the solvent front. In a similar manner, 7 mg of **7b** was reduced to give 4.6 mg of **13b**; 27 mg of **9b** was reduced to give 19 mg of **15b**; and 13 mg of **10b** was reduced to give 8.7 mg of **16b**. These samples were all analyzed without purification. The **a** series triols prepared in the same way were purified by flash chromatography (silica gel, neat ethyl acetate), but this treatment resulted in very poor yields.

Preparation of Trimethylsilyl Ether Derivatives of Triols. A mixture of 1 mg of triol, 0.1 mL of (trimethylsilyl)imidazole, and 0.1 mL of dry pyridine was heated at 80 °C for 30 min. The resulting reaction mixture was then analyzed by GC/MS. The results were shown in Tables VI and VII.

Preparation of the Triacetate Derivatives of Triols. The triacetate derivatives were prepared by stirring the triols with an excess of acetic anhydride in methylene chloride in the presence of 2 equiv of 4-(dimethylamino)pyridine. For example, 6 mg (18 μmol) of **13a**, 50 μL of acetic anhydride, and 5 mg (41 μmol) of (dimethylamino)pyridine in 3 mL of methylene chloride were stirred 15 min at room temperature. The reaction product was then flash chromatographed using 4:1 ether–pentane.

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Supplementary Material Available: Discussion of NMR and MS data on triols, spectroscopic data and experimental details on preparation of hydroperoxides, and tables of NMR, MS, and chromatographic data (15 pages).

Rearrangement and Catalysis in the Seyferth Reaction

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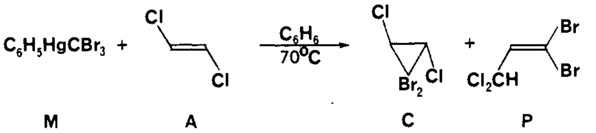
Abstract: The Seyferth reagent $PhHgCBr_3$ reacts with *trans*-1,2-dichloroethene to give two major products, *trans*-1,1-dibromo-2,3-dichlorocyclopropane (C) and 1,1-dibromo-3,3-dichloropropene (P). The stereospecifically formed cyclopropane is consonant with a singlet carbene mechanism, but the rearranged propene requires a second intermediate. Observation that the concentration ratio [P]/[C] is inversely proportional to the concentration of the alkene demonstrates that there are two intermediates, that the cyclopropane comes from the first-formed intermediate, and that the propene comes from the second-formed intermediate. The further observation that [P]/[C] is directly proportional to the concentration of starting material (the Seyferth reagent) requires that an additional mole of $PhHgCBr_3$ react with the first intermediate to form the second intermediate. Thus, the second intermediate must be a complex between the Seyferth reagent and the singlet carbene. Measurement of [P]/[C] as a function of aryl substituent in $ArHgCBr_3$ demonstrates that the Seyferth reagent serves as a Lewis base in the catalytic step. The near absence of rearranged material when phenyl is replaced by cyclohexyl in the Seyferth reagent suggests that the phenyl ring or the phenyl–mercury bond is the basic site. The ratio [P]/[C] is linearly proportional to either σ^+ or arene ionization potential in the series $ArHgCBr_3$, so that the second intermediate probably is a σ or π complex between the carbene and the aryl group. Electron donation from the aryl group increases the nucleophilicity of the carbene and heightens its reactivity with the electron-deficient alkene.

Cyclopropanation by the Seyferth reagent $C_6H_5HgCBr_3$ occurs via a free, singlet carbene, $:CBr_2$, in a reaction that has been well studied.[2] When the alkene is electron deficient, however, the singlet reaction is slow. We found that with dichloroethene a rearrangement pathway occurs in comparable yield to that of cyclopropanation.[3] Furthermore, the rearrangement pathway appeared to be catalyzed by the Seyferth reagent itself.[4] Consequently, we have carried out a thorough examination of the Seyferth reaction with dichloroethene in order to understand the mechanism of catalysis. We report here that the Seyferth reagent serves as a Lewis base in the rearrangement pathway, that the aryl ring is the catalytic site, and that mercury may serve as a template for gathering together carbene and alkene.

Results

trans-Dichloroethene (A) reacts with phenyl(tribromomethyl)mercury (M) in benzene at 70 °C to give two major products, the expected stereospecifically formed cyclopropane (C) and a rearranged propene (P) (eq 1).[5] The cyclopropane is stable to the reaction conditions, so that the propene must be a primary product. *cis*-Dichloroethene undergoes the same reaction but



(1)

Table I. Reaction of 2.5 mol % of $PhHgCBr_3$ with 25 mol % *trans*-CHCl=CHCl as a Function of Temperature[a]

product	60 °C	70 °C	80 °C
propene (P)	0.76	0.75	0.82
cyclopropane (C)	2.69	2.37	2.59
C_6H_5Br[b]	0.41	0.39	0.47
$CHBr_3$[b]	0.17	0.08	0.09
$CBr_2{=}CBr_2$[b]	0.35	0.32	0.34
$Br(CH_2)_6Br$[c]	1.00	1.00	1.00
[P]/[C]	0.28	0.32	0.32

[a] In benzene for 24 h. [b] Observed also in the absence of alkene. [c] Internal standard, not a reaction product.

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[1] (a) This work was supported by the National Science Foundation (Grant No. CHE80-25601). (b) Present address: University of Tokyo, College of General Education. The authors thank Prof. P. P. Gaspar (Washington University, St. Louis, MO) for important discussions.

(2) Seyferth, D.; Mui, J. Y.-P.; Burlitch, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4953–4959.

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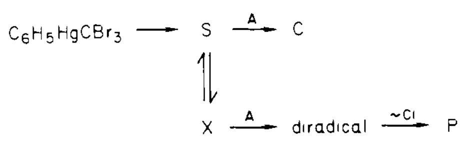
Scheme I



produces the cis cyclopropane as well as the same rearranged propene. Dibromoethene undergoes a similar reaction with this Seyferth reagent, the cis alkene giving the cis cyclopropane from the singlet carbene, the trans form giving the trans cyclopropane, and both forms giving a common rearranged propene. In the case of *trans*-1,2-dichloroethene, which is the subject of the present study, the two products are both formed in significant amounts and comprise about 65% of the material balance. Also produced are tetrabromoethene, bromobenzene, and bromoform. These three products, however, are formed in the absence of dichloroethene and hence are not relevant to this study of the Seyferth reaction. No other product is formed in excess of 5%.

Reaction of 2.5 mol % of phenyl(tribromomethyl)mercury with 25 mol % of *trans*-1,2-dichloroethene in benzene for 24 h at 70 °C (our standard conditions) produces a ratio of rearranged propene to stereospecific cyclopropene of about 0.32. Temperature does not have a large effect on the product distribution, as can be seen from the data in Table I. The data are all for a reaction time of 24 h. Below 60 °C, reaction is incomplete in this amount of time. Effervescence becomes a problem about 80 °C. Because of the very low reactivity of dichloroethene, the products P and C are not observed in solvents with acidic hydrogens, e.g., alcohols or even some ethers. A host of other procedures for generating dibromocarbene thus is eliminated.

Although the cyclopropane reasonably comes from reaction of singlet dibromocarbene with the alkene by the mechanism suggested by Seyferth,[6] the mechanism to produce the propene is unclear. The stereospecificity or high stereoselectivity of the pathway to the cyclopropane would seem to exclude a triplet carbene as a common intermediate, yet this spin state is a possible precursor of the propene. Thus, the alkene A could react with the triplet to produce a diradical, in which a facile[5] 1,2-chlorine shift would give the observed propene (eq 2). Because the 1,2

$$^3{:}CBr_2 + \underset{A}{ClHC{=}CHCl} \rightarrow \dot{C}Br_2{-}CHCl{-}\dot{C}HCl \rightarrow \underset{P}{CBr_2{=}CH{-}CHCl_2} \quad (2)$$

shift occurs very rapidly,[5] there would be little or no time for bond rotation and ring closure to form the cyclopropane with loss of stereochemistry.

The ratio of the two major pathways, which we will designate for the moment as nonsinglet and singlet, is reflected in the ratio of products, [P]/[C]. The kinetic dependence of the alkene concentration [A] is different for the two pathways. Mechanistic divergence occurs at the singlet carbene, which either reacts with alkene or is converted to the second (nonsinglet) intermediate. Such a mechanism is shown in Scheme I. If both products came directly from a common intermediate, the ratio [P]/[C] would be independent of the concentration of alkene. In Scheme I, the singlet carbene [S] is partitioned into two pathways. Production of C has a first-order dependence on [A], whereas conversion of singlet to the second intermediate X is independent of [A]. Definitive proof that there are two intermediates leading to the two products consequently can come from examination of the ratio [P]/[C] as a function of alkene concentration.[6] Figure 1 shows such a plot for the reaction of eq 1, in which the concentration of *trans*-1,2-dichloroethene was varied from 99 to 14.2 mol %. The concentration must be high enough to maintain pseudo-first-order conditions in alkene. The slope is 0.0436 and the correlation coefficient 0.994. The dependence of [P]/[C] on [A] is inverse first order, as predicted by Scheme I. Another run from 99 to 11.1 mol % alkene gave a plot with a slope of 0.0448 and a correlation coefficient of 0.990. A plot of [C]/[P] vs. [A] (Figure 1 with both coordinates inverted) also in linear, whereas a plot of [P]/[C] vs. [A] is extremely nonlinear.

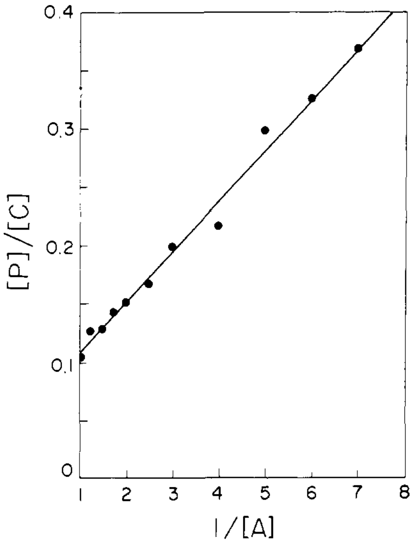


Figure 1. Ratio of products from eq 1, [P]/[C], as a function of the concentration of *trans*-1,2-dichloroethene to the inverse first power.

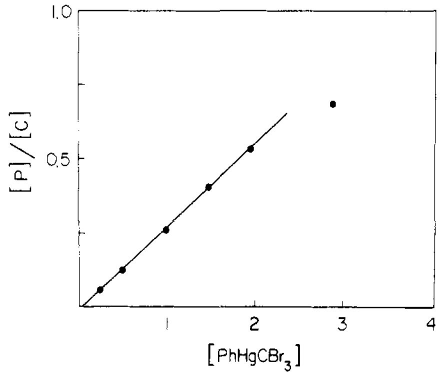


Figure 2. Ratio of products from eq 1 as a function of the concentration of Seyferth reagent.

Variation of other components in the reaction produced a result that is not predicted from the mechanism in Scheme I. The product ratio [P]/[C] depends on the concentration of starting Seyferth reagent, M. Figure 2 shows a plot of the product ratio vs. [M] for the reaction of phenyl(tribromomethyl)mercury with 25 mol % of *trans*-1,2-dichloroethene. There is a first-order dependence of the ratio on [M]; i.e., the amount of the rearranged propene approaches 0 as the concentration of Seyferth reagent goes to 0. The slope of the plot is 0.280, the intercept essentially 0, and the correlation coefficient 0.9998. Another run gave values of 0.274 for the slope and 0.996 for the correlation coefficient.

The mechanism in Scheme I is deficient in some way because it predicts no dependence of the product ratio on the concentration of Seyferth reagent. Thus, we conclude that the second intermediate X could not be the simple triplet dibromocarbene, since intersystem crossing should be fast in the presence of heavy atoms (Br) and not require catalysis. Moreover, singlet $:CBr_2$ is considerably more stable than the triplet.[7]

In order to obtain further information about the nature of the second intermediate, we prepared the series of Seyferth reagents with para substituents in the aromatic ring. The rationale was to probe electron demand in the second intermediate by measuring

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[6] This kinetic approach is due to the following: McConaghy, J. S., Jr.; Lwowski, W. *J. Am. Chem. Soc.* **1967**, *89*, 2357–2364. The same kinetic approach has been used recently: Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *Ibid.* **1980**, *102*, 276–287.

[7] Jones, M., Jr.; Tortorelli, V. J.; Gaspar, P. P.; Lambert, J. B. *Tetrahedron Lett.* **1978**, 4257–4260.

Table II. Relative Product Ratios for the Reaction of p-$XC_6H_4HgCBr_3$ (M) with 25 mol % of *trans*-CHCl=CHCl

X	mol %, M	[P][b]	[C][c]	[X][d]	[S][e]	[P]/[C]
OCH_3	1.0	0.49	1.44	0.20	1.00	0.34
	2.5	0.63	0.95	0.29	1.00	0.66
	4.0	0.43	0.65	0.35	1.00	0.66
H	1.0	0.40	2.95	0.17	1.00	0.14
	2.5	0.62	2.02	0.22	1.00	0.31
	4.0	0.76	1.68	0.26	1.00	0.45
Cl	1.0	0.47	2.70	0.18	1.00	0.17
	2.5	0.86	2.01	0.26	1.00	0.43
	4.0	1.18	1.82	0.35	1.00	0.65
F	1.0	0.44	2.95	0.094	1.00	0.15
	2.5	0.84	2.26	0.18	1.00	0.37
	4.0	1.08	1.92	0.23	1.00	0.56
NO_2	0.5	0.22	2.65		1.00	0.08
	1.0	0.36	3.02		1.00	0.12
	2.5	0.59	2.21	0.098	1.00	0.27
	4.0	0.54	1.58	0.13	1.00	0.34

[a] In benzene for 24 h at 70 °C. Each entry is the average of at least two runs. [b] 1,1-Dibromo-3,3-dichloropropene. [c] *trans*-1,1-Dibromo-2.3-dichlorocyclopropane. [d] Tetrabromoethane. [e] The internal standard, 1,6-dibromohexane.

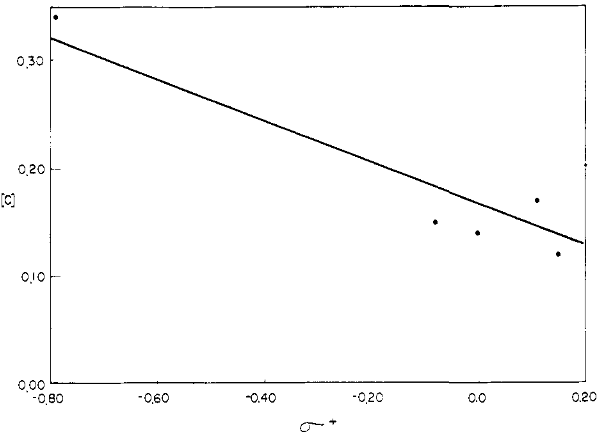


Figure 3. Ratio of products from eq 1 as a function of aryl substitution ($ArHgCBr_3$) as measured by the Hammett σ^+.

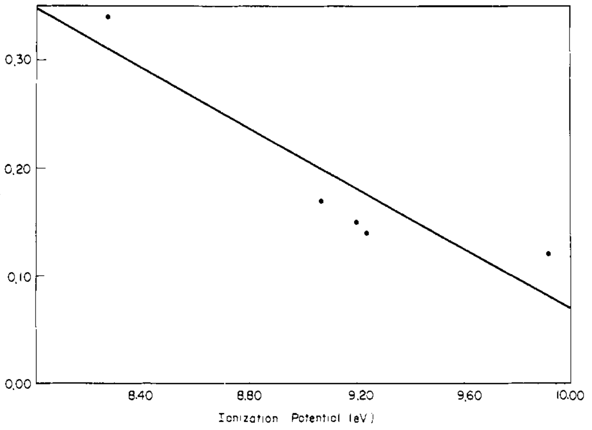


Figure 4. Ratio of products from eq 1 as a function of aryl substitution ($ArHgCBr_3$) as measured by the ionization potential of the analogous arene (ArH).

the effect of the aromatic substituents on the product ratio [P]/[C]. For this purpose we prepared p-$XC_6H_4HgCBr_3$, with X = CH_3O, H, F, Cl, and NO_2, and decomposed them at 70 °C in benzene for 24 h in the presence of 25 mol % of *trans*-1,2-dichloroethene. The reactions were carried out for 1.0, 2.5, and 4.0 mol % of the Seyferth reagent. The product ratios are given in Table II. A relationship between substituent electron demand and product ratio was sought by consideration of various substituent parameters. The plots of [P]/[C] vs. σ_I, σ_p, and σ_R were extremely scattered (correlation coefficients 0.26, 0.70, and 0.78, respectively, for 1.0 mol % Seyferth reagent). The best correlations were obtained with σ^+ and with ionization potential[8] of the arene (anisole, benzene, fluorobenzene, chlorobenzene, nitrobenzene) (correlation coefficients respectively 0.96 and 0.92 for 1.0 mol % and 0.91 and 0.95 for 2.5 mol %). The plots for 1.0 mol % are given in Figures 3 and 4. Only the plots with ionization potential are monotonic.

To test the importance of the presence and location of the phenyl ring in the Seyferth reagent, we examined cyclohexyl(tribromomethyl)mercury and (2-phenylethyl)(tribromomethyl)mercury as the source of dibromomethylene. These reagents were allowed to decompose in the presence of dichloroethene, and the product distributions are given in Table III.

Discussion

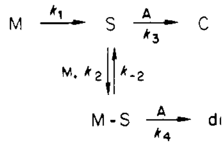
The mechanism of Scheme I correctly predicts the inverse, first-order dependence of [P]/[C] on alkene concentration, but it fails to predict any dependence on the starting material, $PhHgCBr_3$. Both kinetic results can be accommodated by a modification of Scheme I, in which the conversion of the singlet S to the second intermediate X requires a molecule of starting material M, as shown in Scheme II.

Table III. Reaction of $RHgCBr_3$ with *trans*-CHCl=CHCl in Benzene[a]

	R = cyclohexyl	R = $PhCH_2CH_2$		
time, h	24.0	18.0	24.0	48.0
temp, °C	50.0	70.0	70.0	70.0
mol % $RHgCBr_3$	5.0	2.5	2.5	2.5
mol % alkene	25.0	25.0	25.0	25.0
$CBr_2{=}CH{-}CHCl_2$, P	<0.015	0.10	0.10	0.12
cyclopropane, C	0.44	1.81	1.88	1.83
$CHBr_3$	5.54	0.40	0.41	0.36
$Br_2C{=}CBr_2$	0.10	0.25	0.21	0.19
$PhCH_2CH_2Ph$	0.0	0.63	0.67	0.68
$Br(CH_2)_6Br$[b]	1.00	1.00	1.00	1.00
[P]/[C]	<0.034	0.055	0.053	0.066

[a] Products are reported as ratios with an added internal standard, 1,6-dibromohexane. [b] Internal standard, not a reaction product.

Scheme II



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Steady-state treatment of the second intermediate (M–S) gives

$$k_2[\mathrm{M}][\mathrm{S}] = k_4[\mathrm{M{-}S}][\mathrm{A}] + k_{-2}[\mathrm{M{-}S}]$$

or

$$\frac{[\mathrm{M{-}S}]}{[\mathrm{S}]} = \frac{k_2[\mathrm{M}]}{k_4[\mathrm{A}] + k_{-2}}$$

The ratio of products from the two intermediates then is

$$\frac{[\mathrm{P}]}{[\mathrm{C}]} = \frac{\mathrm{d}[\mathrm{P}]/\mathrm{d}t}{\mathrm{d}[\mathrm{C}]/\mathrm{d}t} = \frac{k_4[\mathrm{A}][\mathrm{M{-}S}]}{k_3[\mathrm{A}][\mathrm{S}]}$$

or

$$\frac{[\mathrm{P}]}{[\mathrm{C}]} = \frac{k_4}{k_3}\,\frac{k_2[\mathrm{M}]}{k_4[\mathrm{A}] + k_{-2}}$$

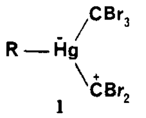
which simplifies to

$$\frac{[\mathrm{P}]}{[\mathrm{C}]} = \frac{k_2[\mathrm{M}]}{k_3[\mathrm{A}]} \tag{3}$$

if $k_4[\mathrm{A}] >> k_{-2}$, i.e., if the mercury–carbene complex goes to product much faster than it returns to the singlet (the inequality is further assisted by the high concentration of alkene that we maintain for pseudo-first-order conditions).

Thus, Scheme II correctly reproduces the observed kinetic dependence of the product ratio on [A] and [M]. A number of mechanisms are clearly eliminated. (1) Production of both products directly from the singlet would require a further arrow in Scheme II from S to the diradical and deletion of k_4. Kinetic analysis of such a mechanism would produce no dependence of the product ratio on alkene concentration. (2) Production of both products from the diradical would eliminate the k_3 pathway and add an arrow from the diradical to C. Again, such a mechanism would exhibit no dependence of the product ratio on alkene concentration. (3) Any mechanism in which the M–S complex precedes formation of the singlet predicts that the product ratio depends on alkene concentration to the first order rather than to the inverse first order. (4) A mechanism whereby $\mathrm{PhHgCBr_3}$ rearranges to give $\mathrm{Ph(HgBr)CBr_2}$ (precursor of P) as the first intermediate, followed by loss of PhHgBr to give the singlet (precursor of C) as the second intermediate, is eliminated. Such a mechanism requires a dependence of the product ratio on [PhHgBr]. We observed that this material is insoluble in benzene and does not affect [P]/[C]. Moreover, such a mechanism does not give the correct dependence on [A]. Thus, the cyclopropane *must* come from the first intermediate, which we are assigning the singlet carbene structure, and the rearranged propene *must* come from the second intermediate, which we are assigning the M–S complex structure. (5) Production of the cyclopropane from the singlet but of the propene directly from the starting material, without any second intermediate, would require an arrow in Scheme II directly from the starting material to the diradical. Again, this mechanism predicts a direct first-order dependence of the product ratio on alkene concentration, contrary to observation. (6) Extremely rapid equilibration between two intermediates ($k_{-2} >> k_4[\mathrm{A}]$) would have predicted no dependence of [P]/[C] on [A]. (7) Finally, the first-order dependence of the product ratio on the starting material M eliminates the mechanism of Scheme I and any other mechanism that does not include a second molecule of starting material on the pathway between the first and second intermediates.

With the overall mechanism defined, the next question to address is the nature of the second intermediate, M–S. Structures **1**–**5** offer a number of possibilities: mercury serving as a Lewis acid (**1**), mercury serving as a Lewis base (**2**), a π complex with the aryl ring (**3**), a σ complex with the aryl ring (**4**), and electron donation by the C–Hg bond (**5**).



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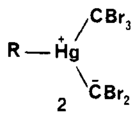

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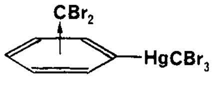

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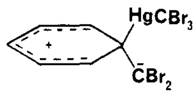

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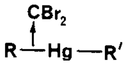

5

There is precedent for mercury(II) acting as a Lewis acid, as in $\mathrm{HgCl_2 + Cl^- \rightarrow HgCl_3^-}$.[9] Thus, structure **1** is feasible, but it requires the electrophilic dibromocarbene (m = 0.65, in the electrophilic range of Moss's scale[10]) to serve as a nucleophile. The experiments with the aryl-substituted Seyferth reagents, however, eliminate this possibility. The [P]/[C] ratio decreases with electron withdrawal, whereas formation of **1** should be favored by electron donation. The slopes of the Hammett-like plots (Figures 3 and 4) indicate that the catalytic molecule of Seyferth reagent is clearly serving as an electron donor or Lewis base.

In the remaining four structures, the Seyferth reagent is the Lewis base and the carbene the Lewis acid, in agreement with the Hammett plots and with the expected role of dibromomethylene. In structure **2**, mercury takes on the unprecedented oxidation state of Hg(IV), in which two electrons must be utilized from the filled 5d orbitals. In contrast, trivalent, negatively charged mercury, as in the eliminated structure **1** or $\mathrm{HgCl_3^-}$, is Hg(II), formed by loss of the two outer electrons in the 6s orbital. Thus, **2** is unlikely on theoretical grounds. The experiments with cyclohexyl(tribromomethyl)mercury appear to eliminate it under any circumstance. This Seyferth reagent produces little or no rearranged product (Table III), indicating that the phenyl ring must be the electron donor. Since cyclohexyl(tribromomethyl)mercury possesses two C–Hg bonds capable of fulfilling the role of Lewis base shown in **5**, this structure also appears to be eliminated. The experiments with (2-phenylethyl)(tribromomethyl)mercury also give very little rearranged propene, in contrast to the expectations from **2** and **5**. A structure, not shown, of the traditional metal-carbene type, $\mathrm{RR'Hg{=}CBr_2}$, is eliminated for the same reason.

The experiments with the aryl, cyclohexyl, and 2-phenylethyl Seyferth reagents eliminate all possibilities except those in which the phenyl ring serves as the Lewis base, namely the σ and π complexes **4** and **3**. The best Hammett-type plots for testing these intermediates are those given in Figures 3 and 4, respectively. The Hammett σ^+ probably is the best probe for the σ complex and the ionization potential of the arenes for the π complex. The correlation coefficients are similar for both plots, although the high value for the σ complex (Figure 3) may be deceptive. The fact that only the ionization potential plot is monotonic suggests that the π complex may be the better model. There actually are several possible σ complexes, in which the carbene is attached at the ipso (shown in **4**), ortho, meta, or para positions with respect to mercury. Use of appropriate linear combinations of σ constants to mimic attachment at the other positions made no improvement on the Hammett plot. A possible side product from a σ complex, $\mathrm{PhCHBr_2}$, was not observed.

Whether the structure of the second intermediate be σ or π complex, the $\mathrm{CBr_2}$ moiety has been changed from an electrophilic carbene into a more nucleophilic carbanionoid species. This alteration of character can explain the catalytic role of the second molecule of Seyferth reagent. Uncomplexed dibromomethylene is electron deficient and reacts very slowly with electron-deficient alkenes such as dichloroethene. In contrast, no rearranged material is observed with electron-rich alkenes, such as 2-butene. Complexation with the phenyl ring in **3** or **4** heightens the nucleophilicity of the carbene and enables it to react more facilely with the alkene.

The final point to be examined is the location and timing of reaction between the second intermediate and the alkene. Reaction

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(9) Davies, J. E. D.; Long, D. A. *J. Chem. Soc. A* **1968**, 2564–2568.

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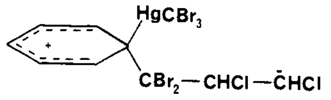
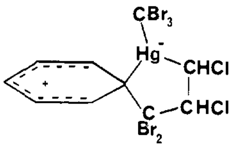
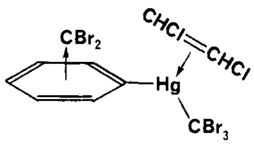
can occur at three or more locations. (1) Reaction at the carbene produces a new complex of the type **6**, shown for the σ complex. (2) Reaction of a cycloaddition type at both the carbene and mercury produces a ring of the type **7**, also illustrated for the σ complex. (3) Reaction at mercury produces a structure, **8**, in which mercury is still in the +2 oxidation state.



6



7



8

In the case of **6**, loss of the trimethylene segment from the σ or π complex gives back the catalytic molecule of Seyferth reagent and produces the diradical ·CBr$_2$–CHCl–CHCl·, or its dipolar equivalent, which leads to the rearranged propene by a 1,2 chlorine shift. The 1,2 chlorine shift could take place prior to dissociation or after formation of the trimethylene fragment. In **7**, a cycloreversion reaction would produce the catalytic molecule of Seyferth reagent and the same diradical as from **6**. We do not observe any possible metathesis products from **7**, e.g., CHCl=CBr$_2$. In **8**, the catalytic molecule of Seyferth reagent has served as a template, gathering the carbene at one site and the alkene at another, for an intramolecular reaction to occur between them, again followed by dissociation and rearrangement. There is ample precedent for mercury–alkene complexes in the electrophilic mercuration of alkenes. Such complexes in fact have been studied under stable conditions by NMR spectroscopy.[11]

Each of these intermediates offers certain attractions and disadvantages, but we are not able to define the mechanism much further. The reactivity of (2-phenylethyl)(tribromomethyl)mercury is suggestive of an intermediate such as **8**. This Seyferth reagent has a phenyl ring but does not give much rearranged propene. It more closely resembles the cyclohexyl than the aryl Seyferth reagents. If the σ or π complex forms on the phenyl ring in the 2-phenylethyl case and if the alkene complexes at mercury, as in **8**, the two reactants may be too far apart, so that the template fails. Such considerations do not apply to **6** and would be a function of ring size in **7**.

Summary

The Seyferth reagent PhHgCBr$_3$, in its reaction with *trans*-1,2-dichloroethene, follows two distinct pathways. A first step, decomposition to form singlet dibromocarbene, is common to both pathways. The uncomplexed carbene reacts directly with dichloroethene to produce *trans*-1,1-dibromo-2,3-dichlorocyclopropane stereospecifically. A second molecule of Seyferth reagent reacts with the carbene in the second pathway to produce a complex, which leads eventually to the rearranged propene. Because the second pathway requires a total of 2 mol of Seyferth reagent and the first pathway only 1 mol, the ratio of propene to cyclopropene, [P]/[C], is directly proportional to the concentration of Seyferth reagent [M]. Because the singlet carbene requires a mole of the alkene for its direct reaction to give cyclopropane but does not react with alkene in its alternative pathway to give the mercury–carbene complex, the [P]/[C] ratio depends on alkene concentration to the inverse first power, $[A]^{-1}$. Experiments corroborated these predictions and thus demonstrated that the cyclopropane comes from the first-formed intermediate, that the rearranged propene comes from the second intermediate, and that formation of the second intermediate requires an additional mole of Seyferth reagent (Scheme II).

Electron donation from the aryl ring in aryl(tribromomethyl)mercury increases the proportion of rearranged material. Thus, during complex formation, the carbene is the electrophile and the Seyferth reagent the nucleophile. The absence of significant amounts of rearranged product when the phenyl ring in the Seyferth reagent is replaced by an aliphatic group suggests that complexation occurs at the aryl ring, to form either a σ or a π complex. Linear plots of [P]/[C] with σ^+ and with ionization potential of arenes are consistent with the π or σ complex structure of the second intermediate (**3** and **4**). After complexation, the heightened nucleophilicity of the CBr$_2$ moiety enables it to react with dichloroethene to form one of the intermediates of the types **6**–**8**. Dissociation and rearrangement (or vice versa) then produce the rearranged propene.

After our original report of the rearranged propene,[3] similar rearrangements were observed in three other studies. Jones and co-workers[7] observed that *cis*-1,2-dichloroethene reacts with singlet dicarbomethoxymethylene to give the cis cyclopropane but with the triplet carbene to give (CO$_2$Me)$_2$C=CH—CHCl$_2$, the rearranged propene analogous to our product P. Gaspar and co-workers[12] observed that singlet diphenylmethylene reacts stereospecifically with either *cis*- or *trans*-1,2-dichloroethene to give the cyclopropane. Reaction of these alkenes with the triplet carbene, however, produced the analogous, rearranged propene Ph$_2$C=CH—CHCl$_2$. Schuster and co-workers[13] observed that fluorenylidene (FlC:) reacts in its singlet state with 1,2-dichloroethene to give the cyclopropane and in its triplet state to give the rearranged FlC=CH—CHCl$_2$. The reaction in each of these three cases is of a singlet carbene to give the cyclopropane and of a triplet carbene to give the rearranged propene. The triplet would react with dichloroethene to give a diradical intermediate, R$_2\dot{C}$–CHCl–$\dot{C}$HCl, which would undergo a 1,2-chlorine shift to form the product. The diradical suggested in these triplet reactions must be essentially identical with that formed in the mechanism of Scheme II after dissociation of the catalytic molecule of PhHgCBr$_3$.

Common to all four observations of rearrangement is the substrate that we used in the original study, 1,2-dichloroethene. Its low reactivity with singlet carbene and its ability to lead to an intermediate in which a facile rearrangement can take place are primarily responsible for this new mode of carbenoid reactivity. Substrates like 2-butene, which are electron rich and react rapidly with singlet carbene, or which have no available rearrangement pathway, can be expected to give only the normal carbene product, the stereospecifically formed cyclopropane.

Experimental Section

NMR spectra were taken on Varian T-60 or Perkin-Elmer R20B spectrometers. Infrared spectra were measured on a Perkin-Elmer 283 spectrometer. Gas chromatography was performed on Varian series 1520B or Vista 6000 and Hewlett-Packard series 700 gas chromatographs with $^1/_8$ and $^3/_8$ in. packed columns for analytical and preparative purposes, respectively. Peak areas were measured by multiplying height by width at half-height, by cutting and weighing, or by electronic integration on a Hewlett-Packard 3390A Reporting Integrator. Values shown in the figures were obtained by averaging the results from three or four injections. Mass spectra were obtained on a Hewlett-Packard mass spectrometer, Model 5985.

General Procedures. Vessels for the Seyferth reaction were made from 11-mm Pyrex tubing cut into 14-in. lengths and sealed at one end. All tubes were washed in an Alconox water solution, rinsed thoroughly with water and acetone, and dried at 110 °C for at least 24 h prior to use. The PhHgCBr$_3$ was weighed directly into the tubes on a Mettler balance. Mallinckrodt reagent grade benzene was dried by distillation from sodium, with benzophenone as an indicator of dryness. *trans*-1,2-Dichloroethene (Aldrich) was distilled through a 15-cm silvered vacuum-jacketed column packed with glass helices (bp 48 °C).

Reaction with Variation of Alkene Concentration. The reaction at 25 mol % dichloroethene with 1 mol % PhHgCBr$_3$ is given as an example.

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Table IV. Properties of $R(CBr_3)Hg$ Compounds

R	% yield[a]	mp, °C	anal. C[b]	anal. H[b]
C_6H_5	56	117–118 dec	15.57 (15.88)[c]	0.83 (0.95)[c]
p-FC_6H_4	55	118–119 dec	15.30 (15.36)[d]	0.59 (0.74)[d]
p-$CH_3OC_6H_4$	46	102–103 dec	17.11 (17.18)[e]	1.17 (1.26)[e]
p-ClC_6H_4	38	132–133 dec	14.88 (14.91)[f]	0.60 (0.72)[f]
p-$NO_2C_6H_4$	74	131–132 dec	15.02 (14.64)[h]	0.63 (0.70)[h]
cyclohexyl	16	50–53 dec[i]		
$C_6H_5CH_2CH_2$	35	70–72[j]		

[a] From ArHgCl. [b] Calculated values are given in parentheses. [c] Calculated for $C_7H_5Br_3Hg$. [d] Calculated for $C_7H_4FBr_3Hg$. [e] Calculated for $C_8H_7OBr_3Hg$. [f] Calculated for $C_7H_4Br_3ClHg$. [g] Calculated for $C_8H_4NBr_3Hg$. [h] Calculated for $C_7H_4NO_2Br_3Hg$. [i] Lit.[18] 53–56 °C. [j] Lit.[18] 71–73 °C.

A stock solution of 6.077 g of dichloroethene (0.0627 mol), 14.454 g of benzene (0.187 mol), and 0.079 g (3.2×10^{-4} mol) of 1,6-dibromohexane was prepared. Into a tube containing 0.1320 g of $PhHgCBr_3$ (2.49×10^{-4} mol) was quickly weighed 2.060 g of the stock solution. The tube was stoppered and placed in a 2-propanol/dry ice bath. The reaction mixture was degassed by four repetitions of pumping, thawing, and refreezing on a vacuum line at $1\text{–}5 \times 10^{-2}$ mmHg. After the final degassing cycle, the tube was carefully sealed with a gas-oxygen flame. Individual reaction tubes were marked and stored at dry ice temperature until an entire set had been prepared and sealed. The tubes were then immersed in a Haake constant temperature bath at 70 °C. After 5 min, the tubes were individually removed and inverted several times until the $PhHgCBr_3$ dissolved, and the solution was thoroughly mixed. The tubes were then returned to the bath, and the reactions were allowed to go 24 h. At that time the tubes were removed from the bath, relabeled, and stored in a 2-propanol/dry ice bath until workup. Workup consisted of opening the reaction tube, thawing the solution, filtering the solid PhHgBr, washing the solid with 2 mL of diethyl ether, and removing most of the solvent at reduced pressure. Analysis of the solution by gas chromatography gave the relative yields of products. An 8 ft × $^1/_8$ in. 25% diethylene glycol succinate on NAW Chromosorb W 60/80 mesh column was used for analysis of the products. Retention times of 6.5 and 10 min at 120 °C and a flow rate of 75 cm^3/min were obtained for 1,1-dibromo-3,3-dichloropropene and *trans*-1,1-dibromo-2,3-dichlorocyclopropane, respectively. Each run was injected three or four times. No corrections were made for relative thermal conductivities. Thus, our ratios do not reflect absolute concentrations.

Arylmercuric Chlorides.[14] The p-Cl, p-F, and p-CH_3O systems were prepared by the following procedure, illustrated for p-Cl. Into a 500-mL, three-necked flask, equipped with a N_2 inlet, a condenser, and a 250-mL addition funnel, were added 8.0 g (0.32 mol) of Mg turnings and 100 mL of diethyl ether. A solution of 38.3 g (0.20 mol) of p-bromochlorobenzene in 100 mL of ether was added over a 3-h period. The reaction mixture was refluxed an additional hour, after which time the solution was transferred via Tygon tubing to an addition funnel that contained a sintered glass filter. The solution was added over 30 min to a 500-mL, three-necked flask, equipped with a condenser and containing 65.0 (0.24 mol) of $HgCl_2$ and 100 mL of ether. The mixture was refluxed 2.5 h and then stirred overnight. A solution of 45 g of KCl, 3.0 mL of concentrated HCl, and 100 mL of H_2O was added to the reaction mixture over 20 min. The solid was filtered and recrystallized in 1,4-dioxane to give 50.3 g of white crystals (72%), mp 229–230 °C (lit.[15] 239–240 °C). For p-F, the yield was 32%, mp 278–280 °C (lit.[16] 259–261 °C). For p-CH_3O, the yield was 66%, mp 234–236 °C (lit.[15] 244–245 °C).

The p-NO_2 system[17] was prepared by the following procedure. A mixture of 27.6 g (0.20 mol) of p-nitroaniline, 60 mL of concentrated HCl, and 200 g of ice was cooled to 0 °C, and 13.8 g (0.20 mol) of NaONO, dissolved in 50 mL of H_2O, was added at a rate that kept the solution temperature below 5 °C. The diazonium salt mixture was added to a paste of 54.4 g (0.20 mol) of $HgCl_2$, 39.6 g (0.40 mol) of CuCl, and 40 mL of concentrated HCl in a 2-L beaker at a rate that kept the reaction temperature below 10 °C. Nitrogen was vigorously expelled during the addition. After 15 min of stirring, the brown solid was filtered and washed with 200 mL of 3 M HCl, 150 mL of H_2O, and 200 mL of EtOH. The solid was dried in a vacuum desiccator: 21.33 g (30%) of brown solid, mp 261–263.5 °C (lit.[15] 265–266 °C).

Cyclohexyl(tribromomethyl)mercury was prepared by the method of Seyferth[18] (see Table IV).

Aryl(tribromomethyl)mercury and (2-Phenylethyl)(tribromomethyl)mercury. All preparations closely followed the standard Seyferth procedures.[19] The new compounds are characterized in Table IV.

Registry No. p-$MeOC_6H_4CBr_3$, 89922-19-0; $PhCBr_3$, 2489-03-4; p-$ClC_6H_4CBr_3$, 89922-20-3; p-$FC_6H_4CBr_3$, 24572-48-3; p-$NO_2C_6H_4CBr_3$, 14505-17-0; *trans*-CHCl=CHCl, 156-60-5; CBr_2=$CHCHCl_2$, 56020-81-6; CBr_2=CBr_2, 79-28-7; $Ph(CH_2)_2Ph$, 103-29-7; $Ph(CH_2)_2HgCBr_3$, 58926-17-3; p-BrC_6H_4Cl, 106-39-8; $HgCl_2$, 7487-94-7; p-$NO_2C_6H_4NH_2$, 100-01-6; p-$NO_2C_6H_4N_2^+Cl^-$, 100-05-0; CuCl, 7758-89-6; *trans*-1,1-dibromo-2,3-dichlorocyclopropane, 70063-97-7; cyclohexyl(tribromomethyl)mercury, 40347-48-6.

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