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Pentachlorophenyl Derivatives. V.[1] The Preparation and Absorption Spectra of Some ω-Substituted Pentachlorostyrenes

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ω-Chloro, ω-bromo and ω-ethoxypentachlorostyrene have been synthesized, and the mechanisms and stereochemistry of the reactions involved are discussed. Acid cleavage of ω-ethoxypentachlorostyrene gives pentachlorophenylacetaldehyde. The ultraviolet absorption spectra of these compounds have been determined and are discussed.

In previous reports from this Laboratory it was shown that ethylpentachlorobenzene is chlorinated predominately in the β-position[2a,c] but is brominated exclusively in the α-position.[2b] It was also shown that halogen in the α-position of ethylpentachlorobenzene will undergo a displacement reaction under conditions where halogen in the β-position proves inert.[2a,b] We have now taken advantage of these facts to prepare ω-substituted pentachlorostyrenes and establish their structures.

Photobromination of 1-pentachlorophenyl-2-chloroethane[2a] results in two products, 1-pentachlorophenyl-1-bromo-2-chloroethane (I) and another product analyzing correctly for $C_8H_3Cl_5Br_2$. This latter product is probably the result of both substitution in the 2-position and replacement of one of the ring chlorine atoms by bromine, but its structure has not been definitely established. When I is refluxed with potassium carbonate or one equivalent of sodium methoxide in methanol, hydrogen bromide is eliminated and ω-chloropentachlorostyrene (II) is formed. The same product, II, results from the reaction of methanol and potassium carbonate with 1-pentachlorophenyl-1,2-dichloroethane, which was prepared by the addition of chlorine to pentachlorostyrene in carbon tetrachloride.

Reaction of 1-pentachlorophenyl-1,2-dibromoethane with either potassium carbonate or equivalent sodium methoxide in methanol gives ω-bromopentachlorostyrene (III). In all three of the above dehydrohalogenation reactions it is the halogen in the α-position which is eliminated, as indicated by the fact that the dibromide leads to III whereas the dichloride and the 1-bromo-2-chloride both lead to II.

Treatment of the dihaloethylpentachlorobenzenes or the ω-halopentachlorostyrenes with either excess potassium hydroxide or sodium ethoxide in ethanol results in the formation of ω-ethoxypentachlorostyrene (IV). The structure of IV was confirmed by acidic cleavage to pentachlorophenylacetaldehyde (V).

The three ω-substituted pentachlorostyrenes, which we prepared can exist in both *cis*- and *trans*-forms. However, in the preparations of both ω-chloro and ω-bromopentachlorostyrene only a single isomer was isolated, and, in both cases, the yields were high. Construction of a Fisher–Hirschfelder model of even 1,2-dichloroethylpentachlorobenzene indicates the presence of an appreciable barrier to free-rotation about both the bond between C_1 and the ring and the bond between C_1 and C_2 of the ethyl group. This hindrance to free-rotation coupled with the steric requirement of *trans* elimination in the E_2 reaction[3] may impose on the transition state of the elimination reaction a preferred orientation resulting in the observed stereospecificity. Alternatively, the stereospecificity may be due merely to a sufficient difference in the stability of the two isomers and sufficient free-rotation during some stage of the reaction to permit formation of the more stable isomer. However, the isolation of both the *cis*- and *trans*-forms of ω-bromostyrene from the dehydrohalogenation of α,β-dibromocinnamic acid casts some doubt on this latter explanation.[4]

In contrast to the above stereospecificity, the preparation of ω-ethoxypentachlorostyrene always results in a mixture of both the *cis*- and *trans*-forms. This is the case whether the starting material for the preparation is any one of the three dihaloethylpentachlorobenzenes or either of the two ω-halopentachlorostyrenes. The latter compounds, II and III, are undoubtedly intermediates even when the starting material is one of the dihaloethylpentachlorobenzenes, and we need consider only the stereochemistry involved in the transformation of a single form of II or III to a mixture of the *cis*- and *trans*-forms of IV.

That the crude ω-ethoxypentachlorostyrene is a mixture of both geometric forms is shown by crystallization from methanol which permits the separation of one isomer in the pure state and the partial separation of the other isomer. In one fortuitous crystallization we obtained crystals sufficiently large to permit mechanical separation, and this resulted in a small quantity of the less available isomer. The less available and lower melting isomer does not result from isomerization of the higher melting isomer under the alkaline reaction conditions, for refluxing the latter in alcoholic sodium methoxide does not result in any detectable conversion to the lower melting form. The ultraviolet absorption spectra (Fig. 1) of the two forms is indicative of structural similarity. More important, either of the individual isomers or their mixtures can be cleaved in excellent yield to pentachlorophenylacetaldehyde (V). This establishes the fact that we are dealing with geometric rather than structural isomers.

Since II and III are unaffected by refluxing ethanol and potassium carbonate, and the conversion to

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[1] For the fourth paper in this series see S. D. Ross and M. Markarian, THIS JOURNAL, **71**, 2756 (1949).

[2] (a) S. D. Ross, M. Markarian and M. Nazzewski, *ibid.*, **69**, 1914 (1947); (b) *ibid.*, **69**, 2468 (1947); (c) *ibid.*, **71**, 396 (1949).

[3] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937); E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941); S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3329 (1951).

[4] C. Dufraisse, *Compt. rend.*, **171**, 960 (1920); A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928).

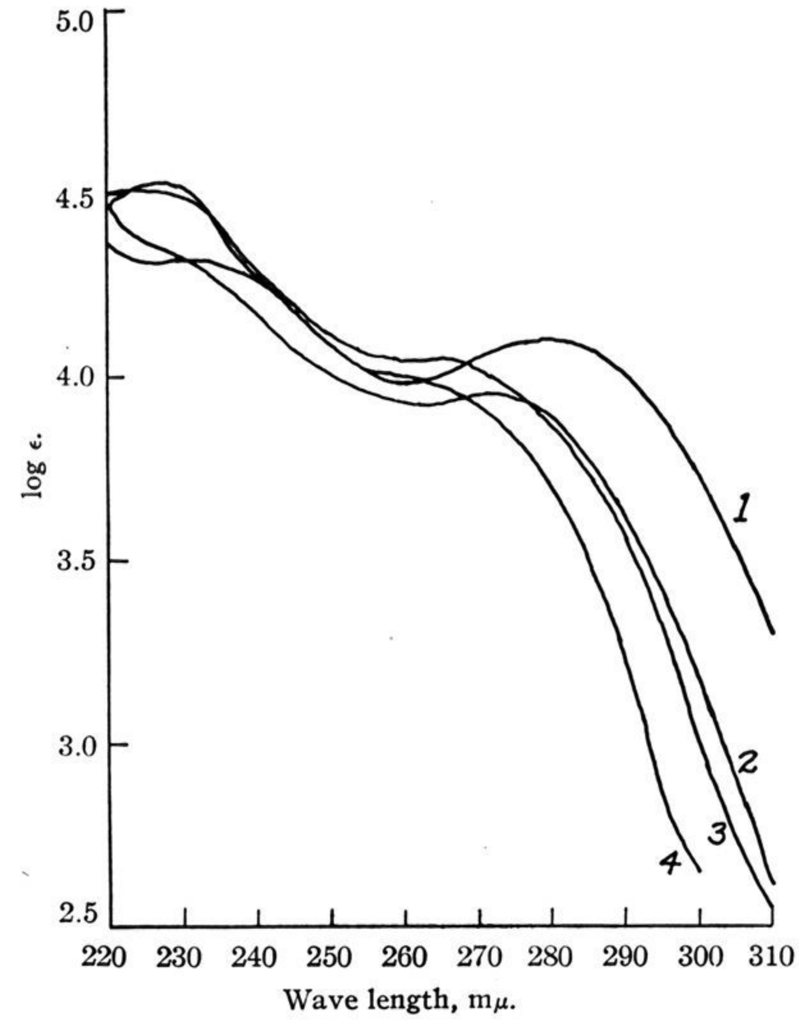


Fig. 1.—Ultraviolet absorption spectra of ω-substituted pentachlorostyrenes: 1, ω-ethoxypentachlorostyrene, high melting isomer; 2, ω-ethoxypentachlorostyrene, low melting isomer; 3, ω-bromopentachlorostyrene; 4, ω-chloropentachlorostyrene.

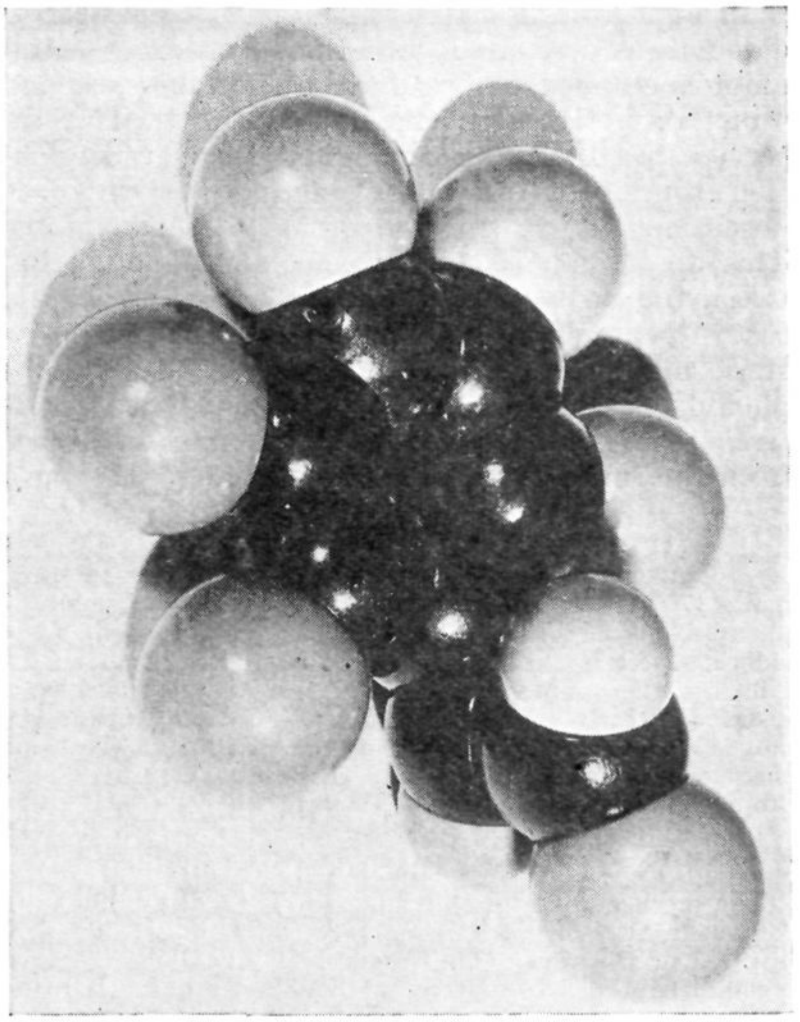
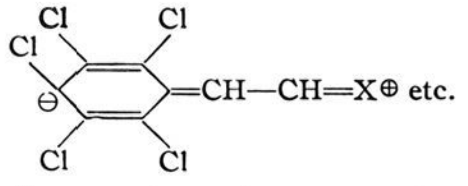


Fig. 2.—Stuart–Hirschfelder model of *trans*-ω-chloropentachlorostyrene.

IV, in both cases, requires a strong base such as alcoholic sodium ethoxide or potassium hydroxide, the reaction is presumably of the S_N2 type. The usual S_N2 attack on a saturated carbon atom follows a definite steric course and is accompanied by Walden inversion.[5] We might, therefore, expect that a single geometric isomer of II or III would result in only one form of IV. Consideration of a Stuart–Hirschfelder model of *trans*-ω-chloropentachlorostyrene (Fig. 2) makes it apparent that the formulation of the path of an S_N2 reaction is not obvious. In particular the point of attack of the ethoxide ion needs clarification. The point of most facile attack by ethoxide ion is that position on the carbon holding the halogen which is furthest from the sphere of influence of the carbon–halogen bond. This position is best defined as a point on the face of the tetrahedron opposite the apex occupied by the halogen atom, and a simple formulation which is in accord with the observed stereochemical result is shown in Fig. 3. Identical considerations, of course, obtain for *cis*-ω-chloropentachlorostyrene.

The ultraviolet absorption spectra of the ω-substituted pentachlorostyrenes shown in Fig. 1 all show a second maximum beyond 260 mμ, and this must be attributed to contributing structures of the type shown below. The model of *trans*-ω-chloropentachlorostyrene (Fig. 2) would predict a considerable barrier to achievement of the planarity required for a large contribution from structures of the type indicated above, but opposed to this steric limitation is the fact that these are structures of large electric moment and transitions to a state involving a larger contribution from such structures would occur with strong absorption.



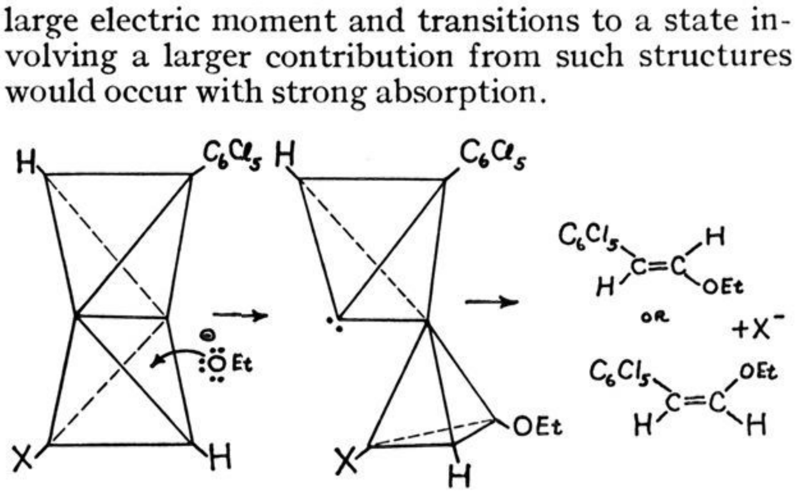


Fig. 3.

The spectra of the high and low melting forms of IV suggest strongly that the former is the *trans*-isomer and the latter the *cis*-isomer. *cis*- and *trans*-isomers differ in the intensity of the maxima more than in the wave length positions, the wave length and intensity at the maximum being usually, but not always, higher for the more linear *trans*-isomers.[6]

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[5] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 181.

[6] P. Ramart-Lucas, see V. Grignard, "Traite de Chimie Organique," Vol. 2, Masson, Paris, 1936, p. 59; see also A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931); L. Zechmeister and J. H. Pinckard, THIS JOURNAL, **69**, 1930 (1947).

In Fig. 4 the spectrum of pentachlorophenylacetaldehyde is compared with the spectra of pentachloroacetophenone,[7] pentachlorobenzaldehyde and 4-methoxytetrachlorobenzaldehyde.[1] It will be observed that the latter two aldehydes show absorption from 265–275 mμ and that such absorption is absent in the case of the other two compounds. This absorption is attributable to interaction between the carbonyl function and the ring. In the case of pentachloroacetophenone it is absent due to steric inhibition of resonance. With pentachlorophenylacetaldehyde, which forms aldehyde derivatives readily, the carbonyl function is insulated from the ring by the intervening methylene group.

Experimental[8]

1-Pentachlorophenyl-1-bromo-2-chloroethane (I).—Bromine (175 g., 1.1 moles) was added slowly to 1-pentachlorophenyl-2-chloroethane (313 g., 1.0 mole) in carbon tetrachloride (5 liters). The solution was illuminated and maintained at the boiling point by a 1000-watt projection bulb inserted directly into the solution. The solvent was removed and the crude product was crystallized twice from acetic acid and three times from ethanol to yield the desired bromochloride; yield 90 g. (23%); m.p. 96–94°.

Anal. Calcd. for $C_8H_3Cl_6Br$; C, 24.51; H, 0.77. Found: C, 24.18, 24.32, 24.53, 24.39; H, 0.76, 0.64, 0.61, 0.77.

The mother liquors from the above crystallizations were combined, the solvent was removed, and the product was distilled at 0.8 mm. The fraction of b.p. 163–171° was crystallized repeatedly from methanol containing a little chloroform to yield finally 59 g. of a product melting at 73–75° and analyzing correctly for $C_8H_3Cl_5Br_2$. This undoubtedly results from bromination in the α-position and replacement of one of the ring chlorine atoms by bromine.

Anal. Calcd. for $C_8H_3Cl_5Br_2$: C, 22.01; H, 0.69. Found: C, 22.40, 22.28; H, 0.60, 0.48.

1-Pentachlorophenyl-1,2-dichloroethane.—A solution of pentachlorostyrene (27.6 g., 0.1 mole) and chlorine (7.7 g., 0.11 mole) in carbon tetrachloride (500 cc.) was illuminated at room temperature for 60 hours with visible light. The solvent was removed and the crude product was crystallized from acetic acid–methanol (1:1); yield 17 g. (49%); m.p. 97–99°.

Anal. Calcd. for $C_8H_3Cl_7$: C, 27.63; H, 0.87. Found: C, 27.40, 27.65; H, 0.69, 0.71.

ω-Chloropentachlorostyrene (II).—In a typical preparation, the bromochloride, I (3.92 g., 0.01 mole) was refluxed for 20 hours in methanol (175 cc.) containing potassium carbonate (1.38 g., 0.01 mole). The reaction mixture was poured into a large volume of water, and the solid which precipitated was crystallized from acetic acid; yield 3.0 g. (96%); m.p. 115–116°.

Anal. Calcd. for $C_8H_2Cl_6$: C, 30.91; H, 0.65. Found: C, 30.72, 30.86; H, 0.66, 0.61.

Almost identical results were obtained when the reaction was carried out with 1-pentachlorophenyl-1,2-dichloroethane as the starting material.

ω-Bromopentachlorostyrene (III).—When 1-pentachlorophenyl-1,2-dibromoethane was treated with potassium carbonate in methanol as above or refluxed 20 hours with one equivalent of sodium methoxide in methanol, III was obtained; yield 87%; m.p. 113–115°.

Anal. Calcd. for $C_8H_2Cl_5Br$: C, 27.03; H, 0.57. Found: C, 26.77, 26.69, 26.59, 26.70; H, 0.72, 0.64, 0.60, 0.64.

ω-Ethoxypentachlorostyrene (IV).—This product was prepared from I, II, III, 1-pentachlorophenyl-1,2-dibromoethane and 1-pentachlorophenyl-1,2-dichloroethane. Similar results were obtained with all five starting materials. In a typical preparation a solution of 1-pentachlorophenyl-1,2-dibromoethane (8.8 g., 0.02 mole) and sodium ethoxide (0.06 mole) in ethanol (350 cc.) was refluxed five hours. One-half of the ethanol was removed by distillation and the remaining solution was poured into water. The solid which precipitated was crystallized from methanol. The first crop of crystals was recrystallized several times from the same solvent to yield finally 0.8 g. of the high-melting isomer; m.p. 105–107°.

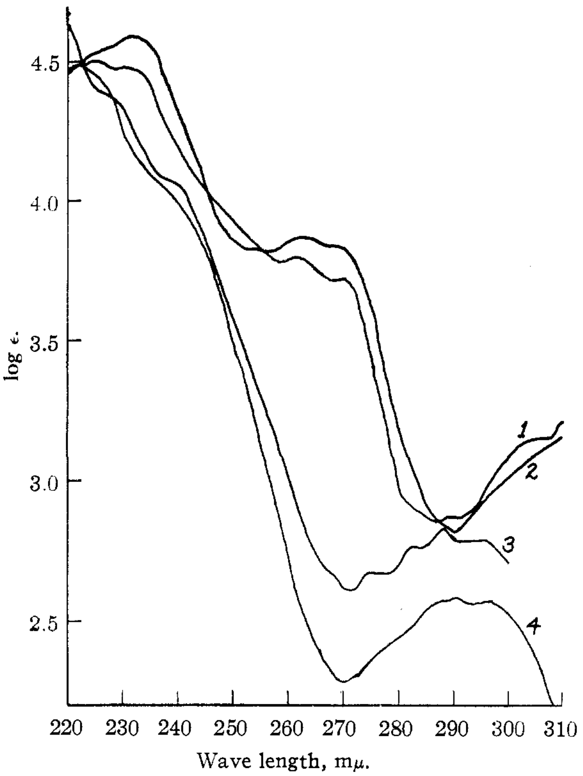

Fig. 4.—Ultraviolet absorption spectra of some chlorinated aldehydes and ketones: 1, pentachlorobenzaldehyde; 2, 4-methoxytetrachlorobenzaldehyde; 3, pentachlorophenylacetaldehyde; 4, pentachloroacetophenone.

Anal. Calcd. for $C_{10}H_7OCl_5$: C, 37.49; H, 2.20. Found: C, 37.00, 37.21; H, 2.39, 2.49.

Concentration of the mother liquors gave 4.3 g. of product; m.p. 63–73°. This product is a mixture of the geometric isomers of IV.

Anal. Calcd. for $C_{10}H_7OCl_5$: C, 37.49; H, 2.20. Found: C, 37.19, 36.92; H, 2.15, 2.32.

In one fortuitous crystallization we obtained crystals of two characteristic shapes and large enough to permit mechanical separation. One form after crystallization from methanol melted at 75–77°. This may be the pure low-melting isomer.

Anal. Calcd. for $C_{10}H_7OCl_5$: C, 37.50; H, 2.20. Found: C, 37.19, 37.00; H, 2.23, 2.08.

Pentachlorophenylacetaldehyde (V).—A mixture of IV (2 g., m.p. 105–107°), dioxane (100 cc.), water (10 cc.) and concentrated sulfuric acid (10 drops) was refluxed 20 hours and poured into water. The crude product was crystallized two times from acetic acid; yield quantitative; m.p. 136–138°.

Anal. Calcd. for $C_8H_3OCl_5$: C, 32.86; H, 1.03. Found: C, 32.40, 32.62; H, 1.23, 1.09.

Identical results were obtained when the starting material was IV of m.p. 63–73° or 75–77°.

The 2,4-dinitrophenylhydrazone of V was prepared in the usual manner; m.p. 212° from acetic acid.

Anal. Calcd. for $C_{14}H_7O_4N_4Cl_5$: C, 35.60; H, 1.50. Found: C, 35.80, 35.51; H, 1.62, 1.76.

Ultraviolet Absorption Spectra.—A Beckman model DU quartz spectrophotometer was employed for the determinations. The solvent employed was, in all cases, Spectro Grade isoöctane (2,2,4-trimethylpentane) from the Phillips Petroleum Company.

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(7) S. D. Ross, *ibid.*, **70**, 4039 (1948).

(8) All microanalyses are by Dr. Carl Tiedcke.