315. *The Reaction of Chlorobenzene with Methyl Radicals.*

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Chlorobenzene reacts with free methyl radicals, generated by thermal decomposition of di-*tert.*-butyl peroxide, to give a complex mixture from which a small quantity of 3 : 3′-dichloro-4 : 4′-dimethyldiphenyl has been isolated. The presence of chlorotoluenes has been detected by vapour-phase chromatography, and confirmed chemically in the case of the *para*-isomer.

3 : 3′-Dichloro-4 : 4′-dimethyldiphenyl, 1 : 2-di-(*p*-chlorophenyl)propane, and some related compounds have been synthesised by conventional methods, and 4 : 4′-dichlorodibenzyl has been prepared by dimerisation of 4-chlorobenzyl radicals.

In a recent investigation [1] of the reactions between anthracene and free methyl radicals, generated by the thermal decomposition of di-*tert.*-butyl peroxide, we found that chlorobenzene was not entirely satisfactory as a solvent since when heated with the peroxide it gave a high-boiling residue, which was separated chromatographically into a yellow amorphous powder and some colourless oils with odours similar to those of the chlorinated diaryls.

From the oily residue of the direct decomposition of di-*tert.*-butyl peroxide in purified chlorobenzene we have now isolated small amounts of a crystalline compound, $C_{14}H_{12}Cl_2$, and this has also been obtained from the reaction of 9 : 10-diphenylanthracene with methyl radicals in chlorobenzene.[2] The infrared spectrum indicated that this product contained 1 : 2 : 4-trisubstituted benzene nuclei and the ultraviolet spectrum was consistent with its formulation as a diphenyl derivative with unsubstituted 2- and 2′-positions. Independent synthesis from 2-chloro-4-iodotoluene shows that it is 3 : 3′-dichloro-4 : 4′-dimethyldiphenyl (III).

The isolation of the substance (III) shows that the attack of free methyl radicals on chlorobenzene occurs, as in methylation of anthracene,[1] by primary *addition* of methyl to give (I), which then dimerises to (II) and is dehydrogenated to (III).

By analogy with the phenylation of chlorobenzene [3] it would be expected that the

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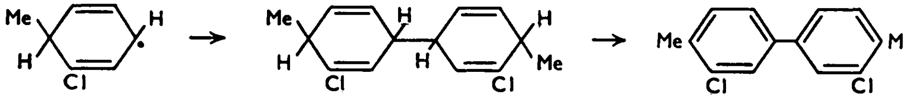
[1] Beckwith and Waters, *J.*, 1956, 1108.
[2] Beckwith and Waters, unpublished work.
[3] Augood, Hey, and Williams, *J.*, 1953, 44.

radical (I) would be formed together with *meta*- and *para*-isomers, but just as the early work on the phenylation of compounds C_6H_5R yielded only the least soluble isomer [4] so it appears that the product (III) has been isolated because it is the most symmetrical one of the diphenyl type. Further, addition of methyl radicals to the *meta*- or *para*-position of chlorobenzene would give isomers of radical (I) in which steric hindrance between vicinal



(I) (II) (III)

groups would decrease the probability of dimerisation and subsequent conversion into a di-*ortho*-substituted diaryl. However, various modes of coupling of radical (I) and its isomers may give rise to twenty-one different diphenyl derivatives, and the colourless oils obtained are probably mixtures of such compounds.

In accordance with the mechanism proposed for the methylation of anthracene [1] it would be expected that the radical (I) and its isomers would be converted, by dehydrogenation, into chlorotoluenes. The production of these substances has now been demonstrated by vapour-phase chromatography of the volatile product which gave a curve very similar to that obtained by identical treatment of a mixture of chlorobenzene with *o*- and *p*-chlorotoluene. Unfortunately, the column used was not capable of resolving the chlorotoluene mixture into the separate isomers but the presence of the *para*-compound was confirmed by its oxidation to *p*-chlorobenzoic acid. Several attempts to detect the presence of chloroxylenes were unsuccessful and it appears that, as in the methylation of anthracene, radicals of type (I) do not undergo coupling with a second methyl radical.

The isolation of the above-mentioned products further confirms the general theory that homolytic aromatic substitution occurs by an addition mechanism and that there is no great distinction between the free-radical reactions of alkyl and aryl radicals.

In the Experimental section we also record the syntheses of 1 : 2-di-(*p*-chlorophenyl)-propane and some related compounds by standard methods, and the preparation of 4 : 4'-dichlorodibenzyl by dimerisation of the free *p*-chlorobenzyl radicals produced when di-*tert*.-butyl peroxide is decomposed in *p*-chlorotoluene. These substances were required for comparison with free-radical reaction products.

EXPERIMENTAL

Reaction of Chlorobenzene with Di-tert.-*butyl Peroxide*.—The experiment was conducted as before [1] with 13 g. of the peroxide in purified chlorobenzene (100 ml.). Acetone and *tert*.-butyl alcohol were removed through a fractionating column, and the solvent and remaining volatile products were collected by rapid distillation under reduced pressure. The involatile residue (4·5 g.) was extracted with hot light petroleum (b. p. 40—60°), and the extract was chromatographed on alumina. Elution of the column with 6 : 1 light petroleum–benzene yielded an oil which crystallised from methanol in plates (0·09 g.), m. p. 92°, of 3 : 3'-dichloro-4 : 4'-dimethyldiphenyl (see below). Other fractions were colourless oils (total 1·1 g.) which on oxidation with chromic acid were converted into solid amorphous acids. There was also isolated a yellow gum (2·1 g.) which was precipitated as a powder by the addition of methanol to an ethereal solution.

A sample (20 μl.) of the crude distillate from the free-radical reaction was subjected to vapour-phase chromatography on a column (150 cm. × 6 mm.) packed with a mixture of dinonyl phthalate (45 parts) and graded Celite 545 (100 parts). The column was operated at 130° under reduced pressure with a carrying stream of nitrogen (20 ml./min.), and the fractions were detected by means of a conductivity gauge and recorded graphically. The resultant graph showed an intense peak with a retention time of 25 min. and a very weak band at 47 min. Pure chlorobenzene, similarly treated, showed a single peak at 25 min., while a mixture of equal

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[4] Hey, *J.*, 1934, 1966.

parts of chlorobenzene, *o*-chlorotoluene, and *p*-chlorotoluene gave a peak at 25 min. and a band at 47 min. The areas beneath the curves were approximately proportional to the amounts of materials present.

Chlorobenzene was removed from the crude distillate by slow distillation through a short fractionating column, and a sample (10 µl.) of the residue (3·2 g.) was then chromatographed. Peaks were recorded at 25 and 47 min. and the graph was very similar in general shape to that shown by the mixture of chlorobenzene with chlorotoluenes. It was estimated that the residue contained approximately 2 g. of chlorobenzene and 1 g. of chlorotoluenes.

When a sample (0·24 g.) of the residue was oxidised with hot 5% aqueous potassium permanganate the product was a mixture of solid acids (70 mg.), which after 3 crystallisations from water yielded *p*-chlorobenzoic acid (12 mg.), m. p. and mixed m. p. 237°.

Preparation of Reference Compounds.—*2-Chloro-4-iodotoluene.* 3-Chloro-4-methylaniline [5] (15 g.) in 50% (v/v) hydrochloric acid (150 ml.) was diazotised with sodium nitrite solution and treated under cooling with potassium iodide (30 g.) in water (60 ml.). After being heated on the steam-bath for 1 hr. the mixture was extracted with ether, and the product was isolated by distillation under reduced pressure. The iodo-compound, b. p. 123—124°/20 mm., gave crystals, m. p. 22° (lit.,[6] m. p. 8°) (Found: C, 33·6; H, 2·0; total hal., 64·7. Calc. for C_7H_6ClI: C, 33·3; H, 2·4; total hal., 64·3%).

3 : *3′-Dichloro-4 : 4′-dimethyldiphenyl.* 2-Chloro-4-iodotoluene (7·1 g.) and copper bronze (8 g.; freshly dried) were heated under nitrogen in a metal-bath at 220°. After 1 hr. the cooled mixture was extracted with hot benzene, and the extract was then passed through a short column of alumina. After removal of the solvent the residual 3 : *3′-dichloro-4 : 4′-dimethyldiphenyl* crystallised from methanol in plates (3·2 g., 90%), m. p. 92° (Found: C, 66·9; H, 4·9; Cl, 28·4. $C_{14}H_{12}Cl_2$ requires C, 66·95; H, 4·8; Cl, 28·2%). The compound showed maximum light absorption (ε 19,000) at 2560 Å, characteristic of diaryls with vacant *ortho*-positions [7] and the infrared spectrum had peaks at 11·4 and 12·4 µ indicating the presence of 1 : 2 : 4-trisubstituted benzene nuclei.

1 : *2-Di-*(p-*chlorophenyl*)*propan-2-ol.* *p*-Chloroacetophenone (11 g.) in ether (30 ml.) was added dropwise to the Grignard reagent from 4-chlorobenzyl chloride (11·4 g.) in ether (100 ml.), and the mixture was stirred for 1 hr. and then treated with ammonium chloride solution. 1 : *2-Di-*(p-*chlorophenyl*)*propan-2-ol* (16·5 g., 83%), which was obtained by removal of the solvent from the ethereal solution, crystallised from light petroleum in needles, m. p. 75° (Found: C, 64·2; H, 5·1. $C_{15}H_{14}OCl_2$ requires C, 64·05; H, 5·0%). Attempts to convert this alcohol into the related chloride were unsuccessful. When the crude mixture obtained by passing dry hydrogen chloride into an ethereal solution was treated with zinc dust in hot acetic acid there were produced small amounts of 1 : 2-di-(*p*-chlorophenyl)propene (see below) and crystals (from methyl acetate) of a compound, m. p. 230°, which may be 1 : 2 : 3 : *4-tetra-*(p-*chlorophenyl*)*-2 : 3-dimethylbutane* (Found: C, 68·1; H, 5·05; Cl, 26·3. $C_{30}H_{26}Cl_4$ requires C, 68·2; H, 5·0; Cl, 26·8%).

1 : *2-Di-*(p-*chlorophenyl*)*propene.* Sulphuric acid (1 ml.) was added to the above-mentioned alcohol (5·0 g.) in acetic acid (20 ml.) and the mixture was heated to boiling. 1 : *2-Di-*(p-*chlorophenyl*)*propene* (4·4 g.), which was precipitated by the addition of water to the cooled mixture, crystallised from alcohol in needles, m. p. 110° (Found: C, 68·4; H, 4·5; Cl, 27·0. $C_{15}H_{12}Cl_2$ requires C, 68·45; H, 4·6; Cl, 26·95%). Light absorption in EtOH: max. at 2825 Å (ε 28,400).

1-(p-*Chlorophenyl*)*ethyl chloride.* *p*-Chloroacetophenone (20 g.) in ether (100 ml.) was reduced with lithium aluminium hydride (1·3 g.) in the usual way. The crude alcohol was not purified but was converted into the chloride by treatment with phosphorus pentachloride (35 g.) in benzene (100 ml.).[8] The required product was a liquid, b. p. 58—60°/0·9 mm. (Found: C, 55·2; H, 4·75; Cl, 40·2. Calc. for $C_8H_8Cl_2$: C, 54·9; H, 4·6; Cl, 40·5%).

1 : *2-Di-*(p-*chlorophenyl*)*propane.* 1-(*p*-Chlorophenyl)ethyl chloride (5·4 g.) in benzene (50 ml.) was added to the Grignard reagent from *p*-chlorobenzyl chloride (5·0 g.) in ether (50 ml.), and the mixture was refluxed under nitrogen for 16 hr. The mixture was then treated with dilute hydrochloric acid and, after removal of the solvent, the crude product was chromatographed on alumina. 1 : *2-Di-*(p-*chlorophenyl*)*propane* (3·8 g., 60%), which was

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[5] Schofield, *J.*, 1927, 2903.

[6] Long and Dains, *Univ. Kansas Sci. Bull.*, 1930, **19**, 205.

[7] O'Shaughnessy and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2906.

[8] Woodcock, *J.*, 1949, 203.

eluted with light petroleum, crystallised from methanol in rhombs, m. p. 69° (Found: C, 67·95; H, 5·3; Cl, 26·3. $C_{15}H_{14}Cl_2$ requires C, 67·95; H, 5·2; Cl, 26·75%).

4 : 4′-*Dichlorodibenzyl*. *p*-Chlorotoluene (82 g.) and di-*tert*.-butyl peroxide were refluxed under nitrogen for 22 hr. *tert*.-Butyl alcohol (10·5 g.) was separated by distillation through a fractionating column and unchanged chlorotoluene (66 g.) was removed by steam-distillation. When the residue (12 g.) was distilled under reduced pressure there was obtained 4 : 4′-dichlorodibenzyl (4·1 g.), b. p. 120°/0·2 mm., which crystallised from light petroleum in rhombs, m. p. 102° (Found: C, 67·2; H, 5·0. Calc. for $C_{14}H_{12}Cl_2$: C, 66·95; H, 4·8%).

We are indebted to Messrs. F. Hastings and A. E. Thompson for carrying out the vapour-phase chromatography. One of us (A. L. J. B.) thanks the Commonwealth Scientific and Industrial Research Organisation of Australia for an overseas studentship.

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[*Received, November 29th*, 1956.]