Registry No.—*p*-Benzoquinone, 106-51-4; **1**, 24097-79-8; **3**, 24097-80-1; **4**, 24097-81-2; ketoquinol diacetate derivative of **4**, 24097-82-3; **5**, 24097-83-4; **6a**, 24215-68-7; **6b**, 24097-84-5; **7a**, 24097-85-6; **7b**, 24097-86-7; **8a**, 24097-87-8; **9**, 24097-88-9; **10**, 24097-89-0.

Halomethyl Metal Compounds. XXXII. Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into Carbon–Hydrogen Bonds. Alkanes and Alkylbenzenes[1]

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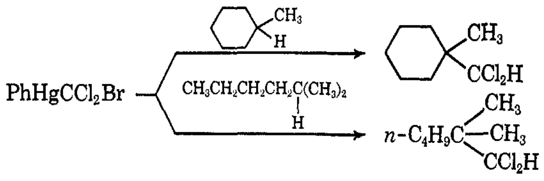
Phenyl(bromodichloromethyl)mercury has been found to insert CCl_2 into aliphatic C–H bonds. Most reactive in this reaction are tertiary C–H bonds; secondary C–H bonds are less reactive and no such insertion into methyl group C–H bonds was observed. The cases of 3-methylcyclohexene and *trans*-$Me_3SiCH{=}CHCHMe_2$ showed that a tertiary C–H bond can even compete for CCl_2 in some measure with a C=C bond. In the case of alkylbenzenes such as ethylbenzene and cumene, CCl_2 insertion occurred exclusively in the benzylic position. These reactions are of preparative utility. A mechanism involving a transition state (III) in which the carbon atom at which the C–H insertion is occurring bears a partial positive charge is suggested. The first case of an insertion of CBr_2 into a C–H bond (of ethylbenzene) is described.

The insertion of singlet state CH_2 into C–H bonds of of alkanes (→ C–CH_3 groups) is a well-known reaction,[6] but in 1962 an analogous insertion of a dihalocarbene into any kind of a C–H bond had not yet been encountered. During our early work on the CX_2 transfer reactions of phenyl(trihalomethyl)mercury compounds,[7] we sought to study the thermolysis of $PhHgCCl_2Br$ and $PhHgCCl_3$ in an inert medium. In view of the apparent lack of reactivity of CCl_2 derived from other sources toward C–H linkages, *n*-heptane was chosen as the "inert" medium. When phenyl(trichloromethyl)mercury was heated at reflux in *n*-heptane solution under nitrogen, phenylmercuric chloride precipitated (*ca.* 80% yield), and one of the volatile products obtained in very low yield upon work-up of the filtrate (glpc) was found by combustion analysis to have the empirical formula $C_8H_{16}Cl_2$, *i.e.*, (C_7H_{16} + CCl_2), an insertion product of CCl_2 into heptane. Because several isomeric (dichloromethyl)heptanes were possible, it was decided to study this novel reaction with a simpler substrate, cyclohexane. The decomposition of phenyl(bromodichloromethyl)mercury in refluxing cyclohexane during 3 hr gave phenylmercuric bromide (77%), tetrachloroethylene[8] (26%), cyclohexyl bromide (22%, based on available bromine), and a new compound identified by analysis and its nmr and ir spectra as (dichloromethyl)cyclohexane (32%). Dichlorocarbene insertion into a completely unactivated C–H bond in a preparatively useful yield was unprecedented and most surprising. Clearly, further studies were called for.

The unactivated secondary C–H bond is very low on the scale of reactivity toward CCl_2. Under the usual conditions which serve in the high yield dichlorocyclopropanation of olefins (3 mol of substrate to 1 mol of $PhHgCCl_2Br$ in benzene solution at 80°), the reaction of phenyl(bromodichloromethyl)mercury with cyclohexane proceeded very poorly, (dichloromethyl)cyclohexane being obtained in only trace yield. However, tertiary aliphatic C–H bonds were found to be more reactive. Thus, under these standard reaction conditions $PhHgCCl_2Br$ served to convert methylcyclohexane to 1-methyl-1-(dichloromethyl)cyclohexane in 15% yield and 2-methylhexane to 1,1-dichloro-2,2-dimethylhexane in 20% yield (eq 1). In neither case



(1)

was any insertion into CH_2 or CH_3 groups observed; insertion into the methine C–H appeared to be the exclusive process. These limited data suggest a reactivity sequence for aliphatic C–H bonds in the order tertiary C–H > secondary C–H > primary C–H. Indirect confirmation for this was provided in experiments with cyclohexene and 3-methylcyclohexene. In the case of the former, reaction with $PhHgCCl_2Br$ at 80° gave 7,7-dichloronorcarane as the sole product (eq 2),[9] but with 3-methylcyclohexene, where a tertiary C–H bond is available to compete with the C=C bond for CCl_2, both C=C addition and C–H insertion were

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[1] (a) Part XXXI: D. Seyferth and K. V. Darragh, *J. Org. Chem.*, **70**, 1297 (1970). (b) preliminary communication: D. Seyferth and J. M. Burlitch, *J. Amer. Chem. Soc.*, **85**, 2667 (1963).

[2] National Institutes of Health Postdoctoral Fellow, 1964–1965.

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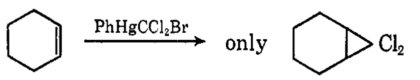
[5] Postdoctoral Research Associate, 1967–1968.

[6] (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, Chapter 2; (b) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, Chapter 2; (c) D. F. Ring and B. S. Rabinovitch, *Can. J. Chem.*, **46**, 2435 (1968), and earlier references cited therein.

[7] First report: D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

[8] Tetrachloroethylene is the product of decomposition of $PhHgCCl_2X$ (X = Cl or Br) in the absence of substrate capable of trapping dichlorocarbene and usually is found in low to moderate yield in reactions where the substrate is only poorly reactive toward CCl_2.[9]

[9] 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).



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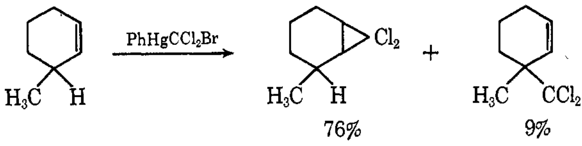
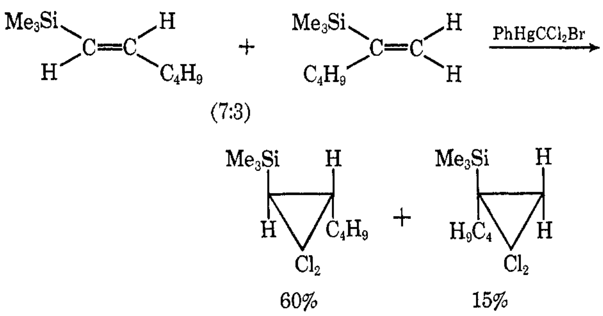


(3)

observed (eq 3).[10] A similar observation was made with vinylic silanes of the type $Me_3SiCH{=}CHR$. A mixture of *cis*- and *trans*-propenyltrimethylsilane gave only the expected C=C addition products,[9] as did a mixture of *trans*-$Me_3SiCH{=}CHC_4H_9$-*n* and $Me_3Si(n\text{-}C_4H_9)C{=}CH_2$ (eq 4). In contrast, the tertiary



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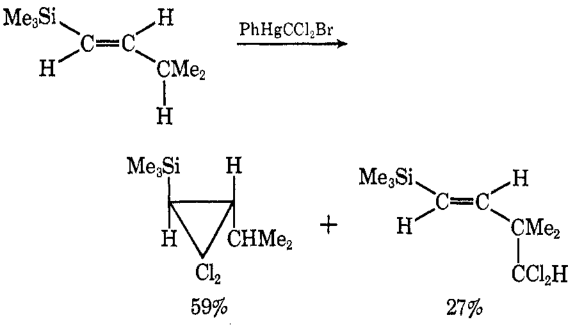
C–H bond of *trans*-$Me_3SiCH{=}CHCHMe_2$ competed effectively with the rather unreactive[12] Me_3Si-substituted C=C bond (eq 5). This tertiary C–H bond is also allylic and, hence, should be more reactive than that of 2-methylhexane.[9]



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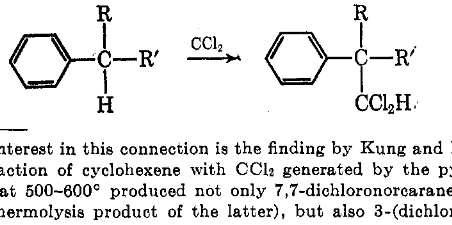
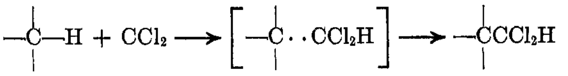
We were diverted from our intention of continuing studies of purely aliphatic systems by the report of Fields[13] that dichlorocarbene (generated *via* sodium trichloroacetate pyrolysis in 1,2-dimethoxyethane) inserted very specifically into benzylic C–H bonds of alkylbenzenes such as ethylbenzene, cumene, *p*-diisopropylbenzene, tetralin, and diphenylmethane (eq 6). The yields ranged from 17 to 39%. It was noteworthy that only minute yields of such insertion products were obtained when the low-temperature $CHCl_3$–*t*-BuOK and CCl_3CO_2Et–NaOMe CCl_2-generating systems were used.[13] Fields commented that it appeared that the additional thermal energy associated with the sodium trichloroacetate procedure (80–85° reaction temperature) was an important factor and suggested that the CCl_2 insertion reaction mechanism may not be identical with the "normal" carbene insertion mechanism, *i.e.* that of CH_2 into C–H bonds.



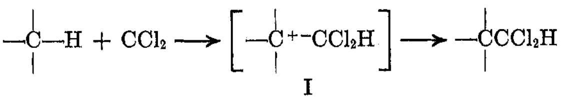
(6)

It was, of course, of interest to study analogous reactions with phenyl(bromodichloromethyl)mercury for purposes of comparison, and we have carried out a brief investigation of the thermolysis of this mercurial in ethylbenzene and in cumene to see if results similar to those of Fields would be obtained. Such was the case, except that our yields of $PhCH(Me)CCl_2H$ and $PhCMe_2CCl_2H$, 35 and 58%, respectively, were approximately double those reported for the sodium trichloroacetate procedure. In the case of the reaction with cumene, two by-products, tetrachloroethylene (4%) and 1,1-dichloro-2-methyl-2-phenylcyclopropane (2%), were identified. Since the cumene used had been rigorously purified of olefins before use, the presence of the latter by-product may be indicative of a free-radical side reaction.[14] An example of the insertion of a CBr_2 moiety into a benzylic C–H linkage was provided by the decomposition of $PhHgCBr_3$ in ethylbenzene at 85°. β,β-Dibromoisopropylbenzene was obtained in 6.5% yield. The low yield probably is not a good indication of the efficiency of the reaction since the isolation and purification of the unstable, high-boiling product proved to be difficult.[15]

We shall defer a more detailed discussion of the mechanism of the insertion of dichlorocarbene into C–H bonds until a later paper of this series. The reactivity sequence observed (tertiary C–H > secondary C–H ≫ primary C–H), as well as the activation by adjacent phenyl groups may be rationalized in terms of either a radical process (eq 7) or a polar process in which a significant partial positive charge is placed on the carbon atom into whose bond to hydrogen the CCl_2 insertion is taking place (eq 8 shows the ionic extreme). To date no evidence for the occurrence of CCl_2 in the diradical triplet state has been reported, and in its well-developed chemistry there has been no indication of radical reactions; all of the reactions of CCl_2 are best rationalized in terms of a singlet configuration.[16] Thus a polar process such as that shown in its extreme ion pair form (I) in eq 8 would be more in agreement with the known reactivity of CCl_2. It is our



$$-\overset{|}{\underset{|}{C}}-H + CCl_2 \longrightarrow \left[-\overset{|}{\underset{|}{C}}\cdot\cdot CCl_2H\right] \longrightarrow -\overset{|}{\underset{|}{C}}CCl_2H \qquad (7)$$



$$-\overset{|}{\underset{|}{C}}-H + CCl_2 \longrightarrow \underset{\text{I}}{\left[-\overset{|}{\underset{|}{C}}{}^{+}{}^{-}CCl_2H\right]} \longrightarrow -\overset{|}{\underset{|}{C}}CCl_2H \qquad (8)$$

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[10] Of interest in this connection is the finding by Kung and Bissinger[11] that the reaction of cyclohexene with CCl_2 generated by the pyrolysis of chloroform at 500–600° produced not only 7,7-dichloronorcarane (and toluene, the thermolysis product of the latter), but also 3-(dichloromethyl)-cyclohexene. Thus the C–H insertion chemistry of dichlorocarbene may depend heavily on thermal activation. Our discussion in this paper is restricted to reactions carried out at 80° or below.

[11] F. E. Kung and W. E. Bissinger, *J. Org. Chem.*, **29**, 2739 (1964).

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

[13] E. K. Fields, *J. Amer. Chem. Soc.*, **84**, 1744 (1962).

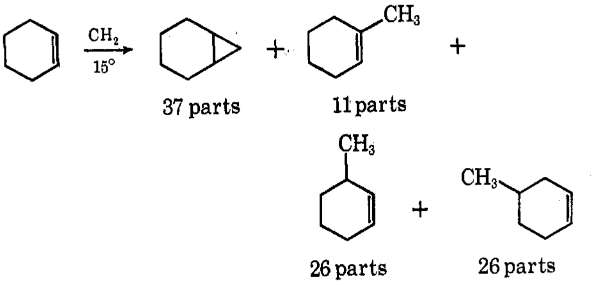
[14] It has been shown that α-methylstyrene (from which the observed cyclopropane must be derived) as well as bicumyl are produced in the irradiation of phenanthraquinone in cumene: R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 3405 (1953).

[15] Our recent report of the insertion of $PhHgCClBr_2$-derived CClBr into the benzylic C–H bond of cumene in 53% yield also should be noted: D. Seyferth, S. P. Hopper, and T. F. Jula, *J. Organometal. Chem.*, **17**, 193 (1969).

[16] Reference 6a, Chapter 8; ref 6b, Chapter 3.

belief that the formation of by-products such as cyclohexyl bromide in the case of the $PhHgCCl_2Br$–cyclohexane reaction and 1,1-dichloro-1-methyl-1-phenylcyclopropane in the $PhHgCCl_2Br$–cumene reaction results from radical side reactions and that their formation is in no way indicative of the mechanism of the insertion of CCl_2 into the C–H bond.

In the reactions under discussion CCl_2 is much more selective than CH_2 in comparable reactions.[17,18] For instance, in the case of cyclohexene, CH_2 (from liquid phase CH_2N_2 photolysis) not only added to the C=C bond but also inserted into all possible C–H bonds (eq 9). With 2,3-dimethylbutane, CH_2 insertion appeared to be nearly random with respect to available primary and tertiary C–H bonds (eq 10). Subsequent work by Doering and Prinzbach[19] suggested that such CH_2 insertion into C–H bonds involved a direct insertion process (transition state II). Our results with CCl_2 are in marked contrast to those found with CH_2, and we believe that the selectivity of CCl_2 observed in these reactions is most reasonably accommodated by a transition state in which there is some development of charge (III). This transition state is analogous to the one we suggested for CCl_2 insertion into the Si–H bond on the basis of the results of a previous study.[20]



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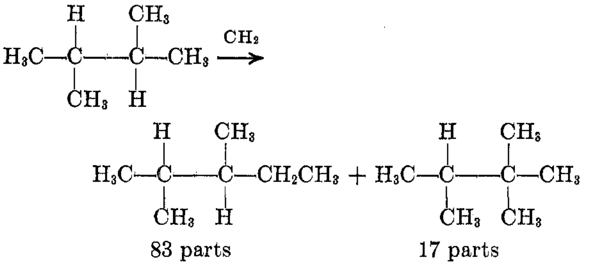

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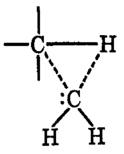

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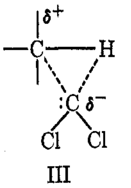

III

A crude estimate of the relative reactivity of an allylic tertiary C–H bond (*vs.* 1-heptene) can be obtained from the results shown in eq 5. Here the total yield of products was 86%, so that the relative yields of the two products obtained can serve, as a first approximation, as a measure of the relative reactivity of the C=C bond and the tertiary C–H bond in the reactant, *trans*-$Me_3SiCH{=}CHCHMe_2$. This value, $k(C—H)/k(C{=}C)$, is 0.46. The relative reactivity *vs.* 1-heptene of the unsubstituted vinyl group attached to silicon in the compound $Me_2EtSiCH{=}CH_2$ toward CCl_2 at 80° is 0.069;[21] so the relative reactivity of the tertiary C–H of *trans*-$Me_3SiCH{=}CHCHMe_2$ would be in the order of 0.03 on that scale. We are assuming that the trimethylsilyl group has no effect on the reactivity of the C–H bond in the γ position; this, however, may not be the case. It is thus understandable why essentially no C–H insertion chemistry is observed with CX_2 generating systems in which a trihalomethide ion source is treated with an alkali metal alkoxide. In such systems the side reactions occurring between the CX_2 and the reagent used in its generation (or the products derived therefrom) become the main processes when the substrate used as CX_2 trap is rather unreactive. The present study thus offers another example of the unique applicability of the phenyl(trihalomethyl)mercury reagents in the study of reactions of dihalocarbenes with poorly reactive substrates.

Experimental Section

General Comments.—All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Infrared spectra were recorded using a Baird Model B or Perkin-Elmer Infracord 237 or 337 spectrophotometers. Nmr spectra were obtained using a Varian Associates A-60 or T-60 spectrometer. Chemical shifts are given in δ units, parts per million downfield from internal TMS. Thin layer chromatographic analysis of reaction mixtures for organomercury compounds was performed as described in a previous paper of this series.[22] Gas–liquid partition chromatography (glpc) was carried out using MIT isothermal units and F & M temperature-programmed gas chromatographs. The columns were packed with 25% General Electric Co. SE-30 silicone rubber gum on Johns Manville Chromosorb W or P, Dow Corning 710 silicone oil on Chromosorb P, or Dow Corning DC 200 silicone oil on Chromosorb P unless otherwise noted. The internal standard method was used in glpc yield determination.

Phenyl(bromodichloromethyl)mercury, phenyl(tribromomethyl)mercury, and phenyl(trichloromethyl)mercury were prepared as described by us previously;[22,23] the preferred procedure is that given in ref 23.

Preparation of Starting Organosilicon Olefins. (a) ***trans*-1-Trimethylsilyl-3-methyl-1-butene.**—A mixture of 6.12 g (0.09 mol) of 3-methyl-1-butyne (Farchan Research Laboratories), 9.0 ml (at −78°) (*ca.* 0.09 mol) of trimethylsilane, and 20 μl of a solution of chloroplatinic acid in 2-propanol (1 g in 5 ml) was sealed in a bomb tube under a nitrogen atmosphere and kept for 2 days at room temperature. The reaction mixture then was filtered from some black solid and distilled at reduced pressure to give 9.92 g (78%) of the monoaddition product [bp 56° (65 mm), $n^{25}D$ 1.4166; lit.[24] bp 124-125°, $n^{20}D$ 1.4180] as well as 0.6 g of material of bp *ca.* 40° (0.6 mm), presumably the diaddition product. Glpc analysis of the monoaddition product (General Electric Co. XF-1112 on Chromosorb W at 100°) showed that two components were present; the peak area ratios were 87:13. An nmr spectrum in CCl_4 of the monoaddition

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(17) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Amer. Chem. Soc.*, **78**, 3224 (1956).

(18) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **82**, 5001 (1960); **83**, 1934 (1961).

(19) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(20) D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, **90**, 2944 (1968).

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

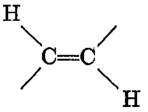
(22) D. Seyferth and J. M. Burlitch, *ibid.*, **4**, 127 (1965).

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

(24) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, **83**, 4385 (1961).

product confirmed this: two different Me_3Si resonances were observed at δ 0.10 and 0.15 ppm, with peak area ratio of 86:14. The pure components were isolated by preparative glpc.

The major component was *trans*-1-trimethylsilyl-3-methyl-1-butene: $n^{25}D$ 1.4156; nmr (neat) δ 6.30–5.41 [six lines, the AB part of an ABX spectrum, J (a) = 18 Hz, J (b) = 5 Hz], 2.33 (1 H, Me_2CH–) m, 1.04 [6 H, $(CH_3)_2C$] d (J = 6.8 Hz), 0.10 ppm (9 H, Me_3Si) s.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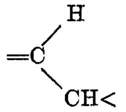
b

Anal. Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.75. Found: C, 67.27; H, 12.57.

The minor component was not obtained in analytical purity: nmr (neat) δ 5.71 (1 H, =CH *trans* to *i*-Pr) double d, 5.42 (1 H, =CH *cis* to *i*-Pr) d (J = 2.4 Hz), 2.49 (1 H, Me_2CH–) m, 1.08 [6 H, $(CH_3)_2C$] d (J = 7.0 Hz), 0.15 ppm (9 H, Me_3Si) s.

Anal. Calcd for $C_8H_{18}Si$: C, 67.51; H, 12.75. Found: C, 68.69; H, 12.96.

(b) **Hydrosilation of 1-Hexyne with Methyldichlorosilane.**—To a mixture of 14.8 g (0.18 mol) of freshly distilled 1-hexyne (Farchan), 40 μl of chloroplatinic acid solution, and 2 ml of dry benzene was added 17.3 g (0.15 mol) of $MeSiHCl_2$ dropwise during 1.5 hr. An exothermic reaction commenced within 30 min. The reaction mixture was heated at 85° for 7.5 hr after the addition had been completed and then was added to 220 ml of 1.58 *M* methyllithium in ether (0.34 mol), slowly, with adequate cooling and stirring. The resulting mixture was heated at reflux for 3 hr and then hydrolyzed with 200 ml of water. Fractional distillation of the dried organic phase gave 17.86 g (80%) of the monoaddition product [bp 48–48.5° (13 mm), $n^{25}D$ 1.4248; lit.[24] bp 60° (20 mm), $n^{20}D$ 1.4260].

Anal. Calcd for $C_9H_{20}Si$: C, 69.14; H, 12.89. Found: C, 69.28; H, 12.79.

Glpc analysis of this product using three different columns (Dow Corning DC 200 silicone fluid at 100°, Carbowax 20M at 100°, General Electric Co. XF 1112 at 120°) suggested that only one component was present. The nmr spectrum, however, indicated the presence of a mixture, showing two different Me_3Si resonances at δ 0.12 and 0.16 ppm in area ratio 70:30. Signals at δ 5.59 and 5.34 characteristic of $=CH_2$ protons indicate that the component present in lesser amount is 2-trimethylsilyl-1-hexene, $Me_3Si(n\text{-}C_4H_9)C=CH_2$.

Insertion Reactions of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbenene. General Procedure.—A three-necked flask of appropriate volume equipped with a reflux condenser topped with an inert gas inlet tube, a magnetic stirring unit, and a thermometer was charged with the mercurial, the substrate, and, in some cases, benzene solvent. The mixture was stirred and heated at reflux in an oil bath maintained at 85–90°, generally for 2.5–3 hr. Initially, the mercurial dissolved as the reaction mixture was heated, and a short time thereafter phenylmercuric bromide began to precipitate. Upon completion of the reaction, the mixture was filtered to remove phenylmercuric bromide (usually formed in above 90% yield). The filtrate was trap-to-trap distilled under vacuum (0.05–0.1 mm) into a receiver cooled to −78°. Glpc analysis of the filtrate usually followed, but, when reactions were carried out on a larger scale, the products were isolated by fractional distillation in vacuum.

Reaction of $PhHgCCl_2Br$ with Cyclohexane.—Thermolysis of 88 g (0.2 mol) of the mercurial was carried out in 275 ml of cyclohexane which was distilled directly into the reaction flask from potassium under argon. Glpc analysis of the trap-to-trap distillate showed the presence of three major components: tetrachloroethylene (26%), cyclohexyl bromide (22%), and (dichloromethyl)cyclohexane (32%) (*n*-butyrophenone internal standard). The first two products were identified by comparison of their glpc retention times and their ir spectra with those of authentic samples. (Dichloromethyl)cyclohexane, $n^{25}D$ 1.4835, showed the following absorptions in its infrared spectrum: 2939 s, 2860 s, 1450 s, 1365 m, 1331 w, 1308 m, 1298 m, 1254 m, 1238 s, 1218 s, 1175 w, 1140 w, 1090 m, 1080 m, 1062 m, 1040 m, 963 s, 927 w, 920 w, 896 m, 885 m, 788 m, 740 s, and 676 s cm^{-1}. Its nmr spectrum showed the following resonances: δ 5.60 (1 H, $-CCl_2H$) d (J = 4.0 Hz), multiplet (11 H) containing two broad resonances at 1.87 and 1.25 ppm.

Anal. Calcd for $C_7H_{12}Cl_2$: C, 50.31; H, 7.24; Cl, 42.44. Found: C, 50.03, 50.31; H, 7.23, 7.47; Cl, 42.29.

The isolated phenylmercuric bromide (77%) was gray in color, which suggests the formation of a minor amount of elemental mercury.

A similar reaction carried out with phenyl(trichloromethyl)mercury (5 days at reflux) gave tetrachloroethylene, cyclohexyl chloride, and (dichloromethyl)cyclohexane in yields of 10, 4, and 16%, respectively.

Reaction of $PhHgCCl_2Br$ with Methylcyclohexane.—A solution containing 4.45 g (10.2 mmol) of the mercurial, 2.91 g (32.8 mmol) of methylcyclohexane, and 15 ml of dry benzene under nitrogen was used. The filtrate was trap-to-trap distilled under vacuum and then fractionally distilled to give 0.27 g of distillate at 90–95° (5 mm). Glpc (General Electric Co. XF 1150) showed that the latter contained a single component; the yield was 14.6%. An analytical sample was isolated by glpc.

Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.02; H, 7.79; Cl, 39.15. Found: C, 53.20; H, 7.80; Cl, 39.31.

The nmr spectrum confirmed that the product was 1-methyl-1-(dichloromethyl)cyclohexane: the $-CCl_2H$ resonance appeared as a singlet at δ 5.54 ppm, and the ring protons and the CH_3 protons were seen as a broad resonance from 0.7 to 1.6 ppm. The $n^{25}D$ was 1.4876.

Reaction of $PhHgCCl_2Br$ with 2-Methylhexane.—A mixture of 6.60 g (15 mmol) of the mercurial and 4.50 g (45 mmol) of 2-methylhexane (Chemical Samples Co.) was used. Fractional distillation of the filtrate gave 1.47 g of 2-methylhexane and 1.06 g of a higher boiling fraction which glpc showed to be *ca.* 90% pure. A yield determination by glpc (20% UC-W98 at 120°) established that the product, 1,1-dichloro-2,2-dimethylhexane, had been formed in 31% yield. An analytical sample, $n^{25}D$ 1.4528, was isolated by glpc: nmr (in CCl_4) δ 5.62 (1 H, $-CCl_2H$) s, 1.43 [6 H, $-(CH_2)_3-$] m, 1.10 [6 H, $(CH_3)_2C-$] s, 0.96 ppm (3 H, CH_3CH_2-) t (J = 7 Hz).

Anal. Calcd for $C_8H_{16}Cl_2$: C, 52.47; H, 8.81; Cl, 38.72. Found: C, 52.53; H, 8.67; Cl, 39.03.

A reaction carried out with 10 mmol of mercurial and 30 mmol of the hydrocarbon in 15 ml of benzene gave this product in 20% yield.

Reaction of $PhHgCCl_2Br$ with 3-Methylcyclohexene.—A mixture of 10 mmol of the mercurial and 30 mmol of the olefin (no solvent) was used. The filtrate was trap-to-trap distilled in vacuum. Analysis of the distillate by glpc (20% Carbowax 20M) showed the presence of two products in 8.2:1 area ratio. The major product, $n^{25}D$ 1.4938, was identified as 7,7-dichloro-2-methylnorcarane: nmr (in CCl_4) δ 1.21 (3 H, CH_3–) d (J = 6.2 Hz), 0.6–2.2 ppm (9 H) complex multiplet.

Anal. Calcd for $C_8H_{12}Cl_2$: C, 53.65; H, 6.75; Cl, 39.60. Found: C, 53.87; H, 6.74; Cl, 39.57.

The minor product was identified as 3-methyl-3-(dichloromethyl)cyclohexene: nmr (neat) δ 5.3–5.9 (2 H, $-CH=CH-$) m, 5.56 (1 H, CCl_2H) s, 0.8–2.2 [6 H, $-(CH_2)_3-$] m, 1.08 ppm (3 H, CH_3) s.

Anal. Found: C, 53.37; H, 6.54.

A yield determination (*n*-undecane internal standard) showed the yields of addition and insertion product to be 76 and 9%, respectively.

Reaction of $PhHgCCl_2Br$ with 1-Trimethylsilyl-3-methyl-1-butene.—The olefin was contaminated with *ca.* 16% 2-trimethylsilyl-3-methyl-1-butene. The reaction was carried out on the same scale using the same procedure. Glpc analysis (20% Carbowax 20M) of the distillate showed the presence of two major products (minor products due to the contaminating isomeric silane were not examined).

The major product (59% yield) was *trans*-1,1-dichloro-2-trimethylsilyl-3-isopropylcyclopropane: $n^{25}D$ 1.4519; nmr (CCl_4) δ 0.9–1.4 (8 H) broad multiplet and a set of four sharp resonances, 0.3 (1 H, Me_3Si–C–H) m, 0.12 ppm (9 H, Me_3Si) s.

Anal. Calcd for $C_9H_{18}Cl_2Si$: C, 47.99; H, 8.06. Found: C, 48.01; H, 8.00.

The minor product (27% yield) was *trans*-1-trimethylsilyl-3,3-dimethyl-4,4-dichloro-1-butene: $n^{25}D$ 1.4645; nmr (in CCl_4) δ 6.10 (1 H, =CH *cis* to Me_3Si) d (J = 19.2 Hz), 5.82 (1 H, $=CHSiMe_3$) d (J = 19.2 Hz), 5.56 (1 H, CCl_2H) s, 1.24 [6 H, $(CH_3)_2C$] s, 0.10 ppm (9 H, Me_3Si) s.

Anal. Found: C, 48.21; H, 8.19.

Reaction of $PhHgCCl_2Br$ with 70:30 Mixture of *trans*-1-Trimethylsilyl-1-hexene and 2-Trimethylsilyl-1-hexene.—The reaction was carried out on the same scale using the same procedure.

Glpc analysis (20% Carbowax 20M) showed the presence of two products in 4:1 ratio based on glpc peak areas. The total yield was 75%.

The major product was *trans*-1,1-dichloro-2-trimethylsilyl-3-*n*-butylcyclopropane: nmr (in CCl_4) δ 1.8–0.8 (10 H), two broad resonances, 0.24 (1 H, Me_3SiCH) m, 0.16 ppm (9 H, Me_3Si) s.

Anal. Calcd for $C_{10}H_{20}Cl_2Si$: C, 50.20; H, 8.43; Cl, 29.63 Found: C, 50.53; H, 8.39; Cl, 29.42.

The minor product was 1,1-dichloro-2-trimethylsilyl-2-*n*-butylcyclopropane: nmr (neat) δ 2.0–0.8 (11 H) m, 0.20 ppm (9 H, Me_3Si) s.

Anal. Found: C, 50.04; H, 8.22; Cl, 29.37.

Reaction of $PhHgCCl_2Br$ with Ethylbenzene.—A mixture of 44.0 g (0.1 mol) of the mercurial in 150 ml of freshly distilled ethylbenzene was used. Glpc analysis of the filtrate at 200° detected only one higher boiling component. Trap-to-trap distillation at 0.1 mm (pot temperature to 95°) gave a clear distillate and 2.6 g of black residue. Glpc examination of the former showed the presence of β,β-dichloroisopropylbenzene in 35% yield. Fractional distillation gave 4.81 g of this product: bp 63–65° (0.85 mm); $n^{25}D$ 1.5374 (lit.[13] bp 57° (0.4 mm); $n^{20}D$ 1.5351); nmr (CCl_4) δ 7.29 (5 H, C_6H_5) s, 5.80 (1 H, CCl_2H) d ($J = 5.0$ Hz), 3.39 (1 H, PhCH) octet, 1.52 ppm (3 H, CH_3) d ($J = 7.5$ Hz).

Anal. Calcd for $C_9H_{10}Cl_2$: C, 57.16; H, 5.33; Cl, 37.50. Found: C, 57.26; H, 5.23; Cl, 37.28.

A similar experiment in which much greater care was taken to exclude air and in which the ethylbenzene was distilled from potassium benzophenone ketyl gave this product in 37% yield. On the other hand, a reaction of 0.01 mol of the mercurial with 0.05 mol of ethylbenzene in 75 ml of benzene at reflux for 2 hr gave the expected product in only 5% yield, as well as tetrachloroethylene in 4.4% yield.

Reaction of $PhHgCCl_2Br$ with Cumene (Isopropylbenzene).—A suspension of the mercurial (0.2 mol) in 300 ml of cumene under argon was used. Color changes from light yellow to dark orange occurred. Filtration gave phenylmercuric bromide in 96% yield. Trap-to-trap distillation of the filtrate in two fractions, (at 0.5 mm, 35°; and at 0.005 mm, 85°) was followed by glpc analysis of the latter (*n*-butyrophenone internal standard). It was found that β,β-dichloro-*t*-butylbenzene was present in 58% yield. Also present were tetrachloroethylene (4%) and 1,1-dichloro-2-methyl-2-phenylcyclopropane[9] (2%). The distillate was fractionally distilled to give 18.7 g (46%) of β,β-dichloro-*t*-butylbenzene: bp 80–84° (1.5 mm); $n^{25}D$ 1.5400 (lit.[13] bp 68–70° (3 mm), $n^{20}D$ 1.5400); nmr (in CCl_4) δ 7.38 (5 H, C_6H_5) s, 5.98 (1 H, CCl_2H) s, 1.53 ppm [6 H, $C(CH_3)_2$] s.

A similar experiment carried out at 70° for 2 hr gave the insertion product in 54% yield.

Reaction of $PhHgCBr_3$ with Ethylbenzene.—A mixture of 52.95 g (0.1 mol) of the mercurial and 175 ml of ethylbenzene was used. By cooling the dark orange filtrate, the precipitation of 7.8 g of brown solid could be effected. Solvent was removed from the filtrate at 0.1 mm and short-path distillation of the residue at 0.07 mm gave 3.15 g of a viscous liquid containing a small amount of white solid; the maximum pot temperature was 140°. Glpc analysis of the distillate (25% SE-30, short column) showed that β,β-dibromoisopropylbenzene (6.5% yield) was present. A pure sample, $n^{25}D$ 1.5867, was collected by glpc: nmr (in CCl_4) δ 7.34 (5 H, C_6H_5) d, 5.88 (1 H, CBr_2H) d ($J = 4.5$ Hz), 3.52 (1 H, PhCH) m, 1.60 ppm (3 H, CH_3) d ($J = 7.0$ Hz).

Anal. Calcd for $C_9H_{10}Br_2$: C, 38.87; H, 3.62; Br, 57.49. Found: C, 39.05; H, 3.71; Br, 57.54.

Registry No.—Phenyl(bromodichloromethyl)mercury, 3294-58-4; *trans*-1-trimethylsilyl-3-methyl-1-butene, 24099-72-7; (dichloromethyl)cyclohexane, 24099-71-6; 1-methyl-1-(dichloromethyl)cyclohexane, 24147-13-5; 1,1-dichloro-2,2-dimethylhexane, 24099-19-2; 7,7-dichloro-2-methylnorcarane, 24099-20-5; 3-methyl-3-(dichloromethyl)cyclohexane, 24099-21-6; *trans*-1,1-dichloro-2-trimethylsilyl-3-isopropylcyclopropane, 24099-73-8; *trans*-1-trimethylsilyl-3,3-dimethyl-4,4-dichloro-1-butene, 24099-74-9; *trans*-1,1-dichloro-2-trimethylsilyl-3-*n*-butylcyclopropane, 24099-75-0; 1,1-dichloro-2-trimethylsilyl-2-*n*-butylcyclopropane, 24099-22-7; β,β-dibromoisopropylbenzene, 24162-41-2.

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Halomethyl Metal Compounds. XXXIII. The Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into Carbon–Hydrogen Bonds. Ethers[1]

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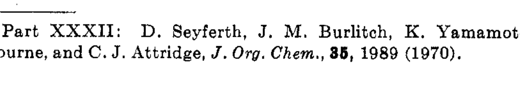
The known insertion of dichlorocarbene into C–H bonds α to the oxygen atom in ethers has received further study using phenyl(bromodichloromethyl)mercury as the dichlorocarbene source. Results are reported for 13 ethers. For C–H bonds α to ether oxygen, the relative reactivity toward CCl_2 was found to be tertiary > secondary, and no insertion was observed at OCH_3 C–H linkages. In over half of the examples cited the insertion product yields were in the preparatively useful range (>40%): diethyl ether, di-*n*-propyl ether, isopropyl methyl ether, benzyl methyl ether, tetrahydrofuran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran.

The insertion of a carbene, CH_2 itself, into a C–H bond of an ether was reported first by Meerwein and his coworkers[3] in 1942 (eq 1 and 2). Subsequent studies by other workers[4–6] have been devoted to obtaining a better understanding of such reactions. An analogous insertion chemistry of dichlorocarbene was developed by Anderson, Lindsay, and Reese,[7]

$$CH_3CH_2OCH_2CH_3 \xrightarrow{CH_2N_2,\ uv} C_2H_5OCH_2CH_2CH_3 + C_2H_5OCH(CH_3)_2 \quad (1)$$



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