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THE "POSITIVE HALOGEN" REACTION BETWEEN BENZOTRICHLORIDES AND POTASSIUM IODIDE

RELEVANT MECHANISTIC AND STERIC ASPECTS*

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Abstract—The "positive halogen" reactions of 2:3:4:5-tetrachlorobenzotrichloride and perchlorotoluene with potassium iodide in aqueous acetic acid, at 100°, have been investigated. In the case of the perchlorotoluene the products are the two isomeric *perchlorostilbenes* along with some 2:3:4:5:6-pentachlorobenzylidene chloride. The chief product of the reaction of 2:3:4:5-tetrachlorobenzotrichloride with potassium iodide is α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-*dodecachlorobibenzyl*; considerable amounts of the two isomeric α:2:3:4:5:α′:2′:3′:4′:5′-*decachlorostilbenes* have been isolated. Under the same conditions the α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl reacts with potassium iodide to give the corresponding decachlorostilbenes.

When the reaction of perchlorotoluene with potassium iodide is performed in aqueous acetic acid containing toluene the yield of 2:3:4:5:6-pentachlorobenzylidene chloride is greatly increased and benzyl iodide is formed.

The mechanisms of these reactions are discussed. It is shown that the results are consistent with the occurrence of the reaction through the intermediate α:α-dichlorobenzyl radicals and α:α:α′:α′-tetrachlorobibenzyls, the latter being formed by dimerization of the former.

The ultra-violet absorption spectra of the geometric isomers of α:α′-dichlorostibene, α:2:3:4:5:-α′:2′:3′:4′:5′-decachlorostilbene and perchlorostilbene are recorded and interpreted. It is shown that the higher-melting isomerides have the *trans* configuration and that, as a result of the strong steric interaction between the *alpha* chloride atoms and the *ortho* atoms, there exists strong inhibition to resonance in the *trans* forms.

INTRODUCTION

The reaction of an organic halide with an inorganic iodide leads usually to substitution of the halogen by iodine. However, with organic halides the halogen of which is bonded to a carbon atom bearing electron-attracting groups, such as carbonyl, carboalkoxyl, nitro, etc, it may result instead in the oxidation of the iodide ion to iodine.[1–7] Such organic halides are said to show "positive halogen" reactivity. This has been attributed to a decreased polar character of the carbon-halogen bond due to the polarization induced by the electron-attracting groups which tends to reverse the normal polarization of the bond.[8] Iodides are not the sole reactants towards which "positive halogen" reactivity is displayed.[9]

From the viewpoint of the nature of the reaction products the "positive halogen" reactions with iodide ion can be grouped into three classes:

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* The present article contains material presented in the XIV and XVI International Congresses of Pure and Applied Chemistry, held in Zurich (1955) and Paris (1957), respectively.

[1] J. V. Backes, R. W. West and M. A. Whiteley, *J. Chem. Soc.* **119**, 359 (1921).

[2] H. Finkelstein, *Ber.* **43**, 1528 (1910).

[3] H. Finkelstein, *Ber.* **43**, 1535 (1910).

[4] M. Weizmann and J. Edlitz, *Bull. Soc. Chim. Fr.* **53**, 1495 (1933).

[5] R. Willstätter and V. Hottenroth, *Ber.* **37**, 1775 (1904).

[6] A. Perret and R. Perrot, *Bull. Soc. Chim. Fr.* **1**, 1547 (1934).

[7] J. E. Leffler, *J. Amer. Chem. Soc.* **75**, 3598 (1953); M. F. Hawthorne, *Ibid.* **77**, 5739 (1955).

[8] W. A. Waters, *The Chemistry of Free Radicals* p. 252. Clarendon Press, Oxford (1946); E. D. Hughes, *Quart. Rev.* **5**, 253, 266 (1951).

[9] R. Altschul and P. D. Bartlett, *J. Org. Chem.* **5**, 623 (1940).

Class 1. Reactions leading to replacement of the "positive halogen" by hydrogen, e.g.: the reaction of phenacyl bromide which gives acetophenone,[1] and the reaction of alkyl bromonitromalonates, which gives alkyl nitromalonates.[5]

Class 2. Reactions yielding condensation products by union of the two groupings bonded to the "positive halogen", e.g.: the reaction of alkyl bromomalonates, which gives alkyl ethanetetracarboxylates.[2,4] When there is more than one "positive halogen" bonded to the same carbon atom the condensation product may undergo vicinal dehalogenation by iodide ion yielding an ethylene. Such is the case of the reaction of alkyl dibromomalonates which gives alkyl ethylenetetracarboxylates,[2,4] and the reaction of dichlorodiphenylmethane, which gives tetraphenylethylene, although the intermediate symmetrical dichlorotetraphenylethane can be isolated as well.[3]

Class 3. Reactions yielding the grouping bonded to the "positive halogen" as a relatively stable free radical, e.g.: the reaction of the triphenylmethyl chloride[6] and the reaction of tris(*p*-nitrophenyl)methyl bromide[7] yielding the corresponding free triarylmethyl radicals.

Each chlorine atom of a trichloromethyl group is subjected at least to the electron-attracting activity of the other two chlorine atoms. It is therefore reasonable to assume that at least one of them may show "positive halogen" reactivity. Accordingly, it is found that trichloromethyl derivatives such as benzotrichloride, 2:3:4:5-tetrachlorobenzotrichloride, 2:3:5:6-tetrachlorobenzotrichloride, perchlorotoluene and trichloroacetic acid react easily with sodium or potassium iodide, in acetic acid solution, with liberation of iodine. Chloroform, carbon tetrachloride and hexachloroethane fail however to react with iodide ion under the same conditions. Nesmeyanov *et al.* have found 1:1:1-trichloroalkanes, such as 1:1:1-trichloropentane, are inert at the trichloromethyl group towards sodium iodide.[10] Apparently, the trichloromethyl group does not display an oxidising character towards iodide ion when bonded to a saturated carbon atom.

As it might be expected, dichloromethyl derivates, such as benzylidene chloride* and pentachlorobenzylidene chloride fail to liberate iodine. However, it has been pointed out[2,3] that dichlorodiphenylmethane reacts with iodide ion. Therefore, a phenyl group can replace a chlorine atom, in this case, without loss of the "positive halogen" reactivity.

The present work has been devised in order to ascertain the nature of the products of the "positive halogen" reaction of benzotrichlorides with potassium iodide, and to obtain information regarding the reaction mechanism. Only the reactions of 2:3:4:5-tetrachlorobenzotrichloride and perchlorotoluene with potassium iodide in acetic acid are to be considered here in detail.

RESULTS

The reaction of perchlorotoluene with potassium iodide in aqueous acetic acid, after 22·5 hr at 100°, gave a mixture of *cis*-perchlorostilbene, m.p. 230·5–231·5°, *trans*-perchlorostilbene, m.p. ca. 400°, and some 2:3:4:5:6-pentachlorobenzylidene chloride. The yields were 47·5 per cent for the *cis* isomer and 36·6 per cent for the *trans* isomer. The pentachlorobenzylidene chloride formed, accounted only for

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* See also reference 6.

[10] A. N. Nesmeyanov, R. K. Freidlina and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR* **96**, 87 (1954); *Quart. Rev.* 330 (1956).

8·9 per cent the initial perchlorotoluene. When the reaction was stopped before completion (2·5 hr) no intermediate was isolated. The reaction takes place very slowly at room temperature. Under the same reaction conditions, but in the absence of potassium iodide, some hydrolysis of perchlorotoluene occurs. When the acetic acid used was not chromic acid-purified the yield of pentachlorobenzylidene chloride increased and, accordingly, the combined yields of perchlorostilbenes diminished.

The reaction took place by substituting iodine for potassium iodide After 22·5 hr at 100° the yields were 21 per cent for the *cis*-perchlorostilbene, 15 per cent for the *trans*-perchlorostilbene, and 40 per cent for the pentachlorobenzylidene chloride.

Ferrous chloride could also be substituted for potassium iodide.

The perchlorostilbenes were obtained by the reaction of perchlorotoluene with powdered copper and pyridine, according to Karrer's method of condensation of organic halides.[11]

The molecular magnitude of the perchlorostilbenes was determined by Rast's method, with camphor.

The structure of the *trans* isomer was ascertained by nuclear perchlorination of *trans*-α:α-dichlorostilbene with Silberrad's chlorinating agent[12] which gave a good yield of the product.

The isomerisation of *cis*-perchlorostilbene into the *trans* form was performed in dioxane solution by ultra-violet light. The yield was 62 per cent. No isomerisation took place, starting from either isomer, using iodine as a catalyst and working under the condensation conditions.

Attempts to convert the perchlorostilbenes into a common derivative failed. Dechlorination (with powdered zinc) of the *trans* isomer yielded a product giving the chlorine analysis of perchlorotolane, while the *cis* isomer gave a product with a smaller chlorine content. They were not investigated further.

Attempted degradations of the perchlorostilbenes with chromic acid (hot acetic acid solution) or warm fuming nitric acid in the presence of mercuric ions failed, for the perchlorostilbenes are quite stable towards such oxidising agents.

When the reaction of perchlorotoluene with potassium iodide was carried out, under nitrogen, in acetic acid containing 20 per cent of purified toluene, pentachlorobenzylidene chloride accounted for about half the starting perchlorotoluene. Benzyl iodide was also isolated. The yields referred to the initial perchlorotoluene were: pentachlorobenzylidene chloride, 47·5 per cent; *cis*-perchlorostilbene, 23·1 per cent; *trans*-perchlorostilbene, 19·1 per cent. Assuming that from every molecule of pentachlorobenzylidene chloride formed a molecule of toluene is converted into benzyl iodide, the amount of the latter was 55·3 per cent of the theoretical. The presence of toluene left the ratio of the yields of perchlorostilbenes practically unchanged.

It was found that under the reaction conditions, neither benzyl iodide resulted from attack of the liberated iodine on toluene nor pentachlorobenzylidene chloride by a direct reaction between toluene and perchlorotoluene.

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[11] P. Karrer, W. Wehrli, E. Biedermann and M. dalla Vedova, *Chem. Zentr.* I, 1394 (1928); L. V. Johnson, F. Smith, M. Stacey and J. C. Tatlow, *J. Chem. Soc.* 4710 (1952).

[12] O. Silberrad, *J. Chem. Soc.* **119**, 2029 (1921); *Ibid.* **121**, 1015 (1922).

The reaction of 2:3:4:5-tetrachlorobenzotrichloride with potassium iodide was less rapid than that of perchlorotoluene under the same conditions. The former, after 5 days at 100°, yielded chiefly α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl, m.p. 252–253°, with *cis*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene, m.p. 141–142° and *trans*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene, m.p. 255–257°.

The reaction was also performed using ferrous chloride instead of potassium iodide.

It was found that α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl reacts with potassium iodide to give a mixture of *cis*- and *trans*-decachlorostilbenes.

The isomerisation of *cis*-decachlorostilbene into its *trans* form was effected in carbon tetrachloride solution by ultra-violet light. The yield was 66·2 per cent.

Attempts to obtain perchlorobibenzyl by nuclear chlorination of α:α:2:4:3:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl with Silberrad's chlorinating agent failed. The result was a mixture containing mostly *trans*-perchlorostilbene (83·8 per cent yield) with some of its *cis* isomer (3·2 per cent yield).

The dodecachlorobibenzyl is stable towards hot concentrated sulphuric acid or boiling acetic acid.

DISCUSSION

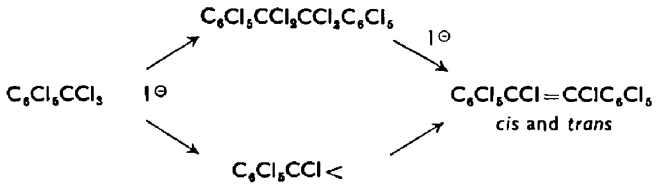
Mechanisms

The α:α:α′:α′-tetrachlorobibenzyls as intermediates. The reaction of perchlorotoluene with iodide ion occurs mostly according to the following stoicheiometry:

$$2C_6Cl_5CCl_3 + 4I^{\ominus} = C_6Cl_5CCl{=}CClC_6Cl_5 + 2I_2 + 4Cl^{\ominus}$$

It belongs therefore to the previously considered class 2, although class 1 reaction is also taking place.

The reaction might proceed either through perchlorobibenzyl as an intermediate, as in the case of the reaction of benzophenone chloride,[3] oi by 1:1-elimination of a molecule of chlorine at the trichloromethyl group giving perchlorobenzylidene radical which would dimerise



Kinetics[13a] as well as structural[13b] evidence has been reported recently for such type of bivalent (carbene) radicals in certain reactions, such as the hydrolysis of chloroform.

In the case of the reaction of 2:3:4:5-tetrachlorobenzotrichloride, the isolation of dodecachlorobibenzyl along the decachlorostilbenes, and the liability of the former to undergo dechlorination with iodide ion under the same condensation conditions shows that the dodecachlorobibenzyl is indeed an intermediate of the reaction. This is circumstantial evidence for the presence of perchlorobibenzyl in the reaction of perchlorotoluene.

The results obtained when the reaction is carried out in the presence of *cyclo*-hexene do not support the bivalent radical mechanism.[14]

[13a] J. Hine, *J. Amer. Chem. Soc.* 72, 2438 (1950); [b] W. von E. Doering and A. K. Hoffmann, *Ibid.* 76, 6162 (1954).

[14] M. Ballester and J. Rosa, unreported experiments.

Assuming that dechlorination of perchlorobibenzyl proceeds more rapidly than its formation from perchlorotoluene its concentration can never reach a substantial value. This is in full agreement with the failure to isolate perchlorobibenzyl when the reaction was stopped before completion.

Steric assistance due to compression between the *ortho* chlorine atoms and those of the *alpha* carbons might be the reason for the extreme readiness with which the perchlorobibenzyl undergoes dechlorination. Such internal steric strain is probably the reason also for the failure to obtain perchlorobibenzyl by nuclear chlorination of dodecachlorobibenzyl.

The α:α-dichlorobenzyls as intermediates. The condensations of benzotrichlorides yielding tetrachlorobibenzyls and/or dichlorostilbenes have also been carried out by means of metals or reducing inorganic ions.[15] The reactions of 2:3:4:5-tetrachlorobenzotrichloride and perchlorotoluene with ferrous chloride described are the best examples that can be given. These reducing agents are known to yield free radicals when reacting with organic halides. Also, the decomposition of benzoyl peroxides in benzotrichlorides give α:α:α′:α′-tetrachlorobibenzyls, presumably by dimerisation of α:α-dichlorobenzyl radicals.[16] On the other hand, the existence of reactions of class 3 shows that, when the grouping bonded to the "positive halogen" is stable enough, iodide ion can give it as a free radical.

There is, therefore, good evidence supporting a mechanism involving perchlorobenzyl radical as a reactive intermediate in the reaction of perchlorotoluene with potassium iodide.

The results of the reaction of perchlorotoluene with iodide ion are therefore consistent with the following sequences.

$$\begin{aligned} \mathrm{C_6Cl_5CCl_3 + 2I^{\ominus}} &\longrightarrow \mathrm{C_6Cl_5\dot{C}Cl_2 + I_2 + Cl^{\ominus}} \\ \mathrm{2C_6Cl_5\dot{C}Cl_2} &\longrightarrow \mathrm{C_6Cl_5CCl_2CCl_2C_6Cl_5} \\ \mathrm{C_6Cl_5CCl_2CCl_2C_6Cl_5 + 2I^{\ominus}} &\longrightarrow \mathrm{C_6Cl_5CCl{=}CClC_6Cl_5 + I_2} \\ &\qquad\qquad \textit{cis and trans} \end{aligned}$$

It is well known that alkylaromatic hydrocarbons having hydrogen bonded to *alpha* carbon atoms can act as hydrogen donors in free radical reactions.[17] This is due to benzyl radical-resonance stabilisation.[18] That fact might be the explanation for the formation of pentachlorobenzylidene chloride in the pyrolysis of perchlorotoluene. In this pyrolysis perchlorobenzyl radical is, presumably, formed by carbon–chlorine bond fission.[19]

Therefore, the results of reaction of perchlorotoluene with potassium iodide in the presence of toluene should be regarded as a hydrogen-atom transfer reaction between toluene and perchlorobenzyl radical, which reaction competes with the dimerisation of the latter. The benzyl radical formed would then react with iodine to give benzyl iodide.

$$\begin{aligned} \mathrm{C_6Cl_5\dot{C}Cl_2 + C_6H_5CH_3} &\longrightarrow \mathrm{C_6Cl_5CHCl_2 + C_6H_5\dot{C}H_2} \\ \mathrm{C_6H_5\dot{C}H_2 + I_2} &\longrightarrow \mathrm{C_6Cl_5CH_2I + I} \end{aligned}$$

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[15] A. Onufrowicz, *Ber.* **17,** 833 (1884); F. Fox, *Ibid.* **26,** 653 (1893); J. Kenner and E. Witham, *J. Chem. Soc.* **97,** 1962 (1910); Y. Ogata and R. Oda, *Chem. Abstr.* **43,** 2194 *d* (1949).

[16] R. L. Dannley and M. Sternfeld, *J. Amer. Chem. Soc.* **76,** 4543 (1954).

[17] M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.* **10,** 401 (1945); J. H. Raley, F. F. Rust and W. E. Waughan, *J. Amer. Chem. Soc.* **70,** 1336 (1948); E. C. Kooyman and A. Strang, *Rec. Trav. Chim.* **72,** 329 (1953); C. S. Rondestvedt and H. S. Blanchard, *J. Amer. Chem. Soc.* **77,** 1769 (1955).

[18] M. Szwarc, *Chem. Rev.* **47,** 75 (1950).

[19] M. Ballester and C. Molinet, *An. Real Soc. Españ. Fís. y Quím.* **54 B,** 151 (1958).

The fact that the molar ratio benzyl iodide pentachlorobenzylidene chloride is only about half the expected value is probably due to solvolysis of benzyl iodide and also by some reaction of benzyl radical with impurities of oxygen.[20]

It has been reported that alkylaromatic hydrocarbons can give hydride-ion transfers to carbonium ions.[21]

Therefore, a carbonium ion mechanism might account for the formation of pentachlorobenzylidene chloride.

$$\mathrm{C_6Cl_5CCl_3} \longrightarrow \mathrm{C_6Cl_5\overset{\oplus}{C}Cl_2} + \mathrm{Cl^{\ominus}}$$

$$\mathrm{C_6Cl_5\overset{\ominus}{C}Cl_2} + \mathrm{C_6H_5CH_3} \longrightarrow \mathrm{C_6Cl_5CHCl_2} + \mathrm{C_6H_5\overset{\oplus}{C}H_2}$$

$$\mathrm{C_6H_5\overset{\ominus}{C}H_2} + \mathrm{I^{\ominus}} \longrightarrow \mathrm{C_6H_5CH_2I}$$

The fact that perchlorotoluene does not yield pentachlorobenzylidene chloride with toluene in the absence of iodide ion, under the same reaction conditions, is inconsistent with such a mechanism.

Ionic mechanisms for the formation of perchlorobibenzyl may also be given. For example:

$$\mathrm{C_6Cl_5CCl_3} \longrightarrow \mathrm{C_6Cl_5\overset{\ominus}{C}Cl_2} + \mathrm{Cl^{\ominus}}$$

$$\mathrm{C_6Cl_5CCl_3} + \mathrm{I^{\ominus}} \longrightarrow \mathrm{C_6Cl_5\overset{\ominus}{C}Cl_2} + \mathrm{ClI}$$

$$\mathrm{C_6Cl_5\overset{\oplus}{C}Cl_2} + \mathrm{C_6Cl_5\overset{\ominus}{C}Cl_2} \longrightarrow \mathrm{C_6Cl_5CCl_2CCl_2C_6Cl_5}$$

and

$$\mathrm{C_6Cl_5CCl_3} + \mathrm{I^{\ominus}} \longrightarrow \mathrm{C_6Cl_5\overset{\ominus}{C}Cl_2} + \mathrm{ClI}$$

$$\mathrm{C_6Cl_5\overset{\ominus}{C}Cl_2} + \mathrm{C_6Cl_5CCl_3} \longrightarrow \mathrm{Cl^{\ominus}} + \mathrm{C_6Cl_5CCl_2CCl_2C_6Cl_5}$$

Regarding the second mechanism, the second step is extremely improbable because of the well-known high steric hindrance in the reactions at the *alpha* carbon atom of 2:6-dichlorophenyl derivatives.[22] This hindrance would, in this case, be in addition increased because of the large volume of the attacking perchlorobenzyl anion and also because of the internal steric strain of the perchlorobibenzyl. Moreover, the inertness of the trichloromethyl group towards nucleophilic displacements at the carbon atom is also well known.[10,23] Furthermore, it appears improbable that perchlorobenzyl anion would be stable enough in acetic acid solution to be such an effective intermediate.

As far as the first ionic mechanism is concerned, although it is known that the tendency of an α-chlorotoluene to give a carbonium ion increases with the number of chlorine atoms bonded to the *alpha* carbon atom,[24] in spite of the solvolysis of perchlorotoluene (presumably taking place by an S_N1 mechanism) is actually

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[20] P. D. Bartlett and J. E. Leffler, *J. Amer. Chem. Soc.* **72**, 3030 (1950).

[21] H. Pines, D. R. Strehlau and V. N. Ipatieff, *J. Amer. Chem. Soc.* **71**, 3534 (1949).

[22] M. S. Reich, *Bull. Soc. Chim. Fr.* **21**, 217 (1917); G. Lock and F. Asinger, *Chem. Abstr.* **26**, 1910 (1932); G. Lock, *Ber.* **66**, 1527 (1933); S. D. Ross, *J. Amer. Chem. Soc.* **70**, 4039 (1948); S. D. Ross and M. Markarian, *Ibid.* **71**, 2756 (1949); S. J. Agyal, P. J. Morris, R. C. Rassack and J. A. Waterer, *J. Chem. Soc.* 2704 (1949); T. Alfrey and W. H. Ebelke, *J. Amer. Chem. Soc.* **71**, 3235 (1949); M. Ballester, *An. Real Soc. Españ. Fis. y Quim.* **50 B**, 765 (1954); P. G. Harvey, F. Smith, M. Stacey and J. C. Tatlow, *J. Appl. Chem.* **4**, 325 (1954).

[23] J. Hine, *Physical Organic Chemistry* p. 131. McGraw-Hill, New York (1956); M. Ballester, *Chem. Rev.* **55** 288, 289 (1955).

[24] E. D. Hughes, *Trans. Faraday Soc.* **38**, 625 (1941).

occurring under the reaction conditions, the required intermediate perchlorobenzyl anion makes it improbable.

No such ionic mechanisms can provide a reasonable account for the results of the reaction in the presence of toluene.

The possibility that perchlorobenzyl iodide could play a role as an intermediate cannot be ruled out. It is reasonable that perchlorobenzyl iodide would appreciably dissociate at the reaction temperature giving perchlorobenzyl radical. In fact, perchlorotoluene and 2:3:5:6-tetrachlorobenzotrichloride begin to decompose appreciably at temperatures as low as 185° and this fact has been attributed to an exceptionally facile homolysis of the carbon–chlorine bonds of the trichloromethyl group when flanked by two *ortho* chlorine atoms, (steric strain).[25]

Moreover, in halides of comparable structures the dissociation energies of the carbon–iodine bonds are about 30 kcal smaller than those of the carbon–chloride bonds.[26] It could be expected therefore a low temperature of decomposition for the perchlorobenzyl iodide.

In view that solvolysis of perchlorotoluene occurs under the reaction conditions, perchlorobenzyl cation could account for the formation of perchlorobenzyl radical either by conversion into labile perchlorobenzyl iodide or by a direct electron-transfer reaction with iodide ion. As far as the mechanism of the formation of the perchlorobenzyl radical is concerned, the evidence here described does not allow any safe decision on the matter.

It has been found[27] that at 100° there is an attack of iodine on acetic acid with the formation of hydrogen iodide. The reaction of iodide with perchlorotoluene in aqueous acetic acid can therefore be explained as a reduction of perchlorotoluene by hydrogen iodide. The greatly increased yield of 2:3:4:5:6-pentachlorobenzylidene chloride may be due to the change in the nature of the iodide. Accordingly, it has been found[28] that hydrogen bromide in acetic acid reduces perchlorotoluene to pentachlorobenzylidene chloride exclusively.

CONFIGURATION AND RELATED STERIC INHIBITION PHENOMENA

Configurations for the stilbenes described have been made on the basis of their ultra-violet spectra.

In general, tri-conjugated *trans* forms absorb more and at longer wave lengths than the *cis* forms. The pair of unsubstituted stilbenes is an example.[29]

In order to apply the ultra-violet spectra to the configurations it was considered convenient to investigate first the spectra of the *cis*- and *trans*-α:α'-dichlorostilbenes which configurations have been well established by Bergmann by dielectric constant measurements.[30]

The absorption spectrum of *trans*-α:α'-dichlorostilbenes shows a general hypsochromic shift with respect to that of its *cis* isomer (Fig. 1a). Accordingly, the latter shows a maximum at longer wavelengths ($\lambda = 281$ mμ; $\varepsilon = 8950$) than the former ($\lambda = 270$ mμ; $\varepsilon = 11{,}400$). Similar anomalous behaviour has been recently found

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[25] M. Ballester and C. Molinet, unpublished results.
[26] C. Walling, *Free Radicals in Solution* p. 50. Wiley, New York (1957).
[27] M. Ballester and J. Ros, unpublished work.
[28] M. Ballester and E. Guardiola, unpublished results.
[29] E. A. Braude and E. S. Waight, *Progress in Stereochemistry* (Edited by W. Klyne), Vol. 1, p. 126. Butterworths, London (1954).
[30] E. Bergmann, *J. Chem. Soc.* 402 (1936).

in α:α′-dialkylstilbenes:[31] the *trans* forms absorb *stronger* and at shorter wavelengths than the *cis* forms.

The anomalous spectra of the α:α′-dichlorostilbenes are attributable to steric inhibition to resonance. It is assumed that resonance in *cis*-stilbene—but not in its *trans* isomer—is sterically inhibited in some extent due to the impossibility of the two benzene nuclei and the central ethylene bond lying in the same plane.[29] By using Stuart atomic models it becomes clear that substitution of both ethylene hydrogen atoms by chlorine in stilbene prevents coplanarity in the *trans* form but leaves the *cis* form almost sterically undisturbed (Fig. 2). Such effect arises mainly from the interaction between the *beta* chlorine atoms and the *ortho* hydrogen atoms.

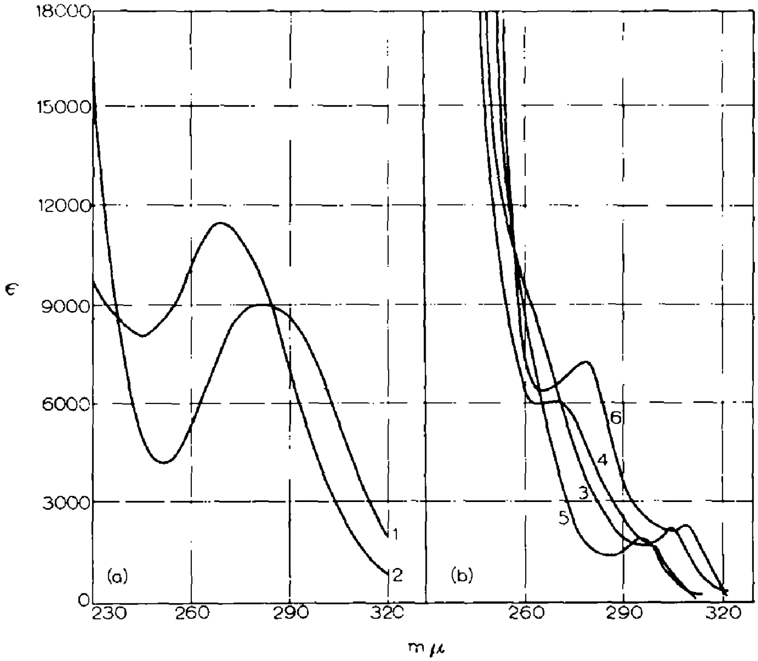

FIG. 1. *cis*-α,α′→-dichlorostilbene, 1; *trans*-α,α′-dichlorostilbene, 2; *trans*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene, 3; *cis*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene, 4; *trans*-perchlorostilbene, 5; *cis*-perchlorostilbene, 6.

Accordingly, while the introduction of two *alpha* chlorine atoms in *cis*-stilbene produces practically no shift of the maximum of absorption and little change in the intensity of the low-frequency band, in the *trans*-stilbene it results in an important hypsochromic shift and a strong reduction of the intensity of absorption.*

In this connexion it has to be mentioned that the ultra-violet spectrum of the *trans*-α:α′-dichlorostilbene was recorded by Arends.[32] However, because its maximum lies closer to that of the *cis*-stilbene, he concluded, according to configurations found in the literature for the known α:α′-dichlorostilbenes,[33] that it was the *cis* isomer.

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* *Cis*-stilbene; λ = 280 mμ; ε = 9800. *Trans*-stilbene; λ = 294 mμ; ε = 27,600.[31]

[31] H. Suzuki, *Bull. Chem. Soc. Japan* **25**, 145 (1952).

[32] B. Arends, *Ber.* **64 B**, 1936 (1931).

[33] A. Blanck, *Liebigs Ann.* **248**, 17 (1888); A. Eiloart, *Amer. Chem. J.* **12**, 231 (1890).

In this connexion it is convenient to indicate that the configurations found in the literature for the $\alpha:o:\alpha':o'$- and $\alpha:p:\alpha':p'$-tetrachlorostilbenes are probably wrong.[34]

In the cases of $\alpha:\alpha'$-dimethyl- and $\alpha:\alpha'$-diethylstilbenes, because of the larger sphere of action of the methyl and the ethyl groups, it can be expected—and it has actually been found—that the absorption is hypsochromically shifted even in their *cis* forms.

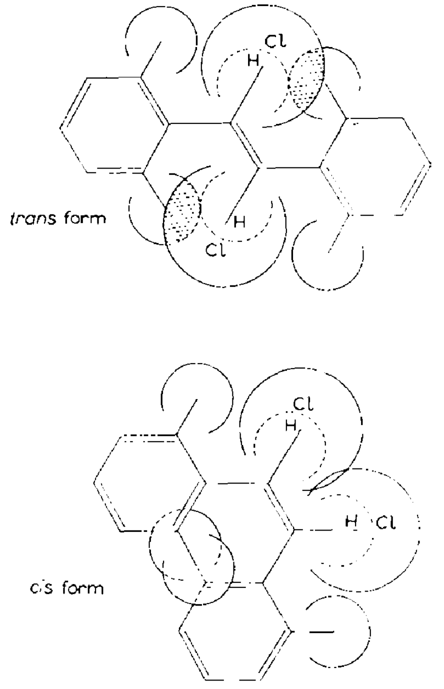

FIG. 2.

It is reasonable to assume that a similar situation occurs in the case of the $\alpha:\alpha:2:3:4:5:\alpha':\alpha':2':3':4':5'$-decachlorostilbenes and the perchlorostilbenes, especially in the latter, where the strong *o*-H × α-Cl interactions in the *trans* forms are all replaced by the stronger *o*-Cl × α-Cl interaction. In fact, as in the case of the $\alpha:\alpha'$-dichlorostilbenes, the ultra-violet spectrum of the higher-melting decachlorostilbene shows, with respect to that of its lower-melting isomer, a general hypsochromic shift (Fig. 1b). This shift is greater in the perchlorostilbenes than in the decachlorostilbenes.

The bathochromic shift of the *cis*-perchlorostilbenes with respect to the *cis*-decachlorostilbene (Fig. 1b) may be ascribed to normal electronic effect due to the substitution.

The configurations thus assigned are consistent with those attributable by the melting point rule, i.e. *trans* configuration for the higher-melting isomeride.

Ultra-violet light usually converts the *trans* isomerides into their *cis* forms.[35]

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[34] F. Fox, *Ber.* **26**, 653 (1893); J. Kenner and E. Witham, *J. Chem. Soc.* 1962 (1910); E. E. Fleck, *J. Amer. Chem. Soc.* **70**, 2173 (1948).

[35] L. Crombie, *Quart. Rev.* **6**, 101 (1952); G. M. Wyman, *Chem. Rev.* **55**, 625 (1955).

The convertions occur here in the opposite direction. These results are probably related to their anomalous ultra-violet absorption spectra. Solubilities may also play a role in such stereomutations by favouring the formation of the less soluble *trans* isomeride. In fact, in the case of the perchlorostilbenes practically all the *trans* form crystallises from solution during the illumination.

EXPERIMENTAL

Reaction of perchlorotoluene with potassium iodide

A mixture of perchlorotoluene[36] (1·4 g), potassium iodide (1·4 g), purified, glacial acetic acid (20 ml) and water (1 ml) was heated (steam-bath) under nitrogen, for 22·5 hr. The mass was then poured into water (200 ml), and after removal of the iodine with sodium bisulphite, it was heated (steam-bath) for half an hour. The suspension was cooled, shaken vigorously with ether (300 ml) and filtered. The insoluble part (0·287 g) consisted of pure trans-*perchlorostilbene*, m.p. ca. 400°. *Ultra-violet*: $\lambda = 296, 305$ mμ; $\varepsilon = 1{\cdot}8 \times 10^3, 2{\cdot}1 \times 10^3$. (Found: C, 28·1; H, 0·1; Cl, 71·6; *mol. wt.* (camphor) 578; $C_{14}Cl_{12}$ requires C, 28·3; H, 0·0; Cl, 71·7% mol. wt. 593·6).

The ether solution, after being extracted with sodium bicarbonate solution, gave cis-*perchlorostilbene* (0·377 g), m.p. 225–229°, which, after crystallisation from ethyl acetate, m.p. 230·0–231·5°. *Ultra-violet*; $\lambda = 279, 309$ mμ; $\varepsilon = 7{\cdot}2 \times 10^3, 2{\cdot}2 \times 10^3$. (Found: C, 28·3; H, 0·1; Cl, 71·8; mol. wt. (camphor) 570; $C_{14}Cl_{12}$ requires C, 28·3; H, 0·0; Cl, 71·7% mol. wt. 593·6). The ethereal mother-liquor gave on evaporation a solid residue (0·081 g), which after extraction with methanol was identified as 2:3:4:5:6-pentachlorobenzylidene chloride by m.p. and mixed m.p. with an authentic sample prepared by photo-chlorination of 2:3:4:5:6-pentachlorotoluene.[37] From the methanol solution more *cis*-perchlorostilbene (0·006 g) was obtained.

Attempted isomerisation of cis-*perchlorostilbenes with iodine*

A mixture consisting of *cis*-perchlorostilbene (0·1 g), iodine (0·04 g) purified acetic acid (7 ml) was heated (steam-bath) during 24 hr. The resulting mixture was poured into water, the iodine destroyed with sodium bisulphite solution and the heating continued for 45 min. Treatment with ether gave no insoluble residue. The ethereal layer was separated, washed with sodium bicarbonate solution and water, and dried over anhydrous sodium sulphate. Removal of the ether gave unchanged perchlorostilbene quantitatively, which was identified by m.p. and mixed m.p.

Attempted isomerisation of trans-*perchlorostilbene with iodine*

A mixture consisting of *trans*-perchlorostilbene (0·1 g), iodine (0·04 g) and purified acetic acid (7 ml) was treated as in the preceeding experiment. The solid obtained (0·093 g) was practically insoluble in ether, and was identified as *trans*-perchlorostilbene by m.p. and mixed m.p. The ethereal layer gave more *trans*-perchlorostilbene (0·002 g).

Reaction of perchlorotoluene and potassium iodide in the presence of toluene

A mixture of perchlorotoluene (2 g), potassium iodide (2·8 g), chromic acid-purified, glacial acetic acid (40 ml), water (2 ml) and purified toluene (10 ml) was heated (22 hr) at 100° under nitrogen. A mixture of water (200 ml) and ether (100 ml) was added to the product, the iodine destroyed with sodium bisulphite solution, and the mass filtered. The residue (0·308 g), was identified as *trans*-perchlorostilbene by chlorine analysis and mixed m.p. with an authentic sample.

The ethereal layer was washed with sodium bicarbonate solution, with water, and dried over sodium sulphate. The solvents were removed at 130° under reduced pressure. The product was distilled (3 mm at 130°) and 0·378 g of crude benzyl iodide distilled and was identified (83%).

The residue of the distillation was redistilled at 0·2 mm. The fraction 100–120° weighed 0·868 g and consisted of 2:3:4:5:6-pentachlorobenzylidene chloride. The residue (0.375 g) was *cis*-perchlorostilbene. These products were identified by mixed m.p. and chlorine analysis.

This reaction was repeated several times and the ratio of amounts of isomeric perchlorostilbenes remained constant (*cis*/*trans* = 1·2), close to the value obtained when the reaction was performed without toluene (1·3). The total yield of the reaction was always around 90 per cent.

[36] M. Ballester and C. Molinet, *Chem. & Ind.* 1290 (1954).

[37] G. Lock, *Ber.* **66**, 1527 (1933); M. Ballester, *Mem. Real Acad. Barcelona* **29**, 271 (1948).

Iodine and toluene under the conditions of the foregoing experiment

A mixture of iodine (0·69 g), potassium iodide (0·6 g), chromic acid-purified, glacial acetic acid (20 ml), purified toluene (5 ml) and water (1 ml) was heated at 100°, under nitrogen during 22·5 hr. No benzyl iodide was detected.

Perchlorotuene and iodine in aqueous acetic acid

A solution containing perchlorotoluene (0·1 g), purified iodine (0·069 g), chromic acid-purified, glacial acetic acid (2 ml) and water (0·1 ml) was heated in a sealed tube at 100° during 22·5 hr. The solid phase formed on standing was filtered and by treatment with ether was resolved into 0·016 g (21 %) of *trans*-perchlorostilbene and 0·011 g (15 %) of *cis*-perchlorostilbene.

The mother liquor was diluted with water, the iodine removed with sodium bisulphite, extracted with ether and decanted. The ethereal layer was washed with sodium bicarbonate solution, dried, and the ether removed. The residue (0·038 g) was digested in hot methanol leaving a residue (0·036 g, 40 %) consisting of 2:3:4:5:6-pentachlorobenzylidene chloride which was identified by m.p. and mixed m.p. with an authentic sample.[37]

This experiment was repeated repurifying the starting materials and the results were reproduced.

Reaction of perchlorotoluene with ferrous chloride

A mixture of perchlorotoluene (0·5 g), $FeCl_2.4H_2O$ (1 g) and purified, glacial acetic acid (10 ml) was heated (steam-bath) for 8 hr. The separation of the reaction products was carried out as in the preceeding reaction and *cis*-perchlorostilbene (0·131 g) and *trans*-perchlorostilbene (0·199 g) were obtained. The yields were 32·5 % and 49·3 %, respectively. The products were identified by mixed m.p. with those obtained from the reaction of perchlorotoluene with potassium iodide.

Hydrolyses of perchlorotoluene with aqueous acetic acid

A solution of perchlorotoluene (0·2 g) in purified, glacial acetic acid (4 ml) was heated at 100° during three days. The solution was poured into water and strongly acidified with a few drops of mineral acid and heated (vapour bath) during 2 hr. The mixture was then extracted with ether, the ethereal layer extracted with sodium bicarbonate solution and discarded . The sodium bicarbonate solution was acidified with concentrated HCl and extracted with ether. Evaporation of the ether yielded 2:3:4:5:6-pentachlorobenzoic acid (0·104 g, 65 %). It was identified by m.p. and mixed m.p. with an authentic sample.

A solution containing perchlorotoluene (0·2 g), purified, glacial acetic acid (5 ml) and water (0·2 ml), was heated at 100° during 22 hr. The resulting solution deposited on cooling perchlorotoluene (0·078 g). The mother-liquor was poured into water and then extracted with ether. The ethereal layer, after extraction with sodium bicarbonate solution, gave (0·094 g) which after crystallization from ethanol gave perchlorotoluene (0·057 g). The sodium bicarbonate solution was acidified with concentrated HCl and extracted with ether. Evaporation of the ether gave 2:3:4:5:6-pentachlorobenzoic acid (0·018 g) identified as above.

Perchlorotoluene in aqueous acetic acid containing toluene

A solution containing perchlorotoluene (0·5 g), purified, glacial acetic acid (10 ml), water (0·5 ml) and purified toluene (2·5 ml) was heated at 100°, during 22 hr. After evaporation of the acid perchlorotoluene (0·446 g) was recovered.

Reaction of perchlorotoluene with copper and pyridine

To an ice-cooled solution of perchlorotoluene (0·5 g) in pyridine (2 ml), freshly precipitated copper (0·095 g) was added. The mixture was heated (steam-bath) during an hour, acidified and heated again. The insoluble part was extracted in a Kumagava extractor with carbon tetrachloride for 25 hr, and *trans*-perchlorostilbene (0·17 g) was obtained. The mother liquor, after evaporation of carbon tetrachloride, gave a residue which, crystallised from ethyl acetate and yielded pure *cis*-perchlorostilbene. The reaction products were identified by m.p. and mixed m.p. with those obtained from the reaction of perchlorotoluene with potassium iodide.

Isomerisation of cis-*perchlorostilbene with ultra-violet light*

In a quartz vessel, a solution of *cis*-perchlorostilbene (0·1 g) in purified dioxane (5 ml) was illuminated during 5·5 hr with the ultra-violet radiation from a 500-watt mercury lamp situated at a distance of 20 cm. The solid phase formed was filtered (0·062 g) and consisted of *trans*-perchlorostilbene, identified by m.p. and mixed m.p.

Nuclear chlorination of trans-$\alpha:\alpha'$-*dichlorostilbene*

A solution of anhydrous aluminium chloride (0·04 g) in sulphuryl chloride (2 ml) was added gradually to a solution containing *trans*-dichlorostilbene[38] (0·05 g), sulphur monochloride (0·04 g), and sulphuryl chloride (2 ml). The resulting solution was gently refluxed during 2·5 hr and then concentrated to one-fourth its original volume. The mass thus obtained was treated, as usual, with warm water, sodium carbonate, and HCl. On filtration a residue (0·123 g) was obtained which after digestion with warm carbon tetrachloride gave an insoluble portion (0·048 g), which was identified as *trans*-perchlorostilbene by mixed m.p. and ultra-violet spectrum. Concentration of the carbon tetrachloride solution yielded another 0·006 g of the compound.

Attempted degradation of cis-*perchlorostilbene with chromic acid*

A mixture of *cis*-perchlorostilbene (0·073 g), chromic acid (0·5 g) and chromic acid purified acetic acid (10 ml) was refluxed during 20 hr. The resulting mixture was poured into water and extracted with ether (100 ml). The part soluble in ether (0·065 g) consisted of *cis*-perchlorostilbene identified by m.p. and mixed m.p.

Reaction of trans-*perchlorostilbene with zinc*

A mixture of *trans*-perchlorostilbene (0·1 g) zinc powder (1 g) and purified dioxane (50 ml) was refluxed during 24 hr. The mass was filtered hot and on cooling a white precipitate formed (0·02 g). The mother liquor gave on concentration 0·06 g of the product. The substance melted at 329–336°. It was purified by sublimation at 190° under 0·001 mm. The substance melted then at 345–348°. (Found: Cl, 67·6; $C_{14}Cl_{10}$ requires Cl, 67·8%).

Reaction of cis-*perchlorostilbene with zinc*

The quantities and conditions were the same as those stated in the preceding experiment. The resulting solution gave on cooling 0·05 g of fine needles, m.p. 260°. (Found: Cl, 55·2; $C_{14}H_4Cl_6$ requires Cl, 55·3%).

Attempted degradation of trans-*perchlorostilbene with fuming nitric acid*

A mixture of *trans*-perchlorostilbene (0·036 g), a droplet of mercury and fuming nitric acid (5 ml) was refluxed during 259 hr. The mixture was then poured into salted water, extracted with ether and filtered. The insoluble portion (0·033 g) was identified as *trans*-perchlorostilbene by m.p. and mixed m.p.

Attempted degradation of cis-*perchlorostilbene with fuming nitric acid*

A mixture of *cis*-perchlorostilbene (0·042 g), a droplet of mercury and fuming nitric acid (10 ml) was refluxed during 196 hr. The mass was poured into water and filtered. The residue, (0·036 g), was identified as *cis*-perchlorostilbene by m.p. and mixed m.p.

Reaction of 2:3:4:5-*tetrachlorobenzotrichloride with potassium iodide*

A mixture of 2:3:4:5-tetrachlorobenzotrichloride[37,39] (4 g), potassium iodide (8 g) and chromic acid-treated, glacial acetic acid (80 ml) was heated at 100°, in a sealed glass container, during 5 days. The mass was treated with water and the iodine formed titrated with standard sodium thiosulphate, 0·0174 equivalents being used up. The resulting mixture was then filtered and residue (3·369 g) was obtained which by treatment with cold petroleum ether gave a solution, A, and a residue, B.

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[38] A. Blank, *Liebigs Ann.* **248**, 17 (1888).

[39] M. Ballester, *An. Real Soc. Españ. Fis. y Quim.* (*Madrid*) **50 B**, 765 (1954).

A, yielded (0·515 g) solids which was submitted to chromatographic purification with alumina grade A. Solid (0·333 g) was obtained, which after treatment with cold petroleum ether gave a residue (0·016 g) which consisted of trans-α:2:3:4:5:α′:2′:3′:4′:5′-*decachlorostilbene*, m.p. 250–254°. *Ultra-violet* data. $\lambda = 297$ mμ; $\varepsilon = 1{\cdot}7 \times 10^3$. (Found: C, 32·4; H, 0·4; Cl, 67·5; $C_{14}H_2Cl_{10}$: requires C, 32·1; H, 0·4; Cl, 67·6%.) On evaporation to dryness the ethereal solution gave cis-α:2:3:4:5:α′:2′:3′:4′:5′-*decachlorostilbene* (0·317 g) m.p. 139–140°. *Ultra-violet*: $\lambda = 270$, 299 mμ; $\varepsilon = 6 \times 10^3$, $1{\cdot}6 \times 10^3$. (Found: C, 32·2; H, 0·7; Cl, 67·7; $C_{14}H_2Cl_{10}$ requires 32·1; H, 0·4; Cl, 67·6%).

On treatment with hot carbon tetrachloride, B (2·854 g) gave α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-*dodecachlorobibenzyl* (1·902 g), m.p. 250–251°. *Ultra-violet*: $\lambda = 295$, 305 mμ; $\varepsilon = 1{\cdot}8 \times 10^3$. (Found: C, 28·3; H, 0·4; Cl, 71·4; $C_{14}H_2Cl_{12}$ requires C, 28·2; H, 0·3, Cl, 71·4%). The soluble portion after treatment with carbon tetrachloride and petroleum ether, yielded dodecachlorobibenzyl (0·004 g) and *trans*-decachlorostilbene (0·065 g). The remaining mixtures, which contained the difficultly separable dodecachlorobibenzyl and *trans*-decachlorostilbene, were analysed for chlorine. On the basis of these analyses it was concluded that they contained dodecachlorobibenzyl (0·46 g) and *trans*-decachlorostilbene (0·22 g).

Reaction of α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-*dodecachlorobibenzyl with potassium iodide*

In a sealed glass container, under nitrogen, a mixture of 1·5 g (0·0025 mole) of α:α:2:3:4:5:-α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl, potassium iodide (6 g) and chromic acid-purified, glacial acetic acid (60 ml) was heated at 100° for 10 days. The mass was then treated with water and the free iodine titrated with sodium thiosulphate, 0·0039 equivalents being used. Filtration gave a precipitate (1·366 g) which was extracted with petroleum ether. The residue, after repeated recrystallisations from carbon tetrachloride gave *trans*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene (0·052 g) identified by mixed m.p. and chlorine analysis (Found: Cl, 67·5; Calc. for 67·6%) and unresolvable mixtures (0·89 g). Part of these mixtures (0·650 g) were analysed for chlorine and the values found were between those calculated for the dodecachlorobibenzyl and *trans*-decachlorostilbene, and were probably mixtures of these two substances. Assuming the decachlorostilbenes are the sole reaction products from the amount of free iodine the composition of the inseparable mixture is dodecachlorobibenzyl (0·345 g) and *trans*-decachlorostilbene (0·542 g).

The portion soluble in petroleum ether (0·424 g), after filtration through activated alumina (0·394 g) and melted at 141–142°. It was identified as *cis*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene by mixed m.p. and chlorine analysis.

Reaction of 2:3:4:5-*tetrachlorobenzotrichloride with ferrous chloride*

A mixture of 2:3:4:5-tetrachlorobenzotrichloride (4 g), $FeCl_2.4H_2O$ (4 g) and chromic acid-purified acetic acid (80 ml) was heated (steam-bath) during 17·5 hr. The mass was then poured into water, acidified with HCl, ether-extracted, and filtered. The insoluble portion (2·472 g) was recrystallised from boiling dioxane yielding α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-decachlorobibenzyl which was identified by m.p., mixed m.p. and chlorine analysis.

Isomerisation of cis-α:2:3:4:5:α′:2′:3′:4′:5′-*decachlorostilbene with ultra-violet light*

A solution of *cis*-α:2:3:4:5:α′:2′:3′:4′:5′-decachlorostilbene (0·05 g) in purified carbon tetrachloride (1·5 ml) contained in a quartz vessel was illuminated, during 21 hr, with the ultra-violet radiation from a 500 W mercury lamp situated at a distance of 20 cm from the vessel. The solid phase formed was filtered (0·038 g) and melted at 245–246°. It was identified as *trans* isomer by mixed m.p. and ultra-violet spectrum.

On evaporation of the mother liquor a residue was obtained which after being washed with cold petroleum ether yielded *trans* isomer (0·015 g, 66·2%).

Attempted hydrolysis of α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-*dodecachlorobibenzyl*

A mixture of α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl (0·2 g) and acetic acid (15 ml) was refluxed during four days. The resulting mass gave on treatment with water and filtration 0·188 g unchanged material.

A mixture of finely ground α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl (0·225 g) and concentrated sulphuric acid (15 ml) was heated at 100° during 6·5 days. The mass was then treated with water and filtered, and, 0·224 g starting material was recovered, and identified.

Nuclear chlorination of α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-*dodecachlorobibenzyl*

A solution of anhydrous aluminum chloride (0·5 g) in sulphuryl chloride (80 ml) was added gradually to a refluxing mixture of α:α:2:3:4:5:α′:α′:2′:3′:4′:5′-dodecachlorobibenzyl (0·5 g), sulphuryl chloride (80 ml) and sulphur monochloride (1 g). The resulting mixture was concentrated to about 40 ml and the heating continued for about 3 hr. It was concentrated further to 5 ml and treated with warm water, slight excess of powdered sodium bicarbonate, excess of HCl and filtered. The solid residue (0·494 g) after treatment with warm carbon tetrachloride, yielded insoluble *trans*-perchlorostilbene (0·419 g). Concentration of the carbon tetrachloride solution gave *cis*-perchlorostilbene (0·016 g) and an oily residue (0·059 g).

The *trans*-perchlorostilbene was identified by m.p. mixed m.p., chlorine analysis and ultra-violet spectrum. The *cis*-perchlorostilbene was identified by m.p., mixed m.p. and ultra-violet spectrum.

Ultra-violet spectra. A "Unicam" ultra-violet spectrophotometer, Mod. SP.500 was used. Benzene-free[40] *cyclo*hexane was used as a solvent. In the case of the unsubstituted α:α′-dichlorostilbenes the spectra were recorded also using purified, absolute ethanol. The *trans*-α:α′-dichlorostilbene was prepared from α:α:α′:α′-tetrachlorobibenzyl[11] by treatment with powdered zinc in boiling ethanol.[38] It melted at 142·5–143·0°.

The *cis*-α:α′-dichlorostilbene was prepared by thermal isomerisation of its *trans* isomer (heating at 280° during four hours in a sealed glass tube). It was purified by careful crystallisations from ethanol and chromatography using neutral alumina, grade A. It melted at 65·5–66·5°.[41]

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[40] A. Gillam and E. S. Stern, *Electronic Absorption Spectroscopy in Organic Chemistry* p. 262. Edward Arnold, London (1954).

[41] F. W. J. Taylor and A. R. Murray, *J. Chem. Soc.* 2078 (1938).