acid-catalyzed run of *m*-chlorobenzhydryl *p*-nitrobenzoate at 114.6° in 90% acetone, for one point 0.6 ml. of a total 7 ml. of developed titer was attributed to solvent decomposition. The largest relative correction applied was in the uncatalyzed hydrolysis of benzhydryl *p*-nitrobenzoate at 114.6° in 90% acetone, where 0.15 ml. out of 0.85 ml. of developed titer was attributed to solvent decomposition.

In the runs in 75% acetone, the solubility of the ester was often a limiting factor in the amount of ester to be solvolyzed. Despite the problems presented by solvent decomposition and limited solubility, rate constants calculated for individual points within a run showed no detectable trend and the mean deviation from the average of these points was generally ±2% or better. The individual points in the very fast reactions, such as *p*-methoxybenzhydryl *p*-nitrobenzoate in 75% acetone at 114.6°, showed deviations of about ±4% from the average. Rates were reproducible from run to run. In general, a run was studied to about 70% reaction, or to 50 hr. if the run was a slow one. Infinity titers were not usually determined. An example of a run requiring large blank corrections (and in which several ampules exploded) is shown in Table VI.

The formation of *p*-nitrobenzoic acid during a run had no detectable effect upon rate constants calculated for various points within that run.[7]

Calculation of Arrhenius Parameters.—The pseudo first-order rate constant for the acid-catalyzed reaction was obtained by subtracting the pertinent uncatalyzed rate constant from the observed rate constant under acid-catalyzed conditions. Second-order rate constants were then calculated by dividing the pseduo first-order rate constant by the acid concentration at the temperature in question[24] and these constants were used in calculating E_a and log A.

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[24] The solvent expansions were determined and were similar to that observed for 80% acetone by Goering and Silversmith.[7]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO 16, ILL.]

Stereochemical Relations in the Pentachlorophenyl-ethanes, -ethenes and -ethyne[1,2]

BY GEORGE HUETT AND SIDNEY I. MILLER

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When either *cis*- or *trans*-ω-bromopentachlorophenylethene is treated with potassium ethoxide, the predominant product is *cis*-ω-ethoxypentachlorophenylethene. The *trans*-ω-ethoxystyrene also found appears to arise from the isomerization of the *cis* compound. It has been shown that pentachlorophenylethyne, which is first formed, adds ethanol in the *trans* sense to give the *cis* ether. In the course of this work several new side-chain bromination products of pentachlorophenylethane were obtained.

What happens when a haloalkene is treated with a base? The answer to this question must be variable and may be complex.[3]

In 1952, Ross and co-workers found that a haloalkene and ethoxide ion gave rise to a *cis-trans* pair of ethoxyalkenes.[4] We considered that a closer look at the reactions involving these compounds, all pentachlorophenyl derivatives, would have broad mechanistic interest. In addition, we prepared pentachlorophenylethyne and several pentachlorophenylethanes and -ethenes. The presence of a highly modified phenyl substituent raised some unusual problems.

Of the several processes which can occur when a haloalkene undergoes substitution in the presence of a base, only two are relevant here. Briefly, the first, elimination-addition, usually leads to a single product formed by *trans* addition to the acetylenic intermediate:

$$\textit{cis}\text{- or }\textit{trans}\text{-RCH=CHX} \xrightarrow{\text{base}} \text{RC}\equiv\text{CH} \xrightarrow{\text{HQ}} \textit{cis}\text{-RCH=CHQ} \qquad (1)$$

The second, addition-elimination, leads primarily to a product of the same configuration as the reactant[3]; secondary processes involving the carbanions or the

$$\textit{cis}\text{-RCH=CHX} \xrightarrow{Q^-} \textit{cis}\text{-RCH-CHQX}^- \longrightarrow \textit{cis}\text{-RCH=CHQ} + X^-$$

$$\textit{trans}\text{-RCH=CHX} \xrightarrow{Q^-} \textit{trans}\text{-RCH-CHQX}^- \longrightarrow \textit{trans}\text{-RCH=CHQ} + X^- \qquad (2)$$

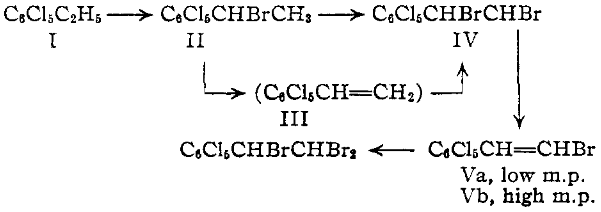
adduct, RCH_2CHQX, could lead to isomerized products.

To obtain key compounds, pentachlorophenylethane (I) was brominated. As in previous work,[5] the chief products were 1-pentachlorophenyl-1-bromoethane (II) and 1-pentachlorophenyl-1,2-dibromoethane (IV).

cis- and *trans*-ω-bromopentachlorostyrene (V) and 1-pentachlorophenyl-1,2,2-tribromoethane (VI) were novel products of the bromination. Chart 1 gives one of many possible schemes to account for all of the identified products.[6]

CHART 1

BROMINATION OF PENTACHLOROPHENYLETHANE



$$\begin{tikzcd}
\underset{\text{I}}{C_6Cl_5C_2H_5} \arrow[r] & \underset{\text{II}}{C_6Cl_5CHBrCH_3} \arrow[r] \arrow[dr] & & \underset{\text{IV}}{C_6Cl_5CHBrCHBr} \arrow[dd] \\
& & \underset{\text{III}}{(C_6Cl_5CH{=}CH_2)} \arrow[ur] & \\
& & C_6Cl_5CHBrCHBr_2 & \underset{\substack{\text{Va, low m.p.} \\ \text{Vb, high m.p.}}}{C_6Cl_5CH{=}CHBr} \arrow[l]
\end{tikzcd}$$

The transformations depicted in Chart 2 were carried out to establish gross structure. To differentiate the ω-bromostyrenes V the rates of ethoxide-catalyzed

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[1] Supported in part by the Office of Ordnance Research, U. S. Army, and in part by the Research Corporation.

[2] In partial fulfillment of the Ph.D. requirements of G. Huett.

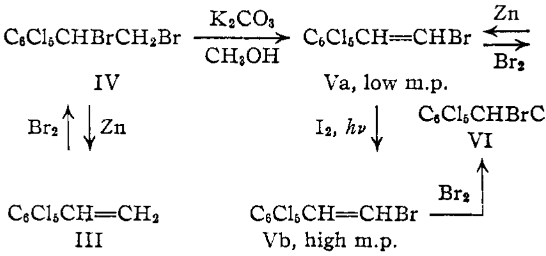
[3] (a) S. I. Miller and P. K. Yonan, THIS JOURNAL, **79**, 5931 (1957); (b) S. I. Miller and W. G. Lee, *ibid.*, **81**, 6313 (1959); (c) F. Montanari, *Boll. sci. fac. Chim. ind.* (*Bologna*), **16**, 31 (1958); (d) D. E. Jones, R. O. Morris, C. A. Vernon and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).

[4] S. D. Ross, W. A. Leach and I. Kuntz, THIS JOURNAL, **74**, 2908 (1952).

[5] S. D. Ross, M. Markarian and M. Nazzewski, *ibid.*, **69**, 2468 (1947).

[6] Ross, *et al.*, suggested that the 1-bromide II dehydrobrominates at 180° to give the styrene from which the 1,2-dibromide is formed.[5] Since we have prepared dibromide in the temperature range 70–130°, it is probable that direct bromination of II also occurs. Elimination-addition steps, however, do account plausibly for the ω-bromostyrenes and the tribromide.

CHART 2



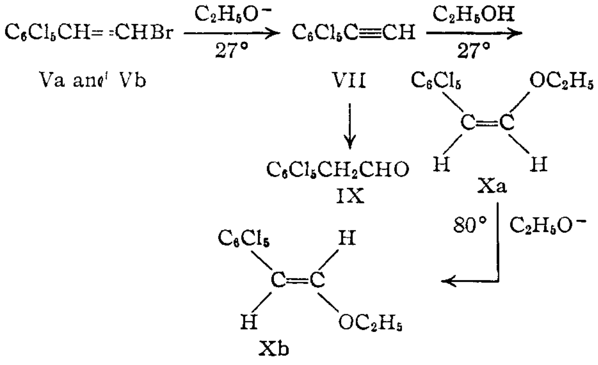
dehydrobromination were measured under comparable conditions. The fact that the rate constant of Va is 1/5 of that of Vb strongly suggests that Va is the *trans* isomer.[7] Conformational analysis also indicates that treatment of the 1,2-dibromide with base or of the tribromide with zinc would lead chiefly to the *trans* isomer.[8] Finally, spectral evidence which will be discussed later is in agreement with this structural assignment.

In the most successful preparations of pentachlorophenylacetylene (VII), ω-bromostyrene (Va) was treated with potassium ethoxide in petroleum ether and any contact with hydroxylic solvents was avoided. The reaction proceeds at room temperature.

In the presence of ethanolic ethoxide and below 60°, both bromostyrenes (V) yield ω-ethoxystyrene Xa; at *ca.* 80°, both ω-ethoxystyrenes (X) are obtained. Since Xa is not isomerized in refluxing ethanol, it would appear that Xb arises from the isomerization of Xa by ethoxide ion. (An ω-methoxystyrene (VIII), presumably *cis*-, was also made from Va in methanolic potassium carbonate.)

From one preparation of X, the aldehyde IX was also isolated. Since basic hydrolysis of the acetal of IX, a plausible product[9] of the ethoxy ethers, is improbable during work-up of the product,[4] it would appear that the aldehyde resulted from the hydration of the acetylene VII. These reactions are summarized in Chart 3.

CHART 3



In the preceding discussion we have explicitly made structural assignments to the ω-ethoxypentachlorostyrenes. That Xa is *cis* is based on its stereospecific formation from VII and that it appears to be less stable than Xb with respect to isomerization.[4] Infrared evidence appears to be more conclusive. In the 940 cm.$^{-1}$ region there is a characteristic C–H bonding frequency in 1,2-*trans* compounds which is absent or of lower intensity in 1,2-*cis* compounds.[9,10] Relevant examples are *trans*- ω-bromopentachlorostyrene (Va), 926 cm.$^{-1}$; *trans*-ω-ethoxypentachlorostyrene (Xb), 947 cm.$^{-1}$; *trans*-*p*-nitro-ω-bromostyrene,[10b] 938 cm.$^{-1}$; *trans*-ω-methoxystyrene,[9] 937 cm.$^{-1}$. Thus, spectral data confirm the *cis* structure of Xa and of Vb and the *trans* structure of Xb and Va.

Experimental

All m.p.'s were uncorrected. Infrared spectra were taken on a Perkin-Elmer model 21 spectrometer with sodium chloride optics. Little reference will be made here to identification by such spectra, but for all compounds, reactants, or products, infrared spectra were recorded and used. Analyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

Bromination of Pentachlorophenylethane (I).—These are variations on the methods of Ross, *et al.*[5] Pentachlorophenylethane, recrystallized from acetone to m.p. 54° (lit.[11] m.p. 57°), was used. A mixture of I (210 g., 0.76 mole) and bromine (130 g., 0.81 mole) was stirred in a Pyrex flask under illumination by an ultraviolet lamp. After 73 hours at 80–130°, the mixture was cooled, aspirated, then treated with acetone. The insoluble residue, chiefly 1-bromopentachlorophenylethane (I), m.p. 120–124°, was obtained in 52% yield. Recrystallization from ethyl ether–petroleum ether yielded a product melting at 124° (lit.[5] m.p. 123–124°).

In another preparation I (54.1 g., 0.195 mole) and bromine (65.5 g., 0.41 mole) were kept at the above conditions for 92 hours. After aspiration, the mixture was crystallized from petroleum ether and acetone (1:1) to yield a 76% yield of crude pentachlorophenyl-1,2-dibromoethane (IV). Further recrystallization gave IV, m.p. 94–94.5° (lit.[5] m.p. 95–96°).

In a third preparation bromine (680 g., 4.25 moles) was added to I (526 g., 1.89 moles) through a capillary extending beneath the surface of the liquid at *ca.* 200° over a period of 45 hr. After 3 hr., the mixture was cooled and taken up in carbon tetrachloride. On cooling, 197 g. of material separated which on recrystallization from acetone yielded (80 g.) of ω-bromopentachlorostyrene (Va), m.p. 113–114.5° (lit.[4] m.p. 113–115°).

Anal. Calcd. for $C_8Cl_5BrH_2$: C, 27.04; H, 0.79. Found: C, 27.21; H, 0.86.

The carbon tetrachloride solution deposited 220 g. of solid. Recrystallization from acetone then petroleum ether–acetone (2:1) yielded 23 g. of 1-pentachlorophenyl-1,2,2-tribromoethane (VI), m.p. 112–114°. Recrystallization from petroleum ether–ethyl ether (1:1) raised the m.p. to 115–115.5°.

Anal. Calcd. for $C_8Cl_5Br_3H_2$: C, 18.65; H, 0.39. Found: C, 18.74; H, 0.57.

Later crops from the original carbon tetrachloride solution deposited numerous impure fractions. These were combined with residues from the earlier crops according to their melting range. Combined portions melting above 115° yielded on several recrystallizations from acetone–petroleum ether 10 g. of ω-bromostyrene Vb, m.p. 135–138°. Further crystallization from petroleum ether–ethyl ether (1:1) raised the m.p. 137.5–139°.

Anal. Calcd. for $C_8Cl_5BrH_2$: C, 27.04; H, 0.79. Found: C, 26.43; H, 0.81.

Pentachlorostyrene (III).—1,2-Dibromo-1-pentachlorophenylethane (IV) (10 g., 0.029 mole) and zinc powder (2.74 g., 0.043 mole) were stirred at reflux temperature for 52 hours in a solvent consisting of 100 ml. of petroleum ether–absolute alcohol (1:1). The mixture was cooled and filtered and the solvent removed. The yield of crude III, m.p. 106–108°, was 90%. Recrystallization from petroleum ether–ethyl ether (1:1) raised the m.p. to 108° (lit.[5] 113–114.5°).

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[7] S. I. Miller and R. M. Noyes, THIS JOURNAL, **74**, 629 (1952).

[8] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Ch. 1.

[9] S. I. Miller, THIS JOURNAL, **78**, 6091 (1956).

[10] (a) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953). (b) The spectra of the *p*-nitro-ω-bromostyrenes were measured by Mr. Peter Yonan.[3a]

[11] P. G. Harvey, F. Smith, M. Stacey and J. C. Tatlow, *J. Appl. Chem.*, **4**, 325 (1954).

Compound III (1.5 g., 0.0054 mole) was treated with bromine (0.87 g., 0.0054 mole) in 100 ml. of carbon disulfide at reflux 24 hr.; 2.17 g. or a 90% yield of IV, m.p. 91–92.5°, was obtained which showed no depression of melting point when mixed with the dibromide obtained from the bromination of I.

Another portion of III (2 g., 0.0072 mole), treated with gaseous hydrogen bromide in 90 ml. of petroleum ether and 15 ml. of glacial acetic acid at reflux (*ca.* 55°), yielded 94% or 2.43 g. of II, m.p. 122–124°; this showed no depression of m.p. when mixed with a sample obtained from the bromination of I. In previous work III could be hydrobrominated only under free radical conditions to yield the 1-pentachlorophenyl-2-bromoethane.[12]

ω-Bromopentachlorostyrene (Va) was prepared by the method of Ross, *et al.*, from the treatment of the 1,2-dibromide IV with potassium carbonate. Crystallization from petroleum ether gave a product melting at 112–113° (lit.[4] m.p. 113–115°).

Compound Va was also obtained in 73% yield from the tribromide VI (5 g., 0.0097 mole) by zinc (2.5 g.) debromination after 48 hours at reflux in petroleum ether–absolute alcohol (1:1). The product had m.p. 112° which showed no depression when mixed with Va obtained from the bromination of I.

1,2,2-Tribromo-1-pentachlorophenylethane (VI).—Compound Va (3.55 g., 0.01 mole) was heated with bromine (1.8 g., 0.011 mole) for 36 hours at 100–120° under an external ultraviolet lamp. The mixture was taken up in carbon tetrachloride, crystallized and then recrystallized from petroleum ether. A 95% yield of the tribromide was obtained, m.p. 113–114°. Further recrystallization from petroleum ether–ethyl ether (1:1) raised the m.p. to 115–115.5°. A mixed m.p. with a sample obtained from the bromination of I showed no depression.

ω-Bromopentachlorostyrene (Vb).—Compound Va (5.5 g., 0.16 mole), m.p. 112–113°, and a few iodine crystals were dissolved in 75 ml. of petroleum ether and 5 ml. of carbon tetrachloride. The solution was illuminated with an ultraviolet lamp for 1 month. Crystallization from the solution gave 3.3 g. of crude Vb, m.p. 134–135°. Recrystallization from petroleum ether–ethyl ether (1:1) raised the melting point to 138–139.5°. This product showed no depression in m.p. when mixed with Vb obtained from the bromination of I.

The tribromide VI, m.p. 115–115.5°, was prepared in almost quantitative yield from Vb by bromination in carbon disulfide.

Base-catalyzed Elimination Rates of the ω-Bromostyrenes (V).—Comparable kinetic runs were made on Va, m.p. 112–113°, and on Vb, m.p. 138–139.5°. Each ω-bromostyrene (0.230 g., 0.000563 mole) was added to 100 ml. of absolute alcohol, 25 ml. of low boiling petroleum ether and potassium ethoxide (0.000661 mole) and allowed to stand at room temperature (*ca.* 27°). Ten-ml. aliquots were taken at intervals and the bromide ion estimated with standard silver nitrate, 0.006 *N*. The initial concentrations were taken as 4.5 mmoles/liter for V and 5.29 mmoles/liter for potassium ethoxide. The concentrations of bromide ion in mmoles/liter are given following the time in hours: for Va: 4, 1.2; 7.75, 2.0; 22, 2.64; 28, 3.0; 52, 3.3; for Vb: 4, 3.0; 7.75, 4.26; 22, 4.86; 28, 4.98; 52, 5.4.

Pentachlorophenylacetylene (VII).—Compound Va (5.7 g., 0.016 mole) was dissolved in 250 ml. of petroleum ether to which had been added potassium (0.68 g., 0.0174 mole) and absolute alcohol (0.80 g., 0.0174 mole). The mixture was refluxed at *ca.* 43° for 1 week. Analysis for inorganic halide showed 90% reaction. The solution was treated with decolorizing carbon, filtered and evaporated. Successive recrystallizations, the last from ethyl ether, gave a 56% yield of VII. The product had infrared bands at 3.06 and 4.74 μ, presumably the C—H and C≡C stretching frequencies. There was no evidence for the presence of reactants or plausible co-products. On heating on the melting block the compound began to turn deep red above *ca.* 140° and finally liquefied at 185–186°. (The red material differs from VII and is being investigated.) Compound VII could be sublimed without apparent change at *ca.* 100° and 1 mm. to give a white product. Analyses on five different samples were unsatisfactory. *Anal.* Calcd. for C_8Cl_5H: C, 35.02; H, 0.37. Found: C, 33.19–33.51; H, 0.72–1.10.

A mercuric acetylide of VII was prepared with alkaline mercuric iodide. It is a white solid, essentially unaffected by most solvents, acids, bases and zinc–acid mixtures. *Anal.* Calcd. for $C_{16}Cl_{10}Hg$: C, 25.78; H, 0.0. Found: C, 25.61; H, 0.18.

ω-Ethoxypentachlorostyrene (X).—Identical runs were made with Va and Vb. Each ω-bromopentachlorostyrene (0.2 g., 0.00056 mole) was dissolved in 100 ml. of absolute ethanol and 25 ml. of petroleum ether containing potassium ethoxide (0.0013 mole) and was stirred for 120 hours at 27°. The mixture was cooled, treated with 2 g. of decolorizing carbon, filtered and evaporated. The residue was taken up in petroleum ether and filtered. After partial removal of solvent and cooling in Dry Ice a solid melting 56–58° was isolated. The infrared pattern of the products from Va and Vb appeared identical; there was no depression of m.p. when they were mixed. Recrystallization raised the m.p. to 71–72°. Since this product was spectroscopically different from its higher melting isomer Xb it is considered that the higher m.p., 75–77°, previously reported must have been for a mixture of Xa and Xb.

Compound Va (9.86 g., 0.0277 mole) was also refluxed in ethanolic ethoxide for 16 hr. The solution was treated with cold water. The crude product on recrystallization yielded 1.9 g. of Xa, m.p. 71–72°; 1.7 g. of Xb, m.p. 106.5–107° (lit.[4] m.p. 105–107°); and 1.8 g. of the aldehyde IX, m.p. 141° (lit.[4] 136–138°) with an infrared carbonyl band at 1730 cm.⁻¹. Sublimation of Xa and Xb could be carried out at 80–100° and 1 mm. However, the low-melting *cis* isomer was isomerized; this was indicated both by the appearance of *trans* bands in its infrared spectrum and by the isolation of *trans*, m.p. 106°; Xa, Xb and IX give DNP's with the same m.p. 214–215° (lit.[4] m.p. 212°).

ω-Methoxypentachlorostyrene (VIII).—Ten grams of a combined portion of the products of bromination, melting range 92–94.5°, was treated with potassium carbonate (0.023 mole) in absolute methanol at reflux for 24 hours. (That the starting material contained *ca.* 75% V and no more than 15% of IV or VI was established partly by product isolation, but chiefly by analysis for inorganic bromide after treatment with base or with zinc.) The mixture was treated with water and extracted with petroleum ether–ethyl ether (2:1). Crystallization from ethyl ether gave 5.6 g. (0.019 mole) of material, m.p. 133–135°, which on further recrystallization was raised to 137.5–139° (lit.[13] 138–139°). If the starting material were pure V (0.028 mole) the yield of VIII would be 65%; if it were either pure IV or the 2,2-dibromide (0.023 mole) the yield of VIII would be 80%. The infrared spectrum of this compound is closely similar to that of Xa; it does not have the carbonyl band of IX and, indeed, the melting point of a mixture of VIII and IX is well below that of either.

1 - Pentachlorophenyl- 1 - substituted Ethanes.—1 - Pentachlorophenyl-1-acetoxyethane was prepared from potassium acetate and II in 70% yield, m.p. 101–102° (lit.[5] m.p. 101–102°). The acetoxy compound was hydrolyzed with base to give 1-pentachlorophenyl-1-hydroxyethane (XI) in almost quantitative yield, m.p. 124° (lit.[5] 124–125°). Compound XI (2.1 g., 0.01 mole) in a solvent of 30 ml. of glacial acetic acid and 50 ml. of petroleum ether was refluxed for 7 hours with potassium dichromate (2 g.), 97% sulfuric acid (2 g.) and water (6.7 g.). The product was recrystallized from 2:1 petroleum ether–acetone yielding, almost quantitatively, pentachlorophenyl methyl ketone, m.p. 90–91.5°. Recrystallization from ethyl ether raised the m.p. to 91–91.5° (lit.[14] m.p. 90–92°); $\nu_{C=O}$ in carbon tetrachloride was 1727 cm.⁻¹.

Attempted Oxidation of I.—It was considered that oxidation of the side chain to corresponding benzoic acids would resolve the question of possible ring *versus* side-chain substitution by base. It was found, however, that pentachlorophenylethane was not oxidized by chromic oxide–sulfuric acid in refluxing acetic acid even after 1 week.

Discussion

When a haloalkene is treated with a base several processes must be considered.[3] Otherwise the stereochemical results of exchange appear to be

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(12) S. D. Ross, M. Markarian, H. H. Young and M. Nazzewski, THIS JOURNAL, **72**, 1133 (1950).

(13) Sidney D. Ross, U. S. Patent 2,643,270, *C. A.*, **48**, 4000 (1954).

(14) S. D. Ross, THIS JOURNAL, **70**, 4039 (1948).

complex or unsystematic.[15] Two of the important processes have been indicated in eq. 1 and 2. The elimination–addition sequence is favored by strong bases and the addition–elimination sequence by bases which are also strong nucleophiles in each system. An example is found in the contrasting behavior of alkoxides and mercaptides toward the β-chlorocrotonic acids.[15] For these two processes one has the useful mechanistic distinction (see also eq. 1 and 2): *when a nucleophile and a haloalkene react under non-isomerizing conditions, a cis product is indicative of elimination–addition while a product of original geometric configuration is indicative of addition–elimination.* It is worth emphasizing that other competing ionic processes or non-ionic isomerization can further complicate the system haloalkene plus base.[3]

Our results indicate that both *cis*- and *trans*- 1-pentachlorophenyl-2-bromoethene are dehydrobrominated by ethoxide to yield the pentachlorophenylethyne. The ethyne then adds ethanol stereospecifically *trans* to give the *cis*-ω-ethoxypentachlorophenylethene (Xa). Subsequently, this ether is isomerized, not thermally, but by ethoxide ion catalysis. It is clear that the displacement mechanism which was first considered to explain these data may now be discarded.[4]

The ionic isomerization would involve the addition–elimination[3]

$$\mathrm{Xa}\ \underset{\text{fast}}{\overset{\mathrm{C_2H_5O^-}}{\rightleftarrows}}\ \underset{\textit{cis}}{\mathrm{C_6Cl_5}\underset{\ominus}{\mathrm{CH}}\mathrm{CH(OC_2H_5)_2}}\ \underset{\text{slow}}{\rightleftarrows}$$

$$\underset{\textit{trans}}{\mathrm{C_6Cl_5}\underset{\ominus}{\mathrm{CH}}\mathrm{CH(OC_2H_5)_2}}\ \underset{\text{fast}}{\overset{\mathrm{C_2H_5O^-}}{\leftrightarrows}}\ \mathrm{Xb} \qquad (3)$$

Such addition is certainly plausible: the methoxide-catalyzed addition of methanol to phenylacetylene yields the *cis*-ω-ether as well as phenylacetaldehyde dimethylacetal.[9] As for the isomerization, Montanari has recently documented an analogous case, the reaction of thiolate with *cis*- and *trans*-mercaptoacrylic acids.[16] Although the *cis*- and *trans*-carbanions of 3 could yield the corresponding acetal, this compound has not been isolated in this or in the previous study.[4] But in other systems this may in fact be the isomerization path: however, the decomposition of such an ethane may be stereoselective, but it is probably not stereospecific. Contrast an early view of Truce who chose to explain certain displacements with retention of configuration on the basis of the *cis* effect operating in equilibrated carbanions (as in eq. 3) or in the corresponding ethane.[17] Clearly, the Law of Microscopic Reversibility requires that if these carbanions are in equilibrium both *cis* and *trans* products will be formed from either isomer.

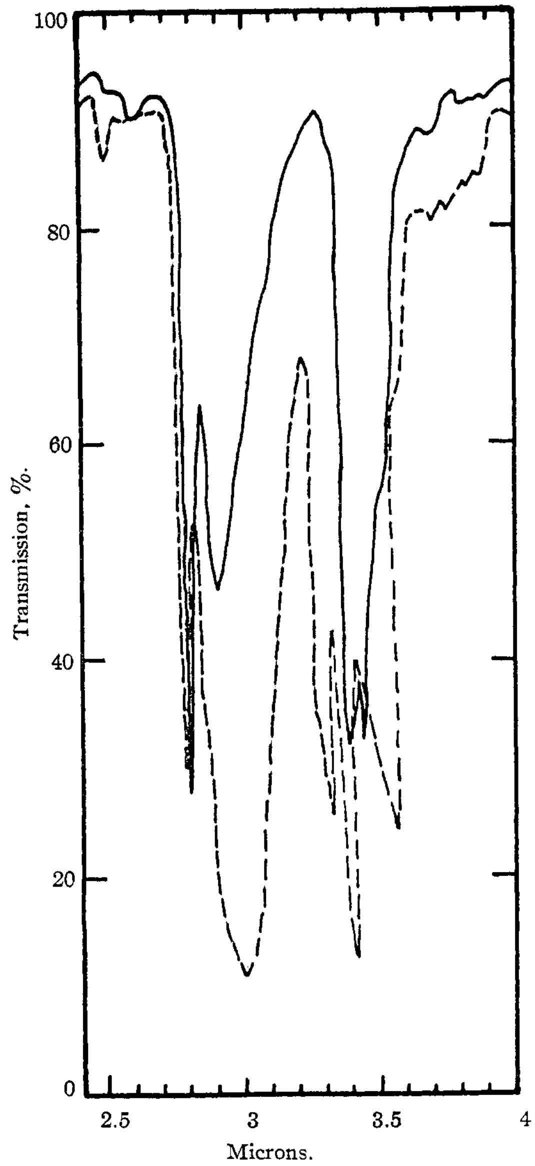

Fig. 1.—The infrared O–H region of $C_6Cl_5CHOHCH_3$ (full line) and $C_6H_5CHOHCH_3$ (broken line), at equal molar concentrations.

Polar Effects of the Pentachlorophenyl Group.—On the Hammett σ-scale, the electron-withdrawing ability of five chlorine atoms on the aromatic nucleus has been rated at $^{\sigma}5\mathrm{Cl} \simeq 3.49$ or about equivalent to about two nitro groups.[18] The 1-pentachlorophenyl group would, therefore, strongly favor processes in which a carbanion or a free radical were generated at the 1-position. Conversely, a positive carbon would be favored at the 2- rather than the 1-position. The following results are consistent with this view (the citations are for systems with which *comparison* is possible): (1) ease of nucleophilic addition of ethanol to pentachlorophenylacetylene[19]; (2) ease of dehydrobromination of pentachlorophenyl-ω-bromostyrene[20]; (3) ease of nucleophilic displacement, *e.g.*, acetate displacement at the 1-carbon of 1-pentachlorophenyl-1-bromoethane[5]; (4) ease of nucleophilic addition at the 2-carbon of the ω-ethoxystyrenes; (5) relatively

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[15] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[16] F. Montanari, *Tetrahedron Letters*, **4**, 18 (1960).

[17] W. E. Truce and R. Kassinger, THIS JOURNAL, **80**, 6450 (1958); for a more recent view, see W. E. Truce, *et al.*, *ibid.*, **82**, 3799 (1960).

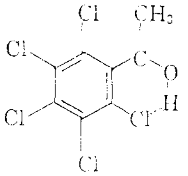
[18] P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **27**, 551 (1957).

[19] S. I. Miller and G. Shkapenko, THIS JOURNAL, **77**, 5038 (1955).

[20] S. J. Cristol and W. P. Norris, *ibid.*, **76**, 3005 (1956).

slow ionic hydrogen bromide addition to pentachlorostyrene to give the 1-pentachloro-1-bromoethane in contrast to the facile radical addition which gives 1-pentachlorophenyl-2-bromoethane[12]; (6) the difficulty of oxidizing pentachlorophenylethane.

The polar effect of the pentachlorophenyl group shows up in another manner. While phenylmethylcarbinol is largely intermolecularly hydrogen-bonded, pentachlorophenylmethylcarbinol is appreciably intramolecularly hydrogen-bonded.[21] Both have sharp free O–H bands at 2.80 μ similar in intensity at comparable molar concentrations in carbon tetrachloride. The former exhibits a broad intermolecular O–H band at 3.0 μ while the pentachloro compound has a weak band at 2.91 μ. It appears that this is an intramolecular O–H band and may be attributed to the structure (see also Fig. 1)



The carbonyl frequency of the aldehyde IX is somewhat above normal at 1730 cm.$^{-1}$.[22] The pentachlorophenyl methyl ketone band at 1727 cm.$^{-1}$ appears to be extremely high for ketone carbonyl[22]; yet it is about what one would predict from a σ (or σ^+) *versus* $\nu_{C=O}$ plot.[23] Both steric and electrostatic (field) effects would tend to shift $\nu_{C=O}$ upward; however, scale models indicate no pronounced interference between the *o*-chloro atoms and the carbonyl oxygen. Thus, strong polar effects of the pentachlorophenyl group are indicated here also.

Previous workers have largely emphasized the steric influence[14] of the pentachlorophenyl group while we have stressed the polar effect. Models indicate that in pentachlorophenylethane rotation is possible between carbon 1 and the ring and carbon 2 and carbon 1 providing there is cog-wheeling between the terminal hydrogens and the *o*-chlorine atoms. Once a 1-substituent is present, rotation between the carbon 1 and the ring is hindered. Thus, in the di- and tribromoethanes, the most stable conformations are also most suitable for *trans* eliminations with base or zinc, to lead almost exclusively to the *trans*-ω-bromostyrene (Va). But these are expected conformational results—the reported inertness of pentachlorophenylmethyl ketone to the usual carbonyl reagents is more striking.[14,24] Only in the sense that these fairly exaggerated polar and steric effects can be rationalized may they be considered "normal."

Acknowledgment.—We wish to thank Mr. L. Clemens for some technical assistance and the Dow Chemical Co. for samples of pentachlorophenylethane.

[21] A. W. Baker and A. T. Shulgin, THIS JOURNAL, **80**, 5358 (1958); G. M. Badger, *Rev. Pure Appl. Chem.*, **7**, 55 (1957).

[22] L. J. Bellamy, "Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Ch. 9.

[23] R. Stewart and K. Yates, THIS JOURNAL, **80**, 6355 (1958).

[24] G. Lock and E. Bock, *Ber.*, **70**, 916 (1937).

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Carbanions. IV. Rearrangements in the Reaction of 2-Chloro-1,1,1-triphenylethane with Lithium and Potassium

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Potassium reacts with 2-chloro-1,1,1-triphenylethane at temperatures of −50 to 66° to give 1,1,2-triphenylethylpotassium as the only detectable monopotassium derivative. On the other hand, lithium reacts with 2-chloro-1,1,1-triphenylethane at temperatures of −65 to −30° to give 2,2,2-triphenylethyllithium which is comparatively stable at these temperatures but rearranges rather readily at temperatures of 0° or higher to give 1,1,2-triphenylethyllithium. These reactions are considered to strengthen the previous interpretation[1] that such rearrangements are rearrangements of the 2,2,2-triphenylethyl carbanion. The ease of rearrangement of 2,2,2-triphenylethylalkali compounds parallels the degree of ionic character of the carbon–metal bond. The structures of the organometallic compounds described here are inferred from the structures of the carboxylic acids obtained after reaction with carbon dioxide.

The reaction of 2-chloro-1,1,1-triphenylethane with sodium has been found to proceed with rearrangement of carbon skeleton *via* 1,2-shift of a phenyl group when the reaction is conducted in refluxing dioxane[1] or in ethyl ether–isoöctane at room temperature.[2] When the reaction was run in a mixture of dioxane and *t*-amyl alcohol, however, 94% of the triphenylethane obtained had the same carbon skeleton as the starting material, while 6% had undergone rearrangement of a phenyl group to give 1,1,2-triphenylethane.[1] These results were most simply explained on the basis that the reaction of 2-chloro-1,1,1-triphenylethane with sodium gives 2,2,2-triphenylethyl carbanion, which in the presence of *t*-amyl alcohol undergoes fast protonation before appreciable rearrangement of phenyl has occurred but which in absence of a proton donor rearranges to give the more stable 1,1,2-triphenylethyl carbanion.[1] If, as seems likely, the reaction

$$\mathrm{Ph_3CCH_2Cl + 2Na \longrightarrow Ph_3CCH_2{\ominus}Na{\oplus}}$$

$$\begin{array}{l} \mathrm{Ph_3CCH_2{\ominus}Na{\oplus}} \xrightarrow{t\text{-AmOH}} \mathrm{Ph_3CCH_3} \\ \quad \llcorner\!\!\longrightarrow \mathrm{(Ph_2CCH_2Ph){\ominus}Na{\oplus}} \end{array}$$

of alkyl halides and of tetraalkylammonium halides with sodium proceeds by a similar mechanism,

[1] E. Grovenstein, Jr., THIS JOURNAL, **79**, 4985 (1957).

[2] H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).