CCCLXVIII.—*Conversion of Hydroaromatic into Aromatic Compounds. Part III. 3 : 5-Dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene and its Behaviour with Chlorine.*

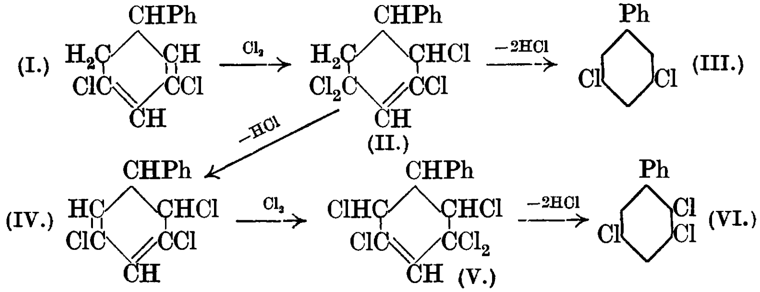
By LEONARD ERIC HINKEL and DONALD HOLROYDE HEY.

IN previous papers (J., 1924, **125**, 1847; this vol., p. 1200) it has been shown that halogenated derivatives of phenyldihydroresorcinol are converted into aromatic compounds much more readily than the corresponding derivatives of dimethyldihydroresorcinol. For instance, 4 : 5 : 5-tribromo-1-phenyl*cyclo*hexan-3-one readily yields an aromatic compound directly, whereas 4 : 5 : 5-trichloro-1 : 1-dimethyl*cyclo*hexan-3-one only does so through the stable intermediate 4 : 5-dichloro-1 : 1-dimethyl-Δ^5-*cyclo*hexen-3-one; and 4 : 5 : 5 : 6-tetrabromo-1-phenyl*cyclo*hexan-3-one yields 4 : 5-dibromo-3-hydroxydiphenyl directly, whereas 4 : 5 : 5 : 6-tetrachloro-1 : 1-dimethyl*cyclo*hexan-3-one readily changes into the stable intermediate 4 : 5 : 6-trichloro-1 : 1-dimethyl-Δ^5-*cyclo*hexen-3-one. Moreover, cleavage of the ring by hydrolysis cannot be achieved in dimethyldihydroresorcinol, but can be readily effected in the case of phenyldihydroresorcinol (Vorländer, *Annalen*, 1897, **294**, 317; *Ber.*, 1894, **27**, 2057; compare also Crossley, J., 1901, **79**, 138).

The greater readiness with which the derivatives of phenyldihydroresorcinol are converted into aromatic compounds is only to be expected, since in the one case the transformation necessitates the migration of a methyl group, whereas in the other the more mobile hydrogen atom is involved, and this is further borne out in the present investigation on 3 : 5-*dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene* (I).

Knoevenagel (*Ber.*, 1894, **27**, 2337) isolated a liquid impure dichlorophenyl*cyclo*hexadiene by the action of phosphorus pentachloride (2 mols.) on phenyldihydroresorcinol, but the structure he assigned to it is no longer tenable (compare Crossley and Le Sueur, J., 1902, **81**, 821). Since both di- and tri-methyldihydroresorcinols on treatment with phosphorus pentachloride give, in addition to a dichloro*cyclo*hexadiene, 3 : 5-dichloro-*o*-xylene and 3 : 5-dichloro-1 : 2 : 6-trimethylbenzene, respectively (Crossley and Le Sueur, J., 1902, **81**, 1533; Crossley and Hills, J., 1906, **89**, 875), 3 : 5-dichlorodiphenyl (III) should in like manner be formed during the action of phosphorus pentachloride on phenyldihydroresorcinol. This has now been shown to be the case. The main product of the action, however, is 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene (I). This compound readily absorbs chlorine, and the *tetrachloro*-compound (II) produced rapidly loses hydrogen chloride (2 mols.) on warming, giving an 80% yield of 3 : 5-dichlorodiphenyl (III). The constitution of (III) has been established by its synthesis as carried out by Scarborough and Waters (J., 1927, 89), who describe it as an oil. The compound has now been obtained by both methods as a crystalline solid.

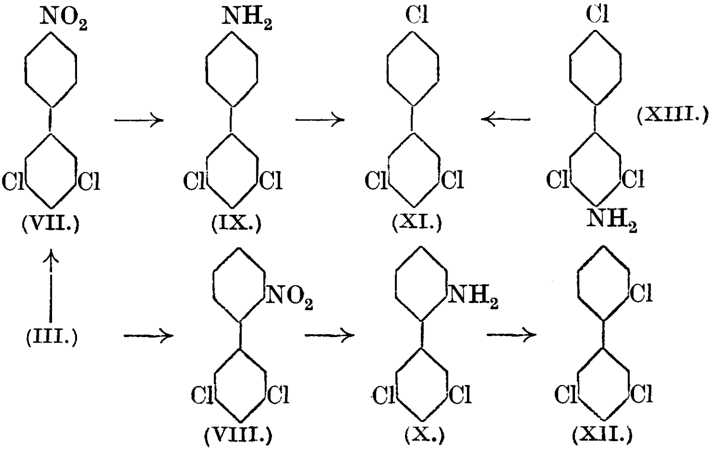
When an excess of chlorine is passed into a hot solution of 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene in chloroform, in addition to 3 : 5-dichlorodiphenyl, a small quantity of 2 : 3 : 5-*trichlorodiphenyl* (VI) is produced, the constitution of which has been confirmed by its synthesis from 3 : 5-dichloro-2-aminodiphenyl. Its formation is explained in the following manner. Loss of one molecule of hydrogen chloride from the tetrachloro-compound (II) gives the trichloro-compound (IV). This may partly lose hydrogen chloride to give 3 : 5-dichlorodiphenyl or may further combine with chlorine, giving an unstable pentachloro-compound (V), which readily loses hydrogen chloride to give 2 : 3 : 5-trichlorodiphenyl (VI) (compare Crossley, J., 1904, **85**, 264; Hinkel, J., 1920, **117**, 1296).



In marked contrast with the action of chlorine on 3 : 5-dichloro-1 : 1-dimethyl-$\Delta^{2:4}$-*cyclo*hexadiene (Hinkel, *loc. cit.*), which gives rise to a pentachlorodimethyl*cyclo*hexene in addition to the two trichloro-*o*-xylenes and tetrachloro-*o*-xylene, no such higher chlorinated products could be obtained in the present investigation. The course of the reactions during the two chlorinations again reveals the influence of the phenyl group in a remarkable manner. In the derivatives of phenyldihydroresorcinol the group $\cdot CCl{:}CH\cdot CCl_2\cdot$ (compounds II and V), although unsaturated, does not further combine with chlorine, whereas in the corresponding derivatives of dimethyldihydroresorcinol further chlorination readily occurs, producing more highly chlorinated derivatives. Since the transformation from the hydroaromatic series yields diphenyl derivatives with substituents in only one of the two rings, such reactions serve as a convenient method for the preparation of diphenyl derivatives of this type.

The separation of the chlorodiphenyls (III) and (VI) obtained as described above is conveniently effected by regulated oxidation with chromic and acetic acids, which converts the dichlorodiphenyl into 3 : 5-dichlorobenzoic acid : the stability of the diphenyl nucleus to oxidation by chromic acid is increased by the introduction of negative substituents, even although these are all in the same ring. A separation may also be effected by means of their nitro-derivatives.

Nitration of 3 : 5-dichlorodiphenyl gives chiefly 3 : 5-*dichloro*-4′-*nitrodiphenyl* (VII) with a smaller quantity of 3 : 5-*dichloro*-2′-*nitrodiphenyl* (VIII). On prolonged boiling (16 hours) with chromic and acetic acids the former gives a small quantity of *p*-nitrobenzoic acid and 3 : 5-dichloro-2′-nitrodiphenyl partly decomposes completely and partly remains unattacked. That in both compounds the nitro-group is in the ring not containing the chlorine atoms is shown by (*a*) oxidation of the corresponding *amines* (IX and X) giving 3 : 5-dichlorobenzoic acid and (*b*) the chlorine atoms being inert towards piperidine (see Le Fèvre and Turner, J., 1927, 1113; this vol., p. 247). The identity of 3 : 5-dichloro-4′-nitrodiphenyl was proved by reduction and conversion of the base into a *trichlorodiphenyl* (XI), m. p. 88°, which was identical with the compound obtained by the elimination of the amino-group from 3 : 5 : 4′-trichloro-4-aminodiphenyl (XIII). The isomeric dichloronitrodiphenyl gave a *trichlorodiphenyl* melting at 58° (XII).



Nitration of 2 : 3 : 5-trichlorodiphenyl readily gives a mononitro-compound which, owing to its exceptional stability towards oxidation by chromic acid and its inertness towards piperidine, is regarded as 2 : 3 : 5-*trichloro-4′-nitrodiphenyl.*

These results of substitution are in agreement with the tentative rules that have been proposed for the orientation of substituents in the diphenyl series (Scarborough and Waters, J., 1926, 557; Blakey and Scarborough, J., 1927, 3000).

EXPERIMENTAL.

Action of Phosphorus Pentachloride on Phenyldihydroresorcinol.—Phenyldihydroresorcinol (94 g.; 1 mol.) was suspended in 200 c.c. of dry chloroform, and phosphorus pentachloride (220 g.; in excess of 2 mols.) gradually added; after an hour the reaction was completed by gentle warming. The chloroform was removed under reduced pressure, and the residue poured on ice and extracted with ether. From the extract, washed with 10% sodium hydroxide solution and with water and dried, 3 : 5-*dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene* (I) (70 g.) was obtained as a colourless oil, b. p. 156°/10 mm. (Found: Cl, 31·2. $C_{12}H_{10}Cl_2$ requires Cl, 31·55%), and also 3 : 5-dichlorodiphenyl, b. p. 166°/10 mm., m. p. 36° (Found: Cl, 31·8. Calc.: Cl, 31·8%).

Action of Chlorine on 3 : 5-*Dichloro*-1-*phenyl*-$\Delta^{2:4}$-cyclo*hexadiene*.—(1) *At room temperature.* Chlorine was slowly passed for 2 hours into a solution of 65 g. of 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene in 50 c.c. of dry chloroform cooled by water. After the evolution of hydrogen chloride had ceased, the chloroform was removed on a boiling water-bath, and the residue left for several days in a vacuum over solid sodium hydroxide. The solution was distilled under reduced pressure and two fractions were collected: (i) b. p. 164—166°/9 mm. (52 g.) and (ii) b. p. 166—200°/9 mm. (14 g.). The main fraction solidified in a freezing mixture, and crystallisation from cold alcohol gave 3 : 5-dichlorodiphenyl as snow-white needles which, alone or mixed with the synthetic product obtained from 3 : 5-dichloro-2-aminodiphenyl (Scarborough and Waters, J., 1927, 89), melted at 36°. Oxidation with chromic and acetic acids gave 3 : 5-dichlorobenzoic acid (m. p. 183°). Fraction (ii) was added to the fractions obtained from the chlorination at the higher temperature.

(2) *In hot solution.* A rapid stream of chlorine was passed into a hot solution of 3 : 5-dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene (56 g.) in dry chloroform (60 c.c.) until the copious evolution of hydrogen chloride had ceased and the solution had regained normal temperature. After removal of the chloroform, the oily residue was dis-

tilled under reduced pressure and three fractions were collected, b. p. 170—175°, 175—180°, and 180—200°/10 mm., respectively. The fraction of b. p. 170—175°/10 mm. (35 g.) gave mainly 3 : 5-dichlorodiphenyl on redistillation. The fraction of b. p. 180—200°/10 mm. was boiled for 6 hours with an excess of chromic acid in glacial acetic acid solution. The solid obtained by dilution with water, after crystallising several times from aqueous alcohol, gave 2 : 3 : 5-trichlorodiphenyl in small, white needles which, alone or mixed with the trichlorodiphenyl obtained from 3 : 5-dichloro-2-aminodiphenyl (Scarborough and Waters, *loc. cit.*) by the Sandmeyer reaction, melted at 41° (Found : Cl, 41·4. $C_{12}H_7Cl_3$ requires Cl, 41·35%). A small quantity of 3 : 5-dichlorobenzoic acid was obtained from the mother-liquor. Treatment of the fraction of b. p. 175—180°/10 mm. in like manner also gave 2 : 3 : 5-trichlorodiphenyl.

Action of Nitric Acid on the Fraction of b. p. 175—180°/10 *mm.*—5 G. of the fraction, dissolved in glacial acetic acid, were gradually treated with 25—30 c.c. of nitric acid (*d* 1·51). The solution, after being warmed, was poured into water and the solid which separated was crystallised repeatedly from alcohol. A small quantity of 2 : 3 : 5-trichloro-4′-nitrodiphenyl and mainly 3 : 5-dichloro-4′-nitrodiphenyl were isolated from the less soluble portions, and concentration of the mother-liquor yielded a small quantity of 3 : 5-dichloro-2′-nitrodiphenyl.

Nitration of 3 : 5-*Dichlorodiphenyl.*—5 G. of 3 : 5-dichlorodiphenyl, dissolved in 12 c.c. of glacial acetic acid, were nitrated by the gradual addition of 50 c.c. of a mixture of equal volumes of fuming nitric and glacial acetic acids. The solid which separated after the addition of water was crystallised from alcohol, 3 : 5-*dichloro*-4′-*nitrodiphenyl* being obtained in small, faintly yellow needles, m. p. 146° (Found : Cl, 26·6. $C_{12}H_7O_2NCl_2$ requires Cl, 26·5%). 3 : 5-*Dichloro-2′-nitrodiphenyl* separated from the mother-liquor and on recrystallisation was obtained in needles, m. p. 75° (Found : Cl, 26·4%).

3 : 5-*Dichloro*-4′-*aminodiphenyl.*—2 G. of 3 : 5-dichloro-4′-nitrodiphenyl, dissolved in 30 c.c. of alcohol, were reduced with 10 g. of stannous chloride in 10 c.c. of concentrated hydrochloric acid. The mixture was heated for several hours on the water-bath and, after evaporation of the alcohol, the *base*, liberated by addition of sodium hydroxide solution, was extracted with ether; it crystallised from aqueous alcohol in flat acicular plates, m. p. 124° (Found : Cl, 29·9. $C_{12}H_9NCl_2$ requires Cl, 29·8%). 3 : 5-*Dichloro*-4′-*acetamidodiphenyl*, prepared from the base in the usual manner, crystallised from alcohol in small white needles, m. p. 188° (Found : Cl, 25·5. $C_{14}H_{11}ONCl_2$ requires Cl, 25·4%).

3 : 5-*Dichloro-2′-aminodiphenyl*, obtained from the corresponding nitro-compound by reduction with stannous chloride in alcoholic solution as described above, separated from aqueous alcohol in needles, m. p. 74° (Found : Cl, 29·8%). Acetylation gave 3 : 5-*dichloro-2′-acetamidodiphenyl*, which crystallised from alcohol in small acicular plates, m. p. 163° (Found : Cl, 25·6%).

3 : 5 : 4′-*Trichlorodiphenyl*.—4 G. of 3 : 5-dichloro-4′-aminodiphenyl were diazotised in hydrochloric acid solution at 0° and then treated with cuprous chloride solution in the usual manner. On distillation with steam 3 : 5 : 4′-*trichlorodiphenyl* was obtained which separated from alcohol in white glistening needles, m. p. 88° (Found : Cl, 41·3. $C_{12}H_7Cl_3$ requires Cl, 41·35%).

3 : 5 : 2′-*Trichlorodiphenyl*.—4 G. of 3 : 5-dichloro-2′-aminodiphenyl were diazotised and treated as described above. The product crystallised from alcohol in faintly yellow needles, m. p. 58° (Found : Cl, 41·4%).

Nitration of 2 : 3 : 5-*Trichlorodiphenyl*.—Fuming nitric acid was gradually added to a solution of 2 : 3 : 5-trichlorodiphenyl in glacial acetic acid. 2 : 3 : 5-*Trichloro-4′-nitrodiphenyl*, obtained by diluting the solution with water, crystallised from alcohol in long, yellow needles, m. p. 155° (Found : Cl, 35·1. $C_{12}H_6O_2NCl_3$ requires Cl, 35·2%).

UNIVERSITY COLLEGE, SWANSEA.

[*Received, July 24th*, 1928.]