159. *A Rearrangement of* o-*Aminodiphenyl Ethers. Part I.*

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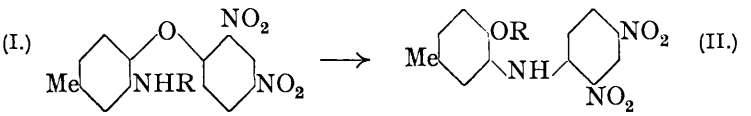
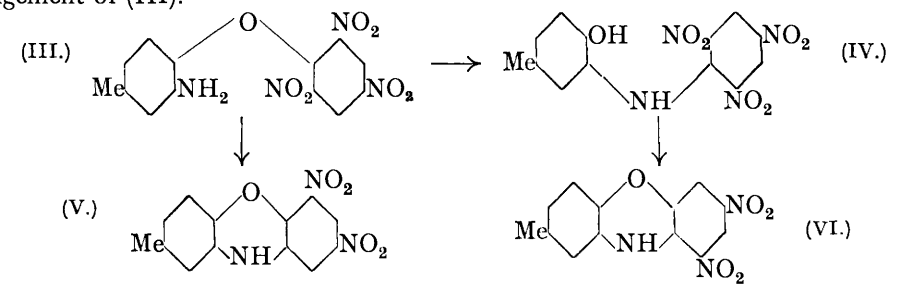
INTRAMOLECULAR change of the type exemplified by the ready conversion of the *O*-acyl derivatives of *o*-aminophenols into the corresponding *N*-acyl derivatives, and by the rearrangement of *o*-thioloxides, 2-hydroxysulphones, and *o*-acetamido-sulphoxides and -sulphones (Smiles and his co-workers, J., 1931, 2207, 3264; 1932, 1040, 1488, 2774; 1933, 1490), could not be effected with *o*-aminodiphenylamines (Roberts, J., 1932, 2358), but has now been brought about in *o*-aminodiphenyl ethers: derivatives of type (I; R = H or acyl) are readily converted in suitable media into the diphenylamines (II).



The rate of change of the *N*-acyl derivatives (I) is slower than that of the parent amino-ethers (I; R = H) and falls off with increasing strength of the acid corresponding to R; *e.g.*, the acetyl derivative is converted more rapidly than the *o*-nitrobenzoyl derivative but less quickly than the parent ether. The expected acceleration of the rearrangement on replacement of the dinitrophenyl by the picryl nucleus with its enhanced positivity at the 1-carbon atom has not been realised, owing partly to the relatively low solubility of the *tri-nitro*-ether (III) in the activating solvents and partly to the ease with which it forms the *phenoxazine* (V). The *trinitrodiphenylamine* (IV) has, however, been obtained by re-arrangement of (III).



A novel feature of the rearrangement of the *N*-acyl derivatives (I) is that the acyl group and not the imino-hydrogen migrates, the product in each of the cases studied being the *O*-acyl derivative (II) of the corresponding hydroxydiphenylamine (contrast the *o*-acetamido-sulphoxides; Levi, Warren, and Smiles, *loc. cit.*). The closest approach to a rearrangement of this type appears to be the exchange of acyl groups between oxygen and nitrogen in diacyl derivatives of *o*-aminophenol (Bell, J., 1931, 2962).

A further notable difference between the changes now described and those recorded by Smiles and others (*locc. cit.*) lies in the means by which they are effected. Whereas the

latter rearrangements take place only under strongly alkaline conditions, those now described are inhibited or strongly retarded by the presence of ions. They are, however, actively promoted by a wide range of basic and hydroxylic solvents such as pyridine, aniline, monohydric alcohols, glycerol, and aqueous solutions of the lower fatty acids (except formic acid), and these, it may be observed, have very low electrolytic dissociation constants. Un-ionisable solvents, on the other hand, whether polar (*e.g.*, nitrobenzene, benzonitrile, acetone, chloroform) or non-polar (*e.g.*, benzene), are inactive. So, too, is the strongly basic piperidine. Aqueous solutions of the effective solvents act more rapidly than do the solvents themselves, although water alone effects the change relatively slowly. This fact may perhaps be ascribed to the breaking up by the water of associated groups of solvent molecules.

A survey of the observations suggests that the action of these media in promoting the change is due in part to the presence of undissociated but ionisable molecules of solvent and in part to the influence of the lone electron-pairs of the oxygen and nitrogen atoms of the solvent molecules. The catalysis of the intramolecular rearrangement of certain aldoximes has been ascribed by Taylor and D. C. V. Roberts (J., 1933, 1439) to a somewhat similar action of undissociated molecules of certain electrolytes (*e.g.*, LiCl, HCl).

The present rearrangements are also effected by the action of heat. Intramolecular changes brought about by this means have been described by Chapman (J., 1927, 1743).

The materials used in the above investigation were synthesised by standard methods. 3-Amino-*p*-cresol condensed readily both with 1-chloro-2 : 4-dinitrobenzene and with picryl chloride to yield the corresponding *hydroxydiphenylamines* (II, R = H; IV), and its sodium derivative reacted with the same chloronitrobenzenes to produce the isomeric *aminodiphenyl ethers* (I, R = H; III).

Experimental.

3-Nitro-*p*-cresol (5 g.) in 2*N*-sodium hydroxide (200 c.c.) was treated at 100° during ½ hour with sodium hydrosulphite until the liquid was decolorised, and 3-amino-*p*-cresol precipitated with acetic acid.

2′ : 4′-*Dinitro*-2-*hydroxy*-5-*methyldiphenylamine* (II; R = H).—3-Amino-*p*-cresol (6·1 g.), 1-chloro-2 : 4-dinitrobenzene (10·1 g.), and sodium acetate (4 g.) were heated in alcohol (100 c.c.) for 2 hours. Addition of water precipitated the *diphenylamine* in 85% yield. It formed bright red needles from alcohol and deep red prisms from benzene or glacial acetic acid, m. p. 183° (Found : C, 54·3; H, 4·2. $C_{13}H_{11}O_5N_3$ requires C, 54·0; H, 3·8%). The substance exhibits chromoisomerism, the red needles rapidly darkening to deep red-brown (m. p. unchanged) on exposure to the air. The sodium derivative (purple plates) is insoluble in aqueous caustic soda. The *acetate* separated in bright yellow, matted needles when water was added to a pyridine–acetic anhydride solution of the diphenylamine which had been boiled for a few minutes; after recrystallisation from alcohol, it had m. p. 191° (Found : N, 12·6. $C_{15}H_{13}O_6N_3$ requires N, 12·6%). The o-*nitrobenzoate*, prepared from the diphenylamine, *o*-nitrobenzoyl chloride, and sodium carbonate in acetone, crystallised from benzene in yellow plates, m. p. 167°, slightly soluble in alcohol (Found : N, 12·6. $C_{20}H_{14}O_8N_4$ requires N, 12·7%). The p-*toluenesulphonate* separated from benzene in bright yellow, thin, matted needles, m. p. 221° (Found : N, 9·15. $C_{20}H_{17}O_7N_3S$ requires N, 9·4%).

2′ : 4′-*Dinitro*-2-*amino*-4-*methyldiphenyl Ether* (I; R = H).—3-Amino-*p*-cresol (6·15 g.), dissolved in ethyl alcohol (60 c.c.) containing sodium (1·15 g.), was added at room temperature to 1-chloro-2 : 4-dinitrobenzene (10 g.) in alcohol (40 c.c.). After 3 hours the solid was collected (the filtrate contained a substantial amount of the isomeric methyldiphenylamine), washed with alcohol and with water (yield, 55%), and recrystallised from benzene, forming bright yellow plates of the *diphenyl ether*, m. p. 142° (Found : C, 54·2; H, 4·3. $C_{13}H_{11}O_5N_3$ requires C, 54·0; H, 3·8%). Treatment of the diphenyl ether with hot aqueous caustic soda yielded a purple solid, which proved to be the sodium derivative of the isomeric diphenylamine. Warmed solutions of the ether in pyridine, aniline, ethyl alcohol, and glycerol rapidly turned red and in all cases the isomeric hydroxydiphenylamine was isolated from the solutions. The rearrangement took place at room temperature in aqueous solutions of pyridine, alcohol, acetic acid, and propionic acid, and was also effected by maintaining the ether above its melting point for 30 minutes, and by long contact of the ether with hot water. Solutions of the ether in formic acid

(pure and aqueous), acetic, and propionic acids, piperidine, nitrobenzene, and benzonitrile all at 100°, and in benzene, chloroform, acetone, and ether at their boiling points were stable, whilst contact with various aqueous alkalis effected the change relatively slowly.

The *acetyl* derivative, prepared by shaking the ether (2 g.) with acetic anhydride (5 c.c.) and dilute acetic acid (10 c.c.), crystallised from benzene in colourless plates, m. p. 146° (Found : N, 12·75. $C_{15}H_{13}O_6N_3$ requires N, 12·6%). When the colourless solution of this substance in pyridine or alcohol was warmed, it became yellow; dilution yielded a yellow solid, m. p. 191° (recryst.), which was identical with the *O*-acetyl derivative of the isomeric diphenylamine. The *o-nitrobenzoyl* derivative, prepared in cold acetone in presence of sodium carbonate, crystallised from benzene in colourless prisms, m. p. 214° (Found : N, 12·85. $C_{20}H_{14}O_8N_4$ requires N, 12·7%), which under conditions similar to those mentioned above underwent rearrangement to the corresponding *O*-acyl derivative of the diphenylamine. When the *o*-nitrobenzoylation of the ether was carried out in warm acetone, only the yellow product of rearrangement, m. p. 167°, was obtained.

Hydrolysis of both the above acyl derivatives with alkali was accompanied by rearrangement to the hydroxydiphenylamine.

2′ : 4′ : 6′-*Trinitro*-2-*hydroxy*-5-*methyldiphenylamine* (IV) resulted when 3-amino-*p*-cresol (3 g.) in alcohol was treated under reflux for 3 hours with picryl chloride (6·1 g.) in presence of sodium acetate. Dilution of the reaction mixture yielded bright scarlet needles of the *trinitrodiphenylamine*, m. p. 177° after recrystallisation from alcohol (Found : C, 47·0; N, 16·8. $C_{13}H_{10}O_7N_4$ requires C, 46·7; N, 16·7%). The substance was soluble in cold dilute caustic soda solution, but the warm reagent caused elimination of nitrous acid and formation of 1 : 3-*dinitro*-8-*methylphenoxazine* (VI), which was difficultly soluble in alcohol and benzene but crystallised from glacial acetic acid in deep crimson plates, m. p. 239° (decomp.) (Found : C, 54·0; H, 3·7; N, 14·9. $C_{13}H_9O_5N_3$ requires C, 54·3; H, 3·15; N, 14·6%). Treatment of (IV) with acetic anhydride and pyridine yielded the *acetate*, which crystallised from acetic acid in orange needles, m. p. 159° (Found: N, 15·1. $C_{15}H_{12}O_8N_4$ requires N, 14·9%).

2′ : 4′ : 6′-*Trinitro*-2-*amino*-4-*methyldiphenyl Ether* (III).—3-Amino-*p*-cresol (6 g.) in absolute alcohol (70 c.c.) in which potassium (2 g.) had been dissolved was slowly added to picryl chloride (12 g.) in alcohol (100 c.c.), maintained below 20°. After 3 hours the solid was isolated (yield, 50%), washed with water and with alcohol, and recrystallised from acetone, forming small, bright yellow prisms, m. p. 241° (decomp.) (Found : N, 16·6. $C_{13}H_{10}O_7N_4$ requires N, 16·7%). The isomeric picrylphenylamine was obtained as a by-product. The *picryl phenyl ether* was insoluble in alcohol and ether and only slightly soluble in glacial acetic acid. It was unchanged by cold aqueous caustic soda, but in contact with the warm reagent a red liquid and a deep red solid were rapidly formed. The former on acidification yielded in small amount a substance identical with (IV), indicating that part of the material had undergone intramolecular rearrangement. The red insoluble solid separated from glacial acetic acid in deep red prisms, m. p. 227°, of a *phenoxazine* (Found : N, 14·5. $C_{13}H_9O_5N_3$ requires N, 14·6%), which depressed the m. p. of (VI) and is probably the isomeride (V). The behaviour of the trinitro-ether with pyridine was similar to that observed with aqueous alkali.

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