

Pentachlorocyclopropane<sup>1</sup>

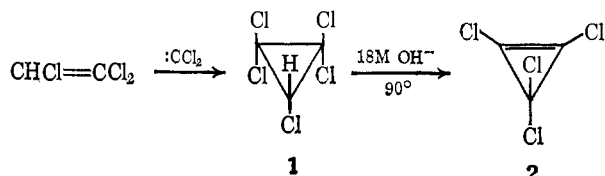
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**Abstract:** Pentachlorocyclopropane (**1**) can be synthesized easily from sodium trichloroacetate and trichloroethylene. With concentrated aqueous potassium hydroxide, **1** is smoothly dehydrochlorinated to tetrachlorocyclopropene (**2**). A related synthesis from sodium trichloroacetate and *cis*-dichloroethylene gives *cis*-1,1,2,3-tetrachlorocyclopropane (**3**) in very low yield; **3** is inert to strong aqueous base. Treatment of **1** with zinc in methanol converts it to *cis*-CHCl=CCl-CH(OCH<sub>3</sub>)<sub>2</sub> (**4**). **1** is thermally unstable, undergoing rapid ring-opening isomerization above 100° to give exclusively 1,1,3,3,3-pentachloropropene (**8**). Treatment of **8** with KOH at 100° converts it to perchloro-1,2-dimethylenecyclobutane (**9**).

In the first paper in this series the synthesis and chemical reactions of hexachlorocyclopropane were described.<sup>2</sup> This paper describes the synthesis, physical properties, and known chemical reactions of pentachlorocyclopropane (**1**), and compares them with those of the fully chlorinated compound.<sup>3</sup> Undoubtedly the single most important reaction of pentachlorocyclopropane is its ready conversion to tetrachlorocyclopropene (**2**) under very mild conditions. This latter compound is a versatile precursor for a wide variety of other cyclopropene compounds, and subsequent papers in this series will describe the chemistry of tetrachlorocyclopropene and its derivatives.<sup>4</sup>

Pentachlorocyclopropane is readily synthesized in one step by the addition of dichlorocarbene to CHCl=CCl<sub>2</sub>. Although other methods of :CCl<sub>2</sub> production have been described which lead to higher yields of highly halogenated cyclopropanes from relatively poor carbene acceptors like trichloroethylene,<sup>5</sup> simple decarboxylation of CCl<sub>3</sub>CO<sub>2</sub><sup>-</sup>Na<sup>+</sup> in 1,2-dimethoxyethane<sup>6</sup> was found to work adequately here. The 22% product yield obtained is modest, but the starting materials are inexpensive and immediately available, and the product is obtained simply and in isomerically pure form. Large-scale preparations which provide **1** in 400-g lots have routinely been carried out.



Pentachlorocyclopropane is a colorless mobile liquid with a faint minty odor, bp 56° (7 mm). The absence of any band in the C=C region and the presence of a strong complex band between 950 and 885 cm<sup>-1</sup> in the infrared spectrum of **1**<sup>3</sup> are consistent with its cyclo-

propane structure and rule out the several open-chain C<sub>3</sub>Cl<sub>5</sub>H isomer possibilities. The proton nmr spectrum of **1** shows a singlet resonance at τ 6.16 flanked by C<sup>13</sup> side bands at ± 96.2 cps. The proton resonance lies well below the τ 9.78 resonance position of cyclopropane itself,<sup>7</sup> and a reasonable distance below the 7.02 value for the -CHCl- proton in chlorocyclopropane.<sup>8</sup> The 192.4-cps C<sup>13</sup>-H coupling constant in **1** is about 30 cps higher than that normally encountered in hydrocarbon cyclopropanes.<sup>7</sup> Although the theoretical prediction that this C<sup>13</sup>-H coupling constant requires 38.5% s character in the carbon orbital bonding to hydrogen<sup>9</sup> is probably not quantitatively<sup>10</sup> accurate (see below), the calculation did suggest that the carbon atom in the -CHCl- grouping of **1** should readily assume a negative charge, and prompted us to attempt the dehydrochlorination of **1** under mild conditions.

When pentachlorocyclopropane is simply shaken with excess 18 M aqueous KOH at 85–95° a moderately exothermic dehydrochlorination of **1** occurs which provides tetrachlorocyclopropene in 85% yield.<sup>11</sup> The requirement for strong aqueous base and the fact that tetrachlorocyclopropene is the sole observed product suggest that loss of HCl from **1** takes place by a concerted β-elimination (E2) mechanism.<sup>12</sup> The successful preparation of **2** from **1** using aqueous base (thus permitting a two-phase system) was most fortunate. Tetrachlorocyclopropene reacts further quite quickly with water, alcohols, and strong bases in a mutual solvent so that isolation of **1** formed under more strenuous conditions would have been much more difficult.<sup>3,4</sup>

In attempting to extend this synthetic method to the preparation of trichlorocyclopropanes **5** and **6** (see below) *cis*-1,1,2,3-tetrachlorocyclopropane (**3**) was synthesized. **3** is obtained in very low yield (0.9%) via decarboxylation of CCl<sub>3</sub>CO<sub>2</sub><sup>-</sup>Na<sup>+</sup> in 1,2-dimethoxyethane at 70° with *cis*-CHCl=CHCl acceptor. The infrared spectrum of **3** clearly indicates a cyclopropane

(1) This paper is taken from the Ph.D. Thesis of S. W. Tobey, The University of Wisconsin, 1965.

(2) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 56 (1964).

(3) For a preliminary report of this work see S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

(4) (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966);

(b) R. West, A. Sadó, and S. W. Tobey, *ibid.*, **88**, 2488 (1966); (c) *ibid.*, in press.

(5) (a) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964), and references cited there; (b) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *ibid.*, **87**, 4259 (1965).

(6) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(7) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(8) Dr. P. von R. Schleyer, Princeton University, private communication.

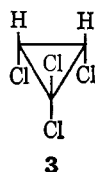
(9) (a) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); (b) J. N. Shoolery, *ibid.*, **31**, 1427 (1959); (c) C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).

(10) G. J. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.*, **86**, 3574 (1964).

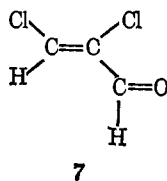
(11) For details of this experiment and the proof of structure of tetrachlorocyclopropene see ref 4a.

(12) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, Chapter 12.

structure. The nmr spectrum of **3** shows a single peak at  $\tau$  6.27. The  $C^{13}$  side bands are the A portion of an AMX spectrum<sup>13</sup> and consist of a pair of doublets flanking the central line at  $\pm 93$  and  $\pm 101$  cps. The 8-cps  $H_a-H_m$  coupling constant in **3** is consistent with the assigned *cis*-hydrogen configuration<sup>14a,b</sup> but is not an unequivocal proof of structure, since *cis* and *trans* coupling constants in certain cyclopropanes have been shown to be nearly equal and near 8 cps.<sup>14c</sup> Compound **3** shows a high  $C^{13}$ -H coupling constant (194 cps) like **1**, which would suggest that it too should undergo ready dehydrochlorination. However, under conditions similar to those used to dehydrochlorinate **1**, **3** appears quite inert. This failure of **3** to undergo deprotonation with aqueous base clearly indicates that the ease of deprotonation of **1** is not *solely* a consequence of the factors which lead to a high  $C^{13}$ -H coupling constant. Possibly the additional chlorine-chlorine interaction in **1** is of crucial importance in destabilizing its ground state relative to the transition state for  $Cl^-$  expulsion.



Like hexachlorocyclopropane, pentachlorocyclopropane is rapidly dehalogenated by zinc in alcohols. In the hexachlorocyclopropane reaction<sup>2</sup> tetrachlorocyclopropene is most probably the initial reaction product, although it cannot be detected in the final reaction product mixture. The spectrum of ester products ultimately isolated is essentially identical with that obtained when tetrachlorocyclopropene is allowed to react directly with the alcohol.<sup>3,4c</sup> When pentachlorocyclopropane is treated with zinc in a large excess of methanol only one product is obtained (40% conversion): the dimethyl acetal of *cis*-2,3-dichloroacrylaldehyde (**4**). On standing, **4** spontaneously hydrolyzes to *cis*-2,3-dichloroacrylaldehyde (**7**). The *cis*-2,3-chlorine configuration of **7** has been established by reduction of the aldehyde to the known *cis*-2,3-dichloroallyl alcohol with  $LiAlH_4$ .<sup>2</sup>



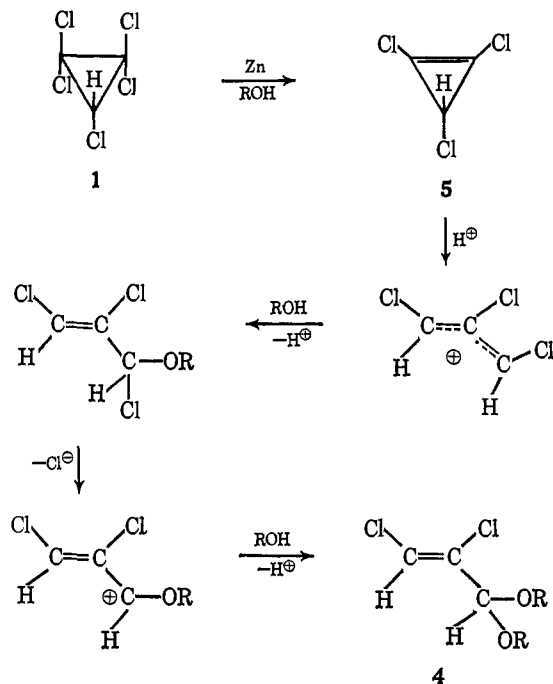
The formation of this product can most satisfactorily be rationalized by assuming the intermediate formation of 1,2,3-trichlorocyclopropene (**5**). Simple acid-catalyzed reaction of this intermediate with methanol solvent, as shown below, would be expected to lead to the observed product.<sup>15</sup> It seems likely that under

(13) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, pp 61-64.

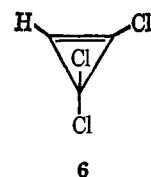
(14) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **85**, 2788 (1963); (c) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 84.

(15) A complete discussion of halocyclopropene ring-opening mechanisms will appear in ref 4c.

appropriate conditions **4** could be isolated, although none could be detected in the reaction product mixture here, and as noted above we have been unable to obtain this product by the reaction of **3** with aqueous base. If the dechlorination of **1** is assumed to give 2,3,3-trichlorocyclopropene (**6**) instead of **5**, ester products



rather than the observed aldehydic product would be predicted according to the mechanism shown.



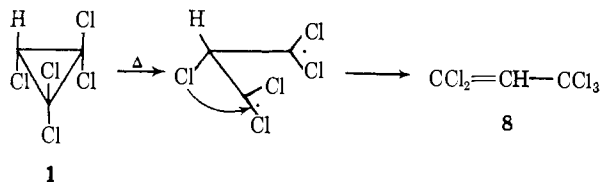
Unlike hexachlorocyclopropane, which can be distilled in air at  $198^\circ$  without apparent decomposition or rearrangement,<sup>2,16</sup> pentachlorocyclopropane undergoes thermal isomerization to 1,1,3,3,3-pentachloropropene (**8**) very easily. This instability of **1** was not anticipated and caused a considerable delay in the early stages of the work reported herein.<sup>17</sup> By carrying out all distillations at reduced pressure with pot temperatures below  $100^\circ$  isomerization of **1** to **8** can be eliminated. Above  $100^\circ$  **8** begins to appear in the distillate, and on slow distillation at  $178^\circ$  under  $N_2$  (740 mm) **1** rearranges to **8** about as fast as it is distilled.

Although the mechanism of isomerization of **1** to **8** has not been investigated further, the following facts are significant. The conversion occurs at a rapid rate at relatively low temperatures. Only one product is formed, and this in quantitative yield. No tarring occurs. No obvious catalyst is required, suggesting a thermally activated homopolar reaction. The isomerization of cyclopropane to propene has been shown

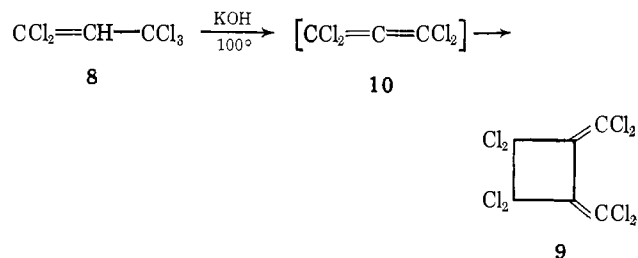
(16) The mass spectral behavior of hexachlorocyclopropane indicates that at higher temperatures it undergoes thermal rearrangement to  $CCl_2=CCl-CCl_2$ ; see E. K. Fields and S. Meyerson, *J. Org. Chem.*, **28**, 1915 (1963).

(17) R. Breslow in "Molecular Rearrangements," Interscience Publishers, Inc., P. de Mayo, Ed., New York, N. Y., 1963, p 234, and references cited therein.

to be a unimolecular reaction in the gas phase,<sup>17,18</sup> and the isomerization of pentachlorocyclopropane is probably similar. The simplest mechanism would involve selective cleavage of the  $-\text{CCl}_2-\text{CCl}_2-$  bond in **1**, followed by (or possibly in concert with) migration of the chlorine from the carbon bearing the hydrogen to an adjacent  $-\text{CCl}_2-$  site.



The structure of the rearranged product (**8**) has been confirmed by the conversion of **8** to  $\text{CCl}_2=\text{CH}-\text{CO}_2-n\text{-Bu}$  with zinc in  $n\text{-BuOH}$ .<sup>2</sup> One other reaction of **8** seems worthy of mention here. When it is heated with 85% KOH at  $100^\circ$ , **8** provides perchloro-1,2-dimethylenecyclobutane (**9**)<sup>19</sup> in good yield. This reaction most probably involves tetrachloroallene (**10**) as an intermediate,<sup>20</sup> and suggests **8** as a readily available precursor for **10**.



## Experimental Section

All syntheses were carried out using purified grades of commercially available starting materials. Gas chromatographic separations were carried out on a Wilkins Instrument and Research, Inc., Aerograph A-90 thermoconductivity detector instrument at  $155\text{--}165^\circ$  using helium carrier gas as a flow rate of 60–80 ml/min through 5 ft  $\times$  0.5 in. columns packed with Dow 11 silicone or Ucon LB550X (20%) on 30–60 mesh firebrick. Infrared spectra in the  $4000\text{--}625\text{-cm}^{-1}$  region were taken between NaCl plates on a Perkin-Elmer Model 237 recording spectrophotometer calibrated in  $\text{cm}^{-1}$ . Listed infrared frequencies are correct within  $\pm 3\text{ cm}^{-1}$ . Proton nmr spectra were recorded on a Varian Associates A-60 instrument. Chemical shifts are for 10% (v/v) solutions in  $\text{CCl}_4$ . Positions of  $\text{C}^{13}$  side bands were measured on the neat liquids. Elemental analyses were performed in the Microanalytical Laboratory of Dr. Alfred Bernhardt at the Max Planck Institut für Kohlenforschung.

**Pentachlorocyclopropane (1).** Trichloroethylene (2500 ml, 27.7 moles) and powdered General Chemical 94% grade  $\text{CCl}_3\text{CO}_2\text{-Na}^+$  (1600 g, 8.1 moles) were placed in a 5-l., three-neck, round-bottom flask fit with a heating mantle, powerful Teflon-blade stirrer, and water takeoff trap leading to a reflux condenser vented through a mineral oil bubbler. Stirring and reflux were continued for 2 hr until all water (5–10 ml) had been removed from the refluxing  $\text{CHCl}=\text{CCl}_2$ . (In control runs where the  $\text{CHCl}=\text{CCl}_2$  was dried and distilled from  $\text{P}_2\text{O}_5$ , and the  $\text{CCl}_3\text{CO}_2\text{-Na}^+$  was dried under vacuum, no significant increase in yield was noted.) In the absence of ether solvent no decarboxylation occurred. To the flask was then added 750 ml of dry 1,2-dimethoxyethane.  $\text{CO}_2$  evolution began almost immediately, as monitored by the bubbler, and

the solution began to darken. (In control runs the 1,2-dimethoxyethane was added in portions.  $\text{CO}_2$  evolution at a reasonable rate began only after 650 ml of ether was present.) Reflux at a pot temperature of  $80^\circ$  caused  $\text{CO}_2$  evolution for 2.5 days, during which time the pot gradually darkened. At no time was all material in solution. In addition to  $\text{CO}_2$ , small amounts of a very irritating and obnoxious smelling gas were evolved (hood). The final reaction mixture was allowed to cool and settle. The upper oily layer was decanted off, and the lower silt layer was drenched with 4 l. of water providing another 500 ml of oil which was dried over  $\text{CaCl}_2$  and combined with the decantate. The combined oils were stripped under vacuum leaving approximately 500 ml of a dark brown oil which was distilled under vacuum through a glass-bead packed column. The distillate boiling around  $75^\circ$  (20 mm) was a colorless, minty smelling oil; 175 ml of dark brown syrup remained in the still pot. Gas chromatographic analysis of the distillate on the silicone column showed one main peak comprising 95% of the material injected, the remainder being 1,2-dimethoxyethane. The infrared spectrum<sup>9</sup> of oil trapped from the main peak was that of pure **1** uncontaminated with  $\text{CCl}_2=\text{CH}-\text{CCl}_3$ . The corrected yield of pentachlorocyclopropane in this typical run was 390 g (1.81 moles, or 22.4% of theoretical based on  $\text{CCl}_3\text{CO}_2\text{-Na}^+$ ). The boiling point of pure **1** is  $55.5\text{--}56.0^\circ$  (7 mm),  $n_{\text{D}}^{27.5\text{D}}$  1.5170.

*Anal.* Calcd for  $\text{C}_3\text{Cl}_5\text{H}$ : C, 16.81; Cl, 82.72; H, 0.47. Found: C, 16.94; Cl, 82.63; H, 0.54.

**cis-1,1,2,2-Tetrachlorocyclopropane (3).** *cis*-Dichloroethylene (700 ml, 9.3 moles) and vacuum-dried  $\text{CCl}_3\text{CO}_2\text{-Na}^+$  (700 g, 3.55 moles) were heated to reflux as described above, and 400 ml of dry 1,2-dimethoxyethane was added in portions until  $\text{CO}_2$  evolution began.  $\text{CO}_2$  evolution was complete after 9 hr, during which time the reaction mixture darkened considerably. The cooled reaction mixture was extracted repeatedly with water and dried over  $\text{CaCl}_2$ , finally providing 500 ml of dark brown oil which was stripped at  $20^\circ$  under vacuum. Gas chromatographic analysis of the volatiles showed no **3**; 100 ml of dark brown, viscous syrup remained. This syrup was evacuated to 4.5 mm and all material volatile up to  $100^\circ$  was trapped out in a Dry Ice-acetone receiver. Above  $100^\circ$  the pot residue began to crack; 10.5 g of pale yellow oil was obtained. Gas chromatographic analysis of this oil on the silicone column showed that it was an approximately 50% (v/v) mixture of 1,2-dimethoxyethane and **3**. The yield of **3** was estimated to be about 6 g, or 0.9% of the theoretical amount based on  $\text{CCl}_3\text{CO}_2\text{-Na}^+$ . **3** is a colorless oil with a banana-like odor. The infrared spectrum (liquid film) of pure **3**,  $n_{\text{D}}^{25.5\text{D}}$  1.5043, in the NaCl region shows bands at 3036 (m), 1310 (m), 1250 (m), 1192 (w,b), 1050 (m), 936 (m), 874 (w,b), 825 (vs,s), and 677 (m)  $\text{cm}^{-1}$ . A 1-ml portion of **3** was heated with 1 ml of 18 M KOH at  $100^\circ$  for 15 min (two-phase system). No obvious reaction occurred, and gas chromatographic analysis of the reaction product showed it was starting material only, unaccompanied by any new compounds.

*Anal.* Calcd for  $\text{C}_3\text{Cl}_4\text{H}_2$ : C, 20.03; Cl, 78.85; H, 1.12. Found: C, 20.20; Cl, 78.51; H, 1.48.

**Dimethyl Acetal of cis-2,3-Dichloroacrylaldehyde (4).** Zinc sand (4.79 g, 0.0733 g-atom) was added to a solution of pentachlorocyclopropane (4.51 g, 0.0254 mole) in dry methanol (6.00 g, 0.188 mole). A vigorous reaction started immediately which brought the reaction temperature up to  $65^\circ$  (reflux). The reaction was maintained at this temperature for 15 min by external cooling, at which time the reaction ceased abruptly. The resulting light tan solution (over excess Zn) was poured into 14 ml of ice-cold water and the yellow liquid which descended was drawn off immediately and dried over  $\text{Na}_2\text{SO}_4$ . The dried oil weighed 2.31 g. The residual zinc weighed 2.82 g, so 1.97 g (0.0302 g-atom) was consumed. Gas chromatographic analysis of the oil on the silicone column showed four peaks. The first small peak was methanol, the second very small peak was *cis*-2,3-dichloroacrylaldehyde (**7**), the third and largest peak was the dimethyl acetal of *cis*-2,3-dichloroacrylaldehyde (**4**), and the fourth peak was recovered pentachlorocyclopropane (**1**). **4** constituted about 75% of the product (1.7 g, 0.010 mole) indicating an over-all 40% conversion of **1** to **4**. After standing overnight, gas chromatographic analysis of this same reaction product mixture showed that the acetal had all but disappeared, and the peak for the parent aldehyde **7** had grown a corresponding amount. Gas chromatographically pure **4** is stable indefinitely if kept in a sealed tube. The liquid film infrared spectrum of **4**,  $n_{\text{D}}^{25.2\text{D}}$  1.4583, in the NaCl region shows vinyl CH at 3085 (m); alkyl CH at 2990 (w), 2955 (m), 2930 (m), 2890 (m), and 2830 (s); no C=O; C=C at 1613 (s); C—O—C at 1133 (vs) and 1066 (vs,b); and other bands at 1443 (m,b), 1348 (s,b), 1193 (s), 991 (s), 884 (s), 810 (s), 751 (s), and 648 (m)  $\text{cm}^{-1}$ . The

(18) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Am. Chem. Soc.*, **86**, 679 (1964).

(19) (a) A. Roedig and F. Baschoff, *Naturwissenschaften*, **49**, 448 (1962); (b) J. Brandmüller, E. Ziegler, and A. Roedig, *ibid.*, **49**, 466 (1962).

(20) (a) K. Pilgram and F. Korte, *Tetrahedron Letters*, 883 (1962); (b) A. Roedig, G. Märkl, and B. Heinrich, *Angew. Chem.*, **75**, 88 (1963).

nmr spectrum of **4** shows a sharp singlet resonance at  $\tau$  76.2 ( $(-\text{OCH}_3)_2$ ); a doublet at 5.20  $J = 1.2$  cps ( $-\text{CH}(\text{OR})_2$ ); and a doublet at  $\tau$  3.31,  $J = 1.2$  cps ( $\text{C}=\text{C}-\text{H}$ ). The peak area ratios are 6:0.9:1.

*Anal.* Calcd for  $\text{C}_3\text{H}_5\text{Cl}_2\text{O}_2$ : C, 35.12; H, 4.72; Cl, 41.46; O, 18.71. Found: C, 34.92; H, 4.74; Cl, 41.75; O, 18.59 (difference).

*cis*-2,3-Dichloroacrylaldehyde (**7**). Spontaneous hydrolysis of the crude dimethyl acetal **4** described above gave a product (**7**) which was obtained in pure form by gas chromatographic separation. Reduction of **7** with  $\text{LiAlH}_4$  in diethyl ether<sup>2</sup> gave the known *cis*-2,3-dichloroallyl alcohol.<sup>21</sup> The liquid film infrared spectrum of **7**,  $n_D^{25}$  1.4980, in the NaCl region shows vinyl CH at 3055 (s); aldehyde CH at 2835 (m,b) and 2715 (w,b);  $\text{C}=\text{O}$  at 1705 (vs);  $\text{C}=\text{C}$  at 1583 (vs); and other bands at 1384 (m), 1287 (m,b), 1128 (vs), 870 (s), 812 (m,b) 706 (w), 674 (s), and 636 (s)  $\text{cm}^{-1}$ . The nmr spectrum of **7** in  $\text{CCl}_4$  shows singlet resonances at  $\tau$  2.57 ( $\text{C}=\text{C}-\text{H}$ ) and 0.61 ( $-\text{CHO}$ ).

*Anal.* Calcd for  $\text{C}_3\text{H}_2\text{Cl}_2\text{O}$ : C, 28.84; H, 1.61; Cl, 56.75; O, 12.80. Found: C, 29.06; H, 1.78; Cl, 56.51; O, 12.65 (difference).

**Thermal Isomerization of Pentachlorocyclopropane (1) to 1,1,3,3,3-Pentachloropropene (8)**. Pentachlorocyclopropane (41.0 g, 0.19 mole) was heated to 160° for 1 hr in a 50-ml distilling flask fit with a 10-cm glass-helix-packed Bantamware column. No darkening of the pot contents occurred. The column was wrapped with heating tape and 32.0 g (78%) of colorless **8**,  $n_D^{22}$  1.5213 ( $n_D^{27}$  1.5202), was distilled off at 177–179° (740 mm) over a 1-hr period; 9 g of pale yellow pot residue remained. The infrared spectrum of the distillate matched that of the pot residue, and both were identical with that of **8** obtained in pure form by gas chromatography.

(21) (a) L. F. Hatch, J. J. D'Amico, and E. V. Ruhnke, *J. Am. Chem. Soc.*, **74**, 123 (1952); (b) L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950).

Although **1** and **8** were *not* resolved on the silicone column, they were readily resolved on a Ucon LB550X column; **8** was eluted first. The liquid film infrared spectrum of **8** in the NaCl region shows vinyl CH at 3060 (s);  $\text{C}=\text{C}$  at 1603 (vs); and other bands at 1280 (vw), 1082 (vs,s), 939 (vs,s), 823 (vs,s), 783 (m,s), 719 (m,s), and 643 (s,s)  $\text{cm}^{-1}$ . The nmr spectrum of **8** shows a single sharp peak at  $\tau$  3.15.

*Anal.* Calcd for  $\text{C}_3\text{Cl}_5\text{H}$ : C, 16.81; Cl, 82.72; H, 0.47. Found: C, 16.97; Cl, 82.75; H, 0.51.

**Chemical Reactions of 1,1,3,3,3-Pentachloropropene (8)**. On warming in *n*-butyl alcohol in the presence of Zn or  $\text{ZnCl}_2$ , **8** reacted vigorously to provide an 80% yield of  $\text{CCl}_2=\text{CH}-\text{CO}_2$ -*n*-Bu identical with authentic material.<sup>2</sup> On warming to 100° over (molten) 85% KOH pellets, **8** reacted quickly to provide a 60% yield of a compound **9** ( $\text{C}_6\text{Cl}_8$ ). The Nujol mull infrared spectrum of **9**, mp 90.8–91.8° (from  $\text{CH}_3\text{OH}$ ) (lit.<sup>19,20</sup> mp 93°), shows a broad complex band in the  $\text{C}=\text{C}$  region with major peaks at 1607–1603 (m, doublet) and 1570 (s); plus other bands at 1144 (m,b) 1112 (m,s), 941 (m,b), 910 (w,s), 898 (vw,s), 779 (vs,s), and 673 (m,vs)  $\text{cm}^{-1}$ . These properties are essentially identical with those of perchloro-1,2-dimethylenecyclobutane<sup>19</sup> obtained in the dimerization of tetrachloroallene (**10**).<sup>20a</sup>

*Anal.* (of **9**) Calcd for  $\text{C}_6\text{Cl}_8$ : C, 20.26; Cl, 79.74. Found: C, 20.56; H, nil; Cl, 79.17.

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## Tetrachlorocyclopropane, Tetrabromocyclopropane, and Some Fluorinated Cyclopropenes and Cyclopropanes<sup>1</sup>

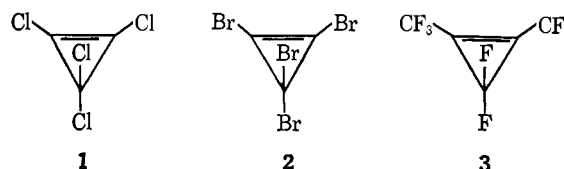
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**Abstract:** The compound  $\text{C}_3\text{Cl}_4$  obtained by dehydrochlorination of pentachlorocyclopropane is shown to be tetrachlorocyclopropane (**1**). **1** is converted in high yield to tetrabromocyclopropane (**2**) on treatment with  $\text{BBr}_3$ . 3-Fluoro-1,2,3-trichlorocyclopropane (**10**), 1,2-dichloro-3,3-difluorocyclopropane (**11**), and 1,2-dibromo-3,3-difluorocyclopropane (**12**) are obtained from the reaction of  $\text{SbF}_5$  with **1** and **2**. Possible mechanisms for these halogen exchange reactions are discussed. The ultraviolet-catalyzed halogenation of the above tetrahalocyclopropenes provides perhalocyclopropanes.

The halogenated cyclopropenes represent an almost totally unexplored class of compounds.<sup>2</sup> As of the time of this writing the only published reference to a cyclopropene compound with covalent halogen substituents, other than preliminary reports of the work described herein,<sup>3,4</sup> is a note by Mahler on 1,2-bis-trifluoromethyl-3,3-difluorocyclopropane (**3**).<sup>5</sup> This paper describes the proof of structure of tetrachlorocyclopropane (**1**), the synthesis of tetrabromocyclo-

propane (**2**) from tetrachlorocyclopropane, and the ready conversion of **1** and **2** to partially fluorinated cyclopropenes. Further chemical reactions of these compounds are outlined in separate papers.<sup>6</sup>



Tetrachlorocyclopropane (**1**) can be easily and efficiently obtained by the dehydrochlorination of

(6) (a) S. W. Tobey and R. West, *ibid.*, **88**, 2478 (1966); (b) *ibid.*, in press.

(1) This paper is taken from the Ph.D. thesis of S. W. T., The University of Wisconsin, 1965.

(2) For a recent review of cyclopropene chemistry see F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

(3) S. W. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).

(4) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964).

(5) W. Mahler, *ibid.*, **84**, 4600 (1962).