

196. *Conversion of Hydroaromatic into Aromatic Compounds. Part V. The Influence of the Methyl Group in 5-Phenyl-2-methyldihydroresorcinol.*

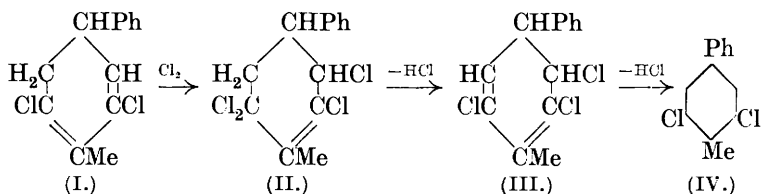
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DIMETHYLDIHYDRORESORCINOL reacts readily with phosphorus trichloride (Crossley and Le Sueur, J., 1903, **83**, 110), but its 2-chloro-derivative is not reacted upon to any appreciable extent even when heated with a large excess of either phosphorus trichloride or oxychloride (Hinkel and Williams, J., 1922, **121**, 2498). In its behaviour with phosphorus pentachloride the chloro-derivative again exhibits a marked difference from dimethyldihydroresorcinol by giving rise to a mixture of chlorinated products (*idem, ibid.*). These peculiarities were ascribed to the presence of the substituent in the 2-position. Similarly, the introduction of a 2-methyl group into a dihydroresorcinol causes the appearance of properties foreign to the general class of dihydroresorcinols, since those containing such a group are unstable on keeping (Vorländer and Erig, *Annalen*, 1897, **294**, 302; Becker and Thorpe, J., 1922, **121**, 1305; Mattar, Hastings, and Walker, J., 1930, 2459) and also give anomalous results on hydrolysis, the reactions being obscured by early secondary reactions (Hinkel, Ayling, Dippy, and Angel, J., 1931, 814). In view of these anomalies a general study of these 2-substituted dihydroresorcinols has been instituted. Since phenyldihydroresorcinol is comparable to some extent with the dimethyl compound in behaviour and a method exists for the ready preparation of 5-phenyl-2-methyldihydroresorcinol (*loc. cit.*), the behaviour of the latter towards the chlorides of phosphorus has been investigated, in order to ascertain whether the influence of a 2-methyl group extends to affect the reactions of a dihydroresorcinol in a manner similar to that of the 2-chloro-substituent.

Although 5-phenyl-2-methyldihydroresorcinol is not strictly comparable with 2-chloro-5:5-dimethyldihydroresorcinol, since the phenyl and *gem*-dimethyl groups themselves cause some differences in the behaviour of the corresponding dihydroresorcinols, yet the 2-methyl in the former does exert an influence of the same character as the 2-chloro-atom in the latter. Thus, whereas the action of either phosphorus trichloride or oxychloride on the former gives the corresponding chloro-ketone, though in small yield, the chloro-ketone does not react with chlorine or bromine in the cold and in this respect resembles the chloro-ketone derived from 2-chloro-5:5-dimethyldihydroresorcinol (Hinkel and Williams, *loc. cit.*).

Again, unlike the previous dihydroresorcinols studied (Hinkel and Hey, J., 1928, 2789; Hinkel and Dippy, J., 1930, 1389), phenyl-methyldihydroresorcinol does not lend itself under similar conditions to the ready conversion into the corresponding dichloro-*cyclohexadiene*. When heated with 1.5 or 2 molecules of phosphorus pentachloride, a large amount of the dihydroresorcinol is recovered unchanged and the product consists of a mixture of the chloro-ketone, dichloro-*cyclohexadiene*, and methyl-dichlorodiphenyl from which the hexadiene cannot be readily separated (compare Crossley and Le Sueur, J., 1903, 83, 121). When the quantity of phosphorus pentachloride is increased to 2.5 molecules, the main product is the methyl-dichlorodiphenyl (compare Crossley, J., 1902, 81, 1533). If the action of the phosphorus pentachloride is moderated by admixture with phosphorus oxychloride, a mixture is obtained from which the hexadiene can be obtained in an almost pure state.

Excess of chlorine at room temperature reacts with the hexadiene (I) to give a liquid which is probably the trichloro-derivative (III) formed through an unstable intermediate (II). The trichloro-derivative (III) readily loses hydrogen chloride when heated, yielding 3:5-dichloro-4-methyldiphenyl (IV).



This reaction is similar to the chlorinations of phenyl- and *m*-nitrophenyl-dichloro-*cyclohexadienes* at room temperature (Hinkel and Hey, Hinkel and Dippy, *loc. cit.*), except that in these cases all the intermediate compounds are unstable.

The constitution of 3:5-dichloro-4-methyldiphenyl was proved by converting its mononitro-derivative into the amine, which on

oxidation gave 3 : 5-dichloro-4-methylbenzoic acid. The methyl group of the dichloromethyldiphenyl resists oxidation by the usual methods, owing probably to a screening effect of the two *o*-chlorine atoms.

EXPERIMENTAL.

Action of the Chlorides of Phosphorus on 5-Phenyl-2-methyldihydroresorcinol.—(a) *Phosphorus trichloride.* A suspension of 5-phenyl-2-methyldihydroresorcinol (74 g.; 2 mols.) in dry chloroform (210 c.c.) was heated under reflux with phosphorus trichloride (18 c.c.; slight excess of 1 mol.) for 6 hours. The chloroform was removed, and the residue added to water and extracted with ether. The ethereal solution, washed with 4% sodium hydroxide solution, then with water and dried, yielded, upon evaporation of the ether, a residue which solidified below 0° and crystallised from well-cooled light petroleum (b. p. 40—60°) in small white prisms of 5-chloro-1-phenyl-4-methyl- Δ^4 -cyclohexen-3-one, m. p. 36°, b. p. 179—180°/10 mm. (Found : Cl, 16.35. $C_{13}H_{13}OCl$ requires Cl, 16.1%). Yield : 16 g.; 20%.

(b) *Phosphorus oxychloride.* Similar treatment (dihydroresorcinol, 12 g., 1 mol.; chloroform, 35 c.c.; phosphorus oxychloride, 6 c.c., slight excess of 1 mol.) yielded 2 g. (16%) of the chlorophenyl-methylcyclohexenone.

(c) *Phosphorus pentachloride.* To a mixture of the dihydroresorcinol (40 g.; 1 mol.) and chloroform (100 c.c.), phosphorus pentachloride (100 g.; 2.5 mols.) was added gradually, and the mixture heated for 2 hours. The chloroform was removed by distillation, and the residue poured on ice and extracted with ether. The ethereal solution after the treatment described under (a) yielded 3 : 5-dichloro-4-methyldiphenyl (22 g.; 42%), which crystallised from alcohol in hair-like needles, m. p. 62°, b. p. 183—184°/11 mm. (Found : Cl, 30.2. $C_{13}H_{10}Cl_2$ requires Cl, 30.0%).

(d) *Phosphorus pentachloride and oxychloride.* The pentachloride (68 g.; 1.7 mols.) was added in small quantities to a well-cooled mixture of the dihydroresorcinol (40 g.; 1 mol.), chloroform (120 c.c.), and phosphorus oxychloride (26 g.; 1.5 mols.), and the whole heated for 1 hour on the water-bath. The subsequent procedure was as in (c). The resulting liquid residue was fractionally distilled under reduced pressure until a liquid, b. p. 163—166°/10 mm., was obtained: this consisted mainly of 3 : 5-dichloro-1-phenyl-4-methyl- $\Delta^{2:4}$ -cyclohexadiene (Found : Cl, 28.6. $C_{13}H_{12}Cl_2$ requires Cl, 29.7%).

The low chlorine value is probably due to the presence of some chloro-ketone, since a higher fraction, b. p. 170—177°/10 mm., though still containing some of the hexadiene, as shown by absorption of bromine, had a chlorine content of 21%, midway between that

of the chloro-ketone and the hexadiene (16.1 and 29.7%), and slowly deposited the chloro-ketone, m. p. 36°, on seeding with a crystal of the latter. The final fraction, b. p. above 180°/10 mm., on cooling in ice and salt, deposited the dichloromethyldiphenyl, m. p. 62°.

Action of Chlorine on 3 : 5-Dichloro-1-phenyl-4-methyl- $\Delta^{2:4}$ -cyclohexadiene.—The above liquid, b. p. 163—166°/10 mm., was dissolved in an equal volume of chloroform, and chlorine passed into the solution at room temperature. Heat was generated and copious evolution of hydrogen chloride occurred. When chlorine was no longer absorbed, the liquid was heated on a steam-bath to remove chloroform and hydrogen chloride. The residual liquid, consisting of 2 : 3 : 5-trichloro-1-phenyl-4-methyl- $\Delta^{3:5}$ -cyclohexadiene, was kept over solid sodium hydroxide in a vacuum desiccator for several days (Found : Cl, 35.0. $C_{13}H_{11}Cl_3$ requires Cl, 38.9%). The low chlorine value is probably due to the presence of the small quantity of chloro-ketone in the original hexadiene and also to partial decomposition. The liquid lost hydrogen chloride at its boiling point : the residue, crystallised from alcohol, melted at 62° and was identical with 3 : 5-dichloro-4-methyldiphenyl (p. 1470).

3 : 5-Dichloro-4' (?) -nitro-4-methyldiphenyl.—To a solution of 3 : 5-dichloro-4-methyldiphenyl (10 g.) in glacial acetic acid (25 c.c.), a mixture of nitric acid (*d* 1.5; 75 c.c.) and glacial acetic acid (75 c.c.) was slowly added. After shaking for some time a solid separated, addition of water and crystallisation from alcohol yielding 3 : 5-dichloro-4' (?) -nitro-4-methyldiphenyl in colourless hair-like needles, m. p. 157° (Found : Cl, 25.3. $C_{13}H_9O_2NCl_2$ requires Cl, 25.2%). Yield : 10 g.; 82%.

3 : 5-Dichloro-4' (?) -amino-4-methyldiphenyl.—A mixture of 3 : 5-dichloro-4' (?) -nitro-4-methyldiphenyl (8.1 g.) in alcohol (120 c.c.) and stannous chloride (40 g.) in concentrated hydrochloric acid (40 c.c.) was heated under reflux on a steam-bath for 3 hours. Removal of alcohol, addition of excess of sodium hydroxide solution, and extraction with ether finally yielded 3 : 5-dichloro-4' (?) -amino-4-methyldiphenyl, which crystallised from benzene-light petroleum (b. p. 40—60°) in small laminæ, m. p. 131° (Found : Cl, 28.5. $C_{13}H_{11}NCl_2$ requires Cl, 28.2%). The *acetyl* derivative, obtained in the usual manner, crystallised from alcohol in colourless needles, m. p. 252—253° (Found : Cl, 24.6. $C_{15}H_{13}ONCl_2$ requires Cl, 24.3%).

Oxidation of 3 : 5-Dichloro-4' (?) -amino-4-methyldiphenyl.—The amino-compound and chromic anhydride were heated in acetic acid under reflux, water added, the solid that separated after several days dissolved in aqueous sodium carbonate, and the filtered solution acidified; 3 : 5-dichloro-4-methylbenzoic acid separated as a white amorphous solid, m. p. 185° (Claus and Böcher, *Annalen*, 1891,

265, 361, record m. p. 188°) (Found: equiv., by titration with baryta, 199. Calc., 205).

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