317. *A Rearrangement of* o-*Aminodiphenyl Ethers. Part IV.* N-*Alphylphenoxazines.*

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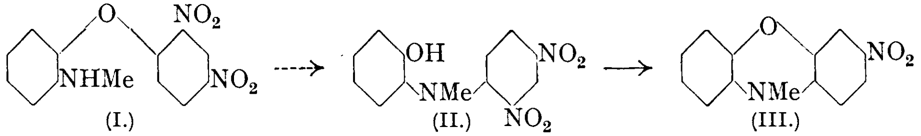
In continuation of the study of the rearrangement of 2-aminodiphenyl ethers to the isomeric 2-hydroxydiphenylamines (J., 1934, 727; this vol., p. 196; preceding paper), 2′ : 4′-*dinitro-2-methylaminodiphenyl ether* (I) has now been investigated.

Conditions designed to favour rearrangement of this substance to the isomeride (II) yield only a phenoxazine (III) identical with that obtained from a synthetic specimen of



(I.) (II.) (III.)

(II). It must therefore be inferred that the sought-for rearrangement occurs only under conditions which preclude direct observation of it.

In (II), chelation between the bridge radical and the adjacent nitro-group is impossible. The facile formation (cf. Kehrmann, *Ber.*, 1920, **53**, 2266) of the phenoxazine (III) from (II) thus affords interesting confirmation of the theory of Brady (J., 1930, 1218) that the non-formation of oxazines from certain 2′-nitro-2-hydroxydiphenylamines is due to chelation between the imino- and the nitro-group.

Similar behaviour was observed with the *O*-dinitrophenyl derivative of 2′ : 4′-dinitro-2-hydroxydiphenylamine, which yielded a nitro-*N*-dinitrophenylphenoxazine.

EXPERIMENTAL.

N-*Methyl*-p-*toluenesulphon*-o-*anisidide*, obtained by treatment of *p*-toluenesulphon-*o*-anisidide under usual conditions, formed colourless needles, m. p. 100°, from alcohol (Found : C, 62·1; H, 5·8. $C_{15}H_{17}O_3NS$ requires C, 61·8; H, 5·8%). It was hydrolysed to *o*-methylaminophenol by heating with fuming hydrochloric acid in a sealed tube at 170° for 5 hours.

2′ : 4′-*Dinitro*-2-*methylaminodiphenyl Ether* (I).—When *o*-methylaminophenol and chlorodinitrobenzene (1 mol. each) in alcohol were treated at room temperature for several hours with sodium ethoxide (1 mol.), the *ether* (I) separated. It formed yellow crystals from benzene, m. p. 182° (Found : C, 53·6; H, 3·7. $C_{13}H_{11}O_5N_3$ requires C, 53·9; H, 3·8%). The substance was stable towards alkali and towards aqueous pyridine, but in a mixture of these solvents, or in aqueous-alcoholic caustic soda, it was slowly converted at 100° into 3-*nitro*-6-*methylphenoxazine* (III), which separated during several hours as a red solid. It formed bright red needles from glacial acetic acid, m. p. 182—183° (Found : C, 64·0. $C_{13}H_{10}O_3N_2$ requires C, 64·4%). Low results were obtained unless the substance was burnt intimately mixed with fine copper oxide.

2′ : 4′-*Dinitro*-2-*hydroxy*-N-*methyldiphenylamine* (II) was isolated from the alcoholic mother-liquor obtained in the preparation of (I). It formed orange plates, m. p. 160°, from alcohol (Found : C, 53·8; H, 4·1. $C_{13}H_{11}O_5N_3$ requires C, 53·9; H, 3·8%). Warm alkaline solutions of the substance in water or in alcohol rapidly deposited a phenoxazine (III) identical with that described above.

ON-*Bis*-2 : 4-*dinitrophenyl*-o-*aminophenol*.—2′ : 4′-Dinitro-2-hydroxydiphenylamine, chlorodinitrobenzene, and sodium ethoxide (0·01 mol. each) in alcohol (100 c.c.) were kept for 48 hours at room temperature. The solid which separated crystallised from benzene and ligroin in deep yellow prisms, m. p. 176° (Found : C, 49·2; H, 2·5. $C_{18}H_{11}O_9N_5$ requires C, 48·9; H, 2·4%). It was insoluble in alcohol and remained unchanged in hot aqueous pyridine, but caustic soda in aqueous pyridine converted it into 3(?)-*nitro*-6-*dinitrophenylphenoxazine*, a deep red substance which, purified from benzene and ligroin, melted at 230—233° (decomp.). It was unaffected by boiling alkali (Found : C, 54·9; H, 2·5. $C_{18}H_{10}O_7N_4$ requires C, 54·8; H, 2·5%). 2′ : 4′-Dinitro-2-aminodiphenyl ether would not condense with chlorodinitrobenzene under conditions which precluded the rearrangement of the ether.

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