

CCCCVII.—*Investigations in the Diphenyl Series. Part  
III. Derivatives of 4-Hydroxydiphenyl.*

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It has been suggested (Turner, *Nature*, 1923, **112**, 439) that the asymmetry of the diphenyl derivatives resolved by Kenner (J., 1922, **121**, 614, *et seq.*) is due to the presence of a permanent bond between the 4. and the 4'-position (I). Abnormal reactivity of the hydrogen atom in the 4'-position subsequent to the introduction of

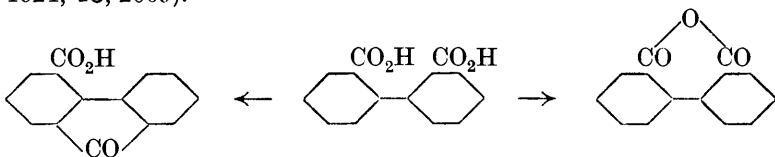
a suitable group in the 4-position would be strongly indicative of such a direct connexion. It is well known that the *p*-hydrogen atom of both dimethylaniline and phenol is specially reactive, but no such reactivity has been found in the corresponding diphenyl derivatives: 4-dimethylaminodiphenyl neither condenses with benzaldehyde nor couples with diazotised aniline or diazotised sulphanilic acid, whilst with nitrous acid it yields 3-nitro-4-dimethylaminodiphenyl (García Banús and Ferrer Tomás, *Anal. Fis. Quím.*, 1921, **19**, 293; Vorländer, *Ber.*, 1925, **58**, 1913).

4-Hydroxydiphenyl couples readily with diazotised aniline; the coupling, however, occurs in the 3-position. Similarly, with nitrous acid the product is 3-nitro-4-hydroxydiphenyl. A structure of type (I) would demand that, in the Reimer-Tiemann reaction, 4-hydroxydiphenyl should give 4-hydroxy-4'-aldehydodiphenyl: although no conclusive proof has been obtained, there is little doubt that the product is 4-hydroxy-3-aldehydodiphenyl.

The experimental results at present available suggest that (1) free rotation of the two nuclei is possible in all lightly-substituted diphenyl derivatives; (2) when free rotation is inhibited, the two nuclei adopt configuration (II), in which they have a common axis but are no longer co-planar.



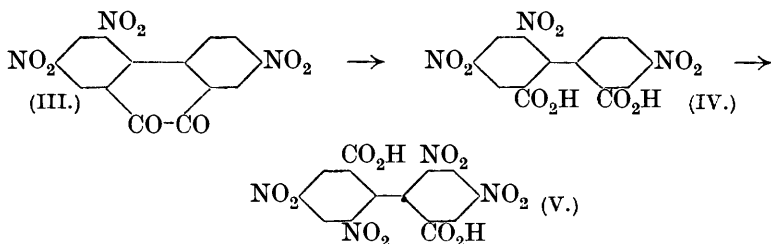
Hypothesis (1) is in harmony with the facts that attempts to resolve diphenic acid and methyl hydrogen diphenate have been unsuccessful\* and that diphenic acid and its derivatives readily yield anhydrides on the one hand and fluorenonecarboxylic acids on the other (Underwood and Kochmann, *J. Amer. Chem. Soc.* 1924, **46**, 2069).



Hypothesis (2) appears to be more in harmony with the experimental facts than the Kaufler configuration, since no evidence exists that the 4:4'-positions are close to each other (compare Le Fèvre and Turner, this vol., p. 2476). Moreover, it obviates the necessity for assuming frequent changes of configuration such as

\* This is in marked contrast with the behaviour of 6-nitrodiphenic acid, which is readily resolvable.

the following, where the method of preparation of (IV) suggests a *cis*-structure, whereas the resolution of (V) requires a *trans*-structure.



4-Methoxydiphenyl on nitration yields a mixture of 3-nitro-4-methoxydiphenyl (about 80%) and 4'-nitro-4-methoxydiphenyl (about 15%); that these derivatives possess the above constitutions was established by preparing them from the corresponding nitrophenols. 4'-Nitro-4-hydroxydiphenyl was described by Schmidt and Schultz (*Annalen*, 1881, **207**, 347), but from the experiments herein described it would appear that the compound obtained by them was, in all probability, 3:4'-dinitro-4-hydroxydiphenyl. 4'-Nitro-4-methoxydiphenyl very readily nitrates to give 3:4'-dinitro-4-methoxydiphenyl, which was also obtained in 50% yield by the nitration of 3-nitro-4-methoxydiphenyl.

Raiford and Colbert (*J. Amer. Chem. Soc.*, 1925, **47**, 1456) have described the dibromination of 4-hydroxydiphenyl and the nitration of the resulting dibromohydroxydiphenyl to give a dibromomononitro-4-hydroxydiphenyl, m. p. 171°. A dibromo-4'-nitro-4-hydroxydiphenyl, m. p. 232—234°, has now been prepared by the bromination of 4'-nitro-4-hydroxydiphenyl and it can scarcely be other than 3:5-dibromo-4'-nitro-4-hydroxydiphenyl. It appears, therefore, that the dibromophenol cannot be, as Raiford and Colbert suggested, 3:5-dibromo-4-hydroxydiphenyl. The halogenation of 4-hydroxydiphenyl is being examined in detail.

4-*p*-Toluenesulphonyloxydiphenyl nitrates mainly, if not exclusively, in the 4'-position, a result which is in marked contrast with the nitration of 4-*p*-toluenesulphonaminodiphenyl, which yields only the 3-nitro-derivative (compare Part II, this vol., p. 2708). It is suggested that the difference in behaviour may be due to substitution being possible *via* the directing group in the former case, whereas in the latter direct substitution only can take place.

#### E X P E R I M E N T A L.

4-Hydroxydiphenyl, prepared in 60% yield by the diazotisation of 4-aminodiphenyl, is readily purified by crystallisation from

benzene. It does not form an additive compound when warmed with *p*-benzoquinone in benzene solution.

*Reaction with Nitrous Acid.*—Sodium nitrite (1 mol.), followed by hydrogen peroxide, was added to a solution of 4-hydroxydiphenyl in warm acetic acid. The mixture was gently heated for a short time and poured into water and the precipitate of 3-nitro-4-hydroxydiphenyl was crystallised from methyl alcohol.

*2-Hydroxy-5-phenylazobenzene.*—Diazotised aniline (1 mol.) was added to a cooled solution of 4-hydroxydiphenyl in dilute aqueous sodium hydroxide. The reddish-brown deposit that formed immediately was filtered off, washed with water, and recrystallised from alcohol, being obtained as brick-red needles, m. p. 129° (Found : C, 78.45; H, 5.2.  $C_{18}H_{14}ON_2$  requires C, 78.8; H, 5.1%).

This compound was reduced by sodium hyposulphite to 3-amino-4-hydroxydiphenyl, m. p. 208° after crystallisation from chloroform. This value agrees with that given by Raiford and so also does that for the diacetyl derivative.

*4-Hydroxy-3(?)-aldehydodiphenyl.*—4-Hydroxydiphenyl (16 g.) was heated under reflux for 3 hours with a mixture of chloroform (20 g.), sodium hydroxide (20 g.), and water (500 c.c.) and the solution was filtered hot. The residue was dissolved in boiling water, and the filtered solution decomposed with hydrochloric acid. The precipitated aldehyde crystallised from alcohol in pale yellow plates, m. p. 102° (Found : C, 79.0; H, 5.3.  $C_{13}H_{10}O_2$  requires C, 78.8; H, 5.1%), which gave an intense violet coloration with ferric chloride. The *phenylhydrazone*, precipitated on addition of phenylhydrazine to a warm alcoholic solution of the aldehyde, crystallised from benzene in needles, m. p. 210° (Found : C, 79.5; H, 5.9.  $C_{19}H_{16}ON_2$  requires C, 79.2; H, 5.5%).

*Attempted Resolution of Diphenic Acid.*—The brucine and quinine salts of diphenic acid were crystallised from various solvents without any sign of resolution being observed. The  $\alpha$ -phenylethylamine salt was obtained as a viscous oil. The strychnine, morphine, and brucine salts of methyl hydrogen diphenate were crystallised from various solvents, but no resolution could be detected. The quinine salt was obtained as a gum.

*Nitration of 4-Methoxydiphenyl.*—To a solution of 4-methoxydiphenyl (7.4 g.) in acetic anhydride (40 c.c.) was added nitric acid (*d* 1.5; 2 c.c.) in acetic anhydride (8 c.c.). Reaction took place with evolution of heat, and after 1 hour the mixture was poured into water. Repeated crystallisation of the precipitated nitro-compounds from alcohol gave 4.2 g. (45%) of 3-nitro-4-methoxydiphenyl. On evaporation of the mother-liquor 5 g. of material, m. p. 50—75°, were obtained. This could not be purified

by further crystallisation and therefore was renitrated in a mixture of nitric acid ( $d$  1.42; 10 c.c.) and acetic acid (10 c.c.). When reaction was complete the mixture was poured into water, and the precipitate, m. p. 125—135°, boiled with alcohol (200 c.c.). The residue, after repeated crystallisation from benzene, acetic acid, or chloroform, melted at 163—166°, but analysis showed that it was contaminated with mononitro-derivatives. It was therefore warmed for a few minutes with nitric acid; an apparently uniform product, m. p. 171°, was then obtained. No other compound could be isolated from the more soluble material (2.5 g., m. p. 125—150°). Addition of nitric acid (1 mol.) to a solution of 4'-nitro-4-methoxydiphenyl in acetic anhydride gave a quantitative yield of the product, m. p. 171°, which was also obtained in 50% yield by treating 3-nitro-4-methoxydiphenyl with warm nitric acid ( $d$  1.42), its identity as 3 : 4'-dinitro-4-methoxydiphenyl thus being established (Found : C, 56.4; H, 3.6.  $C_{13}H_{10}O_5N_2$  requires C, 56.9; H, 3.7%).

Since, under the conditions of the nitration of the product, m. p. 50—75°, 3-nitro-4-methoxydiphenyl suffers only 25% conversion into 3 : 4'-dinitro-4-methoxydiphenyl, it is apparent that the mixture, m. p. 50—75°, must contain about 25% of 4'-nitro-4-methoxydiphenyl. The results indicate that 4-methoxydiphenyl on nitration gives approximately 80% of 3-nitro-4-methoxydiphenyl and 15% of 4'-nitro-4-methoxydiphenyl.

*3-Nitro-4-methoxydiphenyl*, obtained by boiling a solution of 3-nitro-4-hydroxydiphenyl in xylene with potassium carbonate and methyl sulphate, crystallised from alcohol in small needles, m. p. 91—92° (Found : C, 68.3; H, 4.7.  $C_{13}H_{11}O_3N$  requires C, 68.1; H, 4.8%).

*4'-Nitro-4-methoxydiphenyl*.—Small quantities of methyl sulphate and potassium hydroxide were added to a hot solution of 4'-nitro-4-hydroxydiphenyl in dilute aqueous potassium hydroxide until the red colour disappeared; the suspension was filtered hot. The precipitated *4'-nitro-4-methoxydiphenyl* crystallised from alcohol in long, yellow needles, m. p. 111° (Found : C, 68.5; H, 4.9.  $C_{13}H_{11}O_3N$  requires C, 68.1; H, 4.8%).

*3 : 5-Dinitro-4-methoxydiphenyl*, obtained by boiling a solution of 3 : 5-dinitro-4-hydroxydiphenyl in xylene with potassium carbonate and methyl sulphate, crystallised from alcohol in silky, yellow needles, m. p. 137—138° (Found : C, 56.8; H, 3.7.  $C_{13}H_{10}O_5N_2$  requires C, 56.9; H, 3.7%).

*4'-Nitro-4-hydroxydiphenyl*.—4'-Nitro-4-aminodiphenyl (6 g.) was dissolved in boiling dilute hydrochloric acid (500 c.c. of 1%), the clear solution rapidly cooled to 10°, and sodium nitrite (2.4 g.) added. After standing for 1 hour with occasional shaking, the

solution was filtered, dilute sulphuric acid added, and the bulky precipitate of the diazonium sulphate decomposed by passing in steam. The precipitate thus obtained was filtered off and extracted with boiling dilute aqueous potassium hydroxide. The extract was acidified with hydrochloric acid and the crude nitrophenol thus precipitated was filtered off and boiled with alcohol (100 c.c., which leaves any dinitrophenol undissolved), and the filtered alcoholic extract was evaporated to dryness. The residue was crystallised from benzene; 4'-nitro-4-hydroxydiphenyl was then obtained in lustrous, yellow needles, m. p. 203° (yield, 60%) (Found: C, 67·3; H, 4·4.  $C_{12}H_9O_3N$  requires C, 67·0; H, 4·2%).

3 : 4'-Dinitro-4-hydroxydiphenyl, prepared by adding a slight excess of sodium nitrite to a solution of 4'-nitro-4-hydroxydiphenyl in warm acetic acid, crystallised from acetic acid in small needles, m. p. 172° (Found: C, 55·6; H, 3·1.  $C_{12}H_8O_5N_2$  requires C, 55·4; H, 3·1%). Further nitration gave 3 : 5 : 4'-trinitro-4-hydroxydiphenyl. The dinitro-compound reacted with *p*-toluenesulphonyl chloride in pyridine solution and gave a *p*-toluenesulphonate which crystallised from benzene-light petroleum in star-shaped clusters of needles, m. p. 147—148° (Found: C, 54·7; H, 3·5; N, 6·5.  $C_{19}H_{14}O_7N_2S$  requires C, 55·1; H, 3·4; N, 6·75%).

(3 : 5 ?)-Dibromo-4'-nitro-4-hydroxydiphenyl.—4'-Nitro-4-hydroxydiphenyl (1 g.) was heated under reflux with a solution of bromine (2 g.) in chloroform (20 c.c.). The crystals which gradually formed were filtered off and when recrystallised from benzene gave small needles, m. p. 232—234° (Found: C, 39·0; H, 1·9.  $C_{12}H_7O_3NBr_2$  requires C, 38·6; H, 1·9%).

4-*p*-Toluenesulphonyloxydiphenyl, prepared by the interaction of 4-hydroxydiphenyl and *p*-toluenesulphonyl chloride in pyridine solution, crystallised from acetic acid in lustrous plates, m. p. 177° (Found: C, 70·5; H, 5·2.  $C_{19}H_{16}O_3S$  requires C, 70·4; H, 4·9%).

4-*p*-Toluenesulphonyloxy-4'-nitrodiphenyl.—(a) 2·5 G. of the preceding compound were added to a warmed mixture of nitric acid (*d* 1·5; 2·5 c.c.) and acetic acid (3 c.c.) and after  $\frac{1}{2}$  hour the clear solution was poured on to ice. The precipitated plastic mass was extracted with a little hot alcohol to remove impurities. The residue crystallised from benzene-light petroleum in compact needles, m. p. 156—158° (Found: C, 62·3; H, 4·3.  $C_{19}H_{15}O_5NS$  requires C, 61·8; H, 4·1%).

(b) 4'-Nitro-4-hydroxydiphenyl (1 g.) was warmed for 4 hours with a solution of *p*-toluenesulphonyl chloride (1 g.) in diethylaniline (5 c.c.). The solution was digested with hydrochloric acid and filtered; the residue, after crystallisation from benzene, melted at 159°.

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