17. *Studies in the Tetraphenylethylene Series. Part I.*

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The action of chlorine and bromine on tetraphenylethylene and some of its derivatives has been investigated. Tetraphenylethylene dichloride has been found to exist in two isomeric forms, which must owe their existence to restriction of rotation about the ethane link. The *cis*-isomer must exist in mirror image forms. Some new halogen derivatives have been made and some inaccurate statements in the literature corrected.

When chlorine is passed into a solution of tetraphenylethylene in carbon tetrachloride or in chloroform, tetraphenylethylene dichloride is produced in good yield. Finkelstein (*Ber.*, 1910, **43**, 1534), however, using carbon tetrachloride as solvent, gives the melting point of the dichloride as 186° (corr.), while Norris (*J. Amer. Chem. Soc.*, 1916, **38**, 710), using chloroform as solvent, gives the melting point of the purified product as 160—162°. This and some other discrepancies in statements made in the literature suggested the desirability of a re-examination of some of the properties of tetraphenylethylene and its derivatives, and particularly their reactions with chlorine and bromine. The preparations quoted above were therefore repeated. When chlorine, in equivalent quantity or in excess, was passed into a solution of tetraphenylethylene in carbon tetrachloride, tetraphenylethylene dichloride was precipitated, and the purified substance melted at 185° (188·5° corr.). When, however, chloroform was used as solvent, the purified product melted at 172° (175° corr.). Repeated crystallisation from various solvents failed to raise the melting point. In both cases the yields were of the order of 90%. A 50% mixture of the two products melted at about 162°.

Analysis, molecular weight determination, and oxidation with chromic acid to benzophenone showed clearly that both substances were dichlorides of tetraphenylethylene, and indeed this has never been questioned in earlier work. They are therefore either dimorphs or isomers.

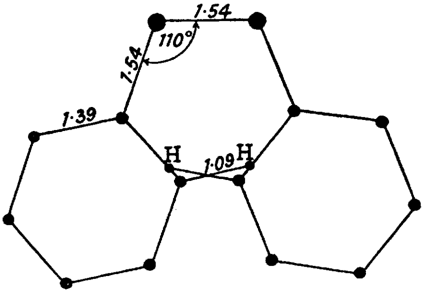
A decision in favour of isomerism was made on the following grounds: (*a*) The substance, m. p. 172°, forms an *addition compound* with carbon tetrachloride containing two molecules of the latter, and a similar *compound* with chloroform. The substance, m. p. 185°, does not form an addition compound with either. (*b*) Sidgwick's method for distinguishing between dimorphs and isomers (*J.*, 1915, **107**, 672) shows the two substances to be isomers. The freezing point of a saturated solution of the more soluble form in benzene is substantially depressed when the less soluble form is added and equilibrium again attained. (*c*) The refractive indices and the dielectric constants of equivalent solutions in benzene are different.

This isomerism can only be due to restriction of rotation about the ethane bond (see Fig.), leading to *cis*- and *trans*-forms. In the *trans*-form the chlorine atoms must lie exactly opposite to one another and there is a plane of symmetry, but in the *cis*-form the chlorine atoms, though on the same side of the molecule, cannot lie in one plane with the ethane carbon atoms and the *cis*-form must exist in two mirror image forms. Tetraphenylethylene dichloride has been prepared by several methods other than the addition of chlorine to the ethylene, and the product appears to be always the higher-melting isomer.

The higher-melting isomer tends to change into that of lower melting point, and this change can be brought about quantitatively when hydrogen chloride is passed for about an hour into a solution of the higher melting compound in, for instance, benzene or chloroform at room temperature; or by refluxing for about 2 hours in benzene, chloroform, or ether, to which a crystal of iodine has been added. If the iodine is omitted, refluxing with ether for 2—3 hours brings about a partial conversion.

Tetraphenylethylene will not add bromine. If it is treated with excess of liquid bromine or of bromine in an inert solvent, the only product is tetrakis-4-bromophenylethylene (Biltz, *Annalen*, 1897, **296**, 231), and the same product is obtained from tetraphenylethylene dichloride (Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2947, 2959). No intermediate compound is recorded, and it is now found that the action of bromine vapour on tetraphenylethylene dichloride gives 1 : 1-*diphenyl*-2 : 2-*bis*-4-*bromophenylethylene*. The formation of this compound is of interest because it shows that the chlorine atoms of the dichloride are expelled during the introduction of the first two bromine atoms. Norris (*loc. cit.*) states that when chlorine in excess is passed into a solution of tetrakis-4-bromophenylethylene in carbon tetrachloride the result is the addition of chlorine to the double bond, with the formation of tetrakis-4-bromophenylethylene dichloride, m. p. 202—203°. This is now found to be true only if the excess of chlorine is slight. When a large excess of chlorine is used, the bromine atoms are expelled and the product is *tetrakis*-4-*chlorophenylethylene dichloride*, m. p. 190—192°, which was in fact what Norris obtained, though he believed it to be tetrakis-4-bromophenylethylene dichloride. His only justification for the identification seems to have been the melting point (190—192°, *loc. cit.*). The structures have now been proved by oxidation to the corresponding substituted benzophenone, which is obtained in over 80% yield in both cases. In neither of these cases did we succeed in obtaining two forms of the dichloride.

Diagram illustrating degree of obstruction to rotation.



Biltz (*loc. cit.*) showed that when tetraphenylethylene is treated with excess of concentrated nitric acid and the mixture kept below 5°, the product is tetrakis-4-nitrophenylethylene, which he obtained as an amorphous yellow powder melting at about 100°. Although it is precipitated in an amorphous condition from most solvents, it is now found to crystallise from glacial acetic acid in small yellow crystals, m. p. 274—276°. No addition compound is formed with chlorine or bromine.

Tetrakis-3 : 5-*dichloro*-4-*methoxyphenylethylene dichloride* was prepared by treatment of tetrakis-4-methoxyphenylethylene (Gattermann and Leick, *Ber.*, 1895, **28**, 2874) with dry chlorine in glacial acetic acid. Bromine, under all conditions that were tried, reacted very vigorously with tetrakis-4-methoxyphenylethylene, but only resinous products were obtained.

EXPERIMENTAL.

(Microanalyses for C and H are by Drs. Weiler and Strauss, Oxford.)

Tetraphenylethylene Dichloride.—(*a*) When chlorine was passed into a solution of tetraphenylethylene in carbon tetrachloride, the dichloride was precipitated in a practically pure state, not as an addition compound with the solvent as stated by Norris, Thomas, and Brown. The dichloride was crystallised from chloroform, m. p. 185° (Found : C, 77·65; H, 4·92; Cl, 17·58; *M*, 389. Calc. for $C_{26}H_{20}Cl_2$: C, 77·42; H, 4·96; Cl, 17·62%; *M*, 403). $n_D^{20^\circ}$ 1·50900, 1·50799, 1·50818; mean 1·50838 (10% w/v in benzene); ϵ^{20° 2·255 (10% w/v in benzene).

(*b*) When a chloroform solution of the ethylene was used no precipitation occurred, and the solution was evaporated to a small bulk; the dichloride then crystallised out. This crude product melted at 160—162° (cf. Norris, *loc. cit.*). Crystallisation from chloroform yielded colourless crystals, m. p. 172°, containing two molecules of chloroform, which were soon lost on exposure to the air (Found : C, 77·63; H, 5·01; Cl, 17·60; *M*, 395. Calc. for $C_{26}H_{20}Cl_2$: C, 77·42; H, 4·96; Cl, 17·62%; *M*, 403). n_D^{20} 1·51139, 1·51121, 1·51212, 1·51175; mean 1·51161 (10% w/v in benzene); ϵ^{20° 2·282 (10% w/v in benzene).

Oxidation using Chromic Acid.—The best conditions for obtaining high yields of benzophenones in all the examples described were found to be as follows.

About 1 g. of the compound is taken and heated for 20 minutes on a water-bath with a solution of 4 g. of chromic acid in 40 c.c. of glacial acetic acid. The liquid is then poured into water and the precipitate formed is filtered off, washed with water, and crystallised from alcohol.

The yields of benzophenone from the two dichlorides were as follows : compound, m. p. 172°, 85%; compound, m. p. 185°, 78%.

The Chloroform and Carbon Tetrachloride Addition Compounds with Tetraphenylethylene Dichloride.—(a) *The compound, m. p.* 172°, *with chloroform.* The compound was crystallised from chloroform and the crystals dried on filter paper, weighed, and exposed to the air (Found : loss in weight after 2 days, 42·55. $C_{26}H_{20}Cl_2,2CHCl_3$ requires loss, 37·17%).

(b) *The compound, m. p.* 172°, *with carbon tetrachloride.* The compound was warmed with carbon tetrachloride (in which it is insoluble) and the crystals treated as for the chloroform addition product. (Found : loss in weight after 2 days, 45·74. $C_{26}H_{20}Cl_2,2CCl_4$ requires loss, 43·26%).

(c) *The compound, m. p.* 185°, *with chloroform.* The same procedure was followed (Found : loss in weight after 2 days, loss, 6·49. Calc. for $C_{26}H_{20}Cl_2,2CHCl_3$: loss, 37·17%).

(d) *The compound, m. p.* 185°, *with carbon tetrachloride* (Found : loss in weight after 2 days, 3·43. Calc. for $C_{26}H_{20}Cl_2,2CCl_4$: loss, 43·26%).

Allowing for the slight loss of weight due to adherent solvent in all cases, it is evident that the compound, m. p. 172°, forms *addition compounds*, while the compound, m. p. 185°, does not. The ready, but unrecognised, conversion of the higher- into the lower-melting compound has caused some confusion in earlier work. Norris, Thomas, and Brown (*loc. cit.*), for instance, state that the former gives a double compound, m. p. 170—171°, with carbon tetrachloride. Evidently they had in fact brought about conversion to the compound, m. p. 172°.

Sidgwick's Method.—A saturated solution of the more soluble form (m. p. 172°) was made in benzene and left overnight with excess of solid. The freezing point was then taken. A small quantity of the less soluble form (m. p. 185°) was added and allowed to attain equilibrium, and the freezing point again noted. Freezing point depression registered : 0·49°, 0·44°.

1 : 1-*Diphenyl*-2 : 2-*bis*-4-*bromophenylethylene.*—Tetraphenylethylene dichloride was left in contact with the vapour of 1 molecular proportion of bromine in a closed vessel for *ca.* 24 hours. The *product* (from chloroform) had m. p. 170° (Found : Br 33·3, 33·6. $C_{26}H_{18}Br_2$ requires Br, 32·6%). Oxidation gave a mixture of benzophenone and 4 : 4′-dibromobenzophenone.

Tetrakis-4-*bromophenylethylene Dichloride.*—This was prepared by passing 1½ molecular proportions of chlorine into a solution of tetrakis-4-bromophenylethylene (10 g.) dissolved in carbon tetrachloride (50 c.c.), so that little or no chlorine escaped. After 5 hours, the carbon tetrachloride was removed, and the residue was crystallised from acetone yielding colourless crystals of the *dichloride* (8 g.) m. p. 203—203° (Found : 0·1460 g. gave 0·2102 g. AgCl + AgBr. $C_{26}H_{16}Cl_2Br_4$ requires 0·2110 g.).

Tetrakis-4-*chlorophenylethylene Dichloride.*—Chlorine was passed into a solution of tetrakis-4-bromophenylethylene (10 g.) dissolved in carbon tetrachloride (50 c.c.) for 8 hours. The carbon tetrachloride was removed, and the residue was crystallised from chloroform yielding the *dichloride* in colourless crystals (8·5 g.), m. p. 190—192° (Found : Cl, 40·31. $C_{26}H_{16}Cl_6$ requires Cl, 39·38%).

Tetrakis - 3 : 5 - *dichloro* - 4 - *methoxyphenylethylene Dichloride.*—Tetrakis - 4 - methoxyphenylethylene (Galtermann and Leick, *loc. cit.*), dissolved in glacial acetic acid, was treated with dry chlorine. After about an hour a fine crystalline precipitate was formed. The *product* had m. p. 195—196° (Found : Cl, 43·3. $C_{30}H_{20}O_4Cl_{10}$ requires Cl, 44·3%). Oxidation yielded 3 : 5 : 3′ : 5′-tetrachloro-4 : 4′-dimethoxybenzophenone.

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