

Small amounts of CCl_2F_2 , CCl_3F , $\text{CCl}_2\text{FCCl}_2\text{F}$, and $\text{CClF}_2\text{CCl}-\text{FCF}_2\text{CCl}_2\text{F}$ ³⁰ were formed.

$\text{CF}_3\text{CClFCClFCF}_3$.—Analysis of the dimer addition product b.p. 62.0°, n_D^{20} 1.3104, 1.3096, by g.l.c. with dioctyl phthalate and hexadecane columns at 25° indicated a pure material and its infrared spectrum was identical with that of authentic $\text{CF}_3\text{CClF}-\text{CClFCCF}_3$; reported³² b.p. 62.9°, n_D^{20} 1.3100. However, its F^{19}

n.m.r. spectrum showed unexpected peaks by comparison with authentic $\text{CF}_3\text{CClFCClFCF}_3$.

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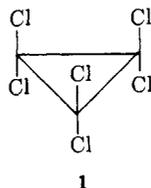
Hexachlorocyclopropane¹

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The synthesis of hexachlorocyclopropane (1) is described, and its physical and spectral properties are presented. Compound 1 is unreactive toward most nucleophilic reagents and is readily attacked by zinc in alcohols to provide *cis*-2,3-dichloroacrylate (6), 3,3-dichloroacrylate (7), 2-chloro-3-alkoxyacrylate (8), and dialkylmalonate (9) esters. The reaction probably proceeds *via* tetrachlorocyclopropane (10) as an intermediate.

Until quite recently the lack of a synthetic route leading to highly halogenated three-membered ring compounds in reasonable yield has been a serious obstacle to a study of their properties. With the discovery in these laboratories^{1,2} that completely chlorinated cyclopropanes and cyclopropenes can be obtained rather simply and in good yield from dichlorocarbene ($:\text{CCl}_2$) and chlorinated olefins, a detailed study of the chemical reactions of these compounds was undertaken. This paper describes the synthesis and physical properties of hexachlorocyclopropane (1) and discusses its known chemical reactions.



When the work described herein was begun the most highly chlorinated cyclopropane reported was 1,1,2,2-tetrachlorocyclopropane (2), obtained by Stevens during a study of the chlorination of cyclopropane.³ The only totally halogenated three-membered ring compound reported was hexafluorocyclopropane (3). This compound is formed in small amounts when Teflon is pyrolytically decomposed⁴ and when $\text{CF}_2=\text{CF}_2$ is passed over a hot filament.⁵ The production of 3 under these conditions can be rationalized in terms of addition of $:\text{CF}_2$ to $\text{CF}_2=\text{CF}_2$. That generation of 3 by this mechanism is feasible has been amply demonstrated by a number of workers. Decomposition of $\text{CF}_3\text{Sn}(\text{CH}_3)_3$,^{6a} $\text{CF}_3\text{Fe}(\text{CO})_4\text{I}$,^{6b} or $(\text{CF}_3)_3\text{PF}_2$ ^{6c} at 100–150° in the presence of $\text{CF}_2=\text{CF}_2$ provides 3 in high yield.

The successful synthesis of hexafluorocyclopropane *via* a carbene mechanism suggested that an attractively straightforward synthesis of 1 might involve addition

of $:\text{CCl}_2$ ⁷ to $\text{CCl}_2=\text{CCl}_2$. However, the addition of $:\text{CCl}_2$ to olefins is well known to be highly sensitive to the electron density in the π -system of the acceptor,⁸ making addition to $\text{CCl}_2=\text{CCl}_2$ inherently unfavorable. Furthermore, unlike $:\text{CF}_2$, $:\text{CCl}_2$ is most conveniently generated in a liquid phase *via* CCl_3^- . These two latter species are known to undergo a variety of rapid degradations when in contact with the reagents from which they are made.⁹ Addition of the $:\text{CCl}_2$ to a double bond must always compete with these reactions.

With the above difficulties in mind, and in the absence of any information on the chemical stability of 1, synthesis under mild conditions was first attempted. Decarboxylation of $\text{CCl}_3\text{CO}_2^- \text{Na}^+$ in 1,2-dimethoxyethane to provide $:\text{CCl}_2$ ¹⁰ with $\text{CCl}_2=\text{CCl}_2$ acceptor provided white, crystalline hexachlorocyclopropane, but in below 1% yield. That this procedure does give 1 in 0.3% yield has been independently verified by Moore and co-workers,¹¹ although Wagner implies this synthesis fails completely.¹²

After preliminary experiments on 1 obtained by the above method demonstrated that it was relatively inert toward strong base, other known successful $:\text{CCl}_2$ syntheses requiring the presence of alkoxide and such materials as $\text{CCl}_3\text{COCCl}_3$,^{13a} $\text{CCl}_3\text{CO}_2\text{Et}$,^{13b} and CHCl_3 ^{13c,d} were tried on a small scale. Gas chromatographic analyses of the product mixtures showed consistently low yields of 1 (<1%). The formation of some 1 in every reaction, but always in microscopic amounts, indicated that $:\text{CCl}_2$ was being formed, but that further degradation took place more readily than addition to $\text{CCl}_2=\text{CCl}_2$.

A study of reaction variables led ultimately to a more satisfactory synthesis of 1, involving a new method for the generation of $:\text{CCl}_2$. The procedure consists of stirring a dilute solution of CHCl_3 in $\text{CCl}_2=\text{CCl}_2$ over fused 85% KOH at 100–110°. The method is emi-

(1) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, Abstracts of Papers, p. 95Q.

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

(3) P. G. Stevens, *J. Am. Chem. Soc.*, **68**, 620 (1946). On further chlorination of 2 Stevens obtained mainly octachloropropane, but also a small quantity of a crystalline product, m.p. 102–102.5°, which showed some hydrogen content. This compound was probably hexachlorocyclopropane.

(4) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 2.

(5) J. Harmon, U. S. Patent 2,404,374 (1946); *cf. Chem. Abstr.*, **40**, 7234² (1946).

(6) (a) H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960); (b) R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3604 (1961); (c) W. Mahler, *Inorg. Chem.*, **2**, 230 (1963).

(7) For the purposes of this discussion, those reactions listed in the literature as involving "dichlorocarbene" will be called $:\text{CCl}_2$ reactions. This is done with the realization that, depending on the particular mode of production, the dichlorocarbene may or may not ever exist as "free" $:\text{CCl}_2$.

(8) (a) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); (b) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

(9) (a) J. Hine, *ibid.*, **72**, 2438 (1950); (b) W. M. Wagner, "Trichloromethyl Anions in Neutral Aprotic Media," University of Leiden, The Netherlands, October, 1962, Introduction and Chapter 4.

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

(11) W. R. Moore, S. E. Krikorian, and J. E. LaPrade, *J. Org. Chem.*, **28**, 1404 (1963).

(12) Reference 9b, p. 14.

(13) (a) P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960); (b) W. E. Parham and E. E. Schweizer, *ibid.*, **24**, 1733 (1959); (c) H. E. Winberg, *ibid.*, **24**, 264 (1959); (d) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

nently straightforward and provides **1** quickly in greater than 10-g. lots from inexpensive and readily available starting materials. The yield, although still only about 5%, is far better than that obtainable by previously known methods.

A possible explanation for the better yield of **1** obtained in this synthesis is that the reaction occurs at the interface between two mutually insoluble phases, $\text{CCl}_2=\text{CCl}_2-\text{CHCl}_3$ and $\text{KOH}-\text{H}_2\text{O}$. According to this explanation, proton abstraction from CHCl_3 occurs at the interface. The resulting CCl_3^- ion (being electrically charged) is trapped in the KOH phase until it splits out Cl^- to form $:\text{CCl}_2$. Some of the $:\text{CCl}_2$ (being electrically neutral) can escape back into the $\text{CCl}_2=\text{CCl}_2$ phase where essentially no OH^- or H_2O is present and where the only available reaction pathway is addition to $\text{CCl}_2=\text{CCl}_2$.¹⁴ The majority of the $:\text{CCl}_2$ reacts further with OH^- or H_2O before escaping and is converted to inorganic salts and CO .^{9a} That a liquid-liquid interfacial reaction is involved is shown by the fact that the otherwise quite violent reaction may be brought to a halt merely by stopping the stirrer, which stops the exposure of fresh KOH , or by cooling the reaction just below 100° so that the KOH resolidifies.

Addition of $:\text{CBr}_2$ to $\text{CCl}_2=\text{CCl}_2$ by the above method to provide 1,1-dibromotetrachlorocyclopropane (**4**) was tried. A very low yield of **4** was obtained ($\sim 0.3\%$) along with a larger amount of CBr_4 ¹⁵ and considerable $\text{CBr}_2=\text{CBr}_2$. The formation of $\text{CBr}_2=\text{CBr}_2$ under these conditions can be rationalized either by assuming $:\text{CBr}_2$ dimerization, or, more reasonably, by postulating attack of $:\text{CBr}_2$ on CBr_3^- followed by loss of Br^- . Addition of $:\text{CBr}_2$ to $\text{CBr}_2=\text{CBr}_2$ to obtain hexabromocyclopropane was also attempted, but none of the desired product could be detected using gas chromatography.

In the interim between our original report of this work¹ and the publication of this paper, Fields and Meyerson have reported raising the yield of **1** via the Wagner method^{9b} to 10%,^{16a} and Seyferth has obtained **1** and **4** in high yield using $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ and $\text{C}_6\text{H}_5\text{HgCBr}_3$.^{16b} The modest success of the synthesis of **1** described herein and the higher yields obtained by these other workers demonstrate conclusively that although $:\text{CCl}_2$ ⁷ may well add preferentially to olefins with high π -electron density, it does add perfectly well to low π -electron density olefins provided its destruction by alternate pathways is suppressed.

The physical properties of **1** are considerably different from those of hexachloropropene (**5**), the other possible C_3Cl_6 isomer, which is an oily liquid.¹⁷ Figure 1 shows the portions of the NaCl region in which **1**, **3**, and **4** show infrared absorption. Although these totally halogenated cyclopropanes all show some absorption near 900 cm^{-1} in the cyclopropane region,¹⁸ there

(14) The dimerization of $:\text{CCl}_2$ has not been reported, although the analogous dimerization of $:\text{CF}_2$ to form $\text{CF}_2=\text{CF}_2$ has been postulated. See, for example, ref. 5a,b,c, and E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963). An alternate reaction mechanism involving addition of CCl_2^- itself to $\text{CCl}_2=\text{CCl}_2$ seems unlikely. The $\text{CCl}_3-\text{CCl}_2-\text{CCl}_2^-$ ion would be expected to provide some $\text{CCl}_3-\text{CCl}_2-\text{CCl}_2\text{H}$ or $\text{CCl}_2=\text{C}(\text{Cl})-\text{CCl}_2$ in addition to **1**. No traces of these side products were found.

(15) H. V. A. Briscoe, J. B. Peel, and J. R. Rowlands, *J. Chem. Soc.*, 1766 (1929).

(16) (a) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **28**, 1915 (1963); (b) D. Seyferth, R. J. Minasz, A. J. H. Treiber, J. M. Burlitch, and S. R. Dowd, *ibid.*, **28**, 1163 (1963). Referee III points out that the mercury reagents most probably do not generate anything approaching free dihalocarbene, but are analogous to the Simmons-Smith reagent. See H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(17) R. R. Dreisbach, "Physical Properties of Chemical Compounds," Vol. II, *Advances in Chemistry Series*, No. 22, American Chemical Society, Washington, D. C., 1959, p. 412.

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1958, p. 29.

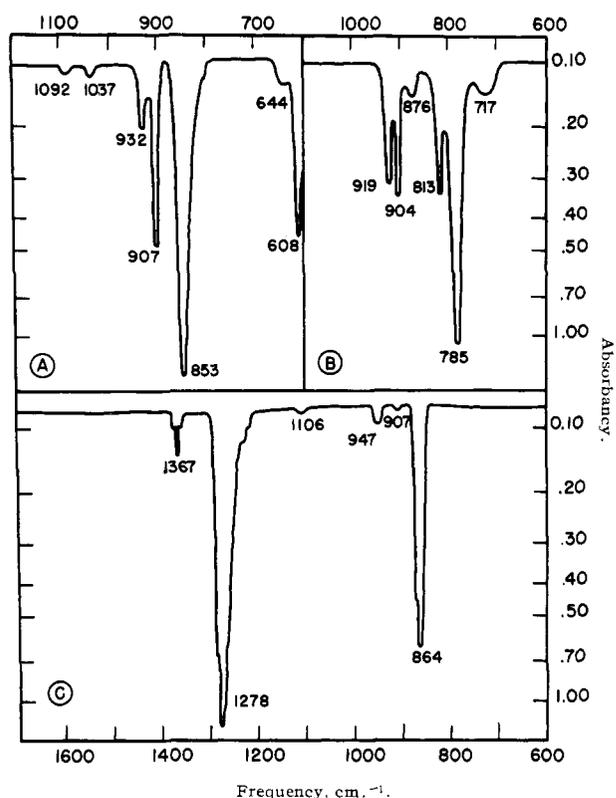


Fig. 1.—Infrared spectra of totally halogenated cyclopropanes: A, hexachlorocyclopropane (**1**), composite of spectra obtained in iso-octane and carbon tetrachloride solutions; B, 1,1-dibromotetrachlorocyclopropane (**4**), Nujol mull; C, hexafluorocyclopropane (**3**), gas spectrum; $P = 2.5\text{ mm.}$ at 25° , cell path = 9 cm.

does not seem to be any single band which is characteristic of them as a class. A complete Raman and infrared study of **1** has been carried out, and a normal coordinate analysis of the data is in progress. The number and type of bands observed agree very well with that predicted for a molecule with D_{3h} symmetry, as shown in Table I, and rule out any lower symmetry.

TABLE I
CONFIRMATION OF D_{3h} SYMMETRY FOR
HEXACHLOROCYCLOPROPANE

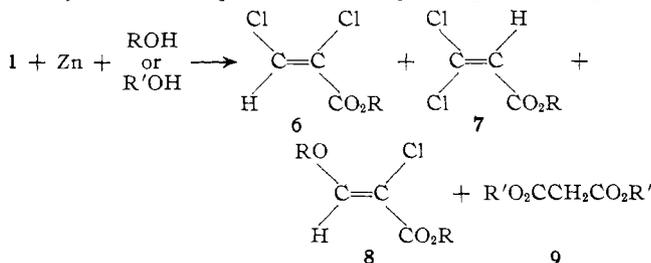
Kind of band	Number predicted ^a	Number obsd.
Raman active	10	8
Polarized Raman	3	2-3
Infrared active	6	5-6
Bands with common frequency in Raman and infrared	4	3

^a G. Herzberg, "Molecular Structure and Molecular Spectra. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1959, p. 351.

The known chemical reactions of hexachlorocyclopropane are consistent with its structure. Under most conditions it is inert. It can be refluxed or distilled in air at 198° without apparent decomposition or rearrangement. Unlike hexafluorocyclopropane, **1** resists ring-opening halogenation.⁵ It is unaffected by Br_2 in CCl_4 or gaseous Cl_2 under ultraviolet irradiation. No attempted nucleophilic substitution reactions on **1** have been successful. Under conditions sufficiently strenuous to displace Cl^- from **1**, no organic products other than unreacted starting material have been recovered. Evidently the severe angle strain and steric crowding generated during either SN1 or SN2 attack

on the cyclopropane system¹⁹ make the required transition state accessible only under conditions drastic enough to cause gross decomposition of any products initially formed. Similarly, most electrophilic reagents fail to react with **1**. Those which do react usually fail to provide well defined organic derivatives.

However, in the presence of zinc (zinc chloride is ineffective) **1** reacts smoothly with methanol or ethanol to provide a mixture of esters **6**, **7**, and **8**. In *n*-butyl alcohol and isopropyl alcohol appreciable amounts of the totally dehalogenated dialkylmalonate ester (**9**) are also formed. Compound **1** and zinc fail to react with *t*-butyl alcohol or phenol even on prolonged heating.



R = Me, Et, *n*-Bu, *i*-Pr; R' = *n*-Bu, *i*-Pr

The relative amounts of the esters obtained from the various alcohols are shown in Table II. The over-all product yields varied between 60 and 80%.

TABLE II
PRODUCT DISTRIBUTION IN THE REACTIONS OF
HEXACHLOROCYCLOPROPANE WITH ZINC AND ALCOHOLS

Alcohol	Fraction of ester in product mixture ^a				Low mol. wt. material ^b
	6	7	8	9	
MeOH	0.83 ± 0.03 ^c	0.06	0.04	0.00	0.07
EtOH	.69	.16	.09	.00	.06
<i>n</i> -BuOH	.59	.21	.02	.11	.07
<i>i</i> -PrOH	.43 ^d	.09	.24	.15	.09
	.37	.08	.26	.20	.09

^a Based on the relative peak areas in gas chromatographic analysis of the product mixtures. ^b Mostly residual alcohol. ^c Approximate reading error. ^d Duplicate runs.

With each alcohol the 2,3-dichloroacrylate ester (**6**) is the predominant reaction product. These esters were found to be identical with those which could be obtained by esterification of the only known 2,3-dichloroacrylic acid,²⁰ m.p. 85.5–87.0°. LiAlH₄ reduction of this acid was found to give exclusively an alcohol which is identical with the known *cis*-2,3-dichloro-2-propen-1-ol.^{21a} Since such reduction has been found by Hatch not to equilibrate the C=C system in substituted acrylic acids,^{21b} the 2,3-dichloroacrylate esters (**6**) and the parent acid must all have the *cis*-chlorine configuration. The esters are easily identified by their conjugated ester infrared carbonyl absorption²² at 1740 ± 2 cm.⁻¹, double bond absorption at 1588 ± 1 cm.⁻¹, and singlet n.m.r. vinyl proton resonance at 2.43 ± 0.03 τ. No *trans* isomers of **6** could be detected using gas chromatographic, infrared, or n.m.r. analysis.²³

(19) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p. 239 ff, and references cited there.

(20) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 263. All *Chem. Abstr.* references to 2,3-dichloroacrylic acid since 1945 were also searched.

(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).

(22) The chlorines present on **6** and **7** raise the carbonyl frequencies 10–20 cm.⁻¹ above those observed in unsubstituted acrylate esters. See ref. 18, Chapter 11.

(23) Assuming a detectability limit of about one mole per cent, this means either that the production of the 2,3-dichloroacrylate esters is stereospecifically *cis*, or that the ester formation reaction proceeds via a mechanism which allows equilibration at the double bond with the *cis*-2,3-dichloro configuration of the esters being thermodynamically favored over the alternate *trans* configuration by at least 3 kcal.

The 2,3-dichloroacrylate esters (**7**) obtained in this work are identical with samples synthesized from the known 2,3-dichloroacrylic acid.²⁴ These esters are characterized by conjugated ester carbonyl absorption²² at 1735 ± 3 cm.⁻¹, double bond absorption at 1608 ± 4 cm.⁻¹, and a singlet n.m.r. vinyl proton resonance at 3.70 ± 0.03 τ.

The structures of the 2-chloro-3-alkoxyacrylate esters (**8**) were assigned on the basis of their elemental analyses and their infrared and n.m.r. spectra. The elemental analysis for each ester showed one chlorine per molecule. The compounds all showed conjugated ester infrared carbonyl absorption at 1723 ± 3 cm.⁻¹ and double bond absorption at 1637 ± 3 cm.⁻¹. The n.m.r. spectra of the esters showed two nonequivalent -OR groups and a single vinyl proton resonance at 2.46 ± 0.03 τ on high band spread indicating the presence of one isomer only.

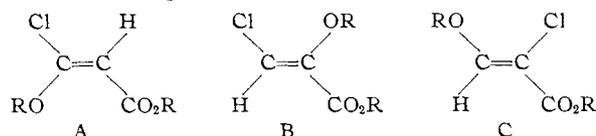
The data shown in Table III allow a decision to be

TABLE III
VINYL PROTON RESONANCES FOR VINYLIC SYSTEMS BEARING ONLY ONE PROTON

Compound	Vinyl proton resonance, τ	Compound	Vinyl proton resonance, τ
	3.70 ± 0.03 ^a		2.43 ± 0.03 ^c
	4.54		3.57
	3.55		

^a Average for the esters (**7**) synthesized in this work. ^b Prepared by the method of H. Crompton and P. L. Vanderstichele, *J. Chem. Soc.*, 691 (1920); b.p. 122–124° (740 mm.), *n*_D²⁵ 1.4509. See also F. M. Montanari and A. Negrini, *Gazz. chim. ital.*, **87**, 1061 (1957). ^c Average for the esters (**6**) synthesized in this work. ^d Prepared by the method of S. M. McElvain and M. J. Curry, *J. Am. Chem. Soc.*, **70**, 3781 (1948); b.p. 123–124° (745 mm.), *n*_D²⁵ 1.4624.

made as to which of the six possible isomers of **8** is most likely. The top three data show that in vinylic systems bearing only one proton, substitution of -OR for -Cl in the *trans*-β-position raises the vinyl proton resonance point 0.99 τ, and substitution of -CO₂R for -Cl in the α-position raises it 0.15 τ. Using these shift values, the vinyl proton resonance in a structure such as A is predicted to be near 4.69 τ. From



the middle three data the vinyl proton resonance for a structure like B is predicted to lie near 3.42 τ. Neither of these values is anywhere near the observed value. Furthermore, it seems unlikely that the vinyl proton resonance of the alternate *cis* or *trans* isomers of these two structures would lie as far down as 2.45 τ.²⁵ However, the last datum in Table III indicates that substitution of -OR for -Cl in the α-position raises the vinyl proton resonance point by only 0.02 τ. Thus, in the third structure, shown above as C, which

(24) Reference 20, p. 237.

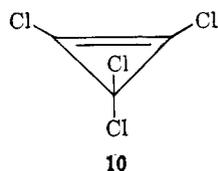
(25) See A. J. Speziale and C. C. Tung, *J. Org. Chem.*, **28**, 1353 (1963), Table III.

can be derived from structure 6 merely by replacing the $-Cl$ α to the vinyl proton with $-OR$, the vinyl proton resonance is predicted to be near 2.45 τ . This value matches exactly the observed vinyl proton resonance value for all the esters (8) within experimental error. This last structure (C) is therefore thought to be the most likely for the 2-chloro-3-alkoxyacrylate esters 8, although the alternate *cis-trans* isomer cannot be definitely excluded.

The totally dehalogenated dialkylmalonate esters (9) were identified by comparing their infrared spectra with those of authentic materials.

In attempting to determine the mechanism by which the observed reaction products are formed, we first eliminated the possibility that hexachlorocyclopropane undergoes rearrangement to hexachloropropene (5) in the presence of Zn or $ZnCl_2$, and that 5 then reacts further to give the observed products. Treatment of 5 with Zn or $ZnCl_2$ in alcohol leads only to the trichloroacrylate ester, along with minor amounts of trichloroacrylyl chloride and products obtained by the dimerization of 5.²⁶ In further experiments it was established that the esters 8 and 9 do not arise from any substitution or Michael type²⁷ reactions on 6 or 7. When refluxed with Zn or $ZnCl_2$ in the corresponding alcohol, 6 and 7 were recovered unchanged and gas chromatographic examination of the reaction mixtures showed no trace of 8, 9, or any other new products.

The observed esters evidently all arise from a common three-carbon intermediate formed earlier in the reaction sequence. The two most likely possibilities are tetrachlorocyclopropane (10), which would be formed in a normal 1,2-dehalogenation of 1, or tetrachloroallene²⁸ formed in a 1,1-dehalogenation on 1.²⁹ Recently we have isolated 10 and demonstrated² that it reacts rapidly with alcohols to produce the same products as do 1 and zinc, although in somewhat different ratios. It therefore seems highly probable that the first step in the reaction of 1 with zinc in alcohols is formation of 10, which then reacts further with the alcohol present to give the observed ester products. The mechanism of this latter reaction is being studied and will be discussed in a full report on tetrachlorocyclopropane.



Experimental³⁰

Hexachlorocyclopropane (1). Method of Wagner.¹⁰—Vacuum-dried $CCl_3CO_2^-Na^+$ (40 g., 0.22 mole) and 75 ml. (0.73 mole) of $CCl_2=CCl_2$ were placed in a 3-neck, 500-ml. flask fit with heating mantle, stirrer, dropping funnel, and reflux condenser. The condenser was capped with a $CaSO_4$ drying tower with an exit tube leading to a $Ca(OH)_2$ bubbler. The mixture was refluxed for 15 min., but no evidence of CO_2 evolution was observed;

(26) See H. J. Prins, *Rec. trav. chim.*, **68**, 419 (1949), for the same reaction catalyzed by copper.

(27) Reference 19, pp. 389–394 and 527–529.

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

(29) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **75** (1958).

(30) 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 155–165° using helium carrier gas at a flow rate of 80 ml./min. through 5 ft. \times 0.5 in. columns packed either with silicone Dow 11 on 30/60 mesh firebrick or 30% tricresyl phosphate on 60/80 mesh Chromosorb P. Melting and boiling points are correct within $\pm 1^\circ$. Infrared spectra were taken on pure liquid films between NaCl plates on a Perkin-Elmer Model 237 recording spectrophotometer calibrated in cm^{-1} . Listed frequencies are correct within ± 3 cm^{-1} . All n.m.r. spectra were run on dilute (1–10%) solutions in CCl_4 with internal tetramethylsilane standard on a Varian Associates Model A-60 spectrometer.

25 ml. of 1,2-dimethoxyethane was then added and reflux resumed. Carbon dioxide evolution began almost immediately (as evidenced by precipitation of $CaCO_3$ in the bubbler) and continued for 16 hr. Removal of the 1,2-dimethoxyethane and excess $CCl_2=CCl_2$ under vacuum left a viscous brown residue which was repeatedly extracted with hexane. The hexane extracts were rinsed with water and dried over Na_2SO_4 . Evaporation of the hexane at 50° left 7 ml. of a deep brown viscous oil. Vacuum distillation of the oil (0.6 mm.) provided approximately 0.3 g. of a white crystalline solid (1) which accumulated in the condenser. This solid was resublimed under vacuum (0.1 mm., 100°) to give 0.3 g. (0.6%) of 1, m.p. 102.5–103.5°. Gas chromatographic analysis of this product on the silicone column showed it to be homogeneous. Examination of the still-pot residue showed it contained more 1, but mostly high polymers.

Anal. Calcd. for C_3Cl_6 : C, 14.50; Cl, 85.50. Found: C, 14.75; Cl, 85.20.

Hexachlorocyclopropane (1). KOH- $CHCl_3$ Method.—A 2-l. 3-neck, round-bottom flask was fit with a Teflon blade stirrer driven by a powerful stirring motor, heating mantle, and 100-ml. by-pass dropping funnel. A 100-cm. high-capacity reflux condenser was attached using a 3-way adapter through which a 0–360° permanent-marking thermometer was inserted so that the bulb would be immersed in the reaction mixture; 500 ml. (4.9 moles) of $CCl_2=CCl_2$, 300 g. of KOH pellets (85% KOH–15% H_2O , 4.5 moles), and 50 ml. of $CHCl_3$ were placed in the flask. An additional 50 ml. of $CHCl_3$ was placed in the dropping funnel (total charge of $CHCl_3$, 1.2 moles). Stirring was begun, and the reaction mixture was heated to 96° quickly. At this temperature the KOH pellets began to soften and the heater was removed immediately. The reaction temperature rose to 100–103° and vigorous reflux began. The temperature was kept below 103° by external cooling with ice-water. The KOH phase turned gradually to a tan sludge. After the reaction had been going a few minutes the temperature was allowed to rise toward 110° and $CHCl_3$ was added so that steady reflux continued. Stirring was continued for 10 min. after all the $CHCl_3$ was added (total reaction time, 45 min.). The supernatant $CCl_2=CCl_2$ solution was filtered off and excess $CHCl_3$ and $CCl_2=CCl_2$ were removed under vacuum between 20 and 35°. The residual hexachlorocyclopropane (1) was recrystallized from CH_3OH (7 ml./g.). The yield of 1 was 15 g. (4.5% based on $CHCl_3$ added) of snow-white crystals with a pine-needle odor, m.p. 103.5–104.5° (lit.^{11,16b} m.p. 103–104°), b.p. 198–199° (740 mm.) in air without decomposition, isopiestic mol. wt. (CH_2Cl_2) 253 \pm 1 (calcd. for C_3Cl_6 248.8). The infrared spectrum of 1 is shown in Fig. 1a.

1,1-Dibromotetrachlorocyclopropane (4).—Tribromomethane (7.5 ml., 0.086 mole), 15 ml. (0.147 mole) of $CCl_2=CCl_2$, and 2.5 g. (0.045 mole) of KOH pellets (85% KOH, 15% H_2O) were heated to 105 \pm 5° for 10 min. while the KOH was triturated. The liquid organic residue (18 ml.) was poured off. Gas chromatographic analysis of 0.1 ml. of the residue on the silicone column showed large peaks for unreacted $CCl_2=CCl_2$ and $CHBr_3$, and, in addition, three small peaks with increasingly longer retention times. Samples of these three peaks were trapped out in U-tubes immersed in ice-water. All three materials were white crystalline solids. The first two peaks were identified as CBr_4 and $CBr_2=CBBr_2$. Their retention times and infrared spectra (Nujol mull) were identical with those of authentic samples. The infrared spectrum of the third peak material (4) shown in Fig. 1b indicated a cyclic structure for the compound. Evaporation of the organic liquid residue from the synthesis left approximately 0.2 g. of white crystalline material (m.p. 95–105°) which was dissolved in 0.4 ml. of CCl_4 and rechromatographed. Just under 50 mg. (0.33%) of 4, m.p. 115–116° (lit.^{16b} m.p. 114–115.5°), was obtained.

Anal. Calcd. for $C_3Cl_4Br_2$: C, 10.67; Cl, 42.00; Br, 47.33. Found: C, 10.78; Cl, 42.24; Br, 47.39.

Chemical Reactions of Hexachlorocyclopropane (1). Halogenation.—Compound 1 did not react with I_2 at reflux (neat), nor with Br_2 in CCl_4 at room temperature, and was unaffected by sublimation through gaseous Cl_2 at atmospheric pressure in a quartz flask under irradiation with a General Electric H4 mercury arc.

Nucleophilic Attack.—Compound 1 reacted slowly without charring with molten 85% KOH, solid $NaOCH_3$, and solid $NaOAc$ at 110–150° to liberate copious amounts of Cl^- . However, gas chromatographic analyses of CCl_4 extracts of the acidified reaction residues showed peaks for unreacted 1 only; 1 dissolved in refluxing pyridine, aniline, and KOH in ethylene glycol but did not react with them.

Electrophilic Attack.—Compound 1 was immiscible with and failed to react with 95% H_2SO_4 at 198°; 1 charred on heating with solid $AlCl_3$, but did not react with Mg, Zn, or Cu powder neat, in tetrahydrofuran or in 1,2-dimethoxyethane. Compound 1 reacted vigorously with phenyllithium in ether to form chlorobenzene in good yield, but no product containing fragments of 1 could be isolated; 1 also reacted with *n*-butyllithium in ether, but again no well-defined product could be isolated.

TABLE IV
 PHYSICAL PROPERTIES OF ACRYLATE ESTERS 6, 7, AND 8

Ester, R =	Carbon, %		Hydrogen, %		Chlorine, %		n_D^{20}	$t, ^\circ\text{C.}$	Infrared spectrum			N.m.r. spectrum		
	Calcd.	Found	Calcd.	Found	Calcd.	Found			frequency, cm.^{-1}	C=C—H	C=O	C=C	Pos., τ (form) ^a	Group
6														
Me	31.00	31.05	2.60	2.61	45.75	45.68	1.4788	21.5	1742	1587	2.40 (1)	—OCH ₃	6.16 (1)	
Et	35.53	35.41	3.58	3.45	41.95	42.08	1.4701	24.2	1740	1588	2.42 (1)	—OCH ₂ —	5.72 (4)	
												—CH ₃	8.66 (3)	
<i>n</i> -Bu	42.67	43.86	5.12	5.37	35.98	35.00	1.4663	25.2	1739	1587	2.43 (1)	—OCH ₂ —	5.78 (3)	
												—CH ₂ CH ₂ —	8.1–8.8 (M)	
<i>i</i> -Pr	39.38	39.61	4.41	4.32	38.75	38.71	1.4638	25.2	1741	1589	2.46 (1)	—CH—	4.95 (7)	
												—(CH ₃) ₂	8.69 (2)	
7														
Me	31.00	30.91	2.60	2.65	45.75	45.55	1.4810	21.5	1738	1613	3.69 (1)	—OCH ₃	6.28 (1)	
Et	35.53	34.62	3.58	3.45	41.95	42.31	1.4710	23.5	1734	1608	3.67 (1)	—OCH ₂ —	5.81 (4)	
												—CH ₃	8.71 (3)	
<i>n</i> -Bu	42.67	42.70	5.12	5.22	35.98	35.56	1.4689	25.3	1735	1606	3.73 (1)	—OCH ₂ —	5.88 (3)	
												—CH ₂ CH ₂ —	8.1–8.8 (M)	
												—CH ₃	9.05 (3)	
<i>i</i> -Pr	39.38	39.54	4.41	4.26	38.75	37.46	1.4652	25.2	1730	1604	3.73 (1)	—CH—	5.00 (7)	
												—(CH ₃) ₂	8.75 (2)	
8														
Me	39.89	39.35	4.69	4.75	23.55	24.73	...		1726	1640	2.51 (1)	—OCH ₃	6.26 (1), 6.06 (1)	
Et	47.07	47.45	6.21	6.73	19.84	19.52	...		1723	1637	2.46 (1)	—OCH ₂ —	5.91 (4), 5.87 (4)	
												—CH ₃	8.70 (3), 8.60 (3)	
<i>n</i> -Bu	60.41	...	8.76	...	16.21	15.90	...		1725	1637	2.46 (1)	—OCH ₂ —	5.90 (3), 5.86 (3)	
												—CH ₂ CH ₂ —	8.1–8.8 (M) ^b	
												—CH ₃	9.01 (3) ^b	
<i>i</i> -Pr	52.40	52.72	7.26	7.28	17.20	17.54	...		1719	1635	2.45 (1)	—CH—	5.75 (7), 5.02 (7)	
												—(CH ₃) ₂	8.73 (2), 8.63 (2)	

^a (1) = singlet, (2) = doublet, (3) = triplet, (4) = quartet, (7) = septet, and (M) = complex multiplet. ^b The alkyl proton resonances were superimposed. Integration of the spectrum showed a vinyl:O-methylene:alkyl proton ratio of 0.9:3.6:14.0; the theoretical ratio is 1.0:4.0:14.0.

Dehalogenation of Hexachlorocyclopropane (1).—Compound 1 reacted vigorously with Mg in alcohols, but no simple organic products could be isolated. Zn in alcohols dehalogenated 1 smoothly, as described below. Compound 1 reacted sluggishly with Al chips in alcohol to give the same products, but in much lower yield.

Compound 1 (2.14 g., 0.0086 mole), 2.46 g. (0.0377 g.-atom) of Zn granules, and 3 ml. (0.051 mole) of absolute ethanol were warmed gently to initiate reaction. Once started the reaction became exothermic and was moderated during its initial stages by external cooling with ice-water. Some volatile material with a pleasant fruity odor bubbled off. The reaction mixture became dark and somewhat viscous over a 15-min. period. The mixture was then warmed gently for 5 more min. and the organic products taken up in 10 ml. of CCl₄. The residual Zn weighed 1.21 g. so 0.0191 g.-atom of Zn was consumed. The CCl₄ was evaporated under vacuum leaving 0.7 ml. of a yellow liquid. Gas chromatographic analysis of 0.1 ml. of this liquid on the silicone column showed five peaks. The first two peaks were CCl₄ and ethanol, and the small fourth peak was unreacted 1. The third peak was a mixture of 6 and 7, and the fifth peak was 8. Compounds 6 and 7 were readily separated on the tricresyl phosphate column; 7 was eluted first. The proportions of the various products are shown in Table II. Gas chromatographic analysis of a portion of the reaction mixture to which a small amount of 9 (R = Et) had been added showed a new peak for 9 which was previously absent.

Identification of Ester Products.—The *cis*-2,3-dichloroacrylate esters (6) were identical with samples prepared³¹ from *cis*-2,3-dichloroacrylic acid, m.p. 85.5–87.0° (lit.²⁰ m.p. 85–86°, 87–88°), and the appropriate alcohol. The n.m.r. vinyl proton resonance for the acid is at 2.21 τ . The characteristic infrared and n.m.r. spectra of the esters are shown in Table IV. All physical data shown in the table were taken on samples obtained from the reaction of 1 and zinc and purified by gas chromatography. The 3,3-dichloroacrylate esters (7) were characterized by the identity of their infrared and n.m.r. spectra to those of the esters prepared³¹ from 3,3-dichloroacrylic acid, m.p. 75–77.5° (lit.²⁴ m.p. 76–77°), and the appropriate alcohol. The n.m.r. vinyl proton resonance for this acid is at 3.61 τ . The physical data

(31) Approximately 0.5 g. of the acid was dissolved in 1 ml. of alcohol. 1 drop of 95% H₂SO₄ was added, and the mixture was refluxed for 5–15 min.; 2 ml. of H₂O was added, the mixture shaken, and the organic layer withdrawn and dried over Na₂SO₄. The ester was obtained pure by gas chromatographic separation.

on the esters 7 shown in Table IV were obtained as for the 6 esters.

The *cis*-2-chloro-3-alkoxyacrylate esters (8) were identified from their elemental analyses and their infrared and n.m.r. spectra as shown in Table IV using the techniques outlined earlier in the discussion.

The dialkylmalonate esters (9) were identified by comparing their infrared spectra with those of authentic materials prepared³¹ from malonic acid and the appropriate alcohol.

Reduction of 2,3-Dichloroacrylic Acid to *cis*-2,3-Dichloro-2-propen-1-ol.—2,3-Dichloroacrylic acid (1.0 g.) was dissolved in 4 ml. of dry ether. A suspension of LiAlH₄ in dry ether was added dropwise to the solution of the acid at 30° over a 1-hr. period. At this time all evidence of reaction had ceased and a considerable excess of LiAlH₄ was present. The excess hydride was destroyed with wet ether, and the reaction mixture was treated with 2 N HCl to dissolve the precipitated aluminum hydroxides. The supernatant ether layer was withdrawn and dried over Na₂SO₄. Evaporation of the ether left a residue having an infrared spectrum identical with that of the known *cis*-2,3-dichloro-2-propen-1-ol.²¹ In addition to bands at 3340 vs. b (—OH), 3075 m, 2930 m, and 2870 m (C—H), and a doublet at 1635 s, 1615 vs (C=C), the spectrum showed bands at 1112 s, 1025 vs, 978 m, 878 m, 839 s, 794 s, and 680 m cm.⁻¹. The presence of these bands, and the absence of bands at 1073 s, 1032 s, 967 m, 819 vs, and 701 m cm.⁻¹, show that the alcohol was the pure *cis* compound, uncontaminated with the *trans* isomer. No bands due to unreacted starting acid were present. The n.m.r. spectrum of the alcohol showed a singlet peak at 6.36 τ (—OH), a doublet at 5.85 τ (—CH₂—), and a triplet at 3.57 τ (C=C—H), $J = 1.4$ c.p.s. This coupling is similar to that observed for other *cis*-vinyl proton-allyl proton interactions.³² The alcohol was completely destroyed by attempted purification using either the silicone or tricresyl phosphate gas chromatography columns.

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2-propen-1-ol for comparison with the product obtained in this work, to Dr. D. C. England of the E. I. du Pont de Nemours Co. for a sample of hexafluorocyclopropane,

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[CONTRIBUTION FROM MONSANTO CHEMICAL CO., RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION, ST. LOUIS, MO.]

Synthesis of Hypophosphite Esters from Orthocarbonyl Compounds

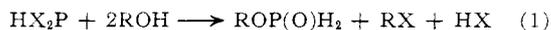
BY STEVEN J. FITCH

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A convenient source of alkyl hypophosphite esters has been found in the reaction of crystalline hypophosphorous acid with orthocarbonates, orthocarboxylates, ketals, or acetals. The only previous preparation of hypophosphite esters was by means of the diazoalkane reaction. Ketals and acetals yield 1-hydroxyphosphinate esters as the final products due to addition of the phosphorus-hydrogen bond of the alkyl hypophosphite to the carbonyl group of the ketone or aldehyde by-product. The reaction between acetone dimethyl ketal and hypophosphorous acid shows an abrupt change in rate, indicating the formation of a weak complex between a reactant and a product, probably the ketal and methyl hypophosphite. P^{31} and H^1 n.m.r. data are presented for the pure esters and some reaction mixtures.

Introduction

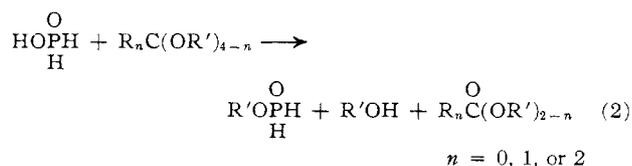
Simple esters of the various oxyacids of nonmetals are usually prepared by the reaction of alcohol with the halide, anhydride, or acid of the central element. None of these methods is applicable to the esterification of hypophosphorous acid since the anhydride, $H_2P(O)OP(O)H_2$, and appropriate halide, XH_2PO or HX_2P , are not known. The dihalophosphine would be an appropriate halide by analogy to the alcoholysis of phosphorus trichloride.



The direct esterification of hypophosphorous acid with alcohol has not been reported, and, if it proceeded at all, would probably result in decomposition of the unstable esters.

These conditions have caused hypophosphite esters to be virtually unknown materials, in striking contrast to the thoroughly studied phosphite esters. The only reported preparation of hypophosphite esters is the formation of the methyl and ethyl esters from the acid and the appropriate diazoalkane.¹ The unspecified yields were undoubtedly low since the esters disproportionate rapidly at the reported boiling points.

A new and convenient synthesis of alkyl hypophosphites has been found, based on the reaction of hypophosphorous acid with compounds having an orthocarbonyl function.



The scope of the reaction was shown with a series of ortho compounds including orthocarbonates ($n = 0$), orthocarboxylates ($n = 1$), and a ketal and an acetal ($n = 2$).

The esterification is nearly quantitative in most cases, although a severe reduction in yield occurs on distillation due to the disproportionation reaction. However, the fresh reaction product, consisting of the hypophosphite ester dissolved in the by-product alcohol and carbonyl compound, decomposes much more slowly than the pure ester. This medium provides a convenient source of compounds which have two hydrogen atoms bonded to a quadruply connected phosphorus atom and which are therefore difunctional analogs of the dialkyl phosphonates. Only the primary phosphine

oxides and hypophosphorous acid, esters, and salts are known to contain this structural unit. Interesting variations on many of the numerous reactions of dialkyl phosphonates should be possible using this reaction mixture as a source of alkyl hypophosphites.

Results and Discussion

The alkyl hypophosphites are prepared simply by mixing crystalline hypophosphorous acid and the ortho compound at room temperature. Two liquid phases are formed, and the system becomes homogeneous as the esterification reaction proceeds. The time required for forming a one-phase system varies from about 1 to 30 min., depending on the ortho compound, the dryness of the acid, and particularly on the rate of agitation. Of the ortho compounds tested, only acetal required heating or long standing to initiate reaction. The course of the esterification in the resulting single-phase system can then be followed by both H^1 and P^{31} n.m.r. to determine when the reaction reaches completion and, in the simpler systems, to determine the stoichiometry by identification of all major components.

The over-all esterification reaction, including the phase change of the crystalline acid, is endothermic, indicating that the entropy increase in forming three molecules from two is an important driving force in the reaction. There is probably an approximate cancellation of the enthalpy effects due to a favorable change in hybridization for carbon and an unfavorable change for phosphorus, in which the π -bond is localized onto only one P-O bond,² leaving the entropy increase as a predominant factor.

Methyl and ethyl hypophosphites prepared from the corresponding orthoformates were isolated by distillation. Yellow solids and phosphine were generated in large amounts during distillation, and the yields were variable, depending on the time and temperature of distillation. No attempt was made to distill the butyl ester since it was expected to decompose completely at distillation temperatures. However, most of the butanol and butyl formate by-products were removed by vacuum evaporation to give a concentrated residue having a stronger n.m.r. signal.

It is not necessary to use completely dry hypophosphorous acid in the reaction since any water present in the acid immediately hydrolyzes the hypophosphite ester, which is then regenerated by reaction with additional ortho compound. In fact, a mixture of ethyl hypophosphite and hypophosphorous acid was obtained

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(2) J. R. Van Wazer, "Phosphorus and its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 437-440.