

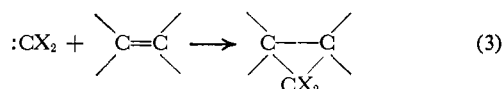
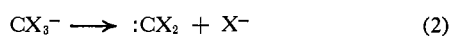
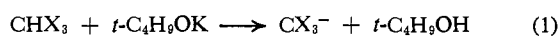
Halomethyl–Metal Compounds. II. The Preparation of *gem*-Dihalocyclopropanes by the Reaction of Phenyl(trihalomethyl)mercury Compounds with Olefins¹

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Phenyl(trihalomethyl)mercury compounds react with olefins to give gem-dihalocyclopropanes in high yield. This new procedure does not involve trihalomethide ion as an intermediate, nor does it require basic reaction conditions. Thus the mercurial route allows the preparation of gem-dihalocyclopropanes from olefins which contain base-sensitive functional groups, which react with trihalomethide ion, or which are only poor nucleophiles. A number of examples are given to illustrate these advantages of the mercurial route in these specific cases over the Doering–Hoffmann and Wagner routes. The conversion of cis and trans olefins to gem-dihalocyclopropanes by the mercurial route occurs with retention of configuration.

Interest in the preparation and reactions of *gem*-dihalocyclopropanes has been high since the initial report by Doering and Hoffmann⁴ that this class of compounds was accessible *via* the addition of dihalocarbenes to olefins.⁵ Their procedure is summarized by eq. 1–3. It and several of its variants^{6–8} leading to



dihalocarbenes are based on the treatment of a trihalomethide ion source with a strong base in the

presence of the olefinic substrate. These procedures can be applied with good success to the preparation of many *gem*-dihalocyclopropanes, but there are cases where these methods give the desired dihalocyclopropane in only very low yield or not at all. If the olefin contains functional groups sensitive to basic reagents, these procedures often are not applicable (*e.g.*, vinyl acetate). If the olefin is only weakly nucleophilic (*e.g.*, ethylene and tetrachloroethylene), these procedures do not give good yields of product because the base used to generate the carbene competes successfully with the olefin for the electrophilic dihalocarbene.

The preparation of *gem*-dihalocyclopropanes by thermal decarboxylation of alkali metal trihaloacetates⁹ avoids the basic reaction conditions of the procedures described above. However, with weakly nucleophilic olefins, a side reaction between the carbene and trihaloacetate ion serves to intercept much of the carbene, thus giving low yields of the desired product.^{9b,10}

Both the Doering–Hoffmann procedure and its variants and the Wagner procedure have one other disadvantage in common: the trihalomethide ion is an intermediate, and with some substrates (*e.g.*, acrylonitrile) this is intercepted in part before it has a chance to decompose to dihalocarbene.

A further route to *gem*-dichlorocyclopropanes is one based on prior formation of trichloromethyl lithium, LiCCl₃, at low temperature. It has been claimed that this reagent reacts directly and rapidly with olefins to give *gem*-dichlorocyclopropanes.¹¹ (See also ref. 12 and 13.)

From the discussion above it is obvious that a general procedure for the preparation of *gem*-dihalocyclopropanes that does not involve basic reaction conditions, that does not proceed *via* nucleophilic intermediates such as trichloroacetate or trichloromethide ion, and that occurs in good yield at relatively low temperatures would be a welcome addition to the list of available procedures. We report here concerning

(1) (a) Part I: D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965). (b) Preliminary communications: D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962); D. Seyferth, R. J. Minasz, A. J.-H. Treiber, J. M. Burlitch, and S. R. Dowd, *ibid.*, **28**, 1163 (1963). (c) Presented in summary form at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 6, 1965.

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(4) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(5) For recent summaries of carbene chemistry see (a) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; (b) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(6) (a) W. E. Parham and F. C. Loew, *J. Org. Chem.*, **23**, 1705 (1958); (b) W. E. Parham, and E. E. Schweizer, *ibid.*, **24**, 1733 (1959).

(7) (a) P. K. Kadaba and J. O. Edwards, *ibid.*, **25**, 1431 (1960); (b) F. W. Grant and W. B. Cassie, *ibid.*, **25**, 1433 (1960).

(8) U. Schöllkopf and P. Hilbert, *Angew. Chem.*, **74**, 431 (1962).

(9) (a) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959); (b) W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. trav. chim.*, **80**, 740 (1961).

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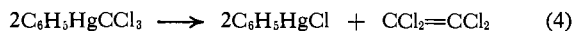
(11) W. T. Miller, Jr., and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964).

(12) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, Abstracts of Papers, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 52P; *J. Am. Chem. Soc.*, in press.

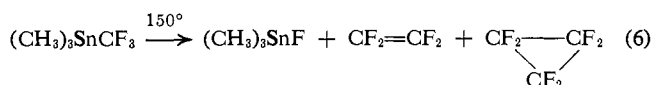
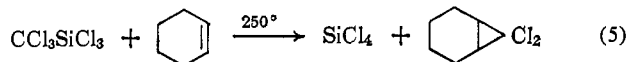
(13) G. Köbrich, K. Flory, and H. R. Merkle, *Tetrahedron Letters*, 973 (1965).

the scope and stereochemistry of a reaction which meets these requirements.

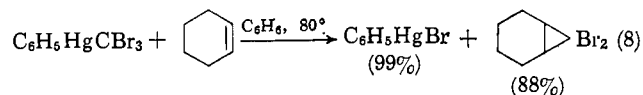
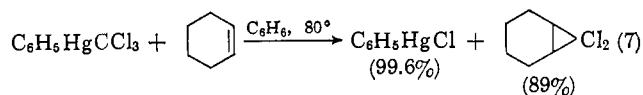
In 1957 Nesmeyanov and co-workers¹⁴ prepared phenyl(trichloromethyl)mercury and reported that it decomposed when heated at 150° to give phenylmercuric chloride in high yield. In 1960–1961 Reutov and Lovtsova described the synthesis of RHgCCl₃ and RHgCBr₃ compounds by another procedure and reported that phenyl(trichloromethyl)mercury when heated in boiling ethanol decomposes in a similar fashion.¹⁵ The other decomposition product(s) were not identified, but a balanced equation nevertheless was written (eq. 4).



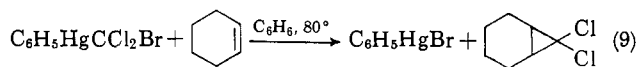
The possibility that the decomposition of RHgCX₃ compounds might proceed by α -elimination of RHgX *via* a dihalocarbene intermediate and that this might possibly be intercepted occurred to us. This possibility was especially attractive in view of previous reports that (trichloromethyl)trichlorosilane and (trifluoromethyl)trimethyltin decomposed in such a manner and that in both cases a dihalocarbene could be intercepted (eq. 5¹⁶ and 6¹⁷). Accordingly, we studied the



reaction of phenyl(trichloromethyl)mercury and phenyl(tribromomethyl)mercury with cyclohexene in excess in refluxing benzene solution. The results are summarized by eq. 7 and 8.



The 7,7-dihalonorcarane yields represent pure product isolated by distillation; hence one may assume that these reactions proceeded quantitatively as written. Such quantitative yields were obtained in reaction 7 only after a reflux period of about 36–48 hr., but the equally high 7,7-dibromonorcarane yield was obtained in reaction 8 under identical conditions in only 2 hr. This suggested that elimination of phenylmercuric bromide was highly favored over elimination of phenylmercuric chloride, and to test this idea, the reaction of phenyl(bromodichloromethyl)mercury with cyclohexene under identical conditions was examined. This reaction proceeded *essentially quantitatively* in 2 hr. as shown in eq. 9. No 7-bromo-7-chloronorcarane



could be detected, a finding in agreement with the great difference in rates of elimination of phenylmercuric bromide and chloride observed in the previous experiments. Exclusive formation in virtually quantitative yield of 7-bromo-7-chloronorcarane was observed in a reaction of phenyl(dibromochloromethyl)mercury with cyclohexene carried out in the same manner. No 7,7-dibromonorcarane was detected in this case.

These initial experiments made it clear that in the phenyl(trihalomethyl)mercurials we had a reagent class which would transfer CX₂ to olefins (to give *gem*-dihalocyclopropanes) in high yield under neutral conditions. No side reactions appeared to complicate matters. The only nucleophile present was the olefinic substrate. As will become clear later, trihalomethyl anions or radicals did not appear to be involved. In any C₆H₅HgCX₂Br (X = Cl or Br) system only C₆H₅HgBr was eliminated, thus allowing specific and exclusive transfer of CCl₂, CClBr, and CBr₂ to the olefin. Another advantage of this new system lies in the insolubility and general inertness of phenylmercuric bromide; it could be filtered off almost quantitatively and recycled to mercurial preparation.¹⁸

The advantages of the phenyl(trihalomethyl)mercurials were shown in striking fashion in their reactions with a number of olefins which contained base-sensitive substituents or which were only poor nucleophiles, and some of which previous workers had been unable to convert to *gem*-dihalocyclopropanes at all, or only in very low yield, because of the complications mentioned in the introductory paragraphs. The results of our mercurial-olefin reaction studies are summarized in Table I. A number of these reactions merit further discussion, in particular, in those cases where the olefin would present special problems in *gem*-dihalocyclopropane synthesis by the CX₃⁻-based routes.

Ethylene. It was reported by Doering and Henderson¹⁸ that dichlorocarbene prepared by the chloroform-potassium *t*-butoxide reaction did not react with ethylene, apparently because the rate of the competing reactions of the carbene with butoxide ion and with *t*-butyl alcohol were faster. The phenyl(trihalomethyl)mercurial reagents, on the other hand, allowed the preparation of 1,1-dibromo- and 1,1-dichlorocyclopropanes from ethylene in yields of 53 and 65%, respectively. These reactions were carried out in an autoclave at 80–100° under 50 atm. of ethylene in benzene solution. Temperature control in the system available to us was poor, and a careful study of reaction conditions very probably would lead to improved yields.

Tetrachloro- and Trichloroethylene. The study of the chemistry of hexa- and pentachlorocyclopropane by Tobey and West has been extremely fruitful.¹⁹ However, the preparation of these compounds was not very satisfactory, the reactions of the poorly nucleophilic tetrachloroethylene and trichloroethylene with dichloro-

(14) A. N. Nesmeyanov, R. Kh. Freidlina, and F. K. Velichko, *Dokl. Akad. Nauk SSSR*, **114**, 557 (1957).

(15) O. A. Reutov and A. N. Lovtsova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1716 (1960); *Dokl. Akad. Nauk SSSR*, **139**, 622 (1961).

(16) W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind. (London)*, 789 (1961).

(17) H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960).

(18) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(19) (a) S. W. Tobey and R. West, *ibid.*, **86**, 56 (1964); (b) Table I, footnote i; (c) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964); (d) *ibid.*, **86**, 4215 (1964).

carbene from the $\text{CHCl}_3 + \text{KOH}$ reaction,^{19a} from the $\text{CHCl}_3 + t\text{-C}_4\text{H}_9\text{OK}$ reaction,²⁰ and from the decarboxylation of sodium trichloroacetate^{19b,20,21} giving only low yields (up to 10% of hexachlorocyclopropane and up to about 25% of pentachlorocyclopropane). In contrast, the reaction of 0.1 mole of phenyl(bromodichloromethyl)mercury with 1 mole of tetrachloroethylene at 90° for 1 hr. resulted in precipitation of phenylmercuric bromide (94%) and hexachlorocyclopropane could be isolated in 83% yield. Similar reactions using the dibromochloromethyl- and tribromomethylmercurials gave bromopentachlorocyclopropane (48%) and 1,1-dibromotetrachlorocyclopropane (26%),²² respectively. A similar procedure served in the preparation of pentachlorocyclopropane. With $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ a reaction time of 5 hr. was used and pentachlorocyclopropane was isolated in 89% yield. With $\text{C}_6\text{H}_5\text{HgCCl}_3$ a 36-hr. period of reflux resulted in a 63% yield of product.

It is not necessary to use the less reactive olefins as their own solvents as was done in these last examples in order to achieve good yields. When the trichloroethylene/mercurial ratio was reduced to 3 and the reaction was carried out during 4 hr. in refluxing benzene solution, pentachlorocyclopropane was produced in 79.4% yield. Tetrachloroethylene also was formed in a yield of 4%. In our experience, tetrachloroethylene appears as a by-product in those cases where the substrate is not very reactive toward our mercurial reagents. In the case of one olefin, perfluorocyclohexene, tetrachloroethylene and hexachlorocyclopropane were the only observed products, formed in yields of 43 and 21%, respectively, based on starting phenyl(bromodichloromethyl)mercury. It may be noted that tetrachloroethylene (accompanied by a trace of bromotrichloroethylene) is the volatile product of the pyrolysis of phenyl(bromodichloromethyl)mercury in the absence of substrate; thus the assumption of Reutov and Lovtsova¹⁵ (eq. 4) is correct.

Vinylsilanes. In the attempted preparation of 1,1-dichloro-2-trimethylsilylcyclopropane the dichlorocarbene-butoxide and dichlorocarbene-butanol reactions also appeared to compete successfully with the olefin dichloromethylenation, since the desired product was obtained in only 0.2% yield by Cudlín and Chvalovský.²³ We were able to prepare this silyl-substituted cyclopropane in 78% yield by the mercurial route, as well as the analogous 1,1-dibromo-2-trimethylsilylcyclopropane in 57% yield. Even more striking is the preparation of 1,1-dichloro-2-chlorodimethylsilylcyclopropane from dimethylvinylchlorosilane *via* phenyl(bromodichloromethyl)mercury. It is doubtful if the very reactive Si-Cl linkage would have been retained intact during the Doering-Hoffmann or the Wagner procedures. In the trimethylvinylsilane reactions a 30-hr. reflux period was required when the $\text{C}_6\text{H}_5\text{HgCX}_2\text{Br}$ mercurials were used, most probably because the reaction temperature was considerably lower than 80° as a result of the 54° boiling point of the vinylsilane.

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

(21) E. K. Fields and S. Meyerson, *ibid.*, **28**, 1915 (1963).

(22) Prepared in 0.3% yield by the $\text{CHBr}_3 + \text{KOH}$ procedure by Tobey and West.^{19a}

(23) J. Cudlín and V. Chvalovský, Table I, footnote *j*.

trans-Stilbene. The attempted addition of dichlorocarbene to *trans*-stilbene gave none of the desired product.²⁴ On the other hand, the reaction of *trans*-stilbene with a slight excess of phenyl(bromodichloromethyl)mercury in benzene at 85° produced 1,1-dichloro-2,3-diphenylcyclopropane in 90% yield. This experiment demonstrates another advantage of the mercurial procedure: high yields of *gem*-dihalocyclopropanes can be obtained in a 1:1 reaction. Thus neither olefin nor mercurial is wasted, and when both olefin and cyclopropane product are solids, work-up of the reaction mixture is facilitated.

Acrylonitrile and Vinyl Acetate. The conversion of acrylonitrile to a 1,1-dihalo-2-cyanocyclopropane by any route involving intermediate trihalomethide ion should present difficulties due to the known nucleophilic addition of CX_3^- to acrylonitrile.^{25,26} Also, bases such as potassium *t*-butoxide and sodium methoxide could not be tolerated, since they react readily with acrylonitrile.²⁷ Noteworthy thus is the preparation of 1,1-dichloro-2-cyanocyclopropane in 78% yield by the mercurial route. Only a slight amount of polymerization of the excess acrylonitrile appeared to have occurred, as evidenced by the isolation of phenylmercuric bromide as a brownish solid with a 275–286.5° melting range.

Wagner, Kloosterziel, and van der Ven^{9b} have reported that the decarboxylation of sodium trichloroacetate in the presence of vinyl acetate in 1,2-dimethoxyethane (DME) solution gives both the expected *gem*-dichlorocyclopropyl acetate (10%) as well as the CCl_3^- addition product, 1-trichloromethylethyl acetate, $\text{CH}_3\text{COOCH}(\text{CCl}_3)\text{CH}_3$, which was obtained in 10% yield. In contrast, the reaction of vinyl acetate with $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$, also carried out in DME at 80°, gave *gem*-dichlorocyclopropyl acetate as sole product in 80% yield. No CCl_2Br^- addition product was observed. (The phenyl(bromodichloromethyl)mercury-vinyl acetate reaction also was carried out in benzene at 80°; within 2 hr. an 85% yield of *gem*-dichlorocyclopropyl acetate was obtained.) It may be noted also that when the $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ -acrylonitrile reaction was carried out in DME, no Michael-type addition product was formed. When CCl_2Br^- was generated in this solvent in the presence of acrylonitrile, $\text{CCl}_2\text{BrCH}_2\text{CH}_2\text{CN}$ was formed.²⁶ These observations suggest strongly that the bromodichloromethide ion is not an intermediate in the mercurial-olefin reaction.

Other olefins containing base-sensitive functionality which were converted readily to the corresponding *gem*-dihalocyclopropanes include allyl bromide,²⁸ allyl isocyanate, mesityl oxide, methyl acrylate, dichloromethyl acrylate, dichloromethyl *trans*-crotonate, and dichloromethyl 3-butenolate.

The reactions of phenyl(bromodichloromethyl)mercury with acrylic, *trans*-crotonic, and 3-butenic acids which led to the latter three esters deserve special

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(25) H. A. Bruson, W. Niederhauser, T. Riener, and W. F. Hester, *J. Am. Chem. Soc.*, **67**, 601 (1945).

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(27) American Cyanamid Co., "The Chemistry of Acrylonitrile," Beacon Press, Inc., New York, N. Y., 1951.

(28) Wagner, *et al.*,^{9b} have converted allyl chloride to 1,1-dichloro-2-(chloromethyl)cyclopropane using their sodium trichloroacetate route.

Table I. *gem*-Dihalocyclopropanes and Other Compounds Prepared by the Reaction of Olefins with Phenyl(trihalomethyl)mercurials

Olefin	Mercurial	Olefin/mercurial ratio	Dihalocyclopropane (% yield) ^a
Cyclohexene	C ₆ H ₅ HgCCl ₂	3	7,7-Dichloronorcarane (89)
Cyclohexene	C ₆ H ₅ HgCCl ₂ Br	3	7,7-Dichloronorcarane (88)
Cyclohexene	C ₆ H ₅ HgCClBr ₂	3	7-Bromo-7-chloronorcarane (85)
Cyclohexene	C ₆ H ₅ HgCBr ₃	3	7,7-Dibromonorcarane (88)
Ethylene	C ₆ H ₅ HgCCl ₂ Br	50 atm. C ₂ H ₄ pressure	1,1-Dichlorocyclopropane (65)
Ethylene	C ₆ H ₅ HgCBr ₃	50 atm. C ₂ H ₄ pressure	1,1-Dibromocyclopropane (53)
Tetrachloroethylene	C ₆ H ₅ HgCCl ₂ Br	<i>b</i>	Hexachlorocyclopropane (83)
Tetrachloroethylene	C ₆ H ₅ HgCCl ₃	<i>b</i>	Hexachlorocyclopropane (74)
Tetrachloroethylene	C ₆ H ₅ HgCClBr ₂	<i>b</i>	Bromopentachlorocyclopropane (48)
Tetrachloroethylene	C ₆ H ₅ HgCBr ₃	<i>b</i>	1,1-Dibromotetrachlorocyclopropane (30)
Trichloroethylene	C ₆ H ₅ HgCCl ₂ Br	<i>b</i>	Pentachlorocyclopropane (89)
Trichloroethylene	C ₆ H ₅ HgCCl ₃	<i>b</i>	Pentachlorocyclopropane (63)
Trichloroethylene	C ₆ H ₅ HgCCl ₂ Br	3	Pentachlorocyclopropane (79)
Trimethylvinylsilane	C ₆ H ₅ HgCCl ₂ Br	3	1,1-Dichloro-2-trimethylsilylcyclopropane (78)
Trimethylvinylsilane	C ₆ H ₅ HgCBr ₃	3	1,1-Dibromo-2-trimethylsilylcyclopropane (57)
Triethylvinylsilane	C ₆ H ₅ HgCCl ₂ Br	0.9	1,1-Dichloro-2-triethylsilylcyclopropane (41)
Dimethylvinylchlorosilane	C ₆ H ₅ HgCCl ₂ Br	<i>b</i>	1,1-Dichloro-2-(chlorodimethylsilyl)cyclopropane (58)
<i>cis</i> -1-Propenyltrimethylsilane	C ₆ H ₅ HgCCl ₂ Br	3	<i>cis</i> -1,1-Dichloro-2-methyl-3-trimethylsilylcyclopropane (78)
<i>trans</i> -1-Propenyltrimethylsilane	C ₆ H ₅ HgCCl ₂ Br	3	<i>trans</i> -1,1-Dichloro-2-methyl-3-trimethylsilylcyclopropane (73)
<i>trans</i> -Stilbene	C ₆ H ₅ HgCCl ₂ Br	0.9	<i>trans</i> -1,1-Dichloro-2,3-diphenylcyclopropane (90) ^m
α -Methylstyrene	C ₆ H ₅ HgCCl ₂ Br	1	1,1-Dichloro-2-methyl-2-phenylcyclopropane (92)
Cyclooctene	C ₆ H ₅ HgCBr ₃	3	9,9-Dibromobicyclo[6.1.0]nonane (73)
Acrylonitrile	C ₆ H ₅ HgCCl ₂ Br	3	1,1-Dichloro-2-cyanocyclopropane (78) ^o
Vinyl acetate	C ₆ H ₅ HgCCl ₂ Br	3	2,2-Dichlorocyclopropyl acetate (85) (80) ^{d,d}
Allyl bromide	C ₆ H ₅ HgCCl ₂ Br	3	1,1-Dichloro-2-bromomethylcyclopropane (76)
Allyl isocyanate	C ₆ H ₅ HgCCl ₂ Br	3	2,2-Dichlorocyclopropylmethylisocyanate (60)
Methyl acrylate	C ₆ H ₅ HgCCl ₂ Br	2.4	Methyl 2,2-dichlorocyclopropanecarboxylate (48)
Acrylic acid	C ₆ H ₅ HgCCl ₂ Br	1	Dichloromethyl acrylate (83)
Acrylic acid	C ₆ H ₅ HgCCl ₂ Br	0.5	Dichloromethyl 2,2-dichlorocyclopropanecarboxylate (35) (+ tetrachloroethylene (7))
<i>trans</i> -Crotonic acid	C ₆ H ₅ HgCCl ₂ Br	1	<i>trans</i> -Dichloromethyl crotonate (87)
<i>trans</i> -Crotonic acid	C ₆ H ₅ HgCCl ₂ Br	0.5	Dichloromethyl 2,2-dichloro-3-methylcyclopropanecarboxylate (51) (+ tetrachloroethylene (7))
3-Butenoic acid	C ₆ H ₅ HgCCl ₂ Br	1	Dichloromethyl 3-butenate (76)
3-Butenoic acid	C ₆ H ₅ HgCCl ₂ Br	0.5	Dichloromethyl 2,2-dichlorocyclopropylacetate (62) (+ tetrachloroethylene (4))
Mesityl oxide	C ₆ H ₅ HgCCl ₂ Br	3	1-Acetyl-2,2-dichloro-3,3-dimethylcyclopropane (83) ^p
<i>cis</i> -Methyl crotonate	C ₆ H ₅ HgCCl ₂ Br	1.35	<i>cis</i> -Methyl 2,2-dichloro-3-methylcyclopropanecarboxylate (62) ^r
<i>trans</i> -Methyl crotonate	C ₆ H ₅ HgCCl ₂ Br	2.5	<i>trans</i> -Methyl 2,2-dichloro-3-methylcyclopropanecarboxylate (76) ^o
<i>cis</i> -2-Butene	C ₆ H ₅ HgCBr ₃	<i>c</i>	<i>cis</i> -1,1-Dibromo-2,3-dimethylcyclopropane (69) ^t
<i>trans</i> -2-Butene	C ₆ H ₅ HgCBr ₃	<i>c</i>	<i>trans</i> -1,1-Dibromo-2,3-dimethylcyclopropane (71) ^u
<i>cis</i> -3-Heptene	C ₆ H ₅ HgCCl ₂ Br	3	<i>cis</i> -1,1-Dichloro-2-ethyl-3- <i>n</i> -propylcyclopropane (82)
<i>trans</i> -3-Heptene	C ₆ H ₅ HgCCl ₂ Br	3	<i>trans</i> -1,1-Dichloro-2-ethyl-3- <i>n</i> -propylcyclopropane (90)
1,3-Butadiene	C ₆ H ₅ HgCCl ₂ Br	<i>c</i>	1,1-Dichloro-2-vinylcyclopropane (58) (+ 2,2,2',2'-tetrachlorobicyclopropyl (10))
1,1-Dichloro-2-vinylcyclopropane	C ₆ H ₅ HgCCl ₂ Br	0.53	2,2,2',2'-Tetrachlorobicyclopropyl (91) (<i>dl</i> and <i>meso</i> , 1:1)
Allene	C ₆ H ₅ HgCCl ₂ Br	<i>c</i>	2,2-Dichloromethylenecyclopropane (64)
2,2-Dichloromethylenecyclopropane	C ₆ H ₅ HgCCl ₂ Br	0.32	1,1,4,4-Tetrachlorospiropentane (59)
4-Vinylcyclohexene	C ₆ H ₅ HgCCl ₂ Br	3	{ 7,7-Dichloro-4-vinylbicyclo[4.1.0]heptane (82.5) { 4(β , β -dichlorocyclopropyl)cyclohexene (9.4) { 1,1-Dichloro-2-ethoxymethylcyclopropane (82) { 4,4-Dichloro-3-ethoxy-1-butene (14)
Allyl ethyl ether	C ₆ H ₅ HgCCl ₂ Br	3	{ 2-Dichloromethyl-2,5-dihydrofuran (52) { 3-Oxa-6,6-dichlorobicyclo[3.1.0]hexane (44)
2,5-Dihydrofuran	C ₆ H ₅ HgCCl ₂ Br	3	2-Dichloromethyltetrahydrofuran (67) (+ tetrachloroethylene (2.5))
Tetrahydrofuran	C ₆ H ₅ HgCCl ₂ Br	3	{ Tetrachloroethylene (39) { Hexachlorocyclopropane (8) { Tetrachloroethylene (43) { Hexachlorocyclopropane (21)
Perfluorocyclohexene	C ₆ H ₅ HgCCl ₂ Br	2	
Perfluorocyclohexene	C ₆ H ₅ HgCCl ₂ Br	<i>b</i>	

^a Underlined numbers represent yields of isolated product; those numbers not underlined are yields determined by g.l.p.c. ^b Olefin used as solvent; olefin/mercurial ratio, 10. ^c Gaseous olefin bubbled into refluxing benzene solution of mercurial; olefin present in excess. ^d Product isolated by g.l.p.c.; b.p. not determined. ^e Doering and Hoffmann⁴ report *n*^{25D} 1.5014. ^f Total silver halide for a 7.620-mg. sample: calcd., 11.980 mg.; found, 12.04 mg. ^g Doering and Hoffmann⁴ report *n*^{25D} 1.5578. ^h V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4928 (1952), report *n*^{25D} 1.4377. ⁱ S. W. Tobey, and R. West, *Tetrahedron Letters*, 1179 (1963), report *n*^{27.5D} 1.5170. ^j J. Cudlín and V. Chvalovský, *Collection Czech. Chem. Commun.*, **27**, 1658 (1962), report *n*^{25D} 1.4554. ^k G.l.p.c. retention time 22.0 min. (25% Dow Corning 710 Fluid on Chromosorb P, jacket at 175°, 15 p.s.i. helium). ^l G.l.p.c. retention time 17.4 min. (same conditions as in *k*). ^m Presumed *trans* isomer. ⁿ W. J. Dale and P. E. Schwartztruber, *J. Org. Chem.*, **24**, 955 (1959), report *n*^{25D} 1.5406. ^o Mol. wt.: calcd. 136, found

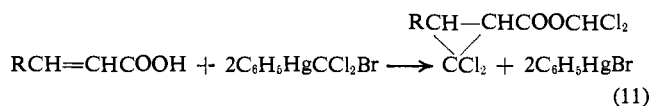
B.p. (mm.) or m.p., °C.	n_D^{20}	Anal.: calcd. (found), %			Br
		C	H	Cl	
73.5–75 (10)	1.5018 (23°) ^e				
42.8–44.7 (0.6)	1.5293 (25°)	40.12 (39.83)	4.81 (4.75)	<i>f</i>	
77.2–78.6 (0.5)	1.5582 (22°) ^g				
75–76 (atm.)	1.4372 (25°) ^h	32.47 (32.66)	3.63 (3.81)	63.90 (63.86)	
59 (81), 48.2 (51)	1.5238 (25°)	18.02 (18.18)	2.02 (2.10)	79.96 (79.72)	
103.5–104.5		14.49 (14.66)		85.51 (85.21)	
106.4–107.6		12.29 (12.18)		60.45 (60.20)	27.26 (27.43)
115–116		10.67 (10.91)		42.00 (42.24)	47.23 (47.24)
107–110 (40), 65 (12)	1.5166 (26°) ⁱ				
80 (50.), 165 (atm.)	1.4558 (25°) ^j	39.34 (39.04)	6.60 (6.37)	38.72 (38.84)	
67–68 (6.5), 84–86 (20)	1.5032 (25°)	26.48 (26.63)	4.45 (4.25)		
54–57 (0.8)	1.4735 (25°)	47.99 (47.69)	8.05 (8.39)	31.48 (31.37)	
68 (11)		29.50 (29.73)	4.46 (4.50)		
89–90 (40) ^k	1.4614 (25°)	42.63 (42.36)	7.16 (7.36)		
86.5–88 (40) ^l	1.4559 (25°)	42.63 (42.53)	7.16 (7.00)	35.96 (36.29)	
39–40.5		68.45 (68.40)	4.59 (4.82)	26.94 (27.21)	
68–69 (1.3)	1.5400 (25°) ⁿ	59.72 (59.75)	5.01 (5.18)	35.26 (34.95)	
62–64 (0.03)	1.5492 (28°)	38.33 (38.20)	5.00 (4.88)		56.67 (56.56)
78–79 (15)	1.4787 (25°)	35.52 (35.58)	2.21 (2.44)	52.17 (51.91)	N, 10.30 (10.10)
<i>d</i>	1.4511 (25°)	35.53 (35.50)	3.58 (3.59)	41.96 (42.61)	
77–78 (23)	1.5150 (25°)	23.56 (23.62)	2.47 (2.57)	34.78 (35.03)	39.19 (38.93)
<i>d</i>	1.4803 (25°)	36.18 (36.49)	3.04 (3.11)	42.72 (42.75)	
<i>d</i>	1.4632 (25°)	35.53 (35.70)	3.58 (3.64)	41.96 (41.94)	
<i>d</i>	1.4526 (25°)	30.99 (31.32)	2.60 (2.85)	45.75 (46.11)	
<i>d</i>	1.4930 (25°)	25.24 (25.51)	1.70 (1.71)	59.62 (58.90)	
<i>d</i>	1.4637 (25°)	35.53 (35.86)	3.58 (3.92)	41.95 (41.04)	
<i>d</i>	1.4961 (25°)	28.61 (28.80)	2.40 (2.54)	56.29 (55.95)	
<i>d</i>	1.4481 (25°)	35.53 (35.72)	3.58 (3.68)	41.95 (41.07)	
<i>d</i>	1.4890 (25°)	28.61 (29.09)	2.40 (2.65)	56.29 (56.31)	
<i>d</i>	1.4784 (25°)	43.23 (43.21) ^o	3.91 (3.99) ^o	19.63 (19.70) ^o	N, 15.51 (15.51) ^o
58–60 (7)	1.4662 (25°)	39.37 (39.39)	4.40 (4.33)		
50 (2–3)	1.4648 (25°)	39.37 (39.64)	4.40 (4.59)	38.75 (38.47)	
74 (40)	1.5150 (29°) ^p	26.34 (26.21)	3.54 (3.50)		70.12 (70.17)
78 (45)	1.5080 (29°) ^q	26.34 (26.15)	3.54 (3.54)		70.12 (70.43)
79–79.5 (20)	1.4530 (25°)	53.05 (53.49)	7.79 (7.76)	39.15 (39.43)	
76–77 (20)	1.4490 (25°)	53.05 (53.39)	7.79 (7.90)	39.15 (38.79)	
<i>d</i>	1.4725 (26°) ^r	43.83 (44.13)	4.42 (4.19)	51.75 (51.57)	
<i>dl</i> , 29–30		32.76 (32.75) ^v	2.76 (2.78) ^v	64.48 (64.47) ^v	
<i>meso</i> , 79–80		32.76 (32.79)	2.76 (2.80)	64.48 (64.39)	
<i>d</i>	1.4852 (26°)	39.06 (39.34)	3.28 (3.25)	57.66 (57.30)	
<i>d</i>	1.5447 (24°)	29.16 (29.57)	1.96 (1.86)	68.88 (68.93)	
<i>d</i>	1.5068 (25°)	56.56 (56.66)	6.41 (6.41)	37.11 (37.28)	
<i>d</i>	1.4975 (25°)	56.56 (56.80)	6.41 (6.44)	37.11 (37.18)	
<i>d</i>	1.4523 (25°)	42.63 (42.71)	5.96 (6.03)	41.94 (41.99)	
<i>d</i>	1.4518 (25°)	42.63 (42.96) ^s	5.96 (6.08) ^s	41.94 (41.82) ^s	
<i>d</i>	1.4888 (25°) ^{aa}	39.25 (39.37)	3.95 (4.07)	46.34 (46.32)	
<i>d</i>	1.4957 (25°) ^{bb}	39.25 (39.33)	3.95 (4.15)	46.34 (46.10)	
<i>d</i>	1.4762 (25°) ^{cc}	38.74 (38.96)	5.20 (5.33)	45.74 (45.56)	

(mass spectry.) 135. ^p Product did not appear to be stable. ^q 2,4-Dinitrophenylhydrazone, m.p. 155.0–156.0°. ^r G.l.p.c. retention time 18.0 min. (20% G.E. SE-30 on Chromosorb P, jacket at 159°, 18.3 p.s.i. helium). ^s G.l.p.c. retention time 16.8 min. (same conditions as in *r*). ^t G.l.p.c. retention time 17.7 min. (20% G.E. SE-30 on Chromosorb W, jacket at 101°, 15 p.s.i. helium). ^u G.l.p.c. retention time 14.7 min. (same conditions as in *t*). ^v W. von E. Doering and P. LaFlamme, *J. Am. Chem. Soc.*, **78**, 5447 (1956), report n_D^{20} 1.5150. ^w W. von E. Doering and P. LaFlamme (footnote *v*) report n_D^{20} 1.5074. ^x R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957), report n_D^{20} 1.4720. ^y Analysis of combined *meso* and *dl* forms. ^z Analysis of combined isomers. ^{aa} J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 4874 (1964), report n_D^{20} 1.4933. ^{bb} J. C. Andrews, D. G. Lindsay, and C. B. Reese (footnote *aa*) report n_D^{20} 1.4980. ^{cc} J. C. Andrews, D. G. Lindsay, and C. B. Reese (footnote *aa*) report n_D^{20} 1.4764. ^{dd} Solvent was DME.

comment. When these reactions were carried out in 1:1 molar ratio, only the dichloromethylation of the O-H bonds was observed. This is in agreement with

$$\text{RCH}=\text{CHCOOH} + \text{C}_6\text{H}_5\text{HgCCl}_2\text{Br} \longrightarrow \text{RCH}=\text{CHCOOCHCl}_2 + \text{C}_6\text{H}_5\text{HgBr} \quad (\text{R} = \text{H and CH}_3) \quad (10)$$

the results of a competition between acetic acid and cyclohexene for this mercurial, in which the acid proved to be considerably more reactive than the olefin.²⁹ Reaction at the C=C bond was observed only after the dichloromethyl esters had been formed in the case of the three acids mentioned above. In all three

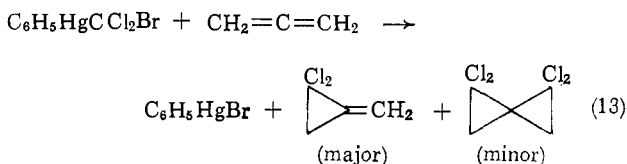
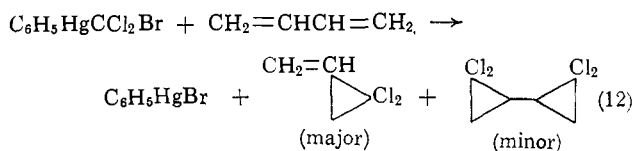


2:1 reactions tetrachloroethylene was found as a by-product in yields of 4–7%. The attempted hydrolysis of the dichloromethyl esters of dichlorocyclopropane-carboxylic acids to the corresponding acids was not successful.

It is noteworthy that acrylonitrile, the acrylic acid esters, vinyl acetate, styrene,³⁰ and butadiene were not polymerized during their reactions with phenyl(bromodichloromethyl)mercury. It already has been suggested that trihalomethide ion is not involved in these reactions, and this absence of polymerization as a complication suggests that free radicals ($\cdot\text{CCl}_2\text{Br}$ or $\text{C}_6\text{H}_5\text{HgCCl}_2\cdot$) also are not involved.

Dienes. It has been shown that butadiene and other 1,3-dienes react with dihalocarbenes in a 1,2-fashion, giving 1,1-dihalo-2-vinylcyclopropanes in the case of butadiene itself.^{9b,31–33} Orchin and Herrick also isolated the dichlorocarbene diaddition product, 2,2,2',2'-tetrachlorobicyclopropyl, apparently as a homogeneous solid with a sharp (79.5–80.5°) melting point. This product should, however, exist in the *dl* and *meso* modifications. The dibromocarbene diaddition product of 1,3-butadiene was, in fact, separated into the *meso* and *dl* forms.³³ Substituted allenes have been treated with dihalocarbenes (e.g., 3-methyl-1,2-butadiene and pentadiene with CBr_2 via bromoform + *t*- $\text{C}_4\text{H}_9\text{OK}$),³⁴ but the reactivity of allene itself does not appear to have been examined.

We have carried out reactions of phenyl(bromodichloromethyl)mercury with 1,3-butadiene and allene simply by passing the respective gaseous diene into a stirred benzene solution of the mercurial maintained at about 80°. A Dry Ice condenser served to minimize gas losses. This procedure was more convenient than bomb tube or autoclave reactions and produced reasonably good yields of products. Thus, such a reaction with 1,3-butadiene gave 1,1-dichloro-2-vinylcyclopropane (58%) and 2,2,2',2'-tetrachlorobicyclopropyl (10%). With allene this procedure resulted in formation of 2,2-dichloromethylenecyclopropane (64%) and 1,1,4,4-tetrachlorospiropentane (10%). This procedure, could be applied with good success to the dibromomethylation of *cis*- and *trans*-2-butene with

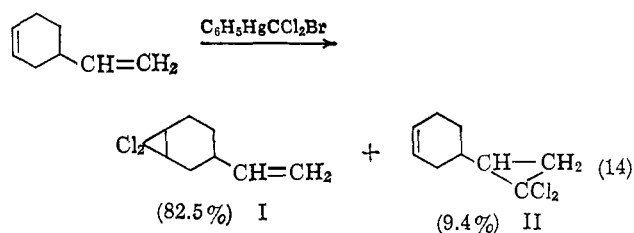


phenyl(tribromomethyl)mercury, but application to the dihalomethylation of ethylene was not successful.

A separate reaction of 1,1-dichloro-2-vinylcyclopropane with phenyl(bromodichloromethyl)mercury gave 2,2,2',2'-tetrachlorobicyclopropyl in 91% yield. Gas chromatographic (g.l.p.c.) analysis³⁵ showed that two products, m.p. 79–80° and 29–30°, in order of increasing retention time, were present in 1:1 ratio. Both were isolated by g.l.p.c. and shown by microanalysis to have the same empirical formula. It seems probable that these were the *dl* and *meso* forms to be expected. The material with shorter g.l.p.c. retention time and higher melting point would be assigned the *meso* structure, in accord with the assignments made by Skattebøl³³ for the analogous tetrabromo derivatives.

A reaction of 2,2-dichloromethylenecyclopropane with phenyl(bromodichloromethyl)mercury produced 1,1,4,4-tetrachlorospiropentane in about 60% yield.³⁶ Its n.m.r. spectrum, two doublets in the dichlorocyclopropyl region at 1.92 and 2.12 p.p.m. ($J = 7$ c.p.s.), served to confirm its structure. The reaction of phenyl(trihalomethyl)mercurials with allenes thus should provide a valuable general route to alkylidene cyclopropanes and to substituted spiro-pentanes.

It was of some interest to determine which double bond of 4-vinylcyclohexene would be more reactive toward our mercurial reagents. The reaction was carried out with $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ and an excess of the diene. Equation 14 summarizes the observed results.



Thus the ratio of addition to the cyclohexene double bond to addition to the vinyl group is 8.77. This diene also was treated with sodium trichloroacetate in refluxing 1,2-dimethoxyethane. In this case the ratio of I:II was 8.5; the total yield of I and II, however, was only 42%. We have already noted the similarity of olefin relative reactivities toward $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ and sodium trichloroacetate and have commented concerning the significance of that striking similarity.³⁰ It will be noted that cyclohexene was found to be 4.2

(29) D. Seyferth, J. Y.-P. Mui, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 2961 (1964).

(30) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

(31) R. C. Woodworth and P. S. Skell, Table I, footnote x.

(32) M. Orchin and E. C. Herrick, *J. Org. Chem.*, **24**, 139 (1959).

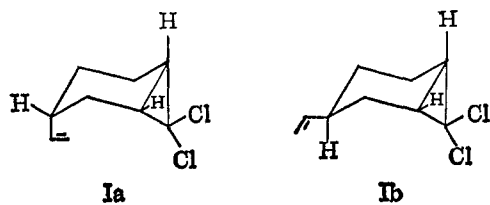
(33) L. Skattebøl, *ibid.*, **29**, 2951 (1964).

(34) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 246 (1961).

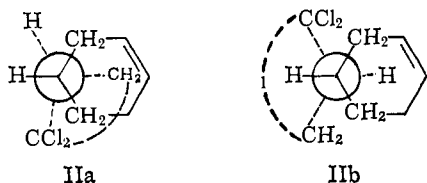
(35) 20% G.E. Co. SE-30 silicone gum on Chromosorb W.

(36) Dihalocarbene addition to *exo*-methylene cyclic compounds, e.g., methylenecyclobutane, methylenecyclopentane, and methylenecyclohexane, has been reported by E. Funakubo, I. Moritani, S. Murahashi, and T. Tuji, *Tetrahedron Letters*, 539 (1962).

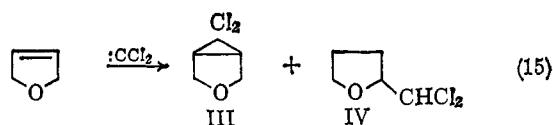
times more reactive toward phenyl(bromodichloromethyl)mercury than was 1-heptene.³⁰ In the present case of an intramolecular competition system in 4-vinylcyclohexene, an additional steric factor due to the cyclohexene ring system should further decrease the reactivity of the vinyl group. Gas chromatographic³⁷ examination of the product mixture comprising I and II showed that each compound was resolved into two peaks. One doublet is probably due to the *cis* and *trans* isomers of the vinylnorcarane, Ia and Ib.



The cyclopropylcyclohexene II contains two asymmetric carbon atoms and thus can exist in both *threo* (IIa) and *erythro* (IIb) forms. These structures probably account for the second doublet.



Unsaturated Ethers. Anderson and Reese³⁸ reported in 1963 the reaction of dichlorocarbene (via $\text{CCl}_3\text{COOCH}_3 + \text{NaOCH}_3$ or NaOCCCl_3 in dioxane) with 2,5-dihydrofuran to give both the double bond addition product (III) and a C-H insertion product (IV) (eq. 15). Further studies by these authors demonstrated that CX_2 insertion into C-H bonds α to oxygen in both unsaturated and saturated cyclic and acyclic ethers is a general reaction.³⁹ The yields of insertion products using conventional CCl_2 sources were poor to moderate. We found that our mercurials give C-H insertion in ethers in good yield. Thus the reaction of 2,5-dihydrofuran with phenyl(bromodichloromethyl)mercury at 80° gave IV and III in yields of 52 and 44%, respectively, that is, in a ratio of 1.18:1.



An experiment in which 2,5-dihydrofuran was allowed to react with dichlorocarbene, generated *via* sodium trichloroacetate at 80°, gave IV and III in yields of 12.9 and 10.4%, respectively, a ratio of 1.24:1. In dioxane at reflux this system gave IV and III in yields of 28.6 and 22%, respectively (IV:III = 1.3:1). Here again we have in the reactions of 2,5-dihydrofuran at 80° a great similarity of the reactivities of the double bond and the C-H linkages α to the oxygen toward sodium trichloroacetate and phenyl(bromodichloromethyl)mercury.

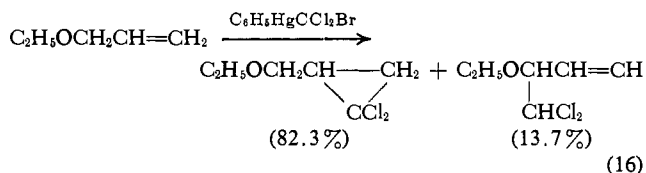
(37) Dow Corning XF-1150 cyanoethylsilicone fluid on Chromsorb P.

(38) J. C. Anderson and C. B. Reese, *Chem. Ind. (London)*, 575 (1963).

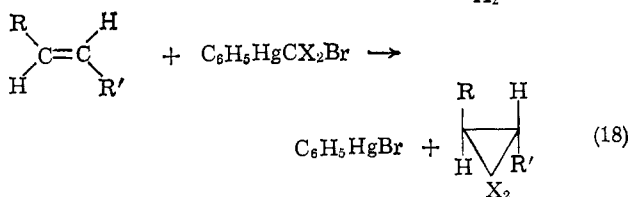
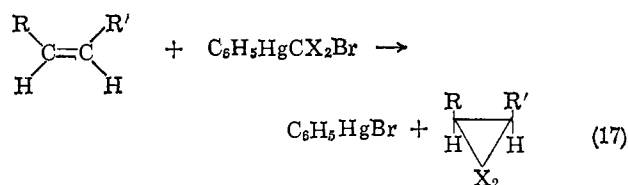
(39) J. C. Anderson D. G. Lindsay, and C. B. Reese, Table I, footnotes *aa*, *bb*, and *cc*.

The high reactivity of cyclic ethers toward the mercurial reagents was confirmed by carrying out a reaction with tetrahydrofuran (THF/mercurial ratio = 3) in refluxing benzene solution. 2-(Dichloromethyl)-tetrahydrofuran was formed in 67% yield. In addition, a 2.5% yield of tetrachloroethylene was noted.

The reaction of allyl ethyl ether with phenyl(bromodichloromethyl)mercury showed greater selectivity toward double bond addition (eq. 16).



Stereochemistry of the Mercurial-Olefin Reaction. It has been shown that the addition of dibromo-⁴⁰ and dichlorocarbene⁴¹ to olefins occurs stereospecifically. We have shown that the mercurial-olefin reaction also occurs in a stereospecific manner (eq. 17



and 18). In the reaction of *cis*- and *trans*-2-butene, respectively, with phenyl(tribromomethyl)mercury, products were obtained in each case which were identical with those obtained by Doering and LaFlamme⁴¹ in the analogous CHBr_3 -*t*- $\text{C}_4\text{H}_9\text{OK}$ -2-butene reactions, and whose geometric configuration these authors had established. In the case of the *cis*- and *trans*-3-heptene + $\text{C}_6\text{H}_5\text{HgCCl}_2\text{Br}$ reactions, the respective 1,1-dichloro-2-ethyl-3-*n*-propylcyclopropanes isolated were identical with the respective products obtained from dichlorocarbene addition to these olefins by the Doering-Hoffmann procedure. It has generally been assumed that Wagner's sodium trichloroacetate route to *gem*-dichlorocyclopropanes involves intermediate $:\text{CCl}_2$, but no studies of the stereochemistry of the CCl_3COONa -olefin reaction have been reported. We have carried out the reactions of *cis*- and *trans*-3-heptene with sodium trichloroacetate in refluxing 1,2-dimethoxyethane. With this reagent also the 1,1-dichloro-2-ethyl-3-*n*-propylcyclopropanes were formed with retention of configuration.

Two other *cis-trans* olefin pairs, the 1-propenyltrimethylsilane and the methyl crotonate isomers, were converted to the *gem*-dichlorocyclopropanes by the mercurial route. In each case the *cis* and *trans* isomers gave different products, as would be expected in a stereospecific reaction. The geometric configuration of

(40) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, 78, 3409 (1956).

(41) W. von E. Doering and P. LaFlamme, Table I, footnote *v*.

the products was, however, not established, but it is reasonable to assume that here also the *cis* olefin gave the *cis* cyclopropane and the *trans* olefin the *trans* cyclopropane.

The finding that the mercurial-olefin reaction occurs stereospecifically provides further evidence against a radical mechanism according to the criteria of previous investigators in the carbene area.^{40,41} This finding does not allow us to distinguish between the possibility of a free carbene mechanism or a bimolecular, direct CX_2 transfer mechanism.

Our work on the mercurial-olefin reaction is continuing. In particular, we are interested in the question of the mechanism of this reaction³⁰ and hope to report fully on our investigations in this area in the near future.

In conclusion, it should be mentioned that the mercurial route appears to be a general reaction. Using phenyl(dihalomethyl)mercurials of type $C_6H_5Hg-CHXBr$ one can prepare in high yield monohalocyclopropanes,⁴² and the $(BrCH_2)_2Hg$ and the $XCH_2HgX + (C_6H_5)_2Hg$ ($X = Br$ and I) systems provide a route to simple cyclopropanes.⁴³ Details concerning these reactions will be published at a later date.

Experimental Section

General Comments. Elemental analyses were performed by Dr. S. M. Nagy and associates, M.I.T. Microchemical Laboratory, the Schwarzkopf Microanalytical Laboratory, and the Galbraith Laboratories. Infrared spectra were recorded using a Baird Model B or a Perkin-Elmer Infracord 337 infrared spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian Associates A-60 n.m.r. spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane.

Reactions of olefins with the phenyl(trihalomethyl)mercurials could be followed conveniently using thin layer chromatography (t.l.c.) on 25×75 mm. microscope slides coated with Brinkman Instruments Co. Silica Gel G. Benzene or a mixture of 20% benzene in cyclohexane was used as eluent. Development was accomplished by first storing the dried plates in an iodine chamber for 5 min., during which time most organic compounds appeared as yellowish brown to dark brown spots, while the organomercurials gave lavender-white spots. Subsequent spraying with 10% Na_2S in 50% aqueous ethanol turned the mercurial spots permanently dark gray or black.

For g.l.p.c. analysis two kinds of glass columns were used: a preparative size column, 8 ft. \times 12 mm. o.d. packed with 25% Dow Corning 710 silicone fluid on 80-100 mesh Johns-Manville Chromosorb P or an analytical column, 7 ft. \times 8 mm. o.d. packed with 25% General Electric Co. SE-30 silicone rubber gum on 80-100 mesh Chromosorb P.

All reactions were carried out under an atmosphere of prepurified nitrogen. The benzene used was either distilled from calcium hydride or passed through Linde molecular sieves and Woelm alumina immediately before use.

Starting Materials. The phenyl(trihalomethyl)mercury compounds used were prepared by the Reutov-

(42) D. Seyferth, H. D. Simmons, Jr., and G. Singh, *J. Organometal. Chem.*, **3**, 337 (1965).

(43) D. Seyferth, M. A. Eisert, and L. J. Todd, *J. Am. Chem. Soc.*, **86**, 121 (1964).

Lovtsova procedure¹⁵; explicit directions are given in part I of this series.^{1a} Most of the olefins used were commercial products. They were examined by g.l.p.c. prior to use and purified by distillation if necessary. *cis*-3-Heptene was prepared in 55% yield by stereospecific reduction of 3-heptyne with diborane using the procedure described by Brown and Zweifel⁴⁴ for the preparation of *cis*-3-hexene. Gas chromatographic analysis of the product using a silver nitrate column (15% $AgNO_3$ in tetraethylene glycol (20%) on Chromosorb P, 50°, 15 p.s.i. helium) showed that the more strongly retained *cis* isomer was contaminated with 2.4% of the *trans* isomer. The propenyltrimethylsilane isomers were prepared using the isomeric 1-propenyllithiums.⁴⁵

Preparation of 7,7-Dichloronorcarane by the Mercurial Route. The procedure used to prepare this compound is typical of the procedure used when both olefin and product were liquids.

In a 100-ml. flask equipped with reflux condenser and magnetic stirrer were placed 0.03 mole of phenyl(bromodichloromethyl)mercury, 0.09 mole of cyclohexene, and 35 ml. of benzene. All of the mercurial dissolved by the time the reflux temperature was reached, and within 15 min., precipitation of a white, flaky solid began. After the reaction mixture had been stirred at reflux for 2 hr., t.l.c. analysis indicated that all of the starting mercurial had decomposed and that only phenylmercuric bromide was present. The reaction mixture was filtered, leaving 10.5 g. (98%) of phenylmercuric bromide, m.p. 284-286°, identified by mixture melting point with an authentic sample. The solvent and excess cyclohexene were removed by trap-to-trap distillation at 25° (5 mm.). The residue was distilled rapidly *in vacuo* into a receiver at -78° and the distillate was fractionally distilled to give 7,7-dichloronorcarane in 89% yield, b.p. 73.5-75° (10 mm.), whose infrared spectrum was identical with that of an authentic sample kindly provided by Professor W. R. Moore.

Equally good yields were obtained if mercurial and olefin were used in a 1:1 molar ratio. Thus reaction of 0.01 mole each of $C_6H_5HgCCl_2Br$ and α -methylstyrene in 20 ml. of benzene at reflux for 2 hr. gave the desired 1,1-dichloro-2-methyl-2-phenylcyclopropane in 92% yield.

With olefins whose boiling point is significantly lower than 80° (and if they are used in excess) longer reaction times are required. Thus a reaction time of about 30 hr. was required to obtain the product yields given in Table I for trimethylvinylsilane (b.p. 54°) when the olefin/mercurial ratio was 3.

Preparation of Hexachlorocyclopropane. A solution of 0.10 mole of phenyl(bromodichloromethyl)mercury in 1.0 mole of redistilled tetrachloroethylene in a 300-ml., three-necked flask, equipped with reflux condenser, was slowly heated to 90° with stirring. After 3 min. light gray flakes began to precipitate; this temperature was maintained for 1 hr. The reaction mixture was cooled and filtered. The residue was washed with 25 ml. of tetrachloroethylene and dried *in vacuo*, giving 33.4 g. (93%) of phenylmercuric

(44) H. C. Brown and G. Zweifel, *ibid.*, **83**, 3834 (1961).

(45) D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.*, **1**, 138 (1963).

bromide as gray flakes, m.p. 285–287°. A second crop of 0.6 g. was obtained by removal of some of the excess olefin from the filtrate at 170–180 mm. The filtrate was concentrated further at 170–180 mm., cooled to 0°, and filtered. The residue was washed with 11 ml. of tetrachloroethylene, leaving 20.6 g. (83%) of white, crystalline solid, m.p. 100–104°. Sublimation of the latter at 40° (0.1 mm.) afforded 18.3 g. (74%) of pure hexachlorocyclopropane, m.p. 103–104°. A mixture melting point with an authentic sample kindly supplied by Professor W. R. Moore showed no depression.

A similar procedure was used in the preparation of the other perhalogenated cyclopropanes.

Preparation of 1,1-Dichloro-2,3-diphenylcyclopropane. This procedure is described to illustrate the advantages of a 1:1 reaction when olefin and product both are solids.

A mixture of 0.0275 mole of phenyl(bromodichloromethyl)mercury and 0.025 mole of *trans*-stilbene in 30 ml. of benzene was stirred and heated (bath at 85–90°) under argon for 2.25 hr., during which time all of the starting materials dissolved, phenylmercuric bromide precipitated, and the mixture became slightly yellow. At this point t.l.c. showed that essentially all of the mercurial had disappeared. The mixture was filtered, leaving 9.50 g. (97%) of phenylmercuric bromide. The volatile materials were removed from the filtrate by trap-to-trap distillation at 30° (0.1 mm.), leaving 7.0 g. of fluffy, cream-colored solid, m.p. 34–38°. Sublimation of the latter at 40–45° (0.001 mm.) afforded 6.0 g. (90%) of white, crystalline solid, m.p. 38–40°. An analytical sample of m.p. 39–40.5° was obtained by two further sublimations.

Preparation of 1,1-Dichloro-2-vinylcyclopropane. This reaction is described to illustrate the procedure which may be used when the olefin is a gas. This procedure, however, is not applicable to the dihalomethylenation of ethylene.

A solution of 0.02 mole of phenyl(bromodichloromethyl)mercury in 60 ml. of benzene was heated to about 70° in a three-necked flask equipped with a thermometer, gas inlet tube, magnetic stirrer, and water-cooled reflux condenser topped with a dewar-type condenser filled with Dry Ice–acetone. The system was flushed with nitrogen and then gaseous 1,3-butadiene was allowed to bubble slowly into the stirred solution at about 80° for 30 min. Phenylmercuric bromide precipitated and the solution became deep yellow in color. The reaction mixture was cooled and 5.7 g. (81%) of phenylmercuric bromide was filtered. G.l.p.c. analysis of the filtrate showed that 1,1-dichloro-2-vinylcyclopropane had been formed in 58% yield and 2,2,2',2'-tetrachlorobicyclopropyl in 10% yield. To a quantity of the above reaction mixture calculated to contain 5 mmoles of 1,1-dichloro-2-vinylcyclopropane was added 10 mmoles of phenyl(bromodichloromethyl)mercury. This mixture was heated at 80° for 8 hr. and then filtered from C₆H₅HgBr (87.5%). Gas chromatography showed that 2,2,2',2'-tetrachlorobicyclopropyl (*dl* and *meso* forms in 1:1 ratio) had been formed in 91% yield. The higher melting form had a shorter retention time on an SE-30 silicone gum column than the lower melting form.

A similar procedure was used in the reaction of allene with C₆H₅HgCCl₂Br and in the reactions of *cis*- and *trans*-2-butene with C₆H₅HgCBr₃.

In the case of ethylene the dihalomethylenations were carried out in an autoclave: 0.073 mole of C₆H₅HgCBr₃ in 100 ml. of benzene, 50 atm. pressure of ethylene, a short time at about 100°, then 24 hr. at about 80°, and 0.06 mole of C₆H₅HgCCl₂Br in 100 ml. of chlorobenzene, 50 atm. pressure of ethylene, at 80° for 30 hr.

Reactions with trans-Crotonic Acid. A. 1:1 Ratio. Anhydrous, crystalline, sublimed *trans*-crotonic acid (0.01 mole) and phenyl(bromodichloromethyl)mercury (0.01 mole) were heated at 80° in 25 ml. of benzene for about 50 min. The mixture was filtered, leaving 3.48 g. (97%) of phenylmercuric bromide. The filtrate was trap-to-trap distilled *in vacuo*. G.l.p.c. analysis of the distillate (20% SE-30 on Chromosorb P, jacket at 112°, 11.2 p.s.i. of helium) showed that *trans*-dichloromethyl crotonate had been formed in 87% yield.

B. 1:2 Ratio. A solution of 0.0313 mole of C₆H₅HgCCl₂Br and 0.0149 mole of *trans*-crotonic acid in 30 ml. of benzene was heated at reflux for 90 min. Filtration (95.4% C₆H₅HgBr) and g.l.p.c. analysis (short column, SE-30 on Chromosorb P) of the filtrate showed the presence of dichloromethyl 2,2-dichloro-3-methylcyclopropane carboxylate (51%), CH₃CH=CHCOOCHCl₂ (21%) and tetrachloroethylene (7%).

Reactions of cis- and trans-3-Heptene with Phenyl(bromodichloromethyl)mercury. A solution of 5 mmoles of mercurial and 15 mmoles of *cis*-3-heptene (containing 2.4% of the *trans* isomer) in 10 ml. of benzene was heated at 80° for 1 hr. Filtration and trap-to-trap distillation *in vacuo* of the filtrate followed. G.l.p.c. analysis of the filtrate using *n*-butyrophenone as internal standard showed that *cis*-1,1-dichloro-2-ethyl-3-*n*-propylcyclopropane had been formed in 82% yield and that only 1.2% of the *trans* isomer was present. The major product had g.l.p.c. retention time (9.2 min. on a 25% SE-30 on Chromosorb W column, jacket at 160°, 25 p.s.i. helium), refractive index, and infrared spectrum identical with those of authentic *cis* isomer prepared by the Doering-Hoffmann procedure.

A similar reaction with *trans*-3-heptene (Chemical Samples Co., 99+ % isomeric purity) gave *trans*-1,1-dichloro-2-ethyl-3-*n*-propylcyclopropane in 90% yield. The identity of the product was established by comparison of its g.l.p.c. retention time (8.3 min. under the conditions stated above for the *cis* isomer), refractive index, and infrared spectrum with those of authentic *trans* isomer prepared by the Doering-Hoffmann route.

A similar procedure was used in the identification of the isomeric products of the reaction of C₆H₅HgCBr₃ with *cis*- and *trans*-2-butene.

Reaction of 2,5-Dihydrofuran with Phenyl(bromodichloromethyl)mercury and Sodium Trichloroacetate. A solution of 0.01 mole of mercurial and 0.03 mole of 2,5-dihydrofuran in 25 ml. of benzene was heated at 80° for 1 hr., cooled, and filtered. The volatiles were trap-to-trap distilled *in vacuo* (to 50° at 0.05 mm.). G.l.p.c. analysis of the distillate indicated the presence of two products, identified by their infrared and n.m.r. spectra as 2-(dichloromethyl)-2,5-dihydrofuran (52%) and 3-oxa-6,6-dichlorobicyclo[3.1.0]hexane (44%).

A similar reaction was carried out between 0.01

mole of sodium trichloroacetate and 0.03 mole of 2,5-dihydrofuran in 25 ml. of 1,2-dimethoxyethane at 80° for 5 hr. A similar work-up procedure was followed by g.l.p.c. analysis. The C—H insertion and C=C addition products had been formed in yields of 12.9 and 10.4%, respectively. An identical reaction carried out in refluxing dioxane for 5 hr. gave these products in yields of 28.6 and 22%, respectively. In these yield determinations a 25% SE-30 silicone gum on Chromosorb P column, jacket temperature 115°, 15 p.s.i. helium, hexachloroethane internal standard, was used.

A reaction of $C_6H_5HgCCl_2Br$ (0.01 mole) and tetrahydrofuran (0.03 mole) in 25 ml. of benzene at 80° for 4 hr. gave C_6H_5HgBr in 92% yield. G.l.p.c. analysis of the distilled filtrate showed the presence of tetrachloroethylene (2.5%) and 2-dichloromethyltetrahydrofuran (67%).

Decomposition of Phenyl(bromodichloromethyl)mercury in Perfluorocyclohexene. The mercurial (0.01 mole) and 17 g. of perfluorocyclohexene (Peninsular Chem Research) were heated at 80° in a sealed, thick-walled Pyrex tube, with agitation, for 8 hr. (heterogeneous reaction). The mixture was filtered and the filtrate was analyzed by g.l.p.c. (20% SE-30 on Chromosorb P, jacket at 157°, 15.7 p.s.i. helium). The only major products were tetrachloroethylene (43%) and hexachlorocyclopropane (21%). The latter was identified by mixture melting point with an authentic sample. Several minor products (yields less than 0.5%) also were present.

Another reaction was carried out between the mercurial (0.01 mole) and perfluorocyclohexene (0.02 mole) in refluxing benzene solution (homogeneous solution). The reaction temperature was only 57–58° due to the 51–52° boiling point of the olefin, and the mixture was heated for 24 hr. T.l.c. analysis at that time indicated that about 15% of the mercurial remained undecomposed. Pure C_6H_5HgBr was recovered in 81% yield. The filtrate was analyzed by g.l.p.c.; two major products were present: tetrachloroethylene (39%) and hexachlorocyclopropane (8%).

Pyrolysis of Phenyl(bromodichloromethyl)mercury. Into a 300-ml., three-necked flask equipped with a mechanical stirrer and a single glass tube outlet to a liquid nitrogen trap and a vacuum system was placed 22.0 g. (0.05 mole) of finely ground mercurial that had been thoroughly mixed with 200 g. of finely ground, reagent grade sodium chloride. The system was evacuated to 2.5 mm. and heated to 95° with stirring. A cream-colored solid began to sublime into the cooler portions of the flask and connecting tube, while a liquid and a dark gray solid collected in the trap. After 1.5 hr. the pressure was reduced briefly to 0.03 mm. and then the heating and evacuation were discontinued. Trap-to-trap distillation of the liquid in the trap (80° at 0.05 mm.) gave 2.42 g. of colorless distillate. G.l.p.c. analysis of the latter on an SE-30 column at 110° showed that the major component of the latter (95%) was tetrachloroethylene. A second component was bromotrichloroethylene (3–5%), identified by comparison of its retention time and infrared spectrum with that of an authentic sample.⁴⁶ The crude yield of tetrachloroethylene was 60%.

(46) D. Seyferth and R. H. Towe, *Inorg. Chem.*, **1**, 185 (1962).

The tan sodium chloride mixture was scraped from the flask, stirred with 500 ml. of distilled water for 3 hr., filtered, and dried to give 16.6 g. (92% yield) of a cream-colored solid, m.p. 250° (began to turn brown-black at 180°). T.l.c. analysis of the latter revealed only the presence of phenylmercuric bromide.

Reduction of 9,9-Dibromobicyclo[6.1.0]nonane with Tri-n-butyltin Hydride. This compound (0.05 mole) was reduced with 2 equiv. of tri-n-butyltin hydride at 25–30°. The more volatile components were removed by trap-to-trap distillation at 1 mm. and then were redistilled to give 2.5 g. (41%) of pure bicyclo[6.1.0]nonane, b.p. 70° (30 mm.), n_D^{25} 1.4662.

Anal. Calcd. for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.08; H, 13.05.

Spectral Data. Spectral data (infrared and/or n.m.r.) of all compounds prepared by previous investigators were compared with those reported by the various investigators. Infrared and n.m.r. spectral data (in all cases compatible with the product structures given in Table I) for some of the new compounds prepared in this study are presented.

1,1-Dibromocyclopropane had infrared (pure liquid) 3080 (w), 3005 (w), 1440 (m), 1420 (m), 1375 (w), 1215 (w), 1119 (s), 1095 (w), 1062 (w), 1031 (s), 941 (m), 757 (w), 640 (m), and 610 (w) cm^{-1} ; n.m.r. (CCl_4) singlet, 1.64 p.p.m.

Bromopentachlorocyclopropane showed infrared (CS_2) 956 (sh), 940 (w), 908 (m), 893 (m), 833 (s), and 815 (s) cm^{-1} ; mass spectrum⁴⁸ (fragment, mass number (percentage)) Cl , 35 (65.0); Cl , 37 (23.7); CCl , 47 (78.5); CCl , 49 (31.1); C_2Cl , 59 (21.4); C_2Cl , 61 (8.5); C_3Cl , 71 (85.3); C_3Cl , 73 (89.4); Br , 79 (16.4); Br , 81 (17.5); CCl_2 , 82 (27.5); CCl_2 , 84 (18.1); C_2Cl_2 , 94 (23.7); C_2Cl_2 , 96 (14.1); C_3Cl_2 , 106 (36.2); C_3Cl_2 , 108 (20.9); C_3Cl_2 , 110 (5.6); CCl_3 , 117 (32.8); CCl_3 , 119 (24.3); CCl_3 , 121 (11.3); C_3Cl_3 , 141 (31.6); C_3Cl_3 , 143 (28.2); C_3Cl_3 , 145 (10.7); C_3Cl_5 , 211 (45.2); C_3Cl_5 , 213 (100); C_3Cl_5 , 215 (42.4); C_3Cl_5 , 217 (16.4); C_3BrCl_4 , 255 (18.1); C_3BrCl_4 , 257 (36.2); C_3BrCl_4 , 259 (27.7); and C_3BrCl_4 , 261 (13.0).

1,1-Dibromotetrachlorocyclopropane gave infrared (CS_2) 941 (w), 919 (m), 902 (m), 877 (w), 811 (m), and 781 (s) cm^{-1} ; mass spectrum (fragment, mass number (percentage)) Cl , 35 (60.0); Cl , 37 (25.8); CCl , 47 (60.8); CCl , 49 (27.5); C_2Cl , 59 (19.1); C_2Cl , 61 (10.8); C_3Cl , 71 (100); C_3Cl , 73 (54.1); Br , 79 (28.3); Br , 81 (25.0); CCl_2 , 82 (22.5); CBr , 91 (20.0); CBr , 93 (14.1); C_2Cl_2 , 94 (20.0); C_2Cl_2 , 96 (11.6); C_3Cl_2 , 106 (46.7); C_3Cl_2 , 108 (34.1); C_3Cl_2 , 110 (20.0); CCl_3 , 117 (28.3); CCl_3 , 119 (26.7); CCl_3 , 121 (14.1); C_3Cl_3 , 141 (39.1); C_3Cl_3 , 143 (36.6); C_3Cl_3 , 145 (18.3); C_3Cl_5 , 211 (14.1); C_3Cl_5 , 213 (19.1); C_3Cl_5 , 215 (13.3); C_3Cl_5 , 217 (6.7); C_3BrCl_4 , 255 (33.3); C_3BrCl_4 , 257 (68.3); C_3BrCl_4 , 259 (61.7); C_3BrCl_4 , 261 (26.7); C_3BrCl_4 , 263 (8.3); $C_3Br_2Cl_3$, 299 (15.0); $C_3Br_2Cl_3$, 301 (27.5); $C_3Br_2Cl_3$, 303 (25.0); $C_3Br_2Cl_3$, 305 (20.0); and $C_3Br_2Cl_3$, 307 (6.7).

1,1-Dibromo-2-trimethylsilylcyclopropane had infrared (pure liquid) 2994 (w), 2903 (m), 2895 (m), 1435 (m), 1405 (w), 1265 (s), 1251 (s), 1205 (m), 1117

(47) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

(48) Determined by R. S. Gohlke, Eastern Research Laboratory, Dow Chemical Co.

(s), 1045 (m), 1009 (s), 969 (s), 905 (s), 842 (s), 757 (s), 695 (m), and 657 (s) cm^{-1} ; n.m.r. (CCl_4) quartets at 1.8, 1.5, and 0.89 (1 H each), and a singlet at 0.17 p.p.m. (9 H).⁴⁹

cis-1,1-Dichloro-2-methyl-3-trimethylsilylcyclopropane showed infrared (pure liquid) 3010 (w), 2960 (s), 2900 (w), 2100 (w), 1940 (w), 1455 (m), 1410 (w), 1380 (m), 1267 (s), 1255 (s), 1226 (w), 1140 (m), 1110 (m), 1031 (s), 985 (s), 917 (s), 850 (s), 801 (s), 777 (s), 762 (m), 748 (s), 694 (m), 651 (m), and 602 (w) cm^{-1} ; n.m.r. (CCl_4) octet at 1.77 (1 H), doublets at 1.35 ($J = 6.2$ c.p.s., 3 H) and 0.83 ($J = 12.4$ c.p.s.,⁵⁰ 1 H), and a singlet at 0.19 p.p.m. (9 H).

trans-1,1-Dichloro-2-methyl-3-trimethylsilylcyclopropane gave infrared (pure liquid) 3000 (w), 2955 (s), 2930 (w), 2895 (w), 2870 (w), 1455 (m), 1410 (w), 1385 (w), 1380 (m), 1310 (w), 1252 (s), 1202 (w), 1141 (m), 1042 (s), 1027 (w), 976 (s), 914 (s), 860 (sh), 844 (s), 795 (s), 758 (w), 744 (m), 694 (m), and 609 (w) cm^{-1} ; n.m.r. (CCl_4) multiplets centered at 1.36 (4 H) and 0.14 p.p.m. (10 H).

trans-1,1-Dichloro-2,3-diphenylcyclopropane had infrared (CS_2) 3050 (m), 3020 (m), 1605 (m), 1220 (w), 1165 (m), 1105 (m), 1085 (s), 1060 (m), 1053 (m), 1028 (m), 910 (w), 859 (s), 766 (w), 752 (s), 738 (m), and 690 (s) cm^{-1} ; n.m.r. (CCl_4) singlets at 7.37 (10 H) and 3.15 p.p.m. (2 H).

1,1-Dichloro-2-cyanocyclopropane showed infrared (pure liquid) 3100 (m), 3045 (m), 2250 (s), 1435 (m), 1365 (w), 1348 (m), 1216 (m), 1111 (s), 1090 (s), 1065 (w), 1002 (m), 923 (m), 879 (m), 780 (s), and 587 (w) cm^{-1} .

2,2-Dichlorocyclopropylmethyl isocyanate gave infrared (CCl_4) 3120 (w), 2940 (w), 2875 (w), 2250 (vs), 2075 (w), 1430 (m), 1380 (s), 1330 (m), 1253 (m), 1225 (m), 1142 (m), 1118 (s), 1057 (m), 1037 (m), 997 (w), 964 (w), 874 (m), 580 (w), and 547 (w) cm^{-1} ; n.m.r. (CCl_4) doublet at 3.48 (2 H), and multiplet centered at 1.71 p.p.m. (3 H).

Methyl 2,2-dichlorocyclopropanecarboxylate had infrared (CCl_4) 3080 (w), 2990 (w), 2945 (m), 2830 (w), 1745 (vs), 1430 (s), 1420 (m), 1320 (s), 1270 (m), 1237 (s), 1200 (s), 1175 (s), 1117 (s), 1070 (m), 1060 (w), 1025 (w), 960 (m), 932 (m), and 888 (w) cm^{-1} ; n.m.r. (CCl_4) singlet at 3.76 (3 H), quartet at 2.54 (1 H), and multiplet centered at 1.90 p.p.m. (2 H).

Dichloromethyl acrylate showed infrared (CCl_4) 3010 (w), 2020 (w), 1940 (w), 1770 (vs), 1640 (m), 1400 (s), 1320 (m), 1290 (m), 1227 (s), 1123 (vs), 1068 (m), 1038 (vs), 1028 (vs), 980 (s), 900 (s), 650 (m), and 600 (w) cm^{-1} ; n.m.r. (CCl_4) singlet at 7.84 (1 H), and a multiplet centered at 6.3 p.p.m. (3 H).

Dichloromethyl 2,2-dichlorocyclopropanecarboxylate gave infrared (CCl_4) 3080 (w), 3040 (w), 3000 (w), 1775 (vs), 1420 (m), 1370 (s), 1315 (w), 1230 (s), 1134 (vs), 1112 (vs), 1080 (m), 1064 (w), 1048 (m), 1026 (vs), 965 (w), 948 (s), 887 (s), 714 (m), and 655 (w) cm^{-1} ; n.m.r. (CCl_4) singlet at 7.82 (1 H), quartet at 2.63 (1 H), and a multiplet centered at 2.06 p.p.m. (2 H).

(49) The n.m.r. spectrum of 1,1-dichloro-2-trimethylsilylcyclopropane has been reported by K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).

(50) Reference 49 reports J_{cis} for 1,1-dichloro-2-trimethylsilylcyclopropane = 12.6 c.p.s.

cis-Methyl 2,2-dichloro-3-methylcyclopropanecarboxylate had n.m.r. (CCl_4) triplet at 3.85 (3 H), multiplet centered at 2.2 (2 H), and a doublet at 1.45 p.p.m. (3 H).

trans-Methyl 2,2-dichloro-3-methylcyclopropanecarboxylate showed n.m.r. (CCl_4) triplet at 3.73 (3 H), quartet centered at 2.15 (2 H), and a doublet at 1.37 p.p.m. (3 H).

1-Acetyl-2,2-dichloro-3,3-dimethylcyclopropane gave infrared (CHCl_3) 3400 (w), 3005 (m), 2960 (m), 2940 (m), 2870 (w), 1720 (s), 1460 (m), 1380 (s), 1203 (s), 1170 (s), 1112 (m), 1091 (m), 1037 (m), 1003 (w), 970 (s), 900 (m), 846 (m), 830 (m), and 600 (m) cm^{-1} ; n.m.r. (CCl_4) singlet at 2.25 (3 H), multiplet centered at 2.20 (1 H), and a doublet at 1.42 p.p.m. ($J = 1.9$ c.p.s., 6 H).

cis-1,1-Dichloro-2-ethyl-3-*n*-propylcyclopropane had infrared (pure liquid) 2995 (m), 2960 (s), 2930 (s), 2875 (s), 1460 (m), 1455 (m), 1380 (m), 1260 (w), 1238 (w), 1229 (w), 1161 (w), 1142 (m), 1040 (w), 990 (w), 940 (w), 898 (w), 859 (w), 850 (w), 815 (s), 800 (m), 790 (m), 756 (m), and 735 (w) cm^{-1} .

trans-1,1-Dichloro-2-ethyl-3-*n*-propylcyclopropane showed infrared (pure liquid) 2997 (m), 2970 (s), 2940 (s), 2880 (s), 2865 (m), 1465 (m), 1450 (m), 1380 (m), 1230 (w), 1216 (w), 1160 (w), 1149 (m), 1104 (w), 1080 (w), 1044 (w), 1032 (w), 1015 (w), 1005 (w), 942 (w), 900 (w), 880 (w), 870 (w), 808 (m), 800 (m), 767 (m), and 735 (w) cm^{-1} .

2,2,2',2'-Tetrachlorobicyclopropyl (*m.p.* 79–80°, *meso* form) gave infrared (CCl_4 , CS_2 composite) 3080 (w), 3030 (m), 3000 (m), 2090 (w), 2060 (w), 1910 (w), 1510 (m), 1425 (s), 1295 (m), 1230 (s), 1122 (s), 1050 (s), 1025 (s), 953 (s), 894 (m), 870 (m), 750 (s), and 650 (w) cm^{-1} .

2,2,2',2'-Tetrachlorobicyclopropyl (*m.p.* 29–30°, *dl* form) had infrared (CCl_4 , CS_2 composite) 3090 (w), 3030 (w), 3010 (m), 2075 (w), 1475 (w), 1425 (m), 1380 (w), 1295 (m), 1236 (m), 1218 (s), 1180 (w), 1120 (s), 1070 (w), 1050 (s), 960 (m), 947 (s), 917 (w), 890 (w), 867 (m), 770 (s), 750 (s), 650 (w), and 590 (m) cm^{-1} .

2,2-Dichloromethylenecyclopropane showed infrared (pure liquid) 3080 (w), 3050 (w), 3000 (w), 2975 (w), 2325 (w), 2075 (w), 2025 (w), 1850 (w), 1820 (w), 1750 (m), 1425 (m), 1400 (m), 1375 (m), 1320 (w), 1265 (w), 1122 (m), 1102 (m), 1045 (s), 980 (m), 925 (sh), 912 (s), 755 (s), and 638 (m) cm^{-1} ; n.m.r. (CCl_4) triplets at 6.03 (1 H), 5.62 (1 H), and 2.1 (2 H) p.p.m.

1,1,4,4-Tetrachlorospiropentane gave infrared (pure liquid) 3075 (m), 2995 (m), 2140 (w), 2080 (w), 2000 (w), 1910 (w), 1790 (w), 1650 (w), 1590 (w), 1550 (m), 1490 (s), 1465 (m), 1425 (m), 1400 (m), 1385 (m), 1200 (w), 1160 (w), 1137 (m), 1100 (s), 1072 (sh), 1064 (s), 1043 (m), 1010 (m), 960 (m), 871 (m), 778 (s), 750 (s), and 550 (m) cm^{-1} ; n.m.r. (CCl_4) doublets (2 H each) at 2.12 and 1.92 p.p.m. ($J = 7.0$ c.p.s.).

7,7-Dichloro-4-vinylbicyclo[4.1.0]heptane had infrared (pure liquid) 3075 (m), 3010 (sh), 2940 (s), 2850 (s), 1825 (m), 1645 (s), 1460 (m), 1450 (s), 1420 (m), 1385 (w), 1345 (m), 1225 (m), 1179 (w), 1115 (w), 1070 (w), 1026 (w), 988 (s), 912 (s), 860 (w), 850 (w), 844 (w), 800 (s), 786 (w), 711 (m), and 607 (w) cm^{-1} ; n.m.r. (CCl_4) multiplets (1 H each) at 5.67, 5.00, and 4.80, and a multiplet at 1.7 p.p.m. (9 H).

4-(β,β -Dichlorocyclopropyl)cyclohexene showed infrared (pure liquid) 3025 (s), 2915 (s), 2840 (s), 1650 (m), 1605 (sh), 1450 (m), 1440 (s), 1390 (m), 1340 (w), 1292 (w), 1271 (w), 1248 (w), 1227 (m), 1211 (m), 1190 (w), 1139 (m), 1123 (m), 1109 (s), 1042 (s), 1008 (m), 957 (m), 932 (w), 910 (m), 895 (w), 872 (m), 841 (w), 793 (w), 752 (s), 723 (w), 650 (s), and 555 (w) cm^{-1} ; n.m.r. (CCl_4) triplet at 5.62 (2 H) and multiplets at 2.05 (6 H), 1.5 (3 H), and 1.05 p.p.m. (1 H).

1,1-Dichloro-2-ethoxymethylcyclopropane gave infrared (pure liquid) 3075 (w), 3000 (sh), 2975 (s), 2925 (w), 2865 (s), 2805 (w), 1480 (m), 1450 (m), 1385 (s), 1370 (w), 1345 (w), 1270 (w), 1247 (w), 1220 (m), 1153 (m), 1105 (s), 1069 (w), 1059 (w), 1035 (w), 975 (m), 942 (w), 891 (w), 871 (w), 850 (w), 817 (w), and 750 (s) cm^{-1} ; n.m.r. (CCl_4) multiplet at 3.6 (4 H), triplet at 1.25, and a multiplet centered at 1.4 p.p.m. (6 H total).

4,4-Dichloro-3-ethoxy-1-butene had infrared (pure liquid) 3075 (m), 3010 (sh), 2975 (s), 2925 (w), 2890 (m), 2865 (s), 2775 (w), 1875 (w), 1650 (m), 1480 (m), 1450 (m), 1425 (m), 1400 (m), 1315 (sh), 1310 (m), 1215 (m), 1175 (m), 1120 (s), 1098 (s), 1070 (m), 1022 (w), 993 (m), 940 (s), 892 (m), 779 (s), 705 (w), and 680 (m) cm^{-1} ; n.m.r. (CCl_4) multiplet centered at 5.6 (4 H, includes dichloromethyl proton), doublet at 3.8 quartet at 3.4 (3 H total), and triplet at 1.25 p.p.m. (3 H).

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The Halogenation of Diazomethane. Study of the Reactivities of Carbenes Derived from Halodiazomethanes¹⁻³

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*Halogenation of diazomethane with less than molar amounts of *t*-butyl hypohalites at -100° gives halodiazomethanes in good yields. Thermolysis at -10° and photolysis of chloro- and bromodiazomethane yield free halocarbenes which undergo insertion reactions and additions to olefins. Halocarbenes from halodiazomethanes are less reactive than methylene but more reactive than the chlorocarbene generated from methylene chloride by α -elimination. Halogenation of diazomethane with 2 equiv. of *t*-butyl hypohalite probably leads to dihalodiazomethanes which are too unstable to be characterized. Product analysis of reactions carried out in olefins as solvent suggests that dihalodiazomethanes decompose instantaneously to nitrogen and dihalomethylenes.*

Ever since the pioneering studies by Hine and Doering halocarbenes have been postulated as intermediates in a great variety of reactions.⁵ Comparison of the reactivities of these carbenes with that established for methylene generated from diazomethane or ketene revealed significant differences between the parent carbene and its halogen derivatives. Perhaps the most

striking discrepancy in the behavior of the postulated intermediates is the fact that methylene inserts into the carbon-hydrogen bond with great ease, while its halogen derivatives undergo this reaction only under very special conditions.⁶ Considering only conventional structure-reactivity relationships, this behavior can be attributed to resonance stabilization in halocarbenes.^{10,11} Although this conclusion is probably qualitatively correct, it does not take into account that the two types of carbenes were generated by two entirely different reactions and under otherwise incomparable conditions. Justification for this reservation is found in the observation that other methylene transfer reagents when produced by α -elimination processes are also considerably more selective and frequently do not give the insertion reaction either.^{12,13} Recently severe doubt has been cast on the notion that any α -elimination necessarily proceeds through a carbene, even when trapping experiments seem to indicate the intermediacy of such species.^{14,15}

(6) Dichloromethylene, for example, will not insert into the C-H bonds of hydrocarbons in the presence of alkoxides.⁷ Only if less nucleophilic reagents such as sodium trichloroacetate⁸ or bromodichloromethylphenylmercury⁹ are used for the formation of dichloromethylene, have C-H bond insertions been observed.

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