normal product of rearrangement; the *N*-methyl group prevents the complication of prototropic change to the *aci*-nitro-form; and a nitro-group seemed preferable for blocking the *para*-position since halogen may be expelled as halogen hydride[3] and an alkyl group may be oxidised.

Decomposition of *N*-methyl-*N*-*p*-nitrophenylnitramine at its melting point is rapid and not easily controlled; the main reaction—formation of *N*-methyl-2,4-dinitroaniline—is accompanied by formation of nitric oxide, formaldehyde, *N*-methyl-*p*-nitroaniline, and a small amount of a nitrosamine. In an indifferent solvent, such as tetrachloroethane, the change proceeds more smoothly with the formation of the same products, together with 2,4-dinitroaniline.

It is evident that the thermal rearrangement is accompanied by oxidation of the *N*-methyl group to formaldehyde and expulsion of the nitro-group as nitric oxide. It was, therefore, of interest to observe how the nitramine behaved in solvents sensitive to oxidation or to nitration, *e.g.*, phenols. It is known[4] that arylnitramines are converted into the corresponding amine with loss of the *N*-nitro-group when heated with phenol, although sulphuric acid is generally added to assist the reaction. Nothing is known of the fate of the phenol in these reactions or yet of the displaced nitro-group.

When phenol and *N*-methyl-*p*-nitrophenylnitramine are heated together, denitration of the nitramine to give *N*-methyl-*p*-nitroaniline was approximately quantitative. Identific-ation of the products from the phenol presented unexpected difficulties. More satisfactory

* Part V, Elkobaisi and Hickinbottom, *J.*, 1960, 1286.

[1] Cf. Hughes and Ingold, *Quart. Rev.*, 1952, **6**, 34.
[2] Bamberger and Landsteiner, *Ber.*, 1893, **26**, 488.
[3] Orton and Smith, *J.*, 1902, **81**, 806; 1905, **87**, 389; 1907, **91**, 146.
[4] Mertens, *Ber.*, 1886, **19**, 2126; Van Romburgh, *Rec. Trav. chim.*, 1886, **5**, 241; 1887, **6**, 370; 1880, **7**, 230; Pinnow, *Ber.*, 1897, **30**, 837, 838; Reverdin, *Bull. Soc. chim. France*, 1911, **9**, 43; 1912, **11**, 485; 1915, **17**, 190; *Ber.*, 1914, **47**, 1537; Reilly and Hickinbottom, *J.*, 1919, **115**, 175; Clarkson, Holden, and Malkin, *J.*, 1950, 1556; Sommer, *J. prakt. Chem.*, 1903, **67**, 534; Hollingsworth, *J.*, 1959, 2424.

results were obtained by using 2,6-dialkylphenols; these are only feebly acidic and cannot act to a major extent as proton-catalysts for the rearrangement; they are also sufficiently sensitive to oxidation to be used as indicators for any oxidising action. In 2,6-di-t-butylphenol, 4-nitro-2,6-di-t-butylphenol was formed in about 70% yield; other products were nitric oxide, 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone, and the corresponding dihydroxybiphenyl. In 2,6-di-isopropylphenol, the yield of the 4-nitrophenol was about 70%; in 2,6-dimethylphenol the yield of nitration product was about 90% and no 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone was detected in the products. 4-Nitro-2,6-di-t-butyl-phenol is known [5] to decompose when heated to give nitric oxide and 3,3′,5,5′-tetra-t-butyl-4,4′-diphenoquinone; when 2,6-di-t-butylphenol is heated with the nitramine, part, at least, of the diphenoquinone is formed by thermal decomposition of the nitrophenol, and this view is confirmed by the fact that by using lower temperatures or other 2,6-dialkylphenols, the yield of nitrophenol may be increased to about 90% at the expense of the diphenoquinone.

That the *N*-nitro-group of the nitramine can be transferred intact to another kind of molecule under suitable conditions is important in considering the course of the rearrangement of arylnitramines to nitroanilines. It strongly suggests that the migration of the nitro-group, brought about thermally, is not intramolecular but involves a rupture of the N–NO₂ bond in such a way that the nitro-group is free to nitrate if conditions are suitable.

It is possible to infer, with some certainty, the nature of this bond fission from observations on the thermal decomposition of the nitramine in diethylaniline. There is no recognisable attack on the aromatic nucleus which is sensitive to electrophilic reagents; the *N*-nitro-group is thus not available as an electrophilic nitrating agent. Instead the *N*-ethyl group is oxidised to acetaldehyde, by, it may be assumed, a free-radical attack; [6] similar oxidation of the *N*-methyl group of *N*-methyl-*p*-nitrophenylnitramine occurs during thermal rearrangement of this nitramine.

A free-radical mechanism for the thermal rearrangement and decomposition of the arylnitramine is supported by the behaviour of *N*-methyl-*p*-nitrophenylnitramine in boiling solution in the alkylbenzenes. The only reactions are oxidation of the side chain of the aromatic hydrocarbon with concurrent replacement of the *N*-nitro-group of the *N*-nitramine by hydrogen; rearrangement of the nitramine to the corresponding *N*-methyl-2,4-dinitroaniline also occurs. Oxidation of the side chain of the alkylbenzene is in accord with all previous observations on the behaviour of alkylbenzenes towards free-radical oxidation and halogenation; it excludes the possibility that the *N*-nitro-group reacts as an electrophilic reagent.

It it is accepted that rearrangement and decomposition of the nitramine are by a free-radical mechanism, the thermal rearrangement can be represented by the annexed scheme. Here nitric oxide and formaldehyde are also formed as minor products and it seems a reasonable assumption that the nitric oxide is derived from nitrogen dioxide as
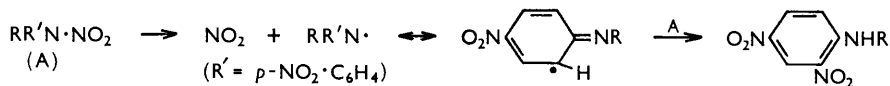
a result of oxidation of the *N*-methyl group to formaldehyde, which is supported by the observations of Glazer *et al.*[7] on the dealkylation of tertiary amines by oxides of nitrogen. An alternative explanation that oxidation of the *N*-methyl group arises from reduction of the *N*-nitramine to an *N*-nitrosamine is, however, not yet excluded by the experimental evidence.

[5] Barnes and Hickinbottom, *J.*, 1961, 953.
[6] Henbest and Thomas, *J.*, 1957, 3032.
[7] Glazer, Hughes, Ingold, James, Jones, and Roberts, *J.*, 1950, 2668.

Nitration of 2,6-dialkylphenols by *N*-methyl-*p*-nitrophenylnitramine can be explained on the scheme propounded for the thermal decomposition of the nitramine. Substantial support for the first stage of the further reactions shown is provided by the isolation of
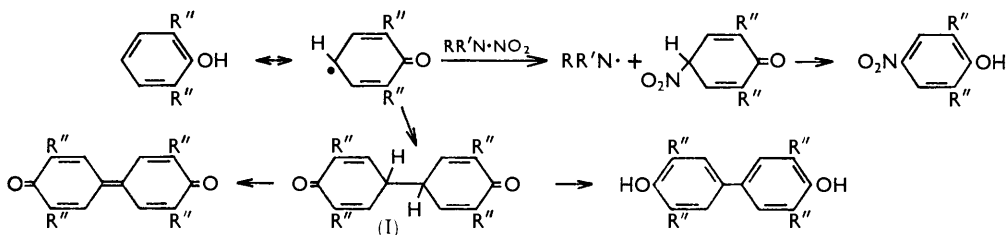
the dihydroxybiphenyl from the products of this nitration. It is already known [5] that compound (I) isomerises readily to the corresponding phenol, and that it can be oxidised to the corresponding diphenoquinone.

<div align="center">EXPERIMENTAL</div>

N-Methyl-*N*-*p*-nitrophenylnitramine, prepared by Hughes and Jones's method,[9] freed from acid by repeated treatment with dilute aqueous ammonia, and crystallised from ethanol, had m. p. 141° (decomp.).

For thermal decomposition of the nitramine, a round-bottomed flask was used, heated by an oil-bath and attached through a condenser to two cold traps, the first cooled in solid carbon dioxide and ethanol, the second by liquid nitrogen. A slow stream of nitrogen was passed through the apparatus during the experiment.

The identity of the products was confirmed whenever practicable by mixed m. p. determination and comparison of the infrared spectrum with that of an authentic specimen.

Thermal Decomposition of N-*Methyl-*N-p-*nitrophenylnitramine.*—(a) *Solid.* The nitramine (20 g.) in contact with the walls of the flask began to darken at 138° (bath-temperature); at 139—140° it melted, with swelling and bubbling. It was often impossible to prevent an evolution of gas so rapid that the connections with the cold trap were forced apart with the development of olive-brown fumes; there was also a smell of formaldehyde and of nitroaniline.

When the decomposition was complete, there remained a dark brown tar, and similar material had been projected into the condenser and carried over into the first cold trap.

The gaseous products were nitric oxide (condensed as a blue solid in the second cold trap) and formaldehyde (dimedone derivative and colour reactions).

From the solid products, *N*-methyl-*p*-nitroaniline (m. p. 150—151°; *N*-nitroso-derivative, m. p. 100—100·5°) was extracted from their benzene solution with hydrochloric acid. The non-basic products, after evaporation of the benzene, were extracted with light petroleum (b. p. 60—80°) to remove a small amount of a nitrosamine, m. p. 91—92·5°, probably *N*-methyl-*N*-*p*-nitrophenylnitrosamine (the amount did not permit identification). The remainder, consisting of *N*-methyl-2,4-dinitroaniline, was purified to m. p. 174—175° by a preliminary crystallisation from aqueous acetic acid, dissolution in benzene to remove more tar, treatment of the benzene solution with charcoal, and filtration through alumina. The ratio of *N*-methyl-*p*-nitroaniline to *N*-methyl-2,4-dinitroaniline was ~1 : 8.

(b) *In* 1,1,2,2-*tetrachloroethane.* A solution of the nitramine (15 g.) in purified tetrachloroethane (150 c.c.) began to darken at about 95° and evolution of gas was first evident at 103°. As the temperature was raised, the solution rapidly became red. In the meantime the evolution of gas continued at the b. p. of the solvent and showed signs of slackening only after 8 hr.; it was substantially complete after 10 hr.

The products were nitric oxide, water, formaldehyde, *N*-methyl-*p*-nitroaniline (2 g., 18%),

[8] Kharasch and Joshi, *J. Org. Chem.*, 1957, **22**, 1439.
[9] Hughes and Jones, *J.*, 1950, 2678.

N-methyl-2,4-dinitroaniline (9·6 g., 64%), and tar (2·1 g.). In the more soluble fractions of the recrystallisation of methyldinitroaniline, the presence of 2,4-dinitroaniline was recognised by diazotisation and coupling with β-naphthol to give the azo-β-naphthol, m. p. and mixed m. p. 302°.

In another experiment the yields were: formaldehyde, as dimedone derivative 4%; *N*-methyl-*p*-nitroaniline, 23%; *N*-methyl-2,4-dinitroaniline, 59%.

(c) *In phenols.* (i) When the nitramine (1·97 g.) and 2,6-di-t-butylphenol (7·2 g.) were heated together, slow evolution of gas began at about 140° and the colour of the melt, initially yellow, darkened as the temperature was raised and as the gas evolution increased. After 2 hr., when the temperature was 200°, there was no perceptible gas evolution.

The only gaseous product was nitric oxide; formaldehyde was not detected.

The phenolic melt was steam-distilled to remove unchanged 2,6-di-t-butylphenol, m. p. 37° (5·05 g.) (Found: C, 81·6; H, 10·6. Calc. for $C_{14}H_{22}O$: C, 81·5; H, 10·7%), and the remainder, dissolved in ether, was extracted with hydrochloric acid to remove *N*-methyl-*p*-nitroaniline (m. p. 152—152·5°; 1·45 g., 95%; nitrosamine, m. p. 100—101°). The non-basic products were separated by treatment with aqueous alkali into 3,5,3′,5′-tetra-t-butyl-4,4′-diphenoquinone, m. p. 247—248° (0·40 g.) (Found: C, 82·5; H, 9·7. Calc. for $C_{28}H_{40}O_{2}$: C, 82·3; H, 9·9%), and 4-nitro-2,6-di-t-butylphenol, m. p. 156·5° (1·85 g., 73%) (Found: C, 66·7; H, 8·2; N, 5·4%; *M*, 247. Calc. for $C_{14}H_{21}O_{3}N$: C, 66·9; H, 8·4; N, 5·6%; *M*, 251) [α-naphthylurethane, m. p. 199·5—200° (Found: C, 71·6; H, 6·5; N, 6·6. Calc. for $C_{25}H_{28}N_{2}O_{4}$: C, 71·4; H, 6·7; N, 6·7%)]. From the more soluble fractions in the purification of the diphenoquinone 0·15 g. of 4,4′-dihydroxy-3,5,3′,5′-tetra-t-butylbiphenyl was isolated as pale yellow needles, m. p. 184°, readily converted into the diphenoquinone even when boiled in alcohol with charcoal.

(ii) The nitramine (1·97 g.) and 2,6-di-isopropylphenol (6·24 g.) were heated together at 110—114° for 90 min. The products were nitric oxide (small yield), 2,6-di-isopropyl-4-nitrophenol, m. p. 112° (1·51 g., 68%) (Found: C, 64·7; H, 7·6; N, 6·5. Calc. for $C_{12}H_{17}NO_{3}$: C, 64·6; H, 7·7; N, 6·3%), 3,3′,5,5′-tetraisopropyl-4,4′-diphenoquinone (Found: C, 81·7; H, 9·0. Calc. for $C_{24}H_{32}O_{2}$: C, 81·8; H, 9·15%), m. p. 214° (0·3 g.), *N*-methyl-*p*-nitroaniline (1·25 g., 82%), and *N*-methyl-*N*-*p*-nitrophenylnitrosamine (0·25 g., 14%). In the isolation of these products, it was more convenient, after the excess of di-isopropylphenol had been removed by steam-distillation, to extract the nitrophenol first with alkali. The remainder of the product was then extracted (Soxhlet) by water; the diphenoquinone remained insoluble. The mixture of methylnitroaniline and nitrosamine was separated by chromatography on a silica–Celite 535 column with benzene–light petroleum (b. p. 40—60°).

(iii) The nitramine (1·97 g.) and 2,6-dimethylphenol (4·28 g.), heated together at 115—128° for 3 hr., gave 2,6-dimethyl-4-nitrophenol, m. p. 172—173° (1·45 g., 87%), and a mixture of *N*-methyl-*p*-nitroaniline with some of its nitrosamine. 3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone was not detected.

(d) *In alkylbenzenes* (in part with C. BEARD). (i) The nitramine (50 g.) and *p*-xylene (100 g.) were boiled together for 3 days during which there was evolution of nitrous fumes. The xylene solution was extracted with aqueous sodium carbonate to remove *p*-toluic acid and then steam-distilled. The residue consisted of *N*-methyl-*p*-nitroaniline, m. p. 150—151°, and *N*-methyl-2,4-dinitroaniline, m. p. 177·5—178·5°. The steam-distillate consisted of *p*-xylene with *p*-tolualdehyde (1·5 g.) (2,4-dinitrophenylhydrazone, m. p. 240—241°; phenylhydrazone, m. p. 112°).

(ii) When the nitramine (15 g.) and mesitylene (50 c.c.) were boiled together for 5 hr., the products were nitric oxide, formaldehyde (0·03 g.), 3,5-dimethylbenzoic acid (0·1 g.), *N*-methyl-*p*-nitroaniline (9·3 g.), *N*-methyl-2,4-dinitroaniline (1·1 g.), and tar (0·9 g.).

(iii) Cumene (50 c.c.) and *N*-methyl-*N*-*p*-nitrophenylnitramine (15 g.), heated together under reflux for 2½ hr., gave formaldehyde (0·25 g., estimated as dimedone derivative), *N*-methyl-*p*-nitroaniline (9·15 g.), *N*-methyl-2,4-dinitroaniline (0·9 g.), acetophenone (1·5 g.) (2,4-dinitrophenylhydrazone), and tar (1·0 g.).

(e) *In* NN-*diethylaniline.* *N*-Methyl-*N*-*p*-nitrophenylnitramine (15 g.) and diethylaniline (40 c.c.) were boiled together for 2 hr. The solution rapidly darkened and nitric oxide and acetaldehyde (2·4 g.) (2,4-dinitrophenylhydrazone, m. p. 167—168°; dimedone derivative, m. p. 140—141°) were evolved. Steam-distillation removed diethylaniline with some monoethylaniline (toluene-*p*-sulphonyl derivative, m. p. 87·5°). From the material not volatile

in steam, *N*-methyl-*p*-nitroaniline (6·7 g.) was isolated. The yield of monoethylaniline was 15—20%.

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