Halomethyl–Metal Compounds. XIV. The Mechanism of the Phenyl(bromodichloromethyl)mercury–Olefin Reaction[1]

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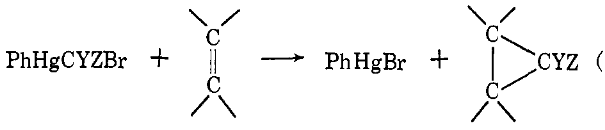
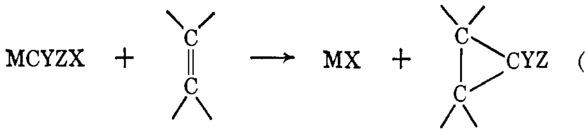
Abstract: A kinetic study of the olefin–phenyl(bromodichloromethyl)mercury reaction (which proceeds virtually quantitatively to give phenylmercuric bromide and a *gem*-dichlorocyclopropane) at 39° in benzene solution, using cyclooctene, 2,3-dimethyl-2-pentene, and 1-heptene, gave results which were interpreted in terms of the mechanism shown in eq 8 and 9.

We have investigated in some detail the scope of the reactions of phenyl(trihalomethyl)mercury compounds ($PhHgCCl_2Br$, $PhHgCClBr_2$, $PhHgCBr_3$, $PhHgCCl_3$) with olefins, in which CX_2 is transferred from the organomercury reagent to the olefin to produce *gem*-dihalocyclopropanes in high yield (eq 1).[3–6] These reactions, in the case of the first three mercurials, proceed rapidly at 80° in an inert solvent and occur at a perceptible rate even at room temperature.[7]

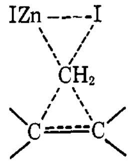

(1)

(Y = Z = Cl; Y = Z = Br; Y = Cl, Z = Br)

In view of its synthetic utility, a study of the mechanism of reaction 1 was of interest to us. Phenyl(trihalomethyl)mercury compounds are by no means the only organometallic divalent carbon transfer agents, and the generalized eq 2 can be written for many elements. Examples are known where M = lithium, sodium, magnesium, zinc, cadmium, mercury, boron, aluminum, indium, silicon, tin, lead, phosphorus, iron, chromium, and iridium. Among organometallic CH_2 transfer agents are $ClCH_2Na$,[8] ICH_2MgI,[9] ICH_2ZnI,[10] $Zn(CH_2X)_2$ (X = Cl, I),[11] $Cd(CH_2I)_2$,[11a] ICH_2HgI,[12] $Hg(CH_2Br)_2$,[12] Et_2AlCH_2Cl,[13] $In(CH_2I)_3$,[11a] π-$C_5H_5Fe(CO)_2CH_2Cl$,[14] and $(Ph_3P)_2(CO)IrCH_2Cl$.[15] CHX transfer (X = Cl, Br) has been effected using $LiCHCl_2$,[16] $Zn(CHCl_2)_2$,[16b] and $PhHgCHXBr$.[17] *gem*-Dichlorocyclopropanes have been prepared using $LiCCl_3$,[18] CCl_3SiCl_3,[19] Me_3SnCCl_3,[20] and Ph_3PbCCl_3[21] as reagents, and CF_2 transfer to olefins was accomplished with Me_3SnCF_3,[22] $(CF_3)_nPF_{5-n}$ (n = 1–3),[23] and $CF_3Fe(CO)_4I$.[24] $PhCCl_2$–boron derivatives have been shown to transfer $PhCCl$[25] and the Me_2BrCC^{+2} ion has beeen used to prepare *gem*-dimethylcyclopropanes.[26] Few definitive mechanistic studies of such systems have been reported to date, but a useful body of indirect evidence has suggested that CYZ transfer reactions of the type shown in eq 2 can proceed by several different mechanisms. Among the possibilities are: (1) a bimolecular, one-step CYZ transfer in which the organometallic reagent reacts directly with the olefin *via* a five-center transition state, suggested to be I in the case of iodomethylzinc compounds;[10] (2) a bimolecular two-step process, for


(2)

(X = halogen)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[1] Part XIII: D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, in press.

[2] (a) Alfred P. Sloan Foundation Fellow, 1962–1966; (b) Postdoctoral Research Associate, 1966–1967; (c) National Institutes of Health Postdoctoral Fellow, 1964–1965.

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[7] Reaction of $PhHgCCl_2Br$ with cyclohexene (1:1 ratio) in benzene at 28° gave after 3 hr, 24 hr, and 11 days, 7,7-dichloronorcarane in yields of 3, 12, and 66%, respectively: D. Seyferth and K. V. Darragh, unpublished results.

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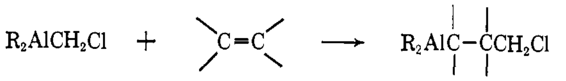
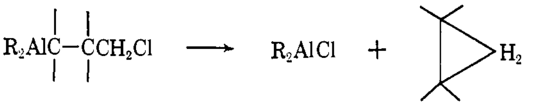
example, of the type suggested by Hoberg[13] for the reactions of chloromethylalanes (eq 3 and 4); (3) a mechanism in which a rate-determining (possibly reversible)



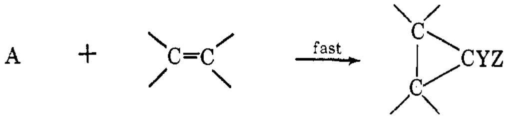
$$\mathrm{R_2AlCH_2Cl} + \mathrm{>C{=}C<} \longrightarrow \mathrm{R_2AlC{-}CCH_2Cl} \qquad (3)$$



$$\mathrm{R_2AlC{-}CCH_2Cl} \longrightarrow \mathrm{R_2AlCl} + \mathrm{>C(CH_2)C<} \qquad (4)$$

decomposition of the organometallic reagent to a reactive intermediate is followed by rapid reaction of this intermediate with the olefin to form the cyclopropane product (eq 5 and 6). Here "A" could be a free carbene

$$\mathrm{MCYZX} \xrightarrow[\text{determining}]{\text{rate}} \mathrm{A} \qquad (5)$$



$$\mathrm{A} + \mathrm{>C{=}C<} \xrightarrow{\text{fast}} \mathrm{>C(CYZ)C<} \qquad (6)$$

(CYZ), a carbene complexed by the metal halide produced in an α-elimination process ($\mathrm{M\ddot{X}{:}}$→CYZ) or by solvent (S:→CYZ), a radical ($\mathrm{M\dot{C}Y\ddot{Z}}$ or $\mathrm{\dot{C}YZX}$), a carbonium ion ($\mathrm{MC^+YZ}$), or a carbanion ($\mathrm{CYZX^-}$). Carbene mechanisms have been suggested for the thermal extrusion of CF_2 from trimethyl(trifluoromethyl)tin[22] and from CF_3-substituted phosphoranes[23] and of CCl_2 from (trichloromethyl)trichlorosilane.[19] For more detailed discussions of "divalent carbon transfer reactions" involving stable or transient organometallic intermediates, see the papers by Simmons, *et al.*,[27] and Hoeg, *et al.*[18c]

Previous observations[3] had definitely ruled out a mechanism involving a CX_3^- intermediate for the thermal $PhHgCX_3$-olefin reaction and provided evidence against radical intermediates. A study of the relative reactivities of olefins toward $PhHgCCl_2Br$ in benzene at 80° had established a reactivity sequence: $Me_2C{=}CMeEt > Et_2C{=}CHMe > n\text{-}Pr(Et)C{=}CH_2 >$ cyclohexene $> n\text{-}C_5H_{11}CH{=}CH_2$, which demonstrated that electrophilic attack with only small steric factors at the olefinic C=C bond was involved.[5] Furthermore, the relative reactivities of a number of different olefins (*vs.* cyclohexene = 1) were found to be identical, within experimental error, with the relative reactivities of these olefins toward sodium trichloroacetate in 1,2-dimethoxyethane (DME)[5] and the [$PhHgCCl_3$ + NaI] reagent,[28] both at 80°, and they paralleled reasonably well those measured for similar (but not identical) olefins at −15° toward the $CHCl_3$-*t*-BuOK system.[29] In contrast, a distinct difference was apparent when they were compared to olefin relative reactivities toward iodomethylzinc iodide, a reagent in whose reactions with olefins electrophilic attack at the C=C bond, but with a pronounced steric factor, was apparent. These relative reactivity studies led us to the tentative conclusion that the $PhHgCCl_2Br$-olefin reaction proceeded *via* a free carbene intermediate.[5] This evidence, however, was only circumstantial in nature, and a kinetic study was required in order to obtain further insight into this question. We report here concerning the results and implications of such a kinetic study.

Results and Discussion

Of immediate interest (in terms of the preceding discussion) was the question of the dependence of the rate of reaction 1 on the olefin and on the mercurial concentrations. Preliminary experiments provided an indication that the rate of product formation was independent of olefin concentration. One set of experiments was carried out in which the reaction of 2,3-dimethyl-2-pentene and $PhHgCCl_2Br$ was allowed to proceed for 1 hr at 60° to about 50% completion. Three such reactions were run under exactly identical conditions, with only the initial olefin concentration being varied. When the olefin/mercurial ratio was 5, the *gem*-dichlorocyclopropane product was obtained in 51% yield; when this ratio was 10, the product yield was 51%; when it was increased to 50, the yield was 49%. Thus there was no increase in product yield despite a tenfold increase in initial olefin concentration.

A kinetic study then was undertaken in which the course of the reaction between cyclooctene and phenyl(bromodichloromethyl)mercury at 39° in benzene (which gives 9,9-dichlorobicyclo[6.1.0]nonane in nearly quantitative yield) was followed by measuring the rate of cyclooctene consumption by gas–liquid partition chromatography (glpc). Because the reaction becomes heterogeneous relatively quickly,[30] we confined ourselves to a study of the early stages of the reaction. A large excess of mercurial was used, so that only a small proportion of the latter was consumed in the whole range of initial rate measurements.

A series of kinetic runs (1, 2, 3, and 4 in Table I) were carried out using different initial concentrations of $PhHgCCl_2Br$ and cyclooctene. A plot of olefin concentration *vs.* time for these experiments is given in Figure 1. The initial rates (dx/dt in moles/l. min, where x = the extent of reaction [31]) were determined from the slopes of these straight lines. Since a change in the initial olefin concentration produces essentially no change in the rate of olefin consumption, one may assume, as a first approximation, that the reaction is zero order in olefin. The rate of olefin consumption, however, was dependent on the initial mercurial concentration, and since an *n*-fold increase in the initial mercurial concentration resulted in an approximately *n*-fold increase in the reaction rate, a first-order dependence on mercurial concentration is indicated. Thus a mechanism in which the mercurial decomposes to give a reactive intermediate in the rate-determining step seems to be operative. However, further experiments showed that the picture was more complicated.

The results thus far suggest the rate law shown in eq 7. If eq 7 were strictly applicable, then the rate of consumption of any olefin should be the same for a given initial

$$dx/dt = k_1[\mathrm{PhHgCCl_2Br}] \qquad (7)$$

mercurial concentration. Experiments were carried

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[30] The solubility of phenylmercuric bromide in benzene at 39° is approximately 0.0055 mole/l.

[31] The exact correspondence of dx/dt with $-d(\text{olefin})/dt$ and $+d(\text{product})/dt$ was established experimentally in the case of cyclooctene by measuring both the rate of olefin consumption and rate of 9,9-dichlorobicyclo[6.1.0]nonane formation with time.

Table I. Olefin-$PhHgCCl_2Br$ Reactions, Kinetic Runs at 39.0° in Benzene Solution

Run no.	Olefin	$[PhHgCCl_2Br]^a$	$[Olefin]^a$	$[PhHgBr]^a$	$dx/dt \times 10^{5\,b}$
1	Cyclooctene	0.099	0.0202	0	7.01 ± 0.17
2	Cyclooctene	0.099	0.010	0	6.83 ± 0.16
3	Cyclooctene	0.200	0.0202	0	12.8 ± 0.4
4	Cyclooctene	0.400	0.0202	0	27.8 ± 0.1
5	Cyclooctene	0.099	0.0202	0.0037	5.92 ± 0.24
6	Cyclooctene	0.099	0.200	0	8.87 ± 0.32
7	Cyclooctene	0.099	0.005	0	3.95 ± 0.09
8	Cyclooctene	0.099	0.005	0.0037	2.78 ± 0.10
9	$Me_2C{=}CMeEt$	0.099	0.0202	0	8.81 ± 0.19
10	$Me_2C{=}CMeEt$	0.099	0.010	0	8.48 ± 0.08
11	$Me_2C{=}CMeEt$	0.099	0.200	0	8.93 ± 0.16
12	$Me_2C{=}CMeEt$	0.099	0.0202	0.0037	8.77 ± 0.08
13	$n\text{-}C_5H_{11}CH{=}CH_2$	0.099	0.0202	0	3.20 ± 0.06
14	$n\text{-}C_5H_{11}CH{=}CH_2$	0.099	0.0202	0.0037	2.22 ± 0.05
15	$Me_2C{=}CMeEt$ (in benzene at 49.9°)	0.099	0.200	0	33.3 ± 0.34
16	$Me_2C{=}CMeEt$ (in benzene at 60.4°)	0.099	0.200	0	108.5 ± 2.4
17	$Me_2C{=}CMeEt$ (in DME at 39°)	0.099	0.100	0	4.92 ± 0.11
18	$Me_2C{=}CMeEt$ (in DME at 39°)	0.099	0.200	0	4.91 ± 0.14

[a] Initial concentration in moles per liter. [b] In moles/l. min.

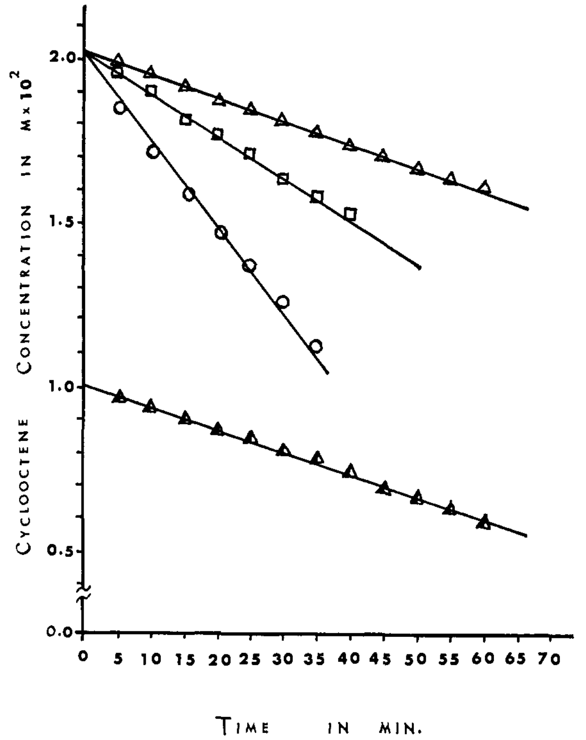


Figure 1. Rate of olefin consumption in the $PhHgCCl_2Br$-cyclooctene reaction in benzene at 39°: Δ, run 1, $C_6H_5HgCCl_2Br$ 0.099 *M*, cyclooctene 0.0202 *M*; ▲, run 2, $C_6H_5HgCCl_2Br$ 0.099 *M*, cyclooctene 0.01005 *M*; □, run 3, $C_6H_5HgCCl_2Br$ 0.20 *M*, cyclooctene 0.0202 *M*; ○, run 4, $C_6H_5HgCCl_2Br$ 0.40 *M*, cyclooctene 0.0202 *M*.

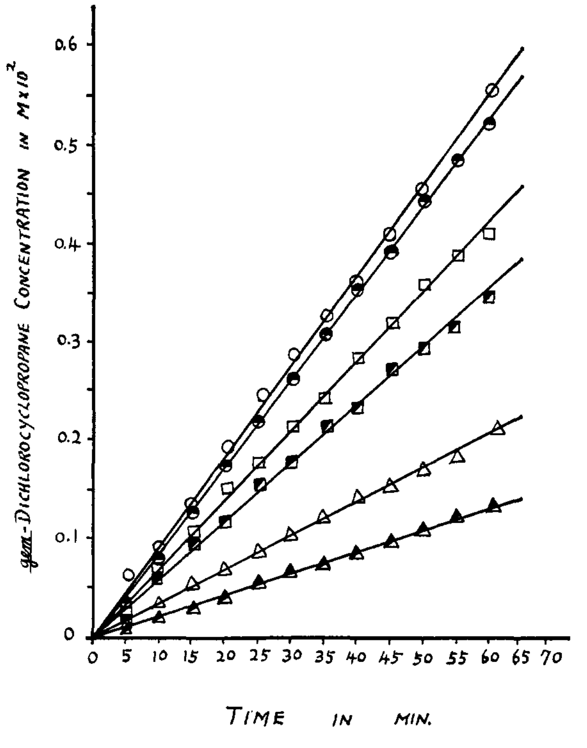
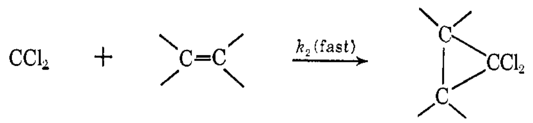


Figure 2. Rate of the $PhHgCCl_2Br$-olefin reaction and effect of added phenylmercuric bromide: □, run 1, $C_6H_5HgCCl_2Br$ 0.10 *M*, cyclooctene 0.02 *M*, C_6H_5HgBr 0; ◩, run 5, same as run 1, with 0.0037 *M* C_6H_5HgBr; ○, run 9, $C_6H_5HgCCl_2Br$ 0.10 *M*, $(CH_3)_2C{=}C(CH_3)C_2H_5$ 0.02 *M*, C_6H_5HgBr 0; ◓, run 12, same as run 9, with 0.0037 *M* C_6H_5HgBr; Δ, run 13, $C_6H_5HgCCl_2Br$ 0.10 *M*, $n\text{-}C_5H_{11}CH{=}CH_2$ 0.02 *M*, C_6H_5HgBr 0; ▲, run 14, same as run 13, with 0.0037 *M* C_6H_5HgBr.

out to test this question using 2,3-dimethyl-2-pentene (k_{rel} = 18.4 *vs.* cyclooctene) and 1-heptene (k_{rel} = 0.184 *vs.* cyclooctene). The results are presented in Table I (runs 9, 10, 11, and 13). Thus we find that the reaction rate for the more reactive olefin is greater than that found with cyclooctene and that the reaction rate for the less reactive olefin is slower. Furthermore, experiments in which the rate of olefin consumption (or *gem*-dichlorocyclopropane formation) was measured in the presence of initially added phenylmercuric bromide (runs no. 5, 12, and 14 in Table I; Figure 2) showed that this compound decreases the rate of the mercurial-olefin reaction in the case of cyclooctene and 1-heptene, but not in the case of 2,3-dimethyl-2-pentene. The low solubility of phenylmercuric bromide in benzene at 39° limited the experiments which could be performed to explore this point, but the rate decreases observed are greater than experimental error.

The picture which now has emerged is as follows. The *initial* rates of the $PhHgCCl_2Br$–olefin reaction are essentially independent of olefin concentration (note that this was found to be the case with 2,3-dimethyl-2-pentene over a tenfold concentration range) and first order in mercurial. They do, however, show a small dependence on the nature of the olefin, the observed reaction rates decreasing as k_{rel} of the olefin toward CCl_2 sources decreases. The initial rates are retarded by added phenylmercuric bromide (which, as eq 1 shows, is formed in the olefin–mercurial reaction). These observations provide strong evidence that the initially rate-determining decomposition of $PhHgCCl_2Br$ is reversible[32] and suggest the following mechanistic scheme (eq 8 and 9).

$$C_6H_5HgCCl_2Br \underset{k_{-1}\ (fast)}{\overset{k_1\ (slow)}{\rightleftharpoons}} C_6H_5HgBr + CCl_2 \qquad (8)$$



(9)

The value of k_2 would 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 as we go from a relatively unreactive olefin such as 1-heptene to a very reactive one such as 2,3-dimethyl-2-pentene (which represents an increase in k_2 by a factor of 100). The rate expression (10) may be derived for the mechanism represented by eq 8 and 9. It will be

$$dx/dt = \frac{k_1[PhHgCCl_2Br]}{1 + \dfrac{k_{-1}[PhHgBr]}{k_2[olefin]}} \qquad (10)$$

noted that in the early stages of the reaction, when $[olefin] \gg [PhHgBr]$ (and if $k_2 \geqslant k_{-1}$), this simplifies to eq 7. If k_1 is calculated from eq 7 using the data from run no. 1 and then is substituted, together with the data from run no. 5, into eq 10, the k_{-1}/k_2 ratio can be calculated to be ~1.1 for the cyclooctene case. In other words, the reverse (Hg–Br insertion) reaction is as rapid as the product-forming reaction. The value of 1.1 is only an approximate figure, since the error is large in this determination which involves the difference between two initial rates.

Figure 2 shows that the effect of added phenylmercuric bromide on the rate of the $PhHgCCl_2Br$–olefin reaction is greatest for 1-heptene, less for cyclooctene, and not perceptible for 2,3-dimethyl-2-pentene. This is as expected. For the latter olefin the ratio $k_{-1}/k_2 = 0.06$ since 2,3-dimethyl-2-pentene is 18.4 times more reactive toward CCl_2 than is cyclooctene. Thus the denominator of eq 10 will be ~1 even when 0.0037 *M* PhHgBr is present initially. For 1-heptene, on the other hand, which is 0.184 as reactive toward CCl_2 as is cyclooctene, the ratio $k_{-1}/k_2 = 6.0$, and in run no. 14 the added phenylmercuric bromide thus has a strong retarding effect on the rate. In this connection we note that for cyclooctene (run no. 1) $dx/dt = 7.0 \times 10^{-5}$ mole/l. min, while with comparable initial olefin and mercurial concentrations $dx/dt = 8.8 \times 10^{-5}$ mole/l. min for 2,3-dimethyl-2-pentene (run no. 9), and for 1-heptene $dx/dt = 3.2 \times 10^{-5}$ mole/l. min. This is explained in the same way. For 2,3-dimethyl-2-pentene the term $k_{-1}/k_2 \times [PhHgBr]/[olefin]$ in eq 10 is negligible, but for the other two olefins for which k_2 is smaller, it is not, and so for the latter two dx/dt will be smaller. The fact that the rate of the olefin–mercurial reaction was the same, within experimental error, for all concentrations of 2,3-dimethyl-2-pentene used (from 0.01 to 0.2 *M*) suggests that with this olefin we are observing the limiting reaction rate, $\sim 8.8 \times 10^{-5}$ mole/l. min, and that for this olefin the simplified rate expression 7 was a good approximation. It was of interest to note that this limiting rate was observed in the case of cyclooctene when the initial olefin concentration was increased to 0.2 *M* (run no. 6), *i.e.*, that at this initial olefin concentration rate eq 7 applied also for this olefin. Conversely, a decrease in the initial rate would be predicted in an experiment in which only a low initial cyclooctene concentration was used, since the amount of phenylmercuric bromide produced would exert a correspondingly greater effect in the early stages of the reaction. The results of an experiment in which the initial cyclooctene concentration was 0.005 *M* (with the initial mercurial concentration 0.099 *M* as usual) are in agreement with this. For this run the plot of cyclooctene concentration *vs.* time showed a noticeable curvature, and the intial rate was estimated to be $\sim 4 \times 10^{-5}$ mole/l. min. Another experiment in which the cyclooctene concentration was this low and in which an initial phenylmercuric bromide concentration of 0.0037 *M* had been added resulted in another drop of the observed initial rate to 2.8×10^{-5} mole/l. min.

The results of these changes in initial reactant concentrations and in the olefin used (*i.e.*, in k_2) are in agreement with what one would predict from the rate eq 10. Further proof for the applicability of this equation to reaction 1 was obtained by demonstrating that it could be used to calculate dx/dt *vs.* time plots which were in good agreement with the experimentally determined curves. For the concentrations used in run no. 4, rate eq 10 takes the form (11), where *M* and *O* are the initial

$$dx/dt = \frac{k_1[M - x]}{1 + \dfrac{B}{[O - x]}} \qquad (11)$$

concentrations of $PhHgCCl_2Br$ and cyclooctene, and *x* is the extent of reaction at time *t*. The constant $B = (k_{-1}/k_2)[PhHgBr]$. The concentration of phenylmercuric bromide was taken as that of its saturated solution in benzene at 39°,[17] and $k_{-1}/k_2 \cong 1.1$, as determined above. The integrated form of eq 11 is given below.

$$\frac{M - B - O}{k_1[M - O]} \ln \frac{[M]}{[M - x]} + \frac{B}{k_1[M - O]} \ln \frac{[O]}{[O - x]} = t \qquad (12)$$

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[32] We have shown[33] that $PhHgCCl_2Br$ reacts with *p*-tolylmercuric chloride in benzene solution at 80° to give $p\text{-}CH_3C_6H_4HgCCl_3$ and PhHgBr in good yield. In this reaction we very likely are dealing with CCl_2 insertion into the Hg–Cl bond, so the insertion of CCl_2 into the Hg–Br bond of phenylmercuric bromide seems quite reasonable. It may be noted that added phenylmercuric chloride and iodide retard the mercurial–olefin reaction.

[33] M. E. Gordon, K. V. Darragh, and D. Seyferth, *J. Am. Chem. Soc.*, **88**, 1831 (1966).

Figure 3 shows a plot of cyclooctene concentration *vs.* time calculated from eq 12 (dotted curve). The dotted straight line represents this plot for the integrated form of eq 7. The solid curve shows the experimental points for this run. Agreement between the experimental curve and that calculated from eq 12 is reasonably good. The fact that the deviation between experimental and calculated curves became larger with the extent of reaction, with the actual rate being smaller than the calculated rate, may find an explanation in terms of a heterogeneous reaction between microcrystalline, freshly formed phenylmercuric bromide and dichlorocarbene. The reaction mixture was observed to become heterogeneous in *ca.* 25 min, which represents about 10% of the total reaction time.

The rate of the 2,3-dimethyl-2-pentene–$PhHgCCl_2Br$ reaction in benzene also was measured at 49.9 and 60.4°. At 49.9°, dx/dt was found to be 33.3×10^{-5} mole/l. min and at 60.4°, 108.5×10^{-5} mole/l. min. The values of k_1 at these temperatures and at 39° were calculated using eq 7, and a plot of the logs of these values of k_1 *vs.* $1/T$ (°*K*) gave a straight line from the slope of which $(E/2.303R)$ the Arrhenius activation energy was calculated to be 24.9 kcal/mole. Using this value and the value of k_1 obtained from eq 7 (run 9, 8.9×10^{-4} min^{-1} or 1.483×10^{-5} sec^{-1}), the activation parameters were calculated: $\Delta F^{\ddagger} = 25.2$ kcal/mole; $\Delta H^{\ddagger} = 24.3$ kcal/mole; $\Delta S^{\ddagger} = -2.8$ eu. A value of about 0.4×10^{13} sec^{-1} was calculated for the frequency factor Z $(p = 1)$. This is of the right order of magnitude for a unimolecular reaction.[34] The numerically small $\Delta S^{\ddagger}$ effectively precludes ionic character in the transition state and argues strongly against ionic intermediates.

It is of interest to calculate the half-life of the phenyl(bromodichloromethyl)mercury reagent in the presence of 2,3-dimethyl-2-pentene at these temperatures. At 39° it is 13 hr; at 49.9°, 3.4 hr; at 60.4°, 63.2 min.

The initial rate of the mercurial–2,3-dimethyl-2-pentene reaction also was measured in 1,2-dimethoxyethane (DME) solution at 39°, since it was known that this solvent also serves well in preparative olefin–mercurial reactions. The effect on the reaction rate of this change from benzene (8.8×10^{-5} mole/l. min) to DME (4.9×10^{-5} mole/l. min) was small. Control experiments established that mercurial-derived CCl_2 did not react with DME under these conditions. Other experiments in which cyclohexene and *trans*-3-heptene were allowed to compete for a deficiency of mercurial-derived dichlorocarbene in various solvents established that there was little if any effect of solvent on the k_2(cyclohexene)/k_2(*trans*-3-heptene) ratio, with the observed k_{rel} values being essentially the same (within experimental error) in cyclohexane, carbon tetrachloride, benzene, DME, and proprionitrile.[35]

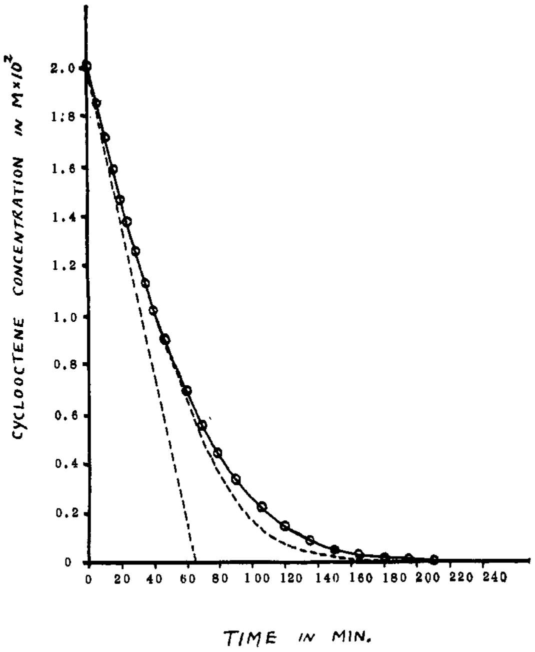

Figure 3. Rate of olefin consumption in the $PhHgCCl_2Br$–cyclooctene reaction; comparison of the experimental with calculated (eq 12) plot: ○, observed rate of consumption of cyclooctene (0.40 *M* $PhHgCCl_2Br$, 0.02 *M* olefin initial concentrations); ---- (curve), calculated plot from eq 12; ---- (straight line), calculated from eq 7.

It is clear from the results presented and the discussion thus far that equation sequence 8–9 is appropriate to the $PhHgCCl_2Br$–olefin system. The evidence most certainly indicates that the mercurial decomposition is reversible. These findings serve to explain the previous observation that when a substrate very unreactive toward CCl_2 is used in mercurial reactions, a rather longer reaction time is required for complete consumption of the mercurial reagent; *i.e.*, poorly reactive substrates, such as paraffinic hydrocarbons, benzene, etc., appear to "stabilize" $PhHgCX_2Br$ compounds. In these cases k_2 is much smaller than in the case of reactive olefins, and so the predominant CCl_2 reaction is regeneration of the mercurial. When $PhHgCCl_2Br$ is decomposed in an inert solvent (*e.g.*, perfluorocyclohexene) or when the substrate is very unreactive toward dichlorocarbene (*e.g.*, cyclohexane, trichloroethylene, etc.), another reaction of dichlorocarbene which produces tetrachloroethylene (and by reaction with the latter, hexachlorocyclopropane) becomes noticeable.[3] It is believed that tetrachloroethylene arises by the process shown in eq 13. The ob-

$$PhHgCCl_2Br + CCl_2 \xrightarrow{k_3} PhHgCCl_2CCl_2Br \longrightarrow PhHgBr + C_2Cl_4 \quad (13)$$

served insertion of ethyl trichloroacetate derived CCl_2 into the C–Hg bond of dialkylmercury compounds to give $RHgCCl_2R$ species is to be noted in this connection.[36]

The question of the nature of the reactive intermediate in the decomposition of phenyl(bromodichloromethyl)mercury now arises. Is it really free dichlorocarbene? The available evidence suggests that it is or that any $PhHgBr$–CCl_2 complex is very weak. This is indicated by the fact that phenylmercuric bromide was found to be kinetically active. If free PhHgBr were not generated in reaction 8, then added phenylmercuric bromide should not have such an effect on the initial rates observed for cyclooctene and 1-heptene. Furthermore, our results speak against a strongly solvent-complexed CCl_2 intermediate. If dichlorocarbene were present as $[S \rightarrow CCl_2]$ in donor solvents as DME and propionitrile,

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(34) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 75.

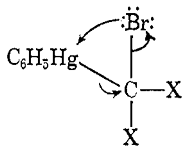
(35) M. E. Gordon, Ph.D. Thesis, Massachusetts Institute of Technology, 1966.

(36) J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **88**, 3545 (1966).

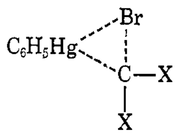
one would have species whose steric requirements and electrophilic nature would be quite different from those of CCl_2 generated in benzene or cyclohexane. In general, the more polar the solvent, the greater would be the degree of solvation and, consequently, the more selective should be the dichlorocarbene reagent toward competing pairs of olefins. The fact that k_2(cyclohexene)/k_2(*trans*-3-heptene) did not change upon change in solvents thus speaks against a strong solvent–CCl_2 complex. Also, if a strong CCl_2–DME complex were formed (*vs.* a weak CCl_2–benzene complex), one might expect an acceleration in the observed initial rate on going from benzene to DME solution with the mercurial–olefin reaction. Instead, we found a slight decrease in initial rate associated with this solvent change. This suggests to us that either more effective solvation of the starting mercurial in DME slows down the extrusion step or more effective solvation of phenylmercuric bromide results in an increase in k_{-1}.

The failure to observe large initial rate increases on going from benzene to DME also speaks strongly against the possible $PhHgCCl_2^+$ intermediate, since its rate of formation should be significantly increased as a result of this change in solvent.

While it seems certain that the slow step of the $PhHgCCl_2Br$–olefin reaction is the extrusion of CCl_2 from the mercurial, the exact nature of this process is not yet understood. We have favored CCl_2 extrusion *via* internal nucleophilic attack by Br at mercury (transition states II or III),[6] and a study currently in progress



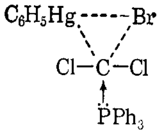
II



III

of the rates of reactions between an olefin and substituted aryl(bromodichloromethyl)mercury compounds, $ZC_6H_4HgCCl_2Br$, hopefully will provide definitive information concerning this question.

As we have reported previously, the $PhHgCHXBr$[17] and $Hg(CH_2X)_2$[12] reagents transfer CHX and CH_2 to olefins. The results of the present study should not, however, be applied to these systems, *i.e.*, it should not be implied that free CHX and CH_2 are involved as intermediates. Indeed, the results of our study of $Hg(CH_2Br)_2$–olefin reactions suggest that this reaction does not involve free CH_2 as an intermediate.[37] Also the results of the present study should not be taken to indicate that all CX_2 transfer reactions of $PhHgCX_2Br$ reagents proceed by a mechanism analogous to eq 8 and 9. Such a mechanism has indeed been found to be operative in mercurial-derived CX_2 insertion into the Si–H bond of triethylsilane,[38] but qualitative evidence suggests that in the case of stronger Lewis bases (tertiary phosphines,[39] tertiary amines,[40] and carbodiimides[41]) a bimolecular reaction occurs with $PhHgCCl_2Br$, possibly involving a transition state such as IV for triphenylphosphine and displacement of CCl_3^- in the case of the $PhHgCCl_3$–triethylamine reaction.



IV

Experimental Section

General Comments. All kinetic runs were carried out under an atmosphere of prepurified nitrogen. The same apparatus was used in all kinetic measurements. Phenyl(bromodichloromethyl)mercury[42] was recrystallized from chloroform–hexane at room temperature or below to avoid thermal decomposition of the purified product and was stored at −5° prior to use. The olefins were dried and distilled from calcium hydride or sodium. Benzene was dried and distilled from calcium hydride, DME from potassium, under a nitrogen atmosphere; both were used immediately after being distilled. All kinetic runs were carried out in a similar manner. One run involving the reaction of $PhHgCCl_2Br$ with cyclooctene is described in detail.

The Reaction of $PhHgCCl_2Br$ with Cyclooctene. Kinetic Run. Apparatus. The reaction vessel was cylindrical in shape (120 × 45 mm), with a large ground-glass joint at the top. It was equipped with a nitrogen inlet tube, a small stoppered entry port, and a low-speed mechanical stirrer extending to about 25 mm above the bottom of the vessel. The reaction vessel was of Pyrex and had a capacity of *ca.* 180 ml. The lower part of the apparatus containing the reaction mixture was immersed in a constant-temperature bath, the temperature of which was regulated by means of an electronic device to ±0.02° of the preset temperature (39.0°). The Nujol oil bath was insulated in a wooden box, and the oil was stirred with a motor-driven stirrer.

Volumetric flasks and pipets were calibrated at room temperature (20–23°). All volumetric measurements above room temperature were subsequently corrected to the equivalent volume at room temperature. Temperature readings from the oil bath have been corrected. A high-vacuum system equipped with a mercury diffusion pump was set up for the distillation of samples and drying of various reagents.

Procedure. A benzene solution (200 ml) of cyclooctene (Cities Service, which had been passed through activated alumina and distilled using a 25-plate spinning-band column, bp 144–145°), 0.6496 g (5.896 mmoles), and chlorobenzene (internal standard), 0.600 g, was prepared in a 200-ml volumetric flask. This solution (100 ml) was pipetted into the dry reaction vessel under nitrogen. The reaction vessel was placed in the oil bath and equilibrated for more than 1 hr. Phenyl(bromodichloromethyl)mercury, 7.4 g, was placed in a 50-ml flask and dried at room temperature (10^{-6} mm) for 30 min. The dry mercurial, 7.209 g (16.36 mmoles), was weighed out directly in a 51.8-ml volumetric flask. Benzene was added to dissolve the mercurial and finally made up to the mark on the flask. The mercurial solution was mixed thoroughly and equilibrated in the oil bath for 15 min. Then 45.6 ml of this solution was pipetted rapidly into the reaction vessel with a stopcock pipet. The latter (also warmed to 39°) allowed rapid measurement and dispensing of a constant volume of solution. The purpose of equilibrating both reactants separately to 39° prior to their reaction was to avoid a large temperature difference between the reaction mixture and the oil bath. This procedure was essential, especially in the initial rate measurements. The mechanical stirrer then was turned on. Timing was started when about one-half of the mercurial solution had been added to the reaction vessel. The amount of cyclooctene and $PhHgCCl_2Br$ used in this reaction had been preselected and then measured accurately prior to the experiment in such a way that the initial concentrations of olefin and mercurial would correspond to the exact concentrations required (0.0202 and 0.099 *M*, respectively) when the two solutions were mixed. A total of 12 samples (*ca.* 4–5 ml each) was taken out of the reaction mixture at 5-min intervals. Each sample was cooled rapidly to −70° (Dry Ice–acetone) immediately after it had been taken out. Samples were stored at this temperature prior to distillation.

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[37] D. Seyferth and R. M. Turkel, to be reported.

[38] D. Seyferth and J. Y.-P. Mui, to be reported.

[39] D. Seyferth, J. K. Heeren, G. Singh, S. O. Grim, and W. B. Hughes, *J. Organometal. Chem.* (Amsterdam), **5**, 267 (1966).

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

[41] D. Seyferth and R. Damrauer, *Tetrahedron Letters*, 189 (1966).

[42] D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.* (Amsterdam), 4, 127 (1965).

Each of the samples was trap-to-trap distilled under high vacuum. The frozen sample was attached to the distillation apparatus and partially evacuated to *ca.* 50 mm at −70°. Then the sample was cooled to −195° (liquid nitrogen) for a period of about 7 min. The apparatus was evacuated to 10^{-5}–10^{-6} mm. The sample then was distilled at or below room temperature into a 25-ml flask cooled to −195°. Subsequently the distillation apparatus was pumped down to *ca.* 10^{-5}–10^{-6} mm through the high-vacuum line for 5 min. Finally, the distillate was warmed to slightly above room temperature while the side wall and upper part of the receiver were cooled with a small amount of Dry Ice–acetone mixture. Benzene was condensed rapidly, thus washing thoroughly the inside of the apparatus. The purpose of this last operation was to ensure that all high-boiling compounds were transferred quantitatively into the receiver. Blank experiments with a mixture containing known quantities of cyclooctene and chlorobenzene showed that such a distillation was quantitative.

In the kinetic runs where an initial concentration of phenylmercuric bromide was added, the benzene solvent used to prepare the cyclooctene–chlorobenzene solution was saturated with PhHgBr.

The distilled samples were analyzed as soon as possible by glpc using an F & M Model 700 gas chromatograph equipped with a dual flame ionization detector. The analysis was carried out at oven temperature 140°, a helium flow rate of 40 cc/min, with a 20-ft (1/8-in. o.d.) aluminum column packed with 20% General Electric Co. SE-30 silicone rubber gum on Johns Manville Chromosorb P. About 0.5–1.0 μl of sample was sufficient. Areas of the cyclooctene and chlorobenzene peaks were measured with an Ott planimeter. Area measurements were traced both clockwise and counterclockwise until at least two opposite measurements agreed within one unit. Sufficient sample was analyzed so that the area of the chlorobenzene and the cyclooctene (first samples) would give a peak area of 200 units or more. The concentrations of cyclooctene in the samples were calculated in the following way. In a typical example, data from run no. 4 are summarized in Table II. Sample no. 0 was a portion of the original cyclooctene–chlorobenzene solution. The peak areas of cyclooctene in column 3 were standardized against an arbitrarily chosen peak area of chlorobenzene (≡300, taken for mathematical convenience), since the concentration of chlorobenzene in each sample was constant. Corrected peak areas of cyclooctene are given in column 4. The peak area of cyclooctene (394.5) of sample no. 0 corresponded to the initial concentration of cyclooctene (0.0202 *M*). The concentrations of cyclooctene in each sample (1–21) were calculated by dividing the corrected peak area of cyclooctene (column 3) of the appropriate sample by 394.5 and multiplying by 0.0202. A plot of cyclooctene concentration *vs.* time for this run is shown in Figure 3. The first eight samples in Table II were used for the initial rate determination (Figure 1); the initial rate, d*x*/d*t*, was given by the slope of the straight line.

Table II. Kinetic Run No. 4 (initial concentration of $C_6H_5HgCCl_2Br$, 0.4 *M*; cyclooctene 2.02 × 10^{-2} *M*)

Sample no.	Peak area: C_6H_5Cl	Peak area: c-C_8H_{14}	c-C_8H_{14}[a] cor	c-C_8H_{14} concn, $M \times 10^2$	Time, min
0	255	335.5	394.5	2.02	0
1	271.5	326.5	360.5	1.847	5
2	256	285.5	334.5	1.713	10
3	283	290.5	308	1.579	15
4	282	269	286	1.466	20
5	282	252	268	1.373	25
6	282.5	232	246.5	1.262	30
7	285	209.5	220.5	1.129	35
8	271.7	188	207.5	1.062	40
9	276	162.5	176.7	0.904	50
10	302	135.5	134.6	0.688	60
11	293.5	104.5	106.8	0.547	70
12	288	82.7	86.2	0.442	80
13	273	57	62.6	0.321	90
14	281	41	43.6	0.223	105
15	273	24.5	26.9	0.138	120
16	293	16	16.4	0.084	135
17	285	9	9.5	0.049	150
18	284	4.8	5.2	0.027	165
19	306	1.8	1.8	0.009	180
20	259	0.9	1.0	0.005	195
21	277	0	0	0.000	210

[a] C_6H_5Cl ≡ 300.

In the run with 0.099 *M* mercurial and 0.20 *M* cyclooctene initial concentrations (run no. 6) the reaction was followed by the rate of appearance of the product, 9,9-dichlorobicyclo[6.1.0]nonane. In this case, 1-chloronaphthalene was used as internal standard; the response factor was 0.710. Glpc analysis of the distilled samples was carried out at oven temperature 200° with a helium flow rate of 50 cc/min, using a 9 ft × 1/8 in. column (25% SE-30 on Chromosorb P).

That the reaction rate could be followed either by measuring the rate of consumption of cyclooctene or the rate of formation of 9,9-dichlorobicyclo[6.1.0]nonane was verified in the following way. A reaction between $PhHgCCl_2Br$ (0.4 *M*) and cyclooctene (0.028 *M*) was carried out in benzene at 39°. Three samples were taken out after 15, 33, and 53 min. The samples were distilled as above and analyzed both for cyclooctene and 9,9-dichlorobicyclo[6.1.0]nonane. The concentrations of cyclooctene consumed in these samples (0.0036, 0.0077, and 0.018 *M*, respectively) were found to be the same, within experimental error, as the concentrations of product formed (0.0038, 0.008, and 0.019 *M*).

Reaction of Phenyl(bromodichloromethyl)mercury with 2,3-Dimethyl-2-pentene. The reaction between mercurial and this olefin (Chemical Samples Co.) was carried out as described above for the cyclooctene case. The reaction was followed by the rate of appearance of 1,1-dichloro-2,2,3-trimethyl-3-ethylcyclopropane. *o*-Dichlorobenzene was used as internal standard; response factor was 1.30. Glpc analysis of the distilled samples was carried out at an oven temperature of 135° and a helium flow rate of 50 cc/min using a 9 ft × 1/8 in. aluminum column (25% SE-30 on Chromosorb P).

Reaction of Phenyl(bromodichloromethyl)mercury with 1-Heptene. The reaction between $PhHgCCl_2Br$ and 1-heptene (Chemical Samples Co.) was carried out as described above for the cyclooctene case. The reaction was followed by the rate of appearance of 1,1-dichloro-2-*n*-amylcyclopropane. *o*-Dichlorobenzene was used as internal standard; the response factor was 1.26. Glpc analysis was carried out at an oven temperature of 140° and a helium flow of 50 cc/min using a 9 ft × 1/8 in. aluminum column (25% SE-30 on Chromosorb P).

Reproducibility. The reproducibility was checked by carrying out duplicate experiments for runs 1 and 5 under the same conditions. For the duplicate of run 1, d*x*/d*t* was determined to be 7.16 (±0.16) × 10^{-5} mole/l. min (*vs.* 7.0 × 10^{-5} in the first experiment); for the duplicate of run 5 d*x*/d*t* = 5.87 (±0.16) × 10^{-5} mole/l. min (*vs.* 5.92 × 10^{-5}). Excellent reproducibility seems indicated.

Relative Reactivity of Cyclooctene *vs.* Cyclohexene. A mixture of 48.5 mmoles of cyclohexene, 48.4 mmoles of cyclooctene, and 10 mmoles of phenyl(bromodichloromethyl)mercury in 15 ml of benzene in a 50-ml, three-necked flask equipped with a condenser, thermometer, nitrogen inlet tube, and a magnetic stirring assembly was heated at 80° under nitrogen for 3 hr. Phenylmercuric bromide (3.30 g, 93%) was filtered, and the filtrate was distilled at 30° (10^{-6} mm). Glpc analysis of the distillate (1,2,4-trichlorobenzene internal standard) was carried out using an oven temperature of 150° with a helium flow rate of 50 cc/min (4 ft × 1/8 in. aluminum column; 10% SE-30 on Chromosorb P). The yields of 7,7-dichlorobicyclo[4.1.0]heptane and 9,9-dichlorobicyclo[6.1.0]nonane were 41.9 and 51.9%, respectively, and these values were used to calculate[5] *k*(cyclooctene)/*k*(cyclohexene) = 1.24.

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