$$RX + \dot{M}g^{+} \longrightarrow R\cdot + Mg^{++} + X^{-} \quad (9)$$

$$R\cdot + Mg: \longrightarrow R:^{-} + \dot{M}g^{+} \quad (10)$$

The question now arises why no Grignard reagent is formed in either the anolyte or catholyte in our electrolysis experiments. The evidence for nonformation of Grignard reagent is two-fold. No benzoic acid is isolated following carbonation and acidification of either solution, and of the isomeric phenylpyridines produced the 4-isomer rather than the 2-isomer predominates. The answer to the question posed at the start of the paragraph is that pyridine functions as an inhibitor of the free radical chain reaction leading to Grignard reagent. As a matter of fact, when bromobenzene is heated with magnesium in pyridine solution containing a small amount of iodine and sodium iodide, 4-phenylpyridine is the predominant isomer formed (see Experimental) and the composition of the basic fraction is identical with that of the anolyte following electrolysis of bromobenzene in pyridine solution between magnesium electrodes.

LAWRENCE, KAN.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Pentachlorophenyl Derivatives. VI.[1] The Preparation and Methanolysis of Pentachlorostyrene Oxide

SIDNEY D. ROSS AND E. ROBERT COBURN, JR.[2]

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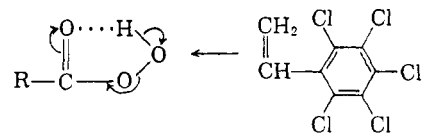
Pentachlorostyrene oxide reacts with methanol in the presence of acid to form 1-pentachlorophenyl-1-methoxy-2-hydroxyethane. In the presence of base, the attack by methoxide ion is on the β-position to give 1-pentachlorophenyl-1-hydroxy-2-methoxyethane. A second product, probably 4-methoxy-2,3,5,6-tetrachlorostyrene oxide, is also formed in this latter reaction. These reactions are discussed.

Pentachlorophenyl derivatives have been of interest because of the frequency with which they react to give atypical products. Some examples which may be cited are the predominant β-chlorination of ethylpentachlorobenzene,[3] the alcoholysis of pentachlorobenzal chloride to give an acetal of a 4-alkoxy-2,3,5,6-tetrachlorobenzaldehyde[4] and the ability of pentachlorostyrene to add hydrogen bromide by a radical mechanism to give β-bromoethylpentachlorobenzene coupled with the complete absence of any evidence for ionic addition in the same system.[5]

For the most part, these abnormal reactions have been attributed to the steric effects rather than the polar effects of the chlorine substituents. In this connection both the preparation and alcoholysis of pentachlorostyrene oxide appeared to be of interest. The failure of pentachlorostyrene to add hydrogen bromide by an ionic mechanism[5] might lead to difficulty in the preparation of the oxide, and the direction of opening of the oxide ring, once formed, might be influenced by polar factors as much as by steric factors.

In actual fact, the preparation of pentachlorostyrene oxide proved to be straightforward, good yields being obtained with either perbenzoic or peracetic acid in chloroform. The success of this reaction, in contrast to the failure of the ionic addition of hydrogen bromide, may be due to the fact that ionic intermediates are probably not involved. One possible rationalization: The reaction involves a π-complex, as depicted below, between the vinyl double bond and an internally hydrogen-bonded form of the peracid, which then collapses to give the final products. This is the mechanism proposed by Overberger and Cummins[6] for the oxidation of *p,p'*-dichlorobenzyl sulfide by perbenzoic acid.



The opening of the oxide ring with methanol proceeds smoothly in the presence of an acid catalyst to give a single methoxyalcohol (I) in good yield. The methanolysis product (I) reacts with thionyl chloride to form a chloro ether and readily forms an acetate and *p*-toluenesulfonate. The structure of I was established by the sequence of reactions shown:

(1) For the previous paper in this series, see S. D. Ross, W. A. Leach, and I. Kuntz, *J. Am. Chem. Soc.*, **74**, 2908 (1952).

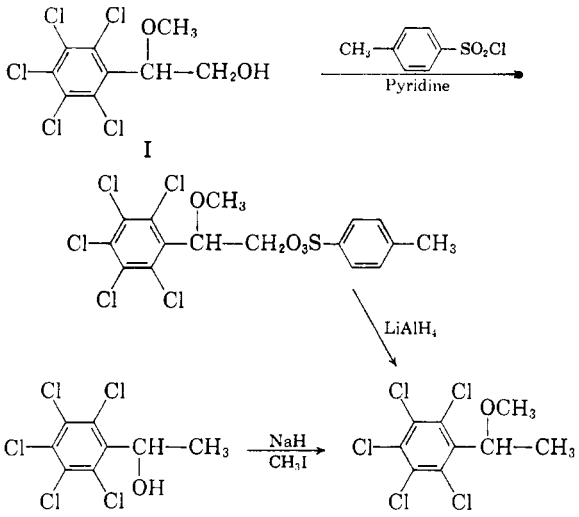
(2) Bennington College, Bennington, Vt.

(3) S. D. Ross, M. Markarian, and M. Nazzewski, *J. Am. Chem. Soc.*, **69**, 1914, 2468 (1947); **71**, 396 (1949).

(4) S. D. Ross and M. Markarian, *J. Am. Chem. Soc.*, **71**, 2756 (1949).

(5) S. D. Ross, M. Markarian, H. H. Young, Jr., and M. Nazzewski, *J. Am. Chem. Soc.*, **72**, 1133 (1950).

(6) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953). See also S. Medvedev and O. Blokh, *J. Phys. Chem.* (*U.S.S.R.*), **4**, 721 (1933); *Chem. Abstr.*, **29**, 6492 (1935).



The *p*-toluenesulfonate was cleaved by lithium aluminum hydride to give an ether, which was shown to be identical with 1-pentachlorophenyl-1-methoxyethane, prepared independently by alkylation of the known methyl pentachlorophenyl carbinol[3,6] with sodium hydride and methyl iodide.

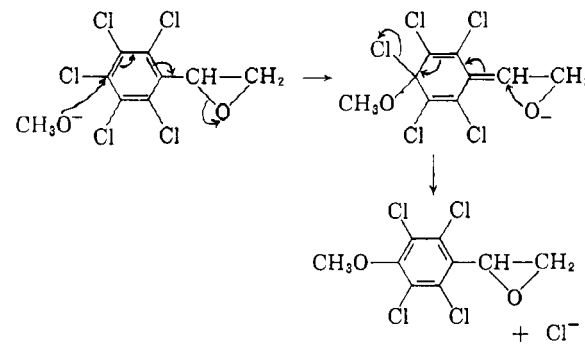
The other possible ether, 1-pentachlorophenyl-2-methoxyethane, was prepared by the reaction of pentachlorostyrene with sodium methoxide in methanol. This ether was different from the ether obtained by degradation of the acid methanolysis product of pentachlorostyrene oxide. The ethyl ether was also obtained in a similar reaction with sodium ethoxide. These reactions permit some insight into the addition reactions of pentachlorostyrene. Unlike the electrophilic reactions of 2- and 4-vinylpyridines,[7] the success of these reactions is probably not due to resonance interaction of the vinyl group and the ring in pentachlorostyrene, since the two *ortho*-chlorine atoms and the vinyl group are sufficiently large so that the latter is forced out of the plane of the benzene ring, reducing the extent of conjugation.[8] Nevertheless, the vinyl group in pentachlorostyrene is strongly polarized by the cumulative inductive effect of the five chlorine atoms and subject to nucleophilic attack at the β-position. Equally important, the attack is by a strong nucleophile, alkoxide ion, and at a point somewhat removed from the *ortho*-chlorine atoms.

The above considerations are also pertinent to the mechanism of the acid catalyzed reaction of the oxide with methanol. The reaction probably involves an S_N1 opening of the conjugate acid of pentachlorostyrene to give a carbonium ion or incipient carbonium ion which then reacts with methanol to give 1-pentachlorophenyl-1-methoxy-2-hydroxyethane (I). If the reaction involved an S_N2 attack by methanol on the conjugate acid of the oxide, the product would be 1-pentachlorophenyl-1-hydroxy-2-methoxyethane both because of the steric barrier to attack at the α-position and the greater ease of displacement at a primary position.

The methanolysis of pentachlorostyrene oxide with sodium methoxide as catalyst resulted in a complex product from which it proved difficult to isolate pure compounds. The crude product was an oil which, when dissolved in a hexane-methanol mixture and stored in a refrigerator, deposited a small amount (~9%) of a crystalline compound (II). The remaining oil on distillation again gave an oil. Analyses indicated this oil was a mixture, but on treatment with acetic anhydride and pyridine, a crystalline acetate (III) developed. The infrared spectrum of III was similar to but not identical with that of the acetate of I, with which it showed a depression on mix melting. The only possible conclusion is that III is the acetate of 1-pentachlorophenyl-1-hydroxy-2-methoxyethane; this is supported by the analytical results.

The S_N2 attack of methoxide ion is thus on the β-carbon atom of the oxide ring. This is in accord with all reasonable expectations, since attack at this primary carbon atom is favored both by electron withdrawal of the chlorine substituents and the steric hindrance at the α-carbon atom.

The only question remaining is the nature of the other product (II) formed in this reaction. The infrared spectrum of II shows strong absorption in the ether regions but no hydroxyl or carbonyl absorption. Analyses lead to the empirical formula, $C_9H_6O_2Cl_4$, and we would suggest that this compound is 4-methoxy-2,3,5,6-tetrachlorostyrene oxide. Such a structure might result from attack by methoxide ion on the *para*- position of the ring as follows:



This reaction sequence is similar to that proposed for the reaction of pentachlorobenzal chloride with methoxide ion to give the dimethylacetal of 4-methoxy-2,3,5,6-tetrachlorobenzaldehyde.[4] To explore the possible generality of reactions of this type, we refluxed both pentachlorobenzaldehyde and pentachloroacetophenone with sodium methoxide in methanol. In both cases the product was

(6) G. Lock, *Ber.*, **66**, 1527 (1933).

(7) W. E. Doering and R. A. N. Weil, *J. Am. Chem. Soc.*, **69**, 2461 (1947).

(8) S. D. Ross, *J. Am. Chem. Soc.*, **70**, 4039 (1948); T. Alfrey, Jr., and W. H. Ebelke, *J. Am. Chem. Soc.*, **71**, 3235 (1949).

pentachlorobenzene. Lock[9] had previously effected the same cleavage reactions with 50% potassium hydroxide. The attack in all four of these cases presumably occurs at the carbonyl carbon atom rather than the 4-position of the ring.

EXPERIMENTAL[10]

Pentachlorostyrene oxide. Pentachlorostyrene (33.2 g., 0.12 mole) was added to a solution of perbenzoic acid (20.5 g., 0.149 mole) in chloroform (275 ml.). The solution was left standing, with occasional shaking, for 20 days in an ice box. The chloroform solution was washed twice with 10% sodium hydroxide solution, then with water, and dried over magnesium sulfate. Removal of the solvent gave 26 g. (74.1%) of the crude oxide, m.p. 115–125°. The yield after crystallization from ligroin (b.p. 90–100°), containing a little benzene, was 18.5 g. (52.7%), m.p. 135–137°.

Anal. Calcd. for $C_8H_3OCl_5$: C, 32.86; H, 1.03. Found: C, 32.83, 32.74; H, 1.13, 1.19.

The same reaction using a 40% solution of peracetic acid in acetic acid for the oxidizing agent gave a 95% yield of crude product and a 55% yield of purified product.

1-Pentachlorophenyl-1-methoxy-2-hydroxyethane (I). Sulfuric acid (15 drops) was added to a solution of pentachlorostyrene oxide (29.2 g., 0.1 mole) in methanol (1250 ml.), and the solution was refluxed 70 hr. Half of the methanol was removed by distillation. The remaining solution was poured into water, and the crude product was filtered and dried in a vacuum desiccator; yield 30.5 g. (94%), m.p. 93–99°. Crystallization from ligroin (b.p. 90–100°) yielded 26.6 g. (82%) of product, m.p. 102–103°. Two additional crystallizations from ligroin did not change the melting point.

Anal. Calcd. for $C_9H_7O_2Cl_5$: C, 33.32; H, 2.17. Found: C, 32.96, 32.79; H, 2.25, 2.33. Found for a second sample: C, 33.00, 32.88; H, 2.05, 2.18.

1-Pentachlorophenyl-1-methoxy-2-chloroethane. Thionyl chloride (6.0 g., 0.05 mole) was added dropwise with stirring to a solution of I (13 g., 0.04 mole) in anhydrous benzene (210 ml.) and dry pyridine (6.4 g., 0.81 mole). The reaction mixture was stirred for 6 hr. and then left standing overnight. The benzene solution was washed with water, 10% hydrochloric acid, 10% sodium hydroxide solution, and then water again. It was dried over magnesium sulfate. Removal of the solvent resulted in an oil to which a little methanol was added. On standing the oil crystallized, yielding 11.5 g. (83.8%) of product; m.p. 108–115°. A sample crystallized for analysis four times from ligroin (b.p. 90–100°) melted at 118–120°. If the crude product is crystallized from acetone, the melting point is 124–127°, and this melting point drops to the lower value if the material, m.p. 124–127°, is crystallized from ligroin.

Anal. Calcd. for $C_9H_6OCl_6$: C, 31.52; H, 1.76. Found for sample from ligroin: C, 31.76, 31.64; H, 1.67, 1.82. Found for sample from acetone: C, 31.00, 31.09; H, 2.23, 2.04.

1-Pentachlorophenyl-1-methoxy-2-acetoxyethane. The acid methanolysis product (I) (1 g.) in pyridine (10 ml.) was treated with acetic anhydride (5 ml.), and the solution was left standing for 5 days at room temperature. When the solution was poured into water a quantitative yield of the crude product resulted, m.p. 103–108°. A sample crystallized twice from ligroin-benzene for analysis had m.p. 113–114°.

Anal. Calcd. for $C_{11}H_9O_3Cl_5$: C, 36.05; H, 2.48. Found: C, 35.81, 36.00; H, 2.44, 2.58.

2-Pentachlorophenyl-2-methoxyethyl-p-toluenesulfonate. A chilled solution of I (6.49 g., 0.02 mole) in pyridine (10 ml.) was treated with a chilled solution of *p*-toluenesulfonylchloride (3.8 g., 0.02 mole) in pyridine (10 ml.), and the mixture was left standing in an ice bath for 2 hr. It was then permitted to come to room temperature and finally warmed at 40–50° for 2 hr. The mixture was poured into water, the water was extracted with benzene, and the benzene solution was dried with magnesium sulfate. Removal of the solvent and crystallization from ligroin (b.p. 90–100°) yielded 5.6 g. (60%) of the tosylate; m.p. 142–145°. A sample crystallized two additional times for analysis had m.p. 144–145°.

Anal. Calcd. for $C_{16}H_{13}O_4SCl_5$: C, 40.15; H, 2.74; Cl, 37.04. Found: C, 40.06; H, 2.63; Cl, 36.92, 37.06, 37.30.

1-Pentachlorophenyl-1-methoxyethane. The above toluene sulfonate (4.67 g., 0.00976 mole) in dry benzene (35 ml.) was added dropwise to a stirred suspension of lithium aluminum hydride (1.04 g., 0.03 mole) in anhydrous ether (100 ml.). The mixture was refluxed 8 hr. with stirring and 12 hr. without stirring. The reaction mixture was decomposed first with water and then with dilute hydrochloric acid. It was extracted twice with benzene, and the benzene extract was dried over magnesium sulfate. The solvent was removed, and the crude product was crystallized from methanol; yield, 1.45 g. (48%), m.p. 87–90°. Three additional crystallizations from methanol raised the m.p. to 99–101°.

Anal. Calcd. for $C_9H_7OCl_5$: C, 35.05; H, 2.29; Cl, 57.48. Found: C, 35.10, 35.31; H, 2.11, 2.33; Cl, 57.42.

Pentachlorophenylmethylcarbinol (10 g., 0.034 mole) in ether (100 ml.), dried with sodium hydride, was added dropwise to a stirred suspension of sodium hydride (1 g., 0.042 mole) in ether (25 ml.). Stirring was continued 3 hr. The mixture was allowed to stand overnight and then stirred for 8 hr. The ether was removed using a water bath, methyl iodide (5 ml., 0.08 mole) was added, and the thick paste that resulted was stirred for 2 hr. and allowed to stand overnight. Ether (50 ml.) was added; the mixture was stirred briefly and filtered. Evaporation of the ether afforded 5 g. of crude ether, m.p. 70–85°. Five crystallizations from methanol gave 0.3 g. of the methyl ether, m.p. 97–98°; mixed m.p. with ether obtained from the *p*-toluenesulfonate, 98–99°.

Anal. Calcd. for $C_9H_7OCl_5$: Cl, 57.48. Found: Cl, 57.62.

1-Pentachlorophenyl-2-methoxyethane. Sodium (6.9 g., 0.3 mole) was allowed to react with methanol (500 ml.). Pentachlorostyrene (13.8 g., 0.05 mole) was added, and the solution was refluxed 140 hr. Half of the methanol was removed by distillation. The remaining solution was poured into water, yielding 12.7 g. (82.5%) of the crude product, m.p. 60–65°. Crystallization from methanol gave 7.9 g. (51.3%), m.p. 72–74°. Three additional crystallizations raised the m.p. to 76–78°.

Anal. Calcd. for $C_9H_7OCl_5$: C, 35.05; H, 2.29; Cl, 57.48. Found: C, 34.78; H, 2.43; Cl, 57.22, 57.08.

1-Pentachlorophenyl-2-ethoxyethane. Pentachlorostyrene reacted with sodium ethoxide in ethanol by the procedure described above for the methyl ether, gave the product in 32% yield, m.p. 90° after three crystallizations from methanol.

Anal. Calcd. for $C_{10}H_9OCl_5$: C, 37.25; H, 2.81; Cl, 54.98. Found: C, 37.00; H, 2.80; Cl, 57.54.

Base catalyzed methanolysis of pentachlorostyrene oxide. Sodium (6.9 g., 0.3 g.-atom) was allowed to react with methanol (1250 ml.). Pentachlorostyrene oxide (29.2 g., 0.1 mole) was added, and the solution was refluxed 90 hr. Part of the methanol was removed by distillation, water was added, and the mixture was extracted with benzene. The aqueous layer was acidified and extracted again with benzene. The benzene extracts were combined and dried over magnesium sulfate. Removal of the solvent gave an oil, which was dissolved in a mixture of hexane and methanol. The solution was stored in a refrigerator until crystals of II precipitated. Concentration of the mother liquors gave two additional crops of II; total yield, 2.6 g. (9%), m.p. 118–123°.

(9) G. Lock, *Ber.*, **66B**, 1527 (1933); **70B**, 916 (1937).

(10) All microanalyses are by the Clark Microanalytical Laboratories.

A sample crystallized twice from methanol had m.p. 125°.

Anal. Calcd. for $C_9H_6Cl_4O_2$: C, 37.54; H, 2.10; Cl, 49.25. Found: C, 36.93; H, 2.45; Cl, 49.14. Found for a second sample: C, 37.14; H, 3.03; Cl, 48.52.

The mother liquors from the above were distilled, b.p. 140–146° at 80 μ, yield 15.8 g. This product was redistilled at 60 μ, yielding the following fractions: (1) b.p. 132–135°, 0.95 g.; (2) b.p. 135–138°, 7.0 g.; (3) b.p. 138°, 4.6 g. Fractions 2 and 3 both showed absorptions in the hydroxyl and ether regions of the infrared.

Anal. Found for Fraction 2: C, 35.27, 35.21; H, 2.92, 3.02; Cl, 50.32. Found for Fraction 3: C, 34.89, 34.92; H, 2.50, 2.51; Cl, 50.69.

The above oil (7 g.; half from Fraction 2 and half from Fraction 3 was dissolved in pyridine (40 ml.) and acetic anhydride (15 ml.), and the solution was left standing at room temperature for 5 days. The reaction mixture was taken up in a large volume of benzene and extracted three times with water. The benzene layer was dried over magnesium sulfate. Removal of the solvent gave the crude product (III); yield, 3.2 g., m.p. 103–107°. After five crystallizations from hexane the melting point was 119–120°. This product shows a melting point depression both with the acetate of I and with II.

Anal. Calcd. for $C_{11}H_{19}O_3Cl_5$: C, 36.05; H, 2.48; Cl, 48.38. Found: C, 35.37, 35.48; H, 2.36, 2.48; Cl, 48.03, 48.14.

Pentachlorobenzene. Sodium (6.9 g., 0.3 g.-atom) was allowed to react with methanol (500 ml.). Pentachlorobenzaldehyde (13.9 g., 0.05 mole) was added and the solution was refluxed 65 hr. Half of the methanol was removed by distillation, water was added, and the mixture was extracted three times with benzene. The benzene solution was dried over magnesium sulfate. Removal of the benzene gave the crude product which was crystallized from ethanol; yield, 6.2 g. (49.6%), m.p. 84–85°.

Anal. Calcd. for C_6HCl_5: Cl, 70.81. Found: Cl, 71.34, 70.33.

Pentachloroacetophenone treated as above gave the same product in 50.4% yield.

NORTH ADAMS, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Reactions of Terpenes. IV.[1] Reaction of α-Pinene Oxide with *p*-Toluenesulfonic Acid and Quinaldine

L. CARROLL KING AND HUGH FARBER[2]

Received May 31, 1960

When α-pinene oxide in quinaldine solution is treated with catalytic amounts of *p*-toluenesulfonic acid, about 30% of the oxide is converted to a mixture of aldehydes. The remainder of the α-pinene oxide is converted to a mixture of hydrocarbons.

The aldehyde fraction consists of α-campholenic aldehyde, 85%, and a new aldehyde identified as 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde. The hydrocarbon fraction consists of four components. One of these is *p*-cymene and two others can be isomerized to *p*-cymene.

All former preparations wherein "α-campholenic aldehyde" was reported as the product of action of acid catalysts on α-pinene oxide are shown to be mixtures consisting of α-campholenic aldehyde as described herein, and 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde.

When α-pinene oxide in quinaldine solution is treated with catalytic quantities of *p*-toluenesulfonic acid, 30% of the α-pinene oxide is converted to aldehydes (Fraction I) and about 70% of the α-pinene oxide is converted to hydrocarbons (Fraction II).

The aldehyde fraction (I) was separated from the hydrocarbon fraction (II) by formation of the water soluble bisulfite adducts, and subsequent decomposition with sodium hydroxide. This fraction formed a derivative, m.p. 137–139°, when treated with semicarbazide, and corresponds to "α-campholenic aldehyde" as reported in the terpene literature.[3,4,5,6,7]

When Fraction I was subjected to analysis by gas chromatography the presence of two substances was indicated. The faster moving component represented 15% of the total aldehyde fraction and was identified as 2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde (III). The slower moving component representing 85% of the aldehyde fraction has the structure IV.

In the terpene literature structure IV has been assigned to "α-campholenic aldehyde," the aldehyde produced when α-pinene oxide is treated with acid catalytists.[3,4,5,6] In view of the results described herein we conclude that all former preparations wherein "α-campholenic aldehyde" was prepared by the action of acid catalysts on α-pinene oxide are mixtures consisting of III and IV in the ratio of about 3:17. As a check on this statement "α-campholenic aldehyde" was prepared by the method of Royals and Harrell.[5] This preparation when treated with semicarbazide hydrochloride provided a derivative, m.p. 137–139°, as reported.[5] When examined by means of

(1) Paper No. III, L. C. King and E. W. Stern, *J. Org. Chem.*, **23**, 1928 (1958).

(2) From the Ph.D. thesis of Hugh Farber, Northwestern University, 1959.

(3) B. A. Arbuzov, *Ber.*, **68**, 1430 (1935).

(4) B. A. Arbuzov and E. G. Isaeva, *Zhur. Obshchei Kim.*, **24**, 1250 (1954).

(5) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).

(6) N. Prileshajew and V. J. Wershuck, *J. Russ. Phys. Chem. Soc.*, **61**, 445–465.

(7) Technical Bulletin No. 82, Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo, N. Y.