

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 CCl₄) δ 1.8–0.8 (10 H), two broad resonances, 0.24 (1 H, Me₃SiCH) m, 0.16 ppm (9 H, Me₃Si) s.

Anal. Calcd for C₁₀H₂₀Cl₂Si: 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, Me₃Si) s.

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

Reaction of PhHgCCl₂Br 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_D²⁰ 1.5374 (lit.¹³ bp 57° (0.4 mm); n_D²⁰ 1.5351); nmr (CCl₄) δ 7.29 (5 H, C₆H₅) s, 5.80 (1 H, CCl₂H) d (*J* = 5.0 Hz), 3.39 (1 H, PhCH) octet, 1.52 ppm (3 H, CH₃) d (*J* = 7.5 Hz).

Anal. Calcd for C₉H₁₀Cl₂: 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 PhHgCCl₂Br 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-phenylcyclopropane⁹ (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_D²⁰ 1.5400 (lit.¹³ bp 68–70° (3 mm), n_D²⁰ 1.5400); nmr (in CCl₄) δ 7.38 (5 H, C₆H₅) s, 5.98 (1 H, CCl₂H) s, 1.53 ppm [6 H, C(CH₃)₃] s.

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

Reaction of PhHgCBr₂ 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_D²⁰ 1.5867, was collected by glpc: nmr (in CCl₄) δ 7.34 (5 H, C₆H₅) d, 5.88 (1 H, CBr₂H) d (*J* = 4.5 Hz), 3.52 (1 H, PhCH) m, 1.60 ppm (3 H, CH₃) d (*J* = 7.0 Hz).

Anal. Calcd for C₉H₁₀Br₂: 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. Ethers¹

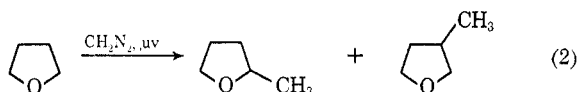
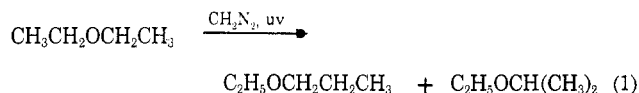
DIETMAR SEYFERTH, VIRGINIA A. MAI, AND MICHAEL E. GORDON²

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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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 CCl₂ was found to be tertiary > secondary, and no insertion was observed at OCH₃ 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, CH₂ itself, into a C-H bond of an ether was reported first by Meerwein and



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

his coworkers³ 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

(2) National Institutes of Health Predoctoral Fellow, 1963–1966.

(3) H. Meerwein, H. Rathjen and H. Werner, *Chem. Ber.*, **75**, 1610 (1942).

(4) W. von E. Doering, L. H. Knox, and M. Jones, Jr., *J. Org. Chem.*, **24**, 136 (1959).

(5) H. M. Frey and M. A. Voisey, *Trans. Faraday Soc.*, **64**, 954 (1968).

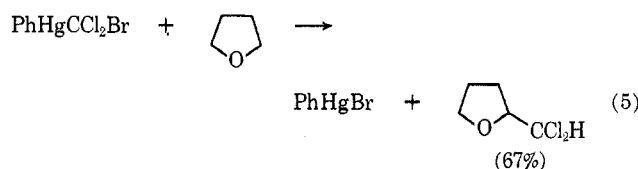
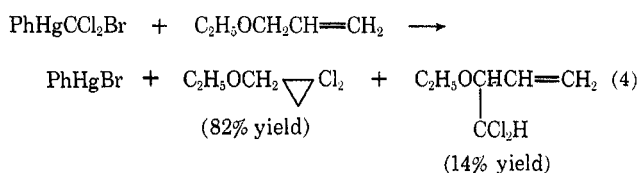
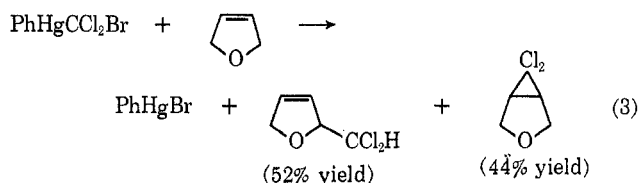
(6) M. A. Voisey, *ibid.*, **64**, 3058 (1968).

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

(b) J. C. Anderson, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc.*, 4874 (1964).

who reported the reactions shown in Table I. Noteworthy in these was (1) the regiospecificity of the CCl_2 insertions which occurred, and (2) the high reactivity of the CH_2 groups of 2,5-dihydrofuran. These reactions did not appear to be very attractive for preparative purposes because of the rather low yields of products which could be realized.

Our previous research had shown that phenyl(bromodichloromethyl)mercury, which releases CCl_2 to a variety of substrates rapidly at 80° , was uniquely useful in transferring dichlorocarbene to reactants which were only poorly reactive toward this intermediate.^{1,8} Accordingly, it was of interest to examine the reactions of $\text{PhHgCCl}_2\text{Br}$ with ethers to see if this interesting but synthetically limited CCl_2 insertion process could not be developed into a more useful one. We have already reported concerning our early work with reactions of this mercury reagent with 2,5-dihydrofuran, ethyl allyl ether, and tetrahydrofuran⁸ (eq 3-5). These initial results indicated that PhHg-

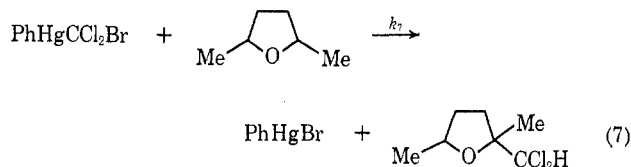
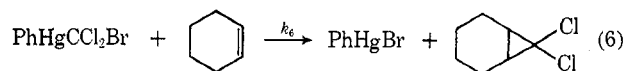


CCl_2Br could be used to good advantage in a study of CCl_2 insertion into C-H bonds of ethers and that the general behavior of this reagent was similar to that of the CCl_2 -generating systems used by the English workers.⁷

The results of Reese, *et al.*,⁷ had led them to suggest that the factor which is most important in these insertion reactions is the effect of the ether oxygen atom in stabilizing a partial positive charge on the adjacent carbon atom into whose bond to hydrogen such CCl_2 insertion is occurring. However, the very limited number of examples studied (Table I) and the generally low yields obtained in all cases except that of 2,5-dihydrofuran led us to investigate in more detail the insertion of CCl_2 into C-H bonds of ethers using phenyl(bromodichloromethyl)mercury as a CCl_2 source.

First, however, it was of some importance to show that in these reactions we were indeed dealing with insertion of dichlorocarbene into the C-H bond and not with a direct reaction of the organomercurial with the ether. Variable concentration competition experiments, in which mixtures of 2,5-dihydrofuran and cyclo-

hexene were allowed to compete for a deficiency of $\text{PhHgCCl}_2\text{Br}$, gave some indication that the former was the case. Equations 6 and 7 show the reactions



involved. Let it be assumed that the rate of 7,7-dichloronorcaradiene formation is n th order in mercurial and m th order in cyclohexene and that the rate of 2,5-dimethyl-2-(dichloromethyl)tetrahydrofuran formation is n' th order in mercurial and m' th order in the ether. Then, in the most general case, we would have the rate equations

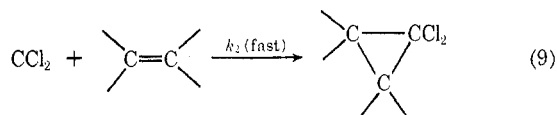
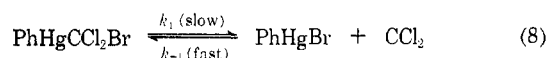
$$-d\text{O}/dt = k_6[\text{PhHgCCl}_2\text{Br}]^n[\text{O}]^m$$

$$-d\text{E}/dt = k_7[\text{PhHgCCl}_2\text{Br}]^{n'}[\text{E}]^{m'}$$

where O = the olefin, cyclohexene; E = the ether, 2,5-dimethyltetrahydrofuran. Dividing the second rate equation by the first gives

$$k_{\text{rel}} = \frac{k_7}{k_6} = \frac{[d\text{E}/dt][\text{PhHgCCl}_2\text{Br}]^n[\text{O}]^m}{[d\text{O}/dt][\text{PhHgCCl}_2\text{Br}]^{n'}[\text{E}]^{m'}}$$

If the experimental finding is that k_{rel} remains constant as the concentrations of the competing reagents are varied, then n must equal n' and m must equal m' . In other words, the orders of the reaction must be the same for both C=C addition and C-H insertion. If k_{rel} is found to change as the reactant concentrations are varied, then one has good indication that C=C addition and C-H insertion proceed by different mechanisms. In the case of the olefin- $\text{PhHgCCl}_2\text{Br}$ reaction the mechanism shown in eq 8 and 9 was found to be operative.⁹ The competition
















of one olefin with another for mercurial-derived CCl_2 involves the second step (k_2). If the ether-mercurial reaction proceeded by a similar course, one would expect to find $k_{\text{rel}} [k(\text{E})/k(\text{O})]$ to be unchanged as the relative concentrations of the ether and the olefin were changed. If, on the other hand, the ether- $\text{PhHgCCl}_2\text{Br}$ reaction proceeded by a mechanism different from that of the olefin- $\text{PhHgCCl}_2\text{Br}$ reaction, such relative starting concentration changes could bring about changes in the observed k_{rel} .

The results of these experiments are shown in Table II. The value of k_{rel} did not change (within experimental error) as the relative concentrations of cyclohexene and 2,5-dimethyltetrahydrofuran were changed from 1:1 to 1:2 to 2:1, respectively. This suggests

(8) 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).

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

TABLE I
REACTIONS OF DICHLOROCARBENE WITH ETHERS^a

Ether	CCl ₂ source	Product (% yield)
	CCl ₃ CO ₂ Et/NaOMe	 (65 parts)
		 (35 parts)
	CCl ₃ CO ₂ Na	 (53 parts)
		 (47 parts)
	CCl ₃ CO ₂ Et/NaOMe	 (2.5)
	CCl ₃ CO ₂ Na	 (3.7)
(CH ₃ CH ₂) ₂ O	CCl ₃ CO ₂ Et/NaOMe	 (20)
(CH ₃) ₂ CHOCH ₃	CCl ₃ CO ₂ Et/NaOMe	 (9)
C ₂ H ₅ OCH ₂ CH=CH ₂	CCl ₃ CO ₂ Et/NaOMe	 (12.7)

^a Reference 7.

(but by no means proves) that the PhHgCCl₂Br-ether reaction involves CCl₂ as an actual intermediate, and in our further discussions we will assume this to be the most reasonable reaction course.

Our investigation proceeded with a study of the reaction of phenyl(bromodichloromethyl)mercury with 13 ethers (Table III). The yields obtained, as expected, were consistently better than those found with other CCl₂ sources. Thus, for instance, CCl₃CO₂Na inserted CCl₂ into diethyl ether in 20% yield, PhHgCCl₂Br in 54% yield. Sodium trichloroacetate inserted CCl₂ into isopropyl methyl ether in 9% yield; PhHgCCl₂Br did so in 39% yield.

The yields obtained with different ethers in reactions with phenyl(bromodichloromethyl)mercury varied markedly with structure. Using our "standard" mercurial reaction conditions—threefold excess of the ether, reaction in benzene medium at reflux for 4 hr—the yields ranged from 90% in the case of 2,5-dimethyltetrahydrofuran to 3% with neopentyl methyl ether. As the ether yields decreased, the yields of tetrachloroethylene, the product of the reaction of CCl₂ with PhHgCCl₂Br,⁸ increased.

The following observations are worth special notice since they are relevant to a discussion of the mechanism of this C-H insertion process.

(1) As in the case of hydrocarbons,¹ CCl₂ insertion into C-H bonds is most favorable where the carbon atom involved could stabilize a partial positive charge. This is shown by the series benzyl methyl ether (71%), isopropyl methyl ether (40%), *n*-propyl methyl ether

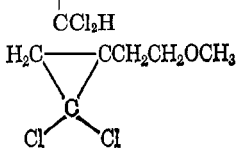

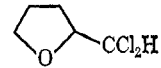
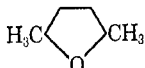
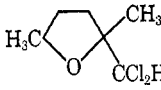
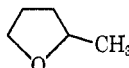
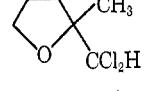
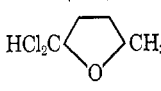

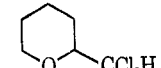
TABLE II
COMPETITION EXPERIMENTS. REACTION OF MIXTURES OF CYCLOHEXENE AND 2,5-DIMETHYLTETRAHYDROFURAN WITH A DEFICIENCY OF PHENYLMERCURIC BROMIDE IN BENZENE at 80 ± 2°

Initial reactant ratio, moles of PhHgCCl ₂ Br/moles of olefin (O)/moles of ether (E)	<i>k</i> _{rel} = <i>k</i> (E)/ <i>k</i> (O)
1/5/5	0.169, 0.174
1/5/10	0.173, 0.165
1/10/5	0.158, 0.162

(10%) (Table III). No insertion into a OCH₃ group was observed in any case. With 2-methyltetrahydrofuran, insertion of CCl₂ into the tertiary C-H bond is favored over insertion into the secondary C-H bond by a factor of 8. Electronegative substituents appear to deactivate C-H bonds in this reaction. Thus in the case of ClCH₂CH₂OCH₂CH₃, dichlorocarbene insertion occurs only into the ethyl group.

(2) Dichlorocarbene insertion into C-H bonds α to the ether function was highly favored. Isobutyl methyl ether with a tertiary C-H bond β to the oxygen and a secondary C-H bond α to the oxygen gave Me₂CHCH(CCl₂H)OMe as the major product on reaction with PhHgCCl₂Br. A minor product, tentatively identified as Me₂(CCl₂H)CCH₂OMe, also was produced. Tetrahydrofuran, with secondary C-H bonds both α and β to the oxygen, underwent reaction only at the former. This is in marked contrast to

TABLE III
REACTIONS OF PHENYL(BROMODICHLOROMETHYL)MERCURY
WITH ETHER

Ether	Insertion product	Yield, %
CH ₃ CH ₂ OCH ₂ CH ₃	CH ₃ CHOCH ₂ CH ₃	58, 51
CH ₃ CH ₂ CH ₂ OCH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CHOCH ₂ CH ₂ CH ₃	42, 40
CH ₃ CH ₂ CH ₂ OCH ₃	CH ₃ CH ₂ CHOCH ₃	10
(CH ₃) ₂ CHOCH ₃	(CH ₃) ₂ COCH ₃	41, 38
(CH ₃) ₃ CCH ₂ OCH ₃	(CH ₃) ₃ CCHOCH ₃	2, 5
(CH ₃) ₂ CHCH ₂ OCH ₃	(CH ₃) ₂ CHCHOCH ₃	7
	(CH ₃) ₂ CCH ₂ OCH ₃ ^a	2
ClCH ₂ CH ₂ OCH ₂ CH ₃	ClCH ₂ CH ₂ OCHCH ₃	16, 14
C ₆ H ₅ CH ₂ OCH ₃	C ₆ H ₅ CHOCH ₃	69, 73
CH ₂ =CHCH ₂ CH ₂ OCH ₃		83
		89
		87, 94
	 (4.2 part)	78, 80
	 (1 part)	
		18, 20

^a Identification tentative.

CH₂ (via CH₂N₂ photolysis) insertion into C-H bonds of ethers. The insertion of CH₂ into tetrahydrofuran was not restricted to the α C-H bonds; insertion into β C-H bonds occurred as well, the α/β C-H insertion ratio being 1.26.⁴ In the case of diethyl ether, the ratio of EtOCH₂CH₂CH₃ to EtOCH(CH₃)₂ formed, 55.5:44.5, was close to the statistical value.⁴

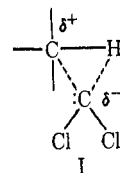
(3) An isolated terminal C=C bond is much more reactive than a C-H bond adjacent to an ether function. With CH₂=CHCH₂CH₂OCH₃ only the expected gem-dichlorocyclopropane was obtained. However, when the double bond is so situated that the C-H bond

adjacent to the oxygen atom is also allylic (e.g., allyl ethyl ether), then this C-H linkage diverts some CCl₂ from the C=C bond (eq 4).⁸ Such a C-H bond becomes even more reactive when it is contained in a five-membered ring (eq 3).

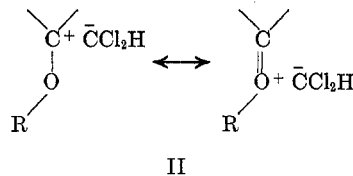
(4) Steric hindrance does appear to play a role. A *t*-butyl group strongly hinders attack at the α C-H bonds of Me₃CCH₂OMe, just as the *t*-amyl group strongly deactivated a vinyl group (in Me₂EtCCH=CH₂) toward CCl₂ addition.¹⁰

(5) Five-membered cyclic ethers enjoy an especially high reactivity, as the comparison between tetrahydrofuran and tetrahydropyran shows. When the C-H bond in question is a tertiary one, adjacent to an ether function and contained in a five-membered ring, the activating influences combine to give maximum reactivity. However, even this most favorable ether is less reactive toward CCl₂ than a "normal" C=C bond. In the case of 2,5-dimethyltetrahydrofuran, the relative reactivity *per C-H bond vs.* the C=C bond of cyclohexene is *ca.* 0.085. By comparison, the relative reactivity of 1-heptene *vs.* cyclohexene is *ca.* 0.24.

In our discussion of CCl₂ insertion into C-H bonds of alkanes and alkylbenzenes,¹ we favored a process in which there is some development of charge in the transition state, as shown in I. Alkyl and aryl sub-

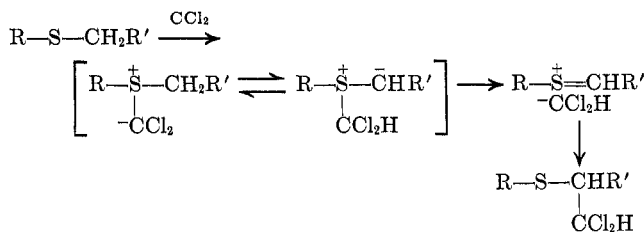


stituents which could by their inductive and resonance effects, respectively, stabilize the partial positive charge on carbon facilitated such insertion. Such a transition state would also serve to explain the activation of C-H bonds toward CCl₂ insertion by an adjacent ether function. In the extreme case, such stabilization would be as shown in II, but complete



ionization need not (and most likely does not) occur for such stabilization to be important.

Similar insertion of CCl₂ into C-H bonds α to a thioether function has been described by Parham and his coworkers, and these reactions were shown to occur by the path indicated below.¹¹ We see no need



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

(11) (a) W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961); (b) W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964); (c) W. E. Parham and S. H. Groen, *ibid.*, **29**, 2214 (1964); (d) *ibid.*, **30**, 3181 (1965); (e) *ibid.*, **30**, 728 (1965).

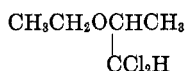
to postulate similar initial attack by CCl_2 at the oxygen atom of the ether molecule undergoing insertion. Further examples of reactions of $\text{PhHgCCl}_2\text{Br}$ with cyclic, allylic methyl ethers will be reported elsewhere.¹²

Experimental Section

General Comments.—All reactions were carried out under an atmosphere of prepurified nitrogen or argon. Infrared spectra were recorded using a Perkin-Elmer 237B or 337 grating infrared spectrophotometer. Nmr spectra were obtained using a Varian Associates A-60 nmr spectrometer. Chemical shifts are given in δ units, parts per million downfield from internal TMS. Gas-liquid partition chromatography (glpc) was accomplished using either an MIT isothermal unit or commercial F & M gas chromatographs (Models No. 700, 776 and 5750). Unless otherwise noted, the columns were packed with 20–25% silicone oil (Dow Corning 200) or silicone rubber gum (General Electric Co. SE-30) on Chromosorb P or W. Phenyl(bromodichloromethyl)mercury was prepared by our published procedures.^{13,14} The ethers used either were commercial products whose purity was checked before use or were prepared in a straightforward manner by the Williamson synthesis. The physical properties (boiling point and refractive index and the ir and/or nmr spectrum in some cases) were in good agreement with those given in the literature.

The Reaction of Phenyl(bromodichloromethyl)mercury with Ethers. General Procedure.—Into a 50- or 100-ml three-necked flask was charged under nitrogen or argon 0.03 mol of the ether, 4.4 g (0.01 mol) of the mercurial, and 15 ml of dry benzene. The reaction flask was equipped with a magnetic stirring assembly and a reflux condenser topped with a nitrogen inlet tube. The reaction mixture was stirred and heated at reflux (oil-bath temperature 88–95°) for 3 hr. During this time flaky, crystalline phenylmercuric bromide precipitated. Upon completion of the heating period the reaction mixture was filtered to remove PhHgBr (the yields were ca. 90%—lower than in the case of reactions with olefins, presumably because of the greater solubility of phenylmercuric bromide in the medium containing unconverted ether). A high-vacuum (0.05–0.2 mm) trap-to-trap distillation of the filtrate followed, and subsequently the distillate was examined by glpc. Products were isolated by preparative glpc and characterized. Yields were determined by glpc using the internal standard method. Details concerning the products obtained in the individual experiments follow below.

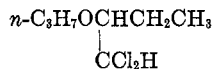
Diethyl ether gave 1,1-dichloro-2-ethoxypropane



in 58% yield (51% in a duplicate experiment), together with tetrachloroethylene in 8% yield. The insertion product had n_D^{25} 1.4371; nmr (microcell, neat) δ 5.8 (1 H, CCl_2H , d, $J = 4$ Hz), 3.6 (3 H, m), 1.2 (6 H, m).

Anal. Calcd for $\text{C}_5\text{H}_{10}\text{OCl}_2$: C, 38.24; H, 6.42; Cl, 45.15. Found: C, 38.58; H, 6.59; Cl, 45.35.

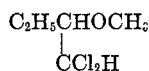
Di-n-propyl ether gave 1,1-dichloro-2-n-propoxybutane



in 42 (40) % yield, as well as tetrachloroethylene (15, 13%). The product had n_D^{25} 1.4398. The CCl_2H resonance was observed as a doublet ($J = 4$ Hz) at 5.65 ppm in the nmr spectrum (CCl_4).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{OCl}_2$: C, 45.42; H, 7.62; Cl, 38.31. Found: C, 45.74; H, 7.60; Cl, 38.27.

n-Propyl methyl ether gave 1,1-dichloro-2-methoxybutane



(12) D. Seyferth and V. A. Mai, in preparation; V. A. Mai, Ph.D. Thesis, MIT, 1969.

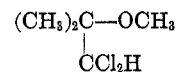
(13) D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, **4**, 127 (1965).

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

n_D^{25} 1.4437, in 10 (5) % yield, as well as tetrachloroethylene (14, 16%): nmr (CCl_4) δ 5.66 (1 H, CCl_2H , d, $J = 9$ Hz), 3.89–3.07 (1 H, $-\text{CHO}-$, m), 3.42 (3 H, OCH_3 , s), 1.67 (2 H, $-\text{CH}_2-$, m), 0.99 (3 H, CH_3CH_2 , t, $J = 13$ Hz).

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{OCl}_2$: C, 38.24; H, 6.42; Cl, 45.15. Found: C, 38.18; H, 6.24; Cl, 44.96.

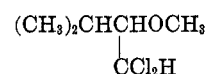
Isopropyl methyl ether gave 2,2-dichloro-1,1-dimethylethyl methyl ether



n_D^{25} 1.4480, in 41 (38) % yield, together with tetrachloroethylene (15, 19%): nmr (CCl_4) δ 5.5 (1 H, CCl_2H , s), 3.13 (3 H, OCH_3 , s), 1.22 [6 H, $(\text{CH}_3)_2\text{C}$, s].

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{OCl}_2$: C, 38.24; H, 6.42; Cl, 45.15. Found: C, 38.15; H, 6.50; Cl, 44.93.

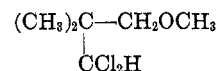
Isobutyl methyl ether gave tetrachloroethylene (24%) and a 1.5/6.25/1.0 mixture of products that could be separated into the individual components using a 20% Carbowax column at 105°. The total product yield was estimated by glpc to be 12%. The major component was 1,1-dichloro-2-methoxy-3-methylbutane



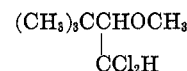
n_D^{25} 1.4436; nmr (neat) δ 5.55 (1 H, CCl_2H , d, $J = 6$ Hz), 3.55 (3 H, OCH_3 , s), 3.15 (1 H, CHOCH_3 doublet of doublets, $J = 4$ and 6 Hz), 2.15 (1 H, Me_2CH , m), 1.0 and 0.9 [6 H, $(\text{CH}_3)_2\text{C}$, two superimposed doublets, $J = 6$ Hz for each]; mass spectrum 170, parent ion ($M:M+2 = 3:2$), 87, molecular ion ($M - \text{CCl}_2\text{H}^+$), 127 = 12% $\text{CH}_3\text{OCHCHCl}_2^+$.

Anal. Calcd for $\text{C}_6\text{H}_{12}\text{OCl}_2$: C, 42.12; H, 7.07. Found: C, 42.47; H, 7.17.

The minor products were not identified. The one with lower glpc retention time showed a band at 2820 cm^{-1} in its ir spectrum (characteristic of an OCH_3 group¹⁵) and also bands attributable to C-Cl linkages [765 (vs), 710 (m)] and thus may be the other isomer



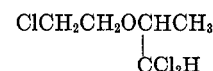
Neopentyl methyl ether gave 1,1-dichloro-2-methoxy-3,3-dimethylbutane



n_D^{25} 1.4538, in 5 (2) % yield and tetrachloroethylene (33, 30%): nmr (CCl_4) δ 5.89 (1 H, CCl_2H , d, $J = 5$ Hz), 3.67 (3 H, OCH_3 , s), 3.5 (1 H, $\text{CH}-\text{OCH}_3$ d, $J = 5$ Hz), 1.01 [9 H, $(\text{CH}_3)_3\text{C}$, s]; mass spectrum 184, parent ion (184:186:188 = 9:6:1, thus 2 chlorines), 92, molecular ion ($184 - \text{Cl} - \text{Me}_3\text{C}^+$), 101 = 83% ($184 - \text{CCl}_2\text{H}^+$).

Anal. Calcd for $\text{C}_7\text{H}_{14}\text{OCl}_2$: C, 45.42; H, 7.62; Cl, 38.31. Found: C, 45.80; H, 7.56; Cl, 38.40.

2-Chloroethyl ethyl ether gave 1,1-dichloro-2- β -chloroethoxypropane



n_D^{25} 1.4750, in 16 (14) % yield, as well as tetrachloroethylene (16, 15%): nmr (CCl_4) δ 5.73 (1 H, CCl_2H , d, $J = 9$ Hz), 3.45–4.0 (5 H, $\text{CH}_2\text{CH}_2\text{OCH}$, m), 1.4 (3 H, CH_3 , d, $J = 12.5$ Hz); mass spectrum 190, parent ion (190:192:194:196 = 27:

(15) K. Nakanishi, "Practical Infrared Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 36.

27:9:1, thus 3 chlorine atoms), 63, molecular ion ($\text{ClCH}_2\text{CH}_2^+$), $107 = 92\%$ ($\text{M} - \text{CCl}_2\text{H}^+$).

Anal. Calcd for $\text{C}_6\text{H}_9\text{OCl}_2$: C, 31.36; H, 4.74. Found: C, 31.39; H, 4.50.

3-Butenyl methyl ether gave 1,1-dichloro-2- β -methoxyethylcyclopropane, n_D^{25} 1.4539, as the sole product in 83% yield: nmr δ 3.24 (3 H, OCH_3 , s), 3.21 (2 H, CH_2O , t, $J = 5.5$ Hz), 1.63 (3 H, $\text{CH}-\text{CH}_2$, m), 1.02 [2 H, CH_2 (ring), m]. No absorptions due to a $\text{C}=\text{C}$ bond were apparent in the ir spectrum.

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{OCl}_2$: C, 42.63; H, 5.96; Cl, 41.94. Found: C, 42.62; H, 5.96; Cl, 42.18.

Benzyl methyl ether gave 1-methoxy-2,2-dichloroethylbenzene, n_D^{25} 1.5305, in 69 (73)% yield, together with a small amount of tetrachloroethylene (3, 6% yield): nmr (CCl_4) δ 7.32 (5 H, C_6H_5 , s), 5.75 (1 H, CCl_2H , d, $J = 11$ Hz), 4.37 (1 H, CHOMe , d, $J = 11$ Hz), 3.28 (3 H, OCH_3 , s); mass spectrum 204, parent ion (204:206:208 = 9:6:1, thus 2 Cl atoms), $77 = 31\%$ C_6H_5^+ , $91 = 17\%$ $\text{C}_6\text{H}_5\text{CH}_2^+$.

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{OCl}_2$: C, 52.71; H, 4.92. Found: C, 52.88; H, 4.98.

2,5-Dimethyltetrahydrofuran gave 2-dichloromethyl-2,5-dimethyltetrahydrofuran,¹⁶ n_D^{25} 1.4645, in 87 (79)% yield: nmr (CCl_4)¹⁶ δ 5.54 (1 H, CCl_2H , s), 4.09 (1 H, CH_2CHO , m), 1.45–2.35 (4 H, CH_2CH_2 , m), 1.38 [3 H, $\text{CH}_3(\text{CCl}_2\text{H})\text{C}$, s], 1.21 (3 H, CH_3CH , d, $J = 7.5$ Hz).

Anal. Calcd for $\text{C}_7\text{H}_{12}\text{OCl}_2$: C, 45.92; H, 6.61; Cl, 38.73. Found: C, 45.80; H, 7.01; Cl, 38.70.

2-Methyltetrahydrofuran gave 2-dichloromethyl-2-methyltetrahydrofuran, n_D^{25} 1.4723, and 2-dichloromethyl-5-methyltetrahydrofuran in 4.2:1 ratio in 78 (80)% combined yield: nmr of the major product (CCl_4) δ 5.53 (1 H, CCl_2H , s), 4.28–4.37 (2 H, CH_2O , m), 1.6–2.5 (4 H, CH_2CH_2 , m), 1.3 (3 H, CH_3 , s). In the nmr spectrum of the minor product a doublet ($J = 8$ Hz) at 5.68 ppm spoke for the structure indicated.

Anal. Calcd for $\text{C}_6\text{H}_9\text{OCl}_2$: C, 42.63; H, 5.96; Cl, 41.94. Found: C, 42.80; H, 6.20; Cl, 41.80.

Tetrahydropyran gave 2-dichloromethyltetrahydropyran in 18 (20)% yield, as well as tetrachloroethylene (12, 12%). The product was rather unstable, turning yellow within a few minutes after isolation by glpc and black within a day in a sealed capillary tube: nmr (CCl_4) δ 5.47 (1 H, CCl_2H , d, $J = 5$ Hz), 3.0–4.1 (3 H, CH_2OCH , m), 1.0 (6 H, m); mass spectrum 188, parent ion (188:200:202 = 9:6:1, thus 2 Cl atoms), 85, molecular ion ($\text{M} - \text{CCl}_2\text{H}^+$).

Anal. Calcd for $\text{C}_6\text{H}_{10}\text{OCl}_2$: C, 42.63; H, 5.96. Found: C, 42.20; H, 6.03.

Competition Study. Reaction of Mixtures of Cyclohexene and 2,5-Dimethyltetrahydrofuran with a Deficiency of Phenyl(bromodichloromethyl)mercury.—In a typical experiment, a

dry, 50-ml flask, equipped with a reflux condenser, a 60-ml pressure-equalizing dropping funnel, a magnetic stirring assembly, and an internal thermometer, was charged with 4.41 g (0.010 mol) of the mercurial, evacuated for 2 hr, and refilled with dry, prepurified nitrogen. Then 15 ml of benzene (distilled from calcium hydride), 4.14 g (0.0504 mol) of cyclohexene (distilled from CaH_2), and 5.19 g (0.0517 mol) of 2,5-dimethyltetrahydrofuran (distilled from CaH_2) were added. The reaction mixture was immersed in an oil bath preheated to $80 \pm 2^\circ$ and stirred at this temperature for 3 hr. During this time the solution turned pale brown and phenylmercuric bromide precipitated. Filtration afforded 3.26 g (92%) of phenylmercuric bromide, mp 284–286°. The filtrate was trap-to-trap distilled at 0.02 mm (pot temperature to 80°). Glpc analysis of the distillate with *o*-dichlorobenzene as internal standard followed. It was established that 7,7-dichloronorcaradiene and 2-dichloromethyl-2,5-dimethyltetrahydrofuran were present in yields of 75.8% and 13.2%, respectively, giving a k_{rel} of 0.169 (calculation by the method of Doering and Henderson¹⁷). A duplicate experiment gave these products in yields of 76.5% and 12.8%; $k_{\text{rel}} = 0.174$.

Registry No.—Phenyl(bromodichloromethyl)mercury, 3294-58-4; 1,1-dichloro-2-ethoxypropane, 923-03-5; 1,1-dichloro-2-*n*-propoxybutane, 24165-84-2; 1,1-dichloro-2-methoxybutane, 24165-85-3; 2,2-dichloro-1,1-dimethylethyl methyl ether, 918-43-4; 1,1-dichloro-2-methoxy-3-methylbutane, 24165-87-5; 1,1-dichloro-2-methoxy-3,3-dimethylbutane, 24165-88-6; 1,1-dichloro-2- β -chloroethoxypropane, 24165-89-7; 1,1-dichloro-2- β -methoxyethylcyclopropane, 24165-90-0; 1-methoxy-2,2-dichloroethylbenzene, 24165-91-1; 2-dichloromethyl-2,5-dimethyltetrahydrofuran, 24165-92-2; 2-dichloromethyl-2-methyltetrahydrofuran, 24215-80-3; 2-dichloromethyl-5-methyltetrahydrofuran, 24165-93-3; 2-dichloromethyltetrahydropyran, 24165-94-4.

Acknowledgments.—The authors are grateful to the U. S. Air Force Office of Scientific Research (SRC)-OAR (USAF Grant No. AFOSR-68-1350) for generous support of this work. This work was supported in part by U. S. Public Health Service Fellowship 5-F1-GM-20,106 (to M. E. G.).

(16) First prepared by S. S. Washburne, Ph.D. Thesis, MIT, 1968.

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