Phenyl(trihalomethyl)mercury Compounds: Exceptionally Versatile Dihalocarbene Precursors

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The area of preparative carbene chemistry began in 1954 with a report by Doering and Hoffmann.[1] They synthesized *gem*-dihalocyclopropanes by the reaction of potassium *tert*-butoxide with haloforms in an inert solvent in the presence of olefins. The subsequent growth of halocarbene chemistry has been spectacular. The developments of the first ten years are documented in two books.[2-4]

The area of organometallic chemistry has made significant contributions to the development of carbene chemistry, or, better, "divalent carbon transfer chemistry," since in the case of some "carbene" reagents free carbenes are not involved as intermediates. In this Account we summarize our present state of knowledge concerning phenyl(trihalomethyl)mercury compounds, their synthesis, and their outstanding utility in the preparation of *gem*-dihalocyclopropanes.

This represents only one aspect of our research on halomethylmercury compounds, the chemistry of which we have developed in considerable breadth and depth at MIT during recent years. However, the PhHgCX₃ reagents and their reactions with olefins represent that aspect of our halomethylmercurial research which is the most useful to other chemists. Also it is these reactions which we understand best in terms of scope and mechanism. For these reasons and because of space limitations, we have chosen to review this relatively narrow area rather than the whole field of halomethylmercury chemistry.

The "Conventional" Dihalocarbene Generating Systems

In order to appreciate the unique reactivity and the very useful synthetic applicability of the phenyl(trihalomethyl)mercury compounds, one must be acquainted with the more "conventional" procedures for generating dihalocarbenes, their scope, and their limitations.

Two broadly applicable procedures for the generation of dihalocarbenes were available in 1961 when we initi-

ated our work in this area. First was the reaction of strong bases with haloforms and other organic trihalomethyl anion sources, *i.e.*, the Doering–Hoffmann (henceforth D–H) procedure[1] and its variations. Some halogenated organic compounds other than haloforms serve in this application[2-4] (esters of trihaloacetic acids, hexahaloacetones, chloral, and carbon tetrahalides), but in general, use of the haloform is preferred. Bases other than *tert*-BuOK may be used.[2-4] At higher temperatures, ethylene oxide in the presence of catalytic quantities of tetraalkylammonium halides serves to generate CX₂ from haloforms.[5] The second procedure was the decarboxylation of alkali metal salts of trihaloacetic acids in aprotic media (generally 1,2-dimethoxyethane or diglyme), reported first by Wagner.[6]

For the majority of intended *gem*-dihalocyclopropane syntheses, these two general procedures for CX₂ generation are perfectly adequate. However, there are some cases where the D–H reaction and its variants give either none of the desired *gem*-dihalocyclopropane or, at best, only very low yields, and there are some (fewer) cases where the Wagner procedure is not successful. Consideration of these systems—reaction conditions, the intermediates involved, and the potential side reactions which could consume CX₂ in competition with its addition to the olefin—serves to explain some of the unsuccessful reactions. Three points merit discussion.

In the D–H reaction and its variants a strong base that usually also is a good nucleophile is used. There are quite a few organic and inorganic functional groups which react with nucleophiles such as RLi and ROK.

All available evidence[7] suggests that dihalocarbenes have a structure in which the three nuclei and a filled carbon sp² orbital lie in a plane and in which a vacant carbon p orbital is perpendicular to this plane. Nearly all of the chemistry of dihalocarbenes is best explained in terms of the interaction of the vacant carbon p or-

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

(2) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964.

(3) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(4) A more up-to-date but less detailed book (in German) by Kirmse has been published: W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim (Bergstr.), 1969.

(5) P. Weyerstahl, D. Klamann, C. Finger, F. Nerdel, and J. Buddrus, *Chem. Ber.*, **100**, 1858 (1967).

(6) (a) W. M. Wagner, *Proc. Chem. Soc. London*, 229 (1959); (b) W. M. Wagner, H. Kloosterziel, and S. Van der Ven, *Recl. Trav. Chim.*, **80**, 740 (1961); (c) W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *ibid.*, **81**, 925, 933 (1962).

(7) Reference 3, Chapter 12.

bital with suitable locii of electron density in the substrate molecule: π-bonding electrons of various C–C multiple linkages, aromatic π electrons, nonbonding lone-pair electrons, especially those on nitrogen, sulfur, and oxygen, and even σ-bonding electrons if π-bonding or nonbonding electrons are not available. In the *gem*-dihalocyclopropane synthesis, if the olefin used is a poor nucleophile for electronic reasons or because reagent access to the C=C bond is sterically hindered, then alternate reaction possibilities are available to the highly reactive dihalocarbene. In the D–H reaction system, three nucleophilic species could in principle compete with the olefinic substrate for CX_2: the *tert*-butoxide ion; the *tert*-butyl alcohol formed in the deprotonation step,[8] especially at the later stages; and possibly even the CX_3^- intermediate. For these reasons, some olefins are not converted to *gem*-dihalocyclopropanes by the *tert*-butoxide–haloform system at all (*e.g.*, ethylene[9] and *trans*-stilbene[10]), and with others the yields obtained are very low (*e.g.*, vinyltrimethylsilane[11] and tetrachloroethylene[12]). Even with the more reactive olefins, better yields are obtained when the olefins are used in considerable excess if the CX_2 is generated by the D–H route.

In the Wagner procedure one is dealing with neutral reaction conditions. However, when the olefinic substrate is poorly reactive toward dihalocarbenes, a side reaction involving the nucleophilic trihaloacetate ion can divert the CX_2 from reaction at the C=C bond.[6c] This reaction appears to be less serious, in terms of interference with formation of the desired product, than the side reactions encountered with the D–H reaction, but, nevertheless, it does limit yields when poorly reactive substrates are used.

In both of the CX_2 procedures discussed above, the trihalomethyl anion is an intermediate. In the case of most olefins this presents no problem, but when the olefinic substrate is relatively electrophilic, *e.g.*, CH_2=CHCN or CH_2=CHCO$_2$R, the CX_3^- ion may be intercepted. The known base-catalyzed addition of chloroform to acrylonitrile[13] is to be noted in this connection. Vinyl acetate also was found to trap a significant portion of the CX_3^- ions formed in the decarboxylation of CCl_3CO_2Na.[6b]

It is evident that improved procedures for dihalocarbene generation were needed.

A New Approach: Organometallic Divalent Carbon Transfer Agents

Results reported in the years 1958–1961 suggested

that organometallic chemistry could contribute significantly to the further development of divalent carbon transfer reactions. An important advance was the discovery by Simmons and Smith[14] that iodomethylzinc iodide[15] reacts with olefins in diethyl ether to produce cyclopropanes. Further studies showed that this reaction does *not* proceed *via* free CH_2, rather that a *direct, bimolecular* transfer reaction between the organozinc reagent and the olefin was involved.[16]

More directly related to CX_2 transfer were two other reports. Trimethyl(trifluoromethyl)tin was found to decompose above its boiling point at *ca.* 150° to give trimethyltin fluoride and hexafluorocyclopropane.[17a] The formation of the observed products was explained in terms of α elimination of trimethyltin fluoride, dimerization of the CF_2 extruded to CF_2=CF_2, and finally addition of CF_2 to tetrafluoroethylene. Similar decomposition of (trichloromethyl)trichlorosilane at 250° was reported by Bevan, *et al.*,[17b] and CCl_2 transfer to cyclohexene could be effected in 60% yield.

These reactions were interesting but seemed of only limited applicability in view of the relatively high temperatures required. For the usual organic and organometallic syntheses, reaction temperatures in the range of 25 to 100° are desirable, and thus what was required was a trihalomethylmetal compound which would extrude its CX_2 (or transfer it directly) at temperatures not too far above room temperature. Trihalomethyl derivatives of mercury fulfill this requirement.

The Advent of Halomethylmercury Reagents

A report by Reutov and Lovtsova[18] that phenyl(trichloromethyl)mercury decomposed to give phenylmercuric chloride in quantitative yield when it was heated in refluxing ethanol called our attention to and aroused our interest in compounds of type $PhHgCX_3$. The temperature of refluxing ethanol is well within the desired temperature range, and the presumed α-elimination reaction seemed to proceed cleanly. Actually, trihalomethyl compounds of mercury had been known for some time. The first one, CBr_3HgBr, reported in 1926,[19] was prepared by a rather obscure route. More recently, Nesmeyanov, *et al.*,[20] prepared $BrHgCCl_3$ by reaction of CCl_3Br with metallic mercury. The reaction of sodium trichloroacetate with phenylmercuric chloride in refluxing 1,2-dimethoxyethane was found to serve well in the preparation of $PhHgCCl_3$,[21,22] but this

(8) For reaction of CCl_2 with alcohols see: D. Seyferth, V. A. Mai, J. Y.-P. Mui, and K. V. Darragh, *J. Org. Chem.*, **31**, 4079 (1966).

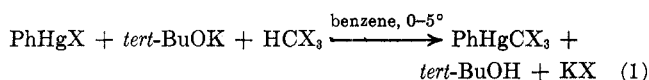(9) W. von E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **80**, 5274 (1958).

(10) H. Komrsová and J. Farkaš, *Collect. Czech. Chem. Commun.*, **25**, 1977 (1960).

(11) J. Cudlín and V. Chvalovský, *ibid.*, **27**, 1658 (1962).

(12) (a) S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **86**, 56 (1964); (b) W. R. Moore, S. E. Krikorian, and J. E. La Prade, *J. Org. Chem.*, **28**, 1404 (1963).

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

(14) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); **81**, 4256 (1959).

(15) G. Emschwiller, *C.R. Acad. Sci.*, **188**, 1555 (1929).

(16) (a) E. P. Blanchard, Jr., and H. E. Simmons, *J. Amer. Chem. Soc.*, **86**, 1337 (1964); (b) H. E. Simmons, E. P. Blanchard, Jr., and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(17) (a) H. C. Clark and C. J. Willis, *ibid.*, **82**, 1888 (1960); (b) W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind.* (*London*), 789 (1961).

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

(19) G. Sachs and L. Balassa, *Z. Anorg. Allg. Chem.*, **152**, 180 (1926).

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

(21) G. A. Razuvaev, N. S. Vasileiskaya, and L. A. Nikitina, *Tr.*

procedure apparently cannot be generalized to bromine-containing trihaloacetic acid salts.[23,24] However, it was the procedure of Reutov and Lovtsova[18] which made a wide range of new halomethyl compounds of mercury available, not only (trihalomethyl)mercurials (eq 1) but also (dihalomethyl)mercury compounds.[25,26]

$$\text{PhHgX} + tert\text{-BuOK} + \text{HCX}_3 \xrightarrow{\text{benzene, 0-5°}} \text{PhHgCX}_3 + \\ tert\text{-BuOH} + \text{KX} \quad (1)$$

The procedure, as originally described, was not well reproducible, and a process study[27] demonstrated the critical importance of several factors. *High-speed* stirring was required since both PhHgX and the *tert*-BuOH solvate of the *tert*-BuOK used were poorly soluble in the reaction medium. Commercially available *tert*-BuOK could not be used successfully; only "homemade" *tert*-BuOK–*tert*-BuOH appeared to be effective in this application. In our hands, at least a fourfold excess of haloform (relative to PhHgX charged) was required. These three factors combined to make this procedure cumbersome, time consuming, and wasteful of haloform.
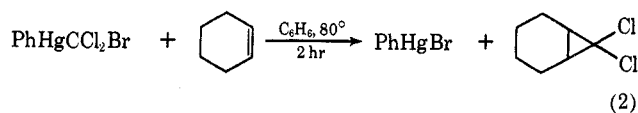
In view of these drawbacks, we developed an improved procedure which has made the PhHgCCl$_n$-Br$_{3-n}$ ($n = 0-3$) easily preparable.[28] A simple change of solvent from benzene to tetrahydrofuran (with concomitant lowering of the reaction temperature to $-25°$) brought the following improvements. (1) High-speed stirring no longer is necessary; a simple paddle stirrer in a three-necked flask suffices. (2) Commercial *tert*-BuOK can be used. (3) A large excess of haloform no longer is required. As synthetic reagents, the PhHgCX$_3$ compounds thus are readily accessible to all who require them.[29]

Applications of Phenyl(trihalomethyl)mercury Compounds in *gem*-Dihalocyclopropane Synthesis

General Comments and Scope. The reported decomposition of PhHgCCl$_3$ in refluxing ethanol to PhHgCl in quantitative yield[18] suggested to us that heating this mercurial in the presence of an olefin might lead to formation of a *gem*-dichlorocyclopropane. Such proved to be the case.[30,31] When a mixture containing PhHg-

CCl$_3$, 3 molar equivalents of cyclohexene, and some benzene diluent was heated at reflux for 48 hr, a reaction giving PhHgCl and 7,7-dichloronorcarane occurred *essentially quantitatively*.

One important fact very quickly became apparent: elimination of PhHgBr is much more favorable than elimination of PhHgCl. Thus a reaction of PhHgCBr$_3$ with cyclohexene was complete, with quantitative product formation, within 2 hr under conditions identical with those used in the experiment with PhHgCCl$_3$. Of importance to CCl$_2$ transfer was the finding that PhHg-CCl$_2$Br reacted *rapidly and exclusively via* PhHgBr elimination (eq 2), although elimination of PhHgCl should

$$\text{PhHgCCl}_2\text{Br} + \underset{}{\bigcirc} \xrightarrow[\text{2 hr}]{\text{C}_6\text{H}_6,\, 80°} \text{PhHgBr} + \underset{}{\bigcirc}\hspace{-0.3em}\triangleleft\hspace{-0.3em}\begin{matrix}\text{Cl}\\\text{Cl}\end{matrix} \quad (2)$$

be favored on a statistical basis. In similar fashion, PhHgCClBr$_2$ was found to act exclusively as a CClBr source.

Fluorine-containing phenyl(trihalomethyl)mercury compounds also have been prepared. PhHgCCl$_2$F has a reactivity comparable to that of PhHgCCl$_3$ and transfers only CClF on being heated with an olefin for 48 hr at 80°.[32] In contrast, no decomposition of PhHg-CF$_3$[33,34] was observed when it was heated at *ca.* 140° in cyclooctene solution for 10 days.

We have devoted considerable effort to a study of the scope of the PhHgCX$_3$–olefin reactions[31,32,35] and have studied the reactions of PhHgCCl$_2$Br in greatest detail.

Some general comments concerning the reactions of the PhHgCCl$_n$Br$_{3-n}$($n = 0-2$) reagents with olefins will serve to illustrate the general utility of these mercurials. A rapid reaction occurs at 80°, but lower temperatures may be used provided that correspondingly longer reaction times are acceptable. For instance, a reaction of PhHgCCl$_2$Br with Me$_3$SiCH=CH$_2$ (bp 54°) in benzene solution, in which the 80° reaction temperature could not be achieved, proceeded in high yield, but required 30 hr. PhHgCCl$_2$Br is an effective CCl$_2$ transfer agent *even at room temperature;* a reaction with cyclohexene in benzene gave 7,7-dichloronorcarane in 66% yield after 11 days at room temperature.

A 1:1 PhHgCX$_3$–olefin stoichiometry is satisfactory for all but the least reactive olefins; an excess of olefin

Khim. Khim. Tekhnol., **1**, 638 (1960); *Chem. Abstr.*, **56**, 15116 (1962).

(22) T. J. Logan, *J. Org. Chem.*, **28**, 1129 (1963); *Org. Syn.*, **46**, 98 (1966).

(23) G. Holan, *Tetrahedron Lett.*, 1985 (1966).

(24) Note, however, the preparation of (CBr$_3$)$_2$Hg *via* CBr$_3$CO$_2$Na: M. Robson and I. E. Dickson, *J. Organometal. Chem.*, **15**, 7 (1968).

(25) O. A. Reutov and A. N. Lovtsova, *Dokl. Akad. Nauk SSSR*, **154**, 166 (1964).

(26) D. Seyferth and H. D. Simmons, Jr., *J. Organometal. Chem.*, **6**, 306 (1966).

(27) D. Seyferth and J. M. Burlitch, *ibid.*, **4**, 127 (1965).

(28) D. Seyferth and R. L. Lambert, Jr., *ibid.*, **16**, 21 (1969).

(29) Other variations of the Reutov–Lovtsova procedure are available, but we see no advantage to their use. The synthesis of PhHgCCl$_3$ can be accomplished by reaction of PhHgCl, CCl$_3$CO$_2$Et, and NaOMe: E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **28**, 851 (1963). Another variation involves preparation of a phenylmercuric alkoxide in a prior step and its subsequent reaction with the haloform: ref 24; G. A. Razuvaev, V. I. Shcherbakov, and S. F. Zhil'tsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2803 (1968); A. J. Bloodworth, *J. Chem. Soc. C*, 2051 (1970).

(30) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(31) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

(32) D. Seyferth and K. V. Darragh, *J. Org. Chem.*, **35**, 1297 (1970).

(33) (a) D. Seyferth, S. P. Hopper, and K. V. Darragh, *J. Amer. Chem. Soc.*, **91**, 6536 (1969); (b) D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, **26**, C62 (1971).

(34) PhHgCF$_3$ can, however, serve very effectively as a source of CF$_2$. Iodide ion (from NaI) displaces CF$_3^-$ from this mercurial at 80°. The CF$_3^-$ ion loses F$^-$ to give CF$_2$, and if this displacement reaction is carried out in the presence of an olefin, a *gem*-difluorocyclopropane is produced in high yield.[33] In similar fashion, CF$_3$HgI can serve as a CF$_2$ precursor. The sodium iodide procedure is a very useful alternative to simple thermolysis for CX$_2$ release from the more stable PhHgCX$_3$ compounds such as PhHgCCl$_3$ and PhHg-CCl$_2$F; see ref 32 and D. Seyferth, M. E. Gordon, J. Y.-P. Mui, and J. M. Burlitch, *J. Amer. Chem. Soc.*, **89**, 959 (1967).

(35) D. Seyferth, S. P. Hopper, and T. F. Jula, *J. Organometal. Chem.*, **17**, 193 (1969).

generally is not required for good yields. This is important if the olefin is expensive or difficult to obtain and also in cases where olefin and cyclopropane product would be difficult to separate. This advantage is due to the fact that the only side reaction encountered in the usual PhHgCX₃ reactions, tetrahaloethylene formation, apparently has a high activation energy. Such byproducts are found only when the substrate is very unreactive toward CX₂ or PhHgCX₃ (*e.g.*, the aliphatic C–H bond, deactivated or very hindered C=C bonds). Even then the effect of this side reaction can be minimized by using a large excess of the substrate or by using the substrate as solvent, as was done in the case of trichloroethylene. Alternatively, if the olefin for some reason must be the limiting reagent and if k(olefin)/k(side reaction) for CX₂ consumption is not favorable, one may use the PhHgCX₃ reagent in large excess; the CX₂=CX₂ formed is a chemically innocuous byproduct which is easily separated. The successful dihalocyclopropanation of several rather unreactive alkenylcarboranes[36] is an example of the application of this technique.

The CX₂=CX₂-forming side reaction proceeds *via* CX₂ insertion into the C–Hg bond of the PhHgCX₂Br reagent followed by β elimination of PhHgBr from the PhHgCX₂CX₂Br thus formed.[31] Such insertions may be used in preparative chemistry, *e.g.*,[37] reaction 3.

$$Me_3SiCCl_2HgBr + PhHgCCl_2Br \longrightarrow$$
$$[Me_3SiCCl_2CCl_2HgBr] + PhHgBr$$
$$\searrow$$
$$Me_3SiCCl=CCl_2 + HgClBr \quad (3)$$
$$(82\%)$$

The solvents that may be used for the PhHgCX₃–olefin reaction can be varied widely, the main requirement being that they be significantly less reactive toward CX₂ than is the substrate of interest. It is desirable that the starting PhHgCX₃ and the substrate be soluble in the reaction medium. Among the solvents that we have used are benzene, cyclohexane, *n*-heptane, carbon tetrachloride, methylene chloride, 1,2-dimethoxyethane, and propionitrile. The two aliphatic hydrocarbons, for instance, undergo CCl₂ insertion into their C–H bonds on reaction with PhHgCCl₂Br in the absence of reactive CX₂ trapping agents.[38]

The progress of PhHgCX₃ reactions can be monitored by following the consumption of starting mercurial using thin-layer chromatography.[31]

Gaseous olefins, with the exception of the most volatile, such as ethylene, may be brought into reaction at atmospheric pressure simply by heating a stirred benzene solution of PhHgCX₃ to 70–75° and bubbling in the gaseous olefin (cold condenser). This procedure served well in the reactions of PhHgCBr₃ with the isomeric 2-butenes and of PhHgCCl₂Br with allene (to give 2,2-dichloromethylenecyclopropane in 64% yield)

and 1,3-butadiene (to give 1,1-dichloro-2-vinylcyclopropane in 58% yield).

Another advantage of the PhHgCX₃ reagents is due to the properties of the phenylmercuric halide formed in their reactions. The PhHgX compounds all are insoluble in common nonpolar organic solvents and precipitate nearly quantitatively during the course of the CX₂ transfer reaction. Thus work-up of such reaction mixtures is quite simple. Furthermore, the phenylmercuric halides are for the most part chemically innocuous. They are very weak electrophiles and in only one instance, the dihalocyclopropanation of vinyltrimethyltin, were they implicated in an undesirable side reaction, cleavage of the Sn-to-vinyl linkage to give vinylmercurials.[39] Even in that case the reaction could be carried out in a manner that minimized the contact between Me₃SnCH=CH₂ and PhHgBr, and thus a 55% yield of the desired 1,1-dichloro-2-(trimethyltin)cyclopropane could be realized. In most reactions, the PhHgX is obtained in good purity and thus can be recycled to PhHgCX₃ preparation with only minor losses, a necessary economic advantage for large-scale application of these reagents.

Some specific examples of the applications of the PhHgCCl$_n$Br$_{3-n}$ (n = 0–2) mercurials in *gem*-dihalocyclopropane synthesis follow. These serve to illustrate the outstanding and often unique capabilities of these organomercury reagents. PhHgCCl₂Br, PhHgCClBr₂, and PhHgCBr₃ react rapidly at 80° with "uncomplicated" olefins of the RCH=CH₂, R₂C=CH₂, *cis*- and *trans*-RCH=CHR (stereospecifically!), R₂C=CHR, and R₂C=CR₂ types, and with cyclic monoolefins (*e.g.*, cyclohexene, cyclooctene) to give the expected *gem*-dihalocyclopropanes in nearly quantitative yields.[31,35] However, the unique advantage of these reagents resides in the fact that they will transfer CX₂ successfully to olefins which are unreactive or only poorly reactive toward the "conventional" CX₂ reagents, to olefins which contain base-sensitive functionality, and to olefins which can trap CX₃⁻ when it is an intermediate. The examples which follow are from our own research and from reports of others.[40,41]

As mentioned above, ethylene[9] and *trans*-stilbene[10] are unreactive toward the D–H reagent. In contrast, *trans*-stilbene was converted to the expected dichlorocyclopropane in 90% yield in a 1:1 reaction between PhHgCCl₂Br and this olefin. Ethylene could be converted to 1,1-dichloro- and 1,1-dibromocyclopropane in yields of 65 and 53%, respectively, using PhHgCCl₂Br and PhHgCBr₃ (in benzene at 80–100°, 50 atm of

(36) D. Seyferth and B. Prokai, *J. Organometal. Chem.*, **8**, 366 (1967).

(37) D. Seyferth, E. M. Hanson, B. Prokai, and R. J. Cross, *ibid.*, **24**, 33 (1970).

(38) D. Seyferth, J. M. Burlitch, K. Yamamoto, S. S. Washburne and C. J. Attridge, *J. Org. Chem.*, **35**, 1989 (1970).

(39) D. Seyferth, T. F. Jula, H. Dertouzos, and M. Pereyre, *J. Organometal. Chem.*, **11**, 63 (1968).

(40) Consideration of the results reported by others shows PhHgCCl₃ and PhHgCBr₃ to be far superior in *gem*-dihalocyclopropane synthesis to the symmetrical mercurials, Hg(CCl₃)₂ (or CCl₃HgCl)[23] and Hg(CBr₃)₂.[26]

(41) A listing as complete as possible of the applications of halomethylmercury compounds, including PhHgCX₃–olefin reactions, is maintained by the author in "Annual Surveys of Organometallic Chemistry." See: (a) D. Seyferth and R. B. King, *Annu. Surv. Organometal. Chem.*, **1**, 44 (1965); **2**, 55 (1966); **3**, 66 (1967); (b) D. Seyferth, *Organometal. Chem. Rev. B*, **4**, 242 (1968); **5**, 292 (1969); **6**, 249 (1970); and future volumes of this series.

ethylene, in an autoclave). Tetrachloroethylene and vinyltrimethylsilane, mentioned above as poorly reactive in the D–H reaction, reacted with $PhHgCCl_2Br$ to give hexachlorocyclopropane (83%) and 1,1-dichloro-2-(trimethylsilyl)cyclopropane (78%), respectively.[42,43] Noteworthy is the survival intact of the very reactive Si–Cl bond of $Me_2ClSiCH=CH_2$ during its conversion to the *gem*-dichlorocyclopropane (57%) with $PhHg-CCl_2Br$. Highly hindered olefins, such as $Me_2EtCCH=CH_2$, whose relative reactivity toward CCl_2 is only 0.01 that of cyclohexene,[44] react with $PhHgCCl_2Br$ to give the *gem*-dichlorocyclopropane in good yield (66% in the example cited[39]). Hindered double bonds in steroids which have not been accessible to the conventional CX_2 sources were reactive toward $PhHgCCl_2Br$ and $PhHgCBr_3$.[45]

The dihalocyclopropanation of some other olefins is worth mentioning. Acrylonitrile, which is susceptible to polymerization initiated by radical and by nucleophilic reagents and which undergoes base-catalyzed $HCCl_3$ addition, was converted smoothly to 1,1-dichloro-2-cyanocyclopropane in 78% yield using $PhHg-CCl_2Br$[31] and to 1-bromo-1-chloro-2-cyanocyclopropane (61%) by $PhHgCClBr_2$.[35] Methyl acrylate also reacted with $PhHgCCl_2Br$, giving methyl 2,2-dichlorocyclopropanecarboxylate in good yield. Vinyl acetate, a CCl_3^- trap as noted above, reacted with $PhHgCCl_2Br$ to give 2,2-dichlorocyclopropyl acetate in 81% yield. *cis*- and *trans*-methyl crotonate reacted stereospecifically with this mercurial, yielding the expected methyl 2,2-dichloro-3-methylcyclopropanecarboxylate isomers in high yield.

The addition of CCl_2 via $PhHgCCl_2Br$ to enol acetates of cyclic ketones was an essential step in the synthesis of ring-enlarged enones by Stork, et al.[46] Also successful was addition of $PhHgCCl_2Br$-derived CCl_2 to vinylene carbonates (eq 4).[47] Enoxysilanes and allyl-

(4)
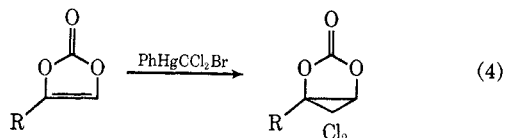
oxysilanes were cyclopropanated by $PhHgCX_3$ reagents, and hydrolysis of the products from the latter gave cyclopropylcarbinols (eq 5).[8] Polymerizable olefins such as styrene, α-methylstyrene, and 1,3-butadiene reacted smoothly with $PhHgCX_3$ without complications; no low or high molecular weight radical-de-

(5)
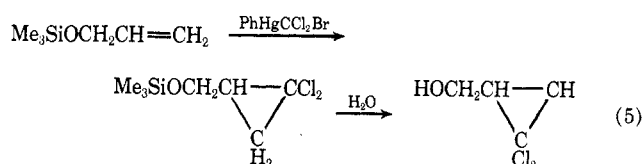
rived by-products were observed.[31] Olefinic ketones, isocyanates, and ethers could be converted to the *gem*-dihalocyclopropanes with $PhHgCX_3$. In the case of the latter, the C=C addition was accompanied by some C–H insertion into allylic ethers (eq 6).[31,48] A

(6)
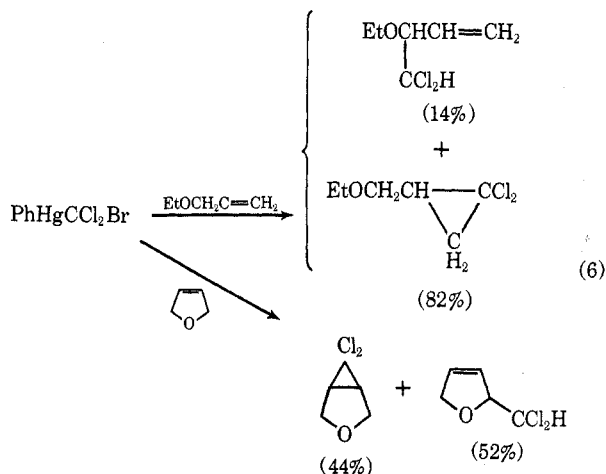
few more examples of *gem*-dihalocyclopropanes prepared by reaction of a $PhHgCX_3$ compound with the corresponding unsaturated compound are given below.

(ref 49)   (ref 50)   (ref 51)

(ref 52)   (ref 53)   (ref 54)

(ref 55)   (ref 31)
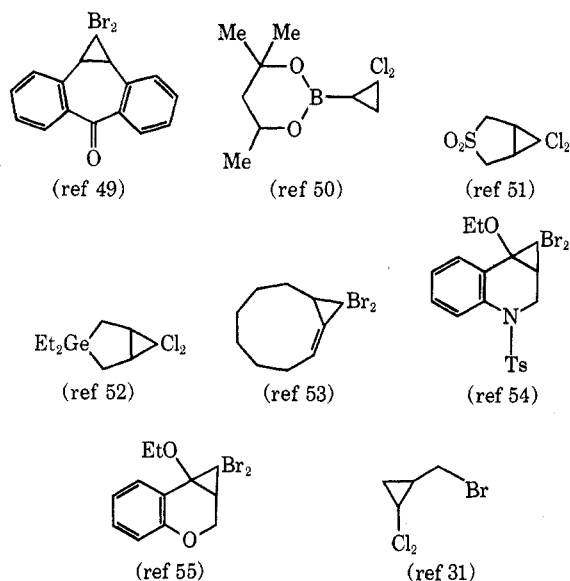
(42) For reactions of $PhHgCX_3$ reagents with other vinylic silanes and germanes, see ref 39.

(43) Other highly chlorinated and fluorinated ethylenes have been converted to the cyclopropanes with $PhHgCX_3$ compounds: (a) M. L. Deem, *Chem. Commun.*, 993 (1969); (b) M. M. Boudakian and G. H. Hofmann, U. S. Patent, 3,349,136 (1967); (c) K. L. Williamson and B. A. Braman, *J. Amer. Chem. Soc.*, **89**, 6183 (1967).

(44) D. Seyferth and H. Dertouzos, *J. Organometal. Chem.*, **11**, 263 (1968).

(45) F. T. Bond and R. H. Cornelia, *Chem. Commun.*, 1189 (1968).

(46) G. Stork, M. Nussim, and B. August, *Tetrahedron Suppl.*, **8**, Part I, 105 (1967).

(47) F. W. Breitbeil, D. T. Dennerlein, A. E. Fiebig, and R. E. Kuznicki, *J. Org. Chem.*, **33**, 3389 (1968)

(48) D. Seyferth, V. A. Mai, and M. E. Gordon, *ibid.*, **35**, 1993 (1970).

(49) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6348 (1967).

(50) W. G. Woods and I. S. Bengelsdorf, *J. Org. Chem.*, **31**, 2769 (1966).

(51) W. L. Mock, *J. Amer. Chem. Soc.*, **92**, 6918 (1970).

(52) D. Seyferth, T. F. Jula, D. C. Mueller, P. Mazerolles, G. Manuel, and F. Thoumas, *ibid.*, **92**, 657 (1970).

(53) W. R. Moore and T. M. Ozretich, *Tetrahedron Lett.*, 3205 (1967).

(54) A. Cromarty and G. R. Proctor, *Chem. Commun.*, 842 (1968).

(55) B. Graffe, M.-C. Sacquet, G. Fontaine, and P. Maitte. *C. R. Acad. Sci., Ser. C*, **269**, 992 (1969).

(n = 5, 6, 8, 10)
(ref 56)

(ref 31)

(ref 57)

(ref 31)

(ref 31)
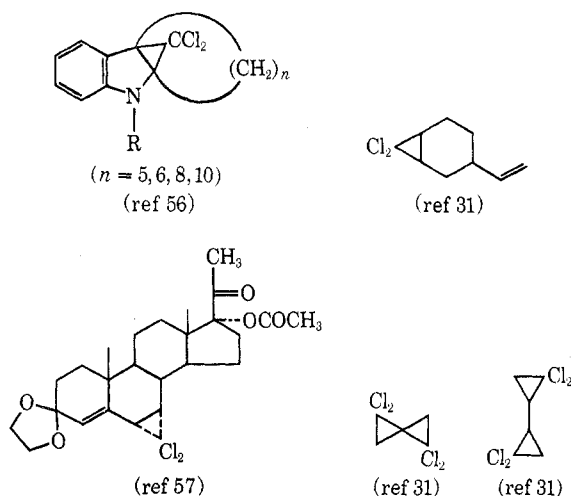
PhHgCX$_3$ compounds are uniquely applicable to the cyclopropanation of C=C bonds in the backbones of polymer chains such as those of polyisoprene, polybutadiene, and polychloroprene.[58] With polyisoprene and polybutadiene the D–H reagents gave only poor conversions to cyclopropane, but with PhHgCCl$_2$Br and PhHgCClBr$_2$ complete saturation of all C=C bonds was realized. Polychloroprene was totally unreactive toward CHCl$_3$–base, but its C=C bonds were converted completely to cyclopropane units with PhHgCCl$_2$Br. Such reactions, coupled with further conversions of the cyclopropane units produced, present interesting possibilities for modification of polymer properties.

There are some functional groups whose presence in olefinic substrates can prevent CX$_2$ addition to the C=C bond. One of these is the O–H group, in alcohols or in carboxylic acids. The reaction of PhHgCCl$_2$Br with unsaturated acids (acrylic, vinylacetic, trans-crotonic) is rapid and gives as the only product, in high yield, the dichloromethyl ester of the acid,[31] e.g., eq 7. The esters thus formed react normally at

$$CH_2=CHCO_2H + PhHgCCl_2Br \xrightarrow{\text{benzene, 80°}}$$
$$PhHgBr + CH_2=CHCO_2CCl_2H \quad (7)$$
$$(83\%)$$
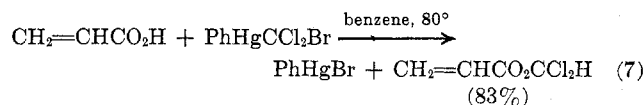
the C=C bond with further mercurial. Insertion of PhHgCCl$_2$Br-derived CCl$_2$ into the O–H bond is a general reaction, occurring readily and in high yield with a wide variety of carboxylic acids, RCO$_2$H (R = CH$_3$, Me$_3$SiCH$_2$, CCl$_3$, Ph, etc.).[59]

With unsaturated alcohols there is a delicate balance of relative reactivities. The reaction of PhHgCCl$_2$Br with allyl alcohol at 80° occurs solely at the O–H bond, giving as products allyl formate, allyl chloride, benzene, and chloroform, but no 2,2-dichlorocyclopropylcar-

(56) W. E. Parham, R. W. Davenport, and J. B. Biasotti, Tetrahedron Lett., 557 (1969).
(57) B. Berkoz, G. S. Lewis, and J. A. Edwards, J. Org. Chem., 35, 1060 (1970).
(58) C. Pinazzi and G. Levesque, C.R. Acad. Sci., Ser. C, 264, 288 (1967); C. Pinazzi, H. Gueniffey, G. Levesque, D. Reyx, and A. Pleurdeau, J. Polym. Sci., Part C, 1161 (1969).
(59) D. Seyferth and J. Y.-P. Mui, J. Amer. Chem. Soc., 88, 4672 (1966).

binol.[8] In contrast, Me$_2$C=CHCH(Me)OH reacted with PhHgCCl$_2$Br to give a 52% yield of the C=C addition product.[60] Thus, increasing the nucleophilicity of the C=C bond by alkyl substitution changes dramatically the nature of the reaction observed. Similarly, French workers[61] have found that the methyl-substituted allenyl alcohol Me$_2$C=C=CHCH(OH)Me reacts with PhHgCBr$_3$ to add CBr$_2$ at the Me$_2$C=C bond.

Similar differences in reactions with PhHgCCl$_2$Br have been noted with the six- through nine-membered cyclic allylic alcohols.[60] 2-Cyclooctenol gave 9,9-dichlorobicyclo[6.1.0]-2-nonanol in 70% yield; mercurial reactions with 2-cycloheptenol and 2-cyclononenol gave the C=C addition products in ca. 30% yield, but with 2-cyclohexenol none of the C=C adduct was detected. Chemical and nmr studies showed that in all cases of PhHgCCl$_2$Br-derived CCl$_2$ addition to bonds of cyclic allylic alcohols, acetates, and methyl ethers, the trans-X,X-dichlorobicyclo[n.1.0]alkane derivatives, I,
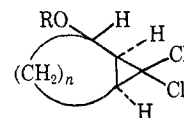
I
(R = H, CH$_3$CO, Me; n = 3-6)

were formed. This observation speaks against any facilitation of reagent approach by complexation with the oxygen functional group.[60]

A lone electron pair on nitrogen also can interfere with dihalocyclopropanations with PhHgCX$_3$. Reactions of allylic amines of type R$_2$NCH$_2$CH=CMe$_2$ with PhHgCCl$_3$ proceed by two alternative paths; which path predominates depends on the nature of R.[62]

$$Et_2NCH_2CH=CMe_2 \xrightarrow{PhHgCCl_3}$$
$$Et_2NCCl=CCl_2 + HCCl_3 + ClCH_2CH=CMe_2 \quad (8)$$
$$(44\%) \qquad (77\%) \qquad (8\%)$$

$$Ph_2NCH_2CH=CMe_2 \xrightarrow{PhHgCCl_3}$$

$$+ Ph_2NCCl=CCl_2 + HCCl \quad (9)$$
$$(<1\%) \qquad (33\%)$$
$$(56\%)$$

$$CH_3CO(Me)NCH_2CH=CMe_2 \xrightarrow{PhHgCCl_3}$$

$$(10)$$

$$(60\%)$$

When the substituents at nitrogen are such that the availability of the nitrogen lone electron pair is decreased, a shift from reaction at nitrogen to reaction at the C=C bond is observed. Actually, a competition

(60) D. Seyferth and V. A. Mai, ibid., 92, 7412 (1970).
(61) M. Bertrand and R. Maurin, Bull. Soc. Chim. Fr., 2779 (1967).
(62) W. E. Parham and J. R. Potoski, J. Org. Chem., 32, 278 (1967).

for CCl_2 by two different reaction sites (N and C=C) is *not* involved. The reaction at nitrogen appears to involve *the mercurial itself*.[62-64]

Finally, some few olefins are truly "inert" toward $PhHgCX_3$. One example is perfluorocyclohexene. When $PhHgCCl_2Br$ was heated in the presence of this olefin at 80°, the only products obtained were tetrachloroethylene and hexachlorocyclopropane.[31]

Mechanism of Transfer of CX_2 from $PhHgCX_3$ to Olefins. It is generally agreed that in all variations of the D–H reaction the transfer of CX_2 to the olefin involves the free dihalocarbene as an intermediate.[2-4,65,66] On the other hand, as mentioned above, CH_2 transfer from a stable organometallic reagent, ICH_2ZnI, to an olefin did *not* proceed *via* free CH_2.[16] How then does transfer of CX_2 from the $PhHgCX_3$ reagents to olefins take place in the thermal reaction?

The discussion above has indicated that in the thermal $PhHgCX_3$–olefin reaction the CX_3^- ion is *not* an intermediate: olefinic substrates which should have trapped it did not do so. Nor was it likely that $X_3C\cdot$ radicals were intermediates at 80° in view of the clean cyclopropanations of styrene, 1,3-butadiene, methyl acrylate, etc. The stereochemistry of the $PhHgCX_3$–olefin reaction (retention[31]) was not useful mechanistic information since both the D–H reaction[2-4] and the ICH_2ZnI–olefin reaction[14] occur with retention of geometric configuration about the C=C bond.

There is available from previous work of Doering[9] a listing of relative rate constants of selected olefins toward *tert*-BuOK–$CHCl_3$ at −15°. However, in view of our application of $PhHgCX_3$ at 80°, comparison with another CCl_2 system seemed desirable. Accordingly, we determined relative rate constants for a series of olefins toward dichlorocyclopropanation by $PhHgCCl_2Br$ in benzene at 80 ± 2° and by sodium trichloroacetate in 1,2-dimethoxyethane (DME) at the same temperature by means of appropriate competition experiments.[67] The results are given in Table I. Since the solvents used with these two reagents differed, a few similar competition experiments were carried out with $PhHgCCl_2Br$ in DME. The relative rate constants were identical with those obtained in benzene.

Noteworthy was the near identity of the k_{rel} values for all olefins toward $PhHgCCl_2Br$ and CCl_3CO_2Na. Also, these values paralleled reasonably well those measured for the same types (but not identical) of alkylsubstituted olefins at −15° for the *tert*-BuOK–$CHCl_3$ system,[9] but with a greater spread of k_{rel} being observed in the latter case. The results shown in Table I would lead one to conclude that the same species is involved

Table I

Relative Reactivities of Olefins toward Phenyl(bromodichloromethyl)mercury and toward Sodium Trichloroacetate

Olefin A	k_A/k for C_6H_5-$HgCCl_2Br^{a,b,e}$	k_A/k for $CCl_3CO_2Na^{c-e}$	Overall yields of dichlorocyclopropanes for C_6H_5Hg-CCl_2Br reactions[g,i]	Overall yields of dichlorocyclopropanes for CCl_3-CO_2Na reactions[h]
$(CH_3)_2C=$				
$C(CH_3)C_2H_5$	22	24.8	94	87.7
$C_6H_5(CH_3)C=CH_2$	7.2	7.35	94	85.7
$(C_2H_5)_2C=CHCH_3$	3.54, 3.55[c]	3.52	93	80.9
n-$C_3H_7(CH_3)C=$				
CH_2	2.07	2.08	92	80.1
$C_6H_5CH=CH_2$	1.22	1.26	93	72.7
Cyclohexene	1.00	1.00		
cis-n-$C_3H_7CH=$				
CHC_2H_5	0.83	0.800[a]	85	49.7
$trans$-n-$C_3H_7CH=$				
CHC_2H_5	0.52, 0.51[c]	0.523	92	63.6
n-$C_5H_{11}CH=CH_2$	0.236	0.219	91	60.6
$Cl_2C=CHCl$	0.015[f]		85	

[a] Reaction time 3 hr at 80 ± 2°. [b] Solvent benzene. [c] Solvent 1,2-dimethoxyethane. [d] Reaction time 8 hr at 80 ± 2°. [e] Compared with cyclohexene; both in fivefold excess unless otherwise specified. [f] Olefins in sevenfold excess. [g] Per cent based on $C_6H_5HgCCl_2Br$. [h] Per cent based on CCl_3CO_2Na. [i] Yields of C_6H_5HgBr isolated: 95–97%.

in the product-forming step in both systems; the most reasonable intermediate common to both systems is free CCl_2.

This general picture was confirmed by means of a kinetic study.[68] The rate of the reaction between cyclooctene and $PhHgCCl_2Br$ at 39° in benzene (which gives 9,9-dichlorobicyclo[6.1.0]nonane and $PhHgBr$ in nearly quantitative yield) was followed by measuring the rate of consumption of the olefin, or the rate of formation of the cyclopropane product (the results were equivalent), by means of glc. Because the reaction becomes heterogenous relatively quickly, we confined ourselves to a study of the early stages of the reaction. A series of kinetic runs was carried out using different initial concentrations of $PhHgCCl_2Br$ and cyclooctene. A twofold change in the initial olefin concentration produced essentially no change in the reaction rate. On the other hand, the reaction rate was dependent on the initial $PhHgCCl_2Br$ concentration, an n-fold increase in the latter resulting in an approximately n-fold increase in reaction rate. These results suggested that the $PhHgCCl_2Br$–cyclooctene reaction is roughly first order in mercurial and zero order in olefin, *i.e.*, that the rate law $dx/dt = k_1[PhHgCCl_2Br]$ applies. If this is so, then the rate of consumption of any olefin should be the same for a given initial mercurial concentration. Experiments were carried out to test this idea using

(63) D. Seyferth, M. E. Gordon, and R. Damrauer, *J. Org. Chem.,* **32,** 469 (1967).

(64) W. E. Parham and J. R. Potoski, *Tetrahedron Lett.,* 2311 (1966).
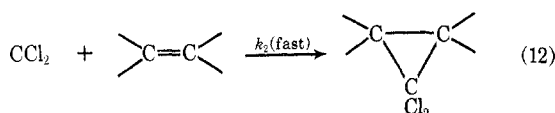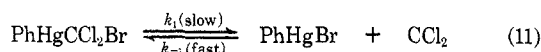
(65) P. S. Skell and M. S. Cholod, *J. Amer. Chem. Soc.,* **91,** 6035, 7131 (1969).

(66) G. Köbrich, H. Büttner, and E. Wagner, *Angew. Chem.,* **82,** 177 (1970).

(67) D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.,* **86,** 2730 (1964).

(68) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *ibid.,* **89,** 4953 (1967).

Me₂C=CMeEt (k_{rel} 18.4 vs. cyclooctene), cyclooctene, and 1-heptene (k_{rel} 0.184 vs. cyclooctene). The reaction rates under identical conditions were in the order of the olefin reactivities (dx/dt = 8.81 × 10⁻⁵, 7.01 × 10⁻⁵, and 3.20 × 10⁻⁵ mole l.⁻¹ min⁻¹, respectively). An explanation was provided by our finding that PhHgBr (within its solubility limits) is kinetically active in these reactions, i.e., that PhHgBr when initially present during PhHgCCl₂Br–olefin reactions retards the initial rates. In other words, the extrusion of CCl₂ from PhHgCCl₂Br is reversible: CCl₂ can insert into the Hg–Br bond of PhHgBr to regenerate PhHgCCl₂Br.[69] These results are nicely accommodated by reactions 11 and 12.

$$PhHgCCl_2Br \underset{k_{-1}(fast)}{\overset{k_1(slow)}{\rightleftharpoons}} PhHgBr + CCl_2 \qquad (11)$$

$$CCl_2 + \underset{}{\overset{}{>}}C=C\underset{}{\overset{}{<}} \xrightarrow{k_2(fast)} \underset{Cl_2}{>C\overset{\triangle}{-}C<} \qquad (12)$$

The value of k_2 will depend on electronic and steric factors in the olefin and so variation in the k_{-1}/k_2 ratio would serve to explain the observed variations of rate. The rate expression 13 may be derived for the mech-

$$dx/dt = \frac{k_1[PhHgCCl_2Br]}{1 + \dfrac{k_{-1}[PhHgBr]}{k_2[olefin]}} \qquad (13)$$

anism represented by eq 11 and 12. From our kinetic data the k_{-1}/k_2 ratio for cyclooctene could be calculated to be about 1.1. In other words, the reverse (Hg–Br insertion) reaction is as rapid as the product-forming reaction. The effect of added PhHgBr on the rate is, as expected, greatest for 1-heptene, less for cyclooctene, and barely perceptible for Me₂C=CMeEt. For Me₂C=CMeEt the rate was the same within experimental error for all olefin concentrations used (0.01–0.2 M), and this suggested that with this olefin we are observing the limiting reaction rate, ~8.8 × 10⁻⁵ mole l.⁻¹ min⁻¹. Further proof of the applicability of the rate equation 13 to the PhHgCCl₂Br–olefin reaction was obtained by demonstrating that it can be used to calculate dx/dt vs. time plots which are in good agreement with the experimentally determined curves.

The rate of the PhHgCCl₂Br–Me₂C=CMeEt reaction at 49.9° was found to be 33.3 × 10⁻⁵ mole l.⁻¹ min⁻¹ and at 60.4°, 108.5 × 10⁻⁵ mole l.⁻¹ min⁻¹. From the derived rate constants the following activation parameters were calculated: $\Delta G^{\ddagger}$ = 25.2 kcal/mole, $\Delta H^{\ddagger}$ = 24.3 kcal/mole, $\Delta S^{\ddagger}$ = −2.8 eu. The half-life of PhHgCCl₂Br in the presence of Me₂C=CMeEt at these temperatures was calculated: 13 hr at 39°; 3.4 hr at 49.9°; 63.2 min at 60.4°.

Further kinetic studies of the reactions of substituted

ArHgCCl₂Br compounds (Ar = p-ZC₆H₄, with Z = H, Cl, F, Me, MeO) with Me₂C=CMeEt in benzene at 39.0° showed that the rate of extrusion of CCl₂ from these mercurials differs only slightly as a function of Z.[70] We take this insensitivity to electronic factors as evidence in support of a concerted CCl₂ extrusion process proceeding via a cyclic transition state, II. Such
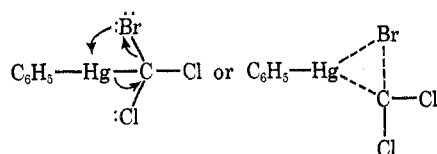
II

a picture provides a satisfactory explanation for the fact that PhHgBr elimination from a PhHgCX₃ compound is so much more facile than is PhHgCl elimination: intramolecular nucleophilic attack at Hg by Br should be more favorable than attack by Cl, and, also, the C–Br bond is weaker than the C–Cl bond.

More information concerning the CCl₂–olefin reaction was obtained in a study of reactions in which two different substituted styrenes were allowed to compete (at 80°) for a deficiency of PhHgCCl₂Br-derived CCl₂.[70] The following relative rate constants were obtained for these ZC₆H₄CH=CH₂ compounds: Z = p-Me, 1.52; H, 1.00; p-F, 0.96; p-Cl, 0.839; m-CF₃, 0.453. The data were found to correlate well with the Hammett equation and gave ρ = −0.619 ± 0.045 using σ^+ constants. This finding is what one would expect in terms of the picture of CX₂ attack at the C=C bond developed by Moore, et al.[71]

We emphasize that our finding that CCl₂ is an intermediate in the PhHgCCl₂Br–olefin reaction should not be generalized to all halomethylmercury systems. We believe that the mechanism described by eq 11 and 12 holds for the reactions of all PhHgCCl_nBr₃₋n (n = 0–3) and PhHgCCl₂F with olefins. However, our studies have shown that the reaction of Hg(CH₂Br)₂ with olefins (eq 14)[72] does not proceed via free CH₂. Thus

$$Hg(CH_2Br)_2 + \bigcirc \longrightarrow BrCH_2HgBr + \bigcirc\!\!\!\triangleright \qquad (14)$$
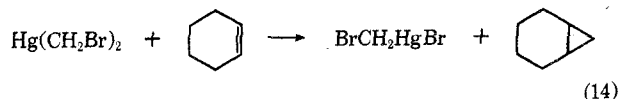
this mercurial is completely stable when heated in refluxing benzene for 20 days. Only in the presence of a CH₂ acceptor does decomposition of the mercurial take place. The initial concentration of the olefin was found to affect the rate of CH₂ transfer, and a very marked dependence of the CH₂ transfer rate on the structure of the olefin was observed. A kinetic study of the Hg(CH₂Br)₂–olefin reaction still must be carried out. The evidence presently available speaks strongly in favor of a mechanism involving a direct reaction be-

(69) Other research showed that PhHgCCl₂Br-derived CCl₂ can insert into the Hg–Cl bond to give the much more stable HgCCl₃ compounds. In this manner, p-MeC₆H₄HgCl was converted to p-MeC₆H₄HgCCl₃. Cf. D. Seyferth, M. E. Gordon, and K. V. Darragh, J. Organometal. Chem., 14, 43 (1968).

(70) D. Seyferth, J. Y.-P. Mui, and R. Damrauer, J. Amer. Chem. Soc., 90, 6182 (1968).

(71) W. R. Moore, W. R. Moser, and J. E. LaPrade, J. Org. Chem., 28, 2200 (1963).

(72) D. Seyferth, R. M. Turkel, M. A. Eisert, and L. J. Todd J. Amer. Chem. Soc., 91, 5027 (1969).

tween $Hg(CH_2Br)_2$ and the olefin. It would appear that the stability of the potential free divalent carbon species which would be released from a halomethylmercury compound is an important factor in determining whether or not a free carbene will be extruded.

However, not all reactions of $PhHgCCl_2Br$ and the other $PhHgCX_3$ compounds proceed by a free carbene mechanism. A free CCl_2 intermediate is involved in the reaction of $PhHgCCl_2Br$ with organosilicon hydrides (which gives $Si-CCl_2H$ compounds),[73] and very likely in CCl_2 insertion (via $PhHgCCl_2Br$) into the C–H bond. On the other hand, reactions of $PhHgCX_3$ compounds with substrates containing atoms with lone-pair electrons, especially nitrogen and phosphorus, are generally much more rapid than reactions with olefins, and the available evidence suggests that initial attack by nitrogen or phosphorus at mercury occurs more rapidly than dihalocarbene extrusion can take place.[68,74] It is quite possible, also, that addition of $PhHgCCl_2Br$-derived CCl_2 to the $C{=}N$,[75] $C{=}S$,[76] and $C{=}O$[77-79] bonds (to give, in many cases, the three-membered heterocycle) does not proceed via free CCl_2.

Concluding Remarks

The present discussion has dealt only with that aspect of halomethylmercury chemistry most generally useful in organic synthesis: the preparation of *gem*-dihalocyclopropanes[80] via $PhHgCX_3$ compounds. There are many other CX_2 transfer reactions (additions to other multiple bonds, insertions into single bonds) of $PhHgCX_3$ compounds which we have developed, and also some other reactions of these mercurials not involving CX_2 transfer. Among these are CX_2 addition to diarylacetylenes[81,82] and to $C{=}N$,[75] $C{=}S$,[76] and $C{=}O$[77,78] bonds, including (presumed) addition–fragmentation processes in reactions with $RN{=}C{=}NR$, $RN{=}C{=}S$, $RN{=}C{=}O$, and CS_2;[83] and insertions into the C–H bond,[35,38,48,84,85] the Si–H bond,[73,86,87] the Ge–H bond,[86] and Sn–Sn[88] Si–Hg, and Ge–Hg bonds,[87] the Sn–X bond,[89] and the B–C bond,[90] and into HCl.[91]

Noteworthy are CCl_2 insertions (via $PhHgCCl_2Br$) into Si–C and Ge–C bonds of silacyclobutane,[92] 1,3-disilacyclobutane,[92] and germacyclobutane[93] ring systems with consequent ring enlargement. Among miscellaneous $PhHgCX_3$ reactions are those with diazoalkanes $(R_2CN_2 \rightarrow R_2C{=}CX_2)$,[94] with trialkyl phosphites $(\rightarrow PhHgCX_2P(O)(OR)_2)$,[95] with tri-*n*-butyltin hydride $(\rightarrow PhHgCX_2H)$,[86] the one-pot Wittig reaction with triphenylphosphine and carbonyl compounds,[74] and deoxygenation of pyridine *N*-oxide.[96]

We and others have prepared useful halomethylmercury compounds other than the $PhHgCX_3$ discussed in this review. These include $Hg(CH_2Br)_2$ and ICH_2HgI,[73,97] $Hg(CH_2I)_2$,[98] $PhHgCHXY$ (X, Y = all combinations of Cl, Br, and I),[26,27] $PhHgCCl_2Ph$,[99] $PhHgCCl_2CH_3$,[100] $PhHgCCl_2CF_3$ and $PhHgCClBrCF_3$,[101] $PhHgCCl_2CO_2Me$ and $PhHgCBr_2CO_2Me$,[102] $PhHgCCl_2CH(OEt)_2$ and $PhHgCCl_2C(R)(ethylenedioxy)$ (R = H, CH_3, Ph),[103] $Hg(CCl_2SiMe_3)_2$ and $Hg(CBr_2SiMe_3)_2$;[104] and $PhHgCCl{=}CCl_2$.[105] All of these are divalent carbon transfer agents with the exception of the alkoxy-substituted 1,1-dichloroethylmercury compounds, whose derived carbenes rearrange more rapidly than they can add to a $C{=}C$ bond.[103]

We cannot discuss these other aspects of halomethylmercury chemistry mentioned so briefly above. However, from the mere listing of these other reactions of $PhHgCX_3$ compounds and the other available halomethylmercury compounds it should be apparent that the halomethylmercury reagents are a potentially large class of organometallic compounds with a very versatile and very useful divalent carbon transfer chemistry.[106]

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(106) NOTE ADDED IN PROOF. An important advance in the chemistry of halomethylmercury compounds not yet realized at the time this Account was written is our recent synthesis of highly reactive phenyl(trihalomethyl)mercury reagents which release dihalocarbenes at room temperature. These are $PhHgCCl_2I$ (CCl_2 transfer; instantaneous reaction at 80°, 24 hr reaction time at room temperature),[107] $PhHgCClBrI$ ($CClBr$ transfer; 3 min reaction time at 80°, 4 days at room temperature),[108] and $PhHgCBr_2F$ ($CFBr$ transfer; 20 min at 80°, 3 days at room temperature).[108] Also,

the scope of PhHgCCl₂Br reactions with olefins at room temperature has been studied with 14 examples, and PhHgCClBr₂ and PhHgCBr₃ also were found to transfer CClBr and CBr₂, respectively, at room temperature in good yield in 15–16-day reaction times.[109]

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Infrared Spectra of Chemisorbed Molecules

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If the surface chemistry of heterogeneous catalysis involves only factors which are found in conventional chemical systems, catalysis by metal surfaces may be viewed as another facet of metal–ligand coordination chemistry. Surface chemists would like to be able to utilize the vast amount of information which is available from studies of coordination chemistry. To do so would require knowledge of the nature of the functional groups in chemisorbed molecules, but this information has been difficult to obtain because the surface ligands comprise such a small fraction of the total sample. Techniques which provide infrared spectra of adsorbed molecules therefore constitute a major advance in studies of surface metal–ligand systems.

Some aspects of the infrared study of adsorbed molecules are as old as infrared spectroscopy. Spectra of adsorbed water were recognized in 1911 by Coblentz.[1] Subsequently, infrared spectroscopy was used quite extensively by mineralogists. Surface infrared spectra of many minerals were found to include bands attributable to adsorbed water and hydroxyl groups.[2] In retrospect, it is difficult to understand why the infrared work of mineralogists did not attract more attention among workers interested in the surface chemistry of catalysis. A probable contributory factor was the low level of interest in infrared spectroscopy in general because of the small number of instruments available. Commercial infrared apparatus was not common before 1945.

The first infrared study of chemisorbed molecules in our laboratory involved ammonia on silica–alumina cracking catalysts.[3] These catalysts are strong acids, and the question of interest was whether the acidity was protonic or of the Lewis type. It was expected that a protonic acid would chemisorb ammonia as NH_4^+, while the NH_3 configuration would be retained

for a Lewis acid. The spectra showed that Lewis acidity was predominant on a carefully dried sample; however, exposure of the Lewis sites to water produced protons. This approach to the study of surface acidity has been widely used. However, this subject is of rather specialized interest and will not be discussed in detail here.

In this Account I shall present examples of the use of infrared in surface chemistry which should be of interest to chemists who are not primarily concerned with catalysis. One example concerns the chemisorption of molecular nitrogen, the study of which has paralleled studies of molecular nitrogen as a ligand. A discussion of carbon monoxide on platinum will emphasize the variable of surface coverage. This variable has no exact counterpart in conventional coordination chemistry. The final example will illustrate how oxygen affects zinc oxide on which it is adsorbed.

Experimental Methods

The metal samples of greatest interest in catalysis are those in which small metal particles are dispersed on supports such as silica or alumina. Particle diameters are commonly in the range of 10–100 Å with 30 to 30,000 metal atoms in a particle. In the smaller particles almost all of the atoms are exposed surface atoms. About one-tenth of the atoms in a 100-Å particle are surface atoms. The supported-metal sample is most often prepared by impregnating the support with a salt of the metal and then reducing the salt with hydrogen at high temperatures. Samples prepared for infrared work usually have metal contents in the range of 2–9 wt % after reduction.

The spectra are obtained by transmission through the powder sample. Many designs of cells suitable for *in situ* infrared study have been used. Desirable design features are: sample temperature controllable over wide ranges both below and above room tempera-

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