Stereomutation in the Seyferth Reaction

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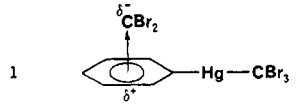
Abstract: The cyclopropanation reaction between dibromomethylene ($:CBr_2$) from the Seyferth reagent ($PhHgCBr_3$) and electron-deficient alkenes is nonstereospecific. Thus fumaronitrile, styrene-*cis*-β-*d*, and *trans*-1,2-dichloroethene give mixtures of the respective cis and trans cyclopropanes. The stereospecific and stereomutated cyclopropanes come from distinct pathways, as the ratio of materials from the two pathways is proportional to $[alkene]^{-1}$. Moreover, the amount of material formed by the nonstereospecific pathway is directly proportional to the concentration of Seyferth reagent. These results are consistent with two parallel product-forming intermediates. The first intermediate, the normal singlet carbene, reacts with alkene stereospecifically. The second intermediate is a complex between carbene and Seyferth reagent, which leads ultimately to an open intermediate such as $\cdot CBr_2CXYCZH\cdot$ in which stereomutation may take place. Examination of a series of para-substituted styrenes showed that the nonstereospecific pathway is favored by electron donation in the alkene. This result is best accommodated by a template intermediate, in which the carbene is complexed with the phenyl ring of the Seyferth reagent and the alkene with the mercury. The components brought together in this fashion may react smoothly to form the diradical or its equivalent.

The reaction of the Seyferth reagent $C_6H_5HgCBr_3$ with the electron-deficient alkene *trans*-1,2-dichloroethene leads to two products by parallel pathways (Scheme I).[2] The singlet carbene ($:CBr_2$) can react with alkenes in the usual fashion to give the cyclopropane (C) stereospecifically. With electron-rich alkenes such as 2-butene, this is the only observed pathway. The poor reactivity of the electrophilic dibromomethylene with the electron-deficient dichloroethene, however, permits a second pathway to surface. Complexation of the singlet carbene with another molecule of the Seyferth reagent produces a material in which the carbenic moiety possesses higher nucleophilicity, as demonstrated by our earlier experiments.[2] This species, which might resemble a π complex, **1**, reacts more rapidly with the electron-



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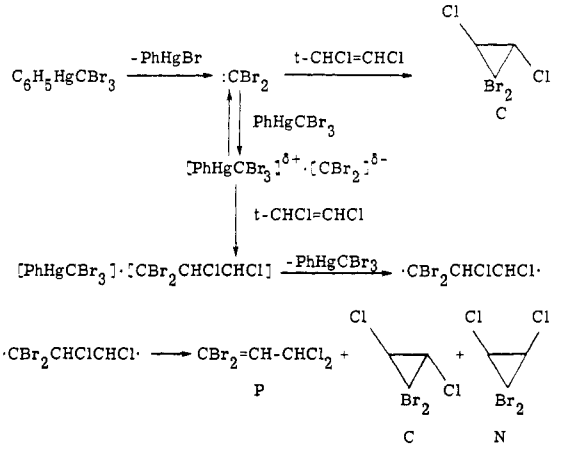
deficient alkene. Loss of the catalytic molecule of Seyferth reagent then gives the diradical shown in Scheme I, which may undergo a rapid 1,2-chlorine shift to produce the indicated alkene (P). Analysis of the ratio of the rearranged propene P to that of the stereospecifically formed cyclopropane C gives a direct measure of the two pathways for dichloroethene. We used the [P]/[C] ratio as a means of defining the mechanism and the structure of the complex, e.g., **1**, through variation of the structure of the Seyferth reagent.[2]

In addition to the 1,2-chlorine shift, it is conceivable that the diradical in Scheme I can ring-close to form the cyclopropane C stereospecifically. Moreover, rotation about the bond between the atoms bearing chlorine, followed by ring closure, could lead to the stereomutated cyclopropane N (Scheme I, final equation). Prior to this study, formation of the stereomutated cyclopropane was known only in cases in which triplet carbenes or alkene–carbene charge-transfer complexes lead to product. Production of the singlet diradical through the complexation pathway of Scheme I provides a novel method for studying their chemistry, in particular their potential for leading to stereomutated cyclopropanes. Our initial examination of the products of the Seyferth reaction with the *trans*- and *cis*-1,2-dichloroethenes failed to reveal stereomutated cyclopropanes.[2] In this case, the availability of the very rapid 1,2-chlorine shift in the diradical made ring closure a poor alternative. Consequently, we have sought electron-deficient alkene substrates that would lead to diradicals that are not likely to undergo 1,2-shifts to rearranged alkenes. Replacement of

Scheme I

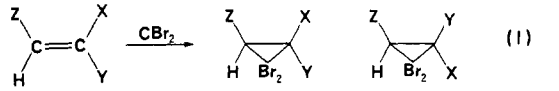


chlorine by groups that have poor migratory aptitude fulfills these conditions. We report herein that such substrates lead to cyclopropane in high yield but with stereomutation.

Results

The Seyferth reagent, $C_6H_5HgCBr_3$, was allowed to decompose in the presence of various alkenes under standard conditions (benzene solvent, 70 °C, 24 h). The products were analyzed by NMR spectroscopy, mass spectrometry, and VPC. Bromoform, bromobenzene, tetrabromoethene, and hexabromocyclopropane were still formed when the Seyferth reagent was decomposed in the absence of alkene, so attention was directed only to the cyclopropane and rearranged propene products.

Electron-rich alkenes and those that were not especially electron deficient gave the stereospecific cyclopropane (analogous to C in Scheme I) as the only major product. These included *trans*-stilbene, *trans*-β-methylstyrene, *trans*-crotonitrile, isocrotonitrile,



(1)

and methyl *trans*-crotonate (Z,Y = C_6H_5; Z = C_6H_5, Y = CH_3; Z = CN, Y = CH_3; Z = CH_3, X = CN; and Z = CO_2Me, Y = CH_3 in eq 1; undesignated letters represent H). For fumaronitrile and styrene-*cis*-β-*d* (Z,Y = CN; Z = C_6H_5, Y = D in eq 1), however, both the stereospecific and the stereomutated cyclopropanes (C and N, respectively) were formed in the reaction. Diethyl fumarate, *trans*-1,2-diodoethene, and *cis*-stilbene gave poor yields and were not considered further.

Additional studies were carried out on fumaronitrile and the deuterated styrene. The product cyclopropanes were stable to the

(1) This work was supported by the National Science Foundation Grant No. CHE83-12285.

(2) Lambert, J. B.; Bosch, R. J.; Mueller, P. H.; Kobayashi, K. *J. Am. Chem. Soc.* **1984**, *106*, 3584–3589.

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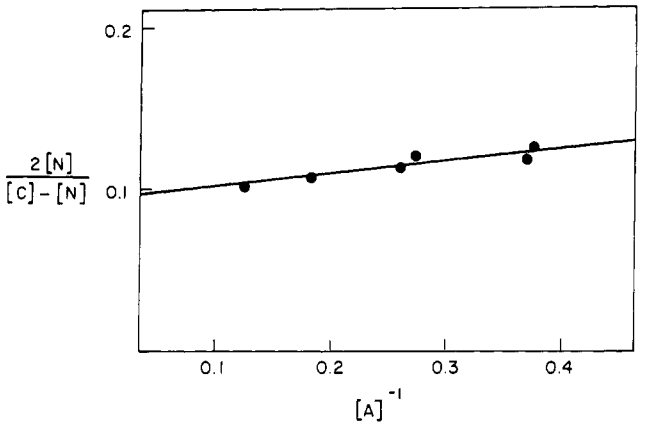


Figure 1. Plot of $2[N]/([C] - [N])$ vs. $[A]^{-1}$ for styrene-*cis*-2-*d* with variation of [A] from 9.3 to 2.7 mol % (slope = 0.156, correlation coefficient = 0.98).

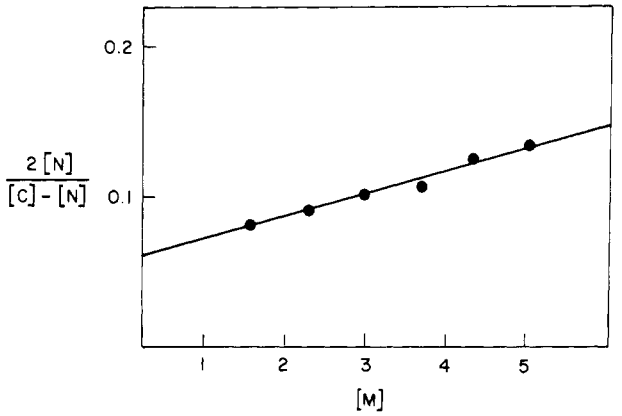


Figure 2. Plot of $2[N]/([C] - [N])$ vs. [M] for styrene-*cis*-2-*d* (slope = 0.149, correlation coefficient = 0.99).

reaction conditions. Moreover, the starting alkenes did not isomerize under reaction conditions. Consequently, both cyclopropanes must constitute primary products. As a standard test for two intermediates, the ratio of products was plotted vs. the reciprocal of the alkene concentration. There is no general method to calculate the amount of C that comes from the diradical intermediate of Scheme I. For styrene, however, we can assume that the diradical $\cdot CBr_2$–CHD–CHPh$\cdot$ is freely rotating, so it leads to equal amounts of N and C. Thus the amount of total product ([N] + [C]) from the diradical is equivalent to 2[N] and can be calculated directly from the observed yield of N. The total concentration of C comprises products from both the stereospecific pathway via the singlet carbene and the nonstereospecific pathway via the complexed carbene and diradical. Since an amount of C equal to N comes from the nonstereospecific pathway, the actual concentration of C from the stereospecific pathway alone is [C] − [N]. Thus the ratio of products from the nonstereospecific and stereospecific pathways is $2[N]/([C] - [N])$, when the diradical leads to equal amounts of C and N. This ratio should be linear in the reciprocal of alkene concentration according to the mechanism of Scheme I. Figure 1 shows a linear plot with slope of 0.156 and correlation coefficient of 0.98 for the products of reaction between styrene and $PhHgCBr_3$.

The radical from fumaronitrile should not necessarily lead to equal amounts of N and C. Nonetheless, such a plot, i.e., of $2[N]/([C] - [N])$ vs. $[alkene]^{-1}$ is linear (r = 0.994). Interestingly, a plot of [N]/[C] vs. $[alkene]^{-1}$ also is linear (r = 0.97). Such a product ratio would be appropriate if the diradical went only to N, and all of C came via the stereospecific singlet reaction (highly unlikely). An intermediate case, in which the radical gave a split of 1/3 to C and 2/3 to N would be represented by a plot of $3[N]/(2[C] - [N])$ vs. $[alkene]^{-1}$, which also proved to be linear (r = 0.993). Apparently, the method is not particularly sensitive to the split of products from the diradical, but the best correlation coefficient was obtained with equal amounts.

Table I. Dependence of Product Ratios on $PhHgCBr_3$ Concentration

alkene[a]	[M][b]	[N][b]	[C][b]	[N]/[C]
fumaronitrile	4.21	0.30	0.70	0.43
	2.95	0.21	0.79	0.26
	2.15	0.15	0.85	0.18
	1.70	0.12	0.88	0.14
	1.30	0.083	0.92	0.090
styrene-*cis*-β-*d*	5.11	0.940	0.060	0.14
	4.36	0.944	0.056	0.13
	3.63	0.951	0.049	0.11
	2.91	0.954	0.046	0.10
	2.18	0.958	0.042	0.092
	1.43	0.962	0.038	0.082

[a] The concentration (mol %) of fumaronitrile was 12.70 (0.22) for each run; that of styrene was 2.95 (0.06) for each run. [b] M is $PhHgCBr_3$; N and C respectively are the nonstereospecifically and the stereospecifically formed cyclopropanes.

Table II. Effect of $PhHgCBr_3$ Concentration on the Product Ratios for the Reaction of $PhHgCBr_3$ with Para-Substituted Styrenes

alkene[a]	[M][a]	[C][a]	[N][a]	[N]/[C]
4-methylstyrene-*cis*-β-*d*[b]	5.07	0.924	0.076	0.18
	4.40	0.928	0.072	0.17
	3.64	0.960	0.040	0.087
	2.90	0.959	0.041	0.089
	2.17	0.971	0.029	0.061
	1.47	0.976	0.024	0.050
4-fluorostyrene-*cis*-β-*d*[b]	4.33	0.939	0.061	0.14
	3.66	0.944	0.056	0.13
	2.94	0.949	0.051	0.11
	2.17	0.961	0.039	0.086
	1.47	0.968	0.032	0.069
4-chlorostyrene-*cis*-β-*d*[b]	5.12	0.970	0.030	0.063
	4.39	0.974	0.026	0.054
	3.58	0.975	0.025	0.052
	2.90	0.976	0.024	0.050
	2.20	0.978	0.022	0.047
	1.81	0.977	0.023	0.047
4-trifluoromethylstyrene-*cis*-β-*d*[b]	5.13	0.854	0.146	*c*
	4.36	0.853	0.147	
	4.06	0.854	0.146	
	2.93	0.839	0.161	
	2.21	0.861	0.139	
	1.45	0.852	0.148	

[a] See footnote *b* in Table I. [b] The alkene concentration (mol %) for 4-methylstyrene was 2.85 (0.06) for each run, for 4-fluorostyrene 2.87 (0.06), for 4-chlorostyrene 2.85 (0.05), and for 4-trifluoromethylstyrene 2.88 (0.06). [c] 4-Trifluoromethylstyrene was an 85/15 mixture of cis/trans isomers to start with. The data show that no stereomutation took palce, so that calculation of [N]/[C] is not relevant as it would reflect only the initial isomer ratio.

The mechanism of Scheme I requires that the ratio of products from the two pathways be directly proportional to the concentration of Seyferth reagent, M. The plot for styrene (Figure 2) is linear with slope 0.115 and correlation coefficient 0.993. The three plots for the product ratios for fumaronitrile vs. [M] also were linear. Table I provides the raw data for these plots. For fumaronitrile, the amount of the nonstereospecific product varied from 8 to 30%. The range for styrene was 4–6%.

A series of para-substituted, cis-deuterated styrenes was prepared in order to explore the effect of electron demand on stereomutation. The substrates were *cis*-*p*-$XC_6H_4CH{=}CHD$, in which X = CH_3, F, Cl, and CF_3. The styrenes were at least 98% deuterated for each case except CF_3, which was only 85% deuterated. Each substrate was decomposed with variation of the concentration of Seyferth reagent (Table II). The plots of $2[N]/([C] - [N])$ vs. [M] were linear in each case, with slopes and correlation coefficients as follows (X, m, r): CH_3, 0.038, 0.94; F, 0.025, 0.99; H, 0.015, 0.99; Cl, 0.0044, 0.94; CF_3, 0.00, 0.98. A Hammett-like plot of these slopes vs. σ^+ was roughly linear (r = 0.90) with a negative slope (ρ = −2.0).

The large amount of stereomutated product for furmaronitrile led us to reexamine the reaction mixtures for dichloroethene and

Table III. Effect of Additives and Solvent on Product Ratios for the Reaction of $PhHgCBr_3$ with *trans*-CHCl=CHCl

solvent	additive	[P]	[C]	[N]	[N]/[P]	[N]/[C]
C_6H_6[a]		0.95	2.87	0.18	0.19	0.06
CCl_4[a]		1.47	2.78	0.30	0.20	0.11
CCl_4[a,b]	toluene	0.77	2.24	0.13	0.17	0.06
C_6H_6[a,c]	Ph_2Hg	0.79	2.98	0.15	0.19	0.05
C_6H_6[a,d]	Ph_2Hg	0.52	3.56	0.086	0.17	0.02

[a] 24 h, 70 °C, 2.5 mol % $PhHgCBr_3$, 25 mol % *trans*-CHCl=CHCl. [b] 10.0 mol % additive. [c] 0.12 mol % additive. [d] 0.25% additive.

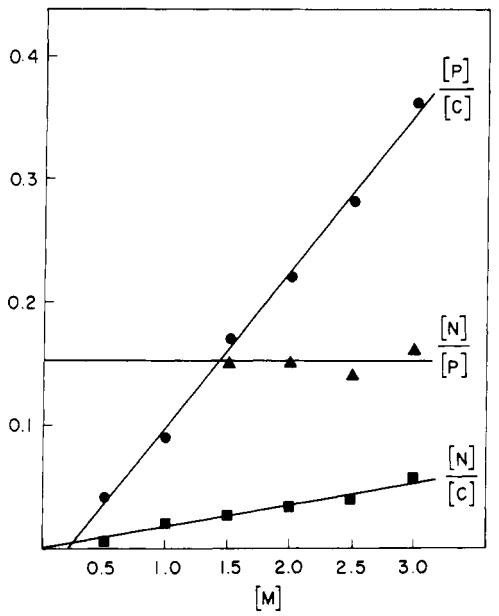


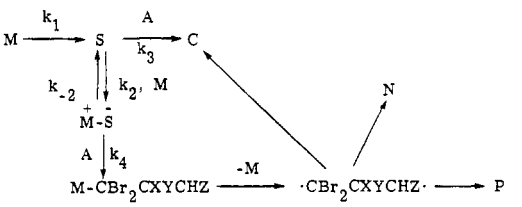
Figure 3. Plot of [P]/[C], [N]/[P], and [N]/[C] vs. [M] for *trans*-CHCl=CHCl.

dibromoethene.[2] Each alkene in fact gave a small amount of nonstereospecific cyclopropane. Table III shows the amount of N from *trans*-CHCl=CHCl in comparison with the major products, P and C. The amount of N, like that of P and C, is dependent on the identity of the solvent and on the presence of additives. Figure 3 presents a plot of [P]/[C], of [N]/[C], and of [N]/[P] vs. [M], analogous to Figure 2. For [P]/[C] the slope is 0.126 and the correlation coefficient 0.997. For [N]/[C], they are 0.0174 and 0.987. Whereas the first two lines are linear with positive slopes, the plot for [N]/[P] is linear and approximately horizontal. Because of the large error in the measurement of N and P for the first two points, they have been dropped in the [N]/[P] plot. The concentration of N was corrected for the small amount of *cis*-dichloroethene that was present in the starting material, *trans*-dichloroethene. The same correction is not necessary for the concentration of C, which is large compared with the concentration of the cis impurity (approximately 0.012 on the scale of the plot).

Discussion

Complete absence of stereomutation in the cyclopropanation reaction has been a hallmark of singlet carbenes, as stated originally in what is now called the Skell hypothesis.[3] Nonetheless, nonstereospecific reactions of singlet carbenes are at least a theoretical possibility[4] and have been suggested when a preequilibrium between carbene and alkene occurs.[5] Our observation

Scheme II



that the ratio of rearranged propene to stereospecific cyclopropane ([P]/[C]) from the reaction of Seyferth reagent with *trans*-1,2-dichloroethene is directly proportional to the inverse of alkene concentration demands at least two intermediates. Thus a singlet-only mechanism is not possible for the production of rearranged propene. We observe in the present work that stereomutated products from both fumaronitrile and styrene provide a similar result; i.e., the ratio of products from the first and second intermediates is directly proportional to [alkene]$^{-1}$ (Figure 1; the fumaronitrile plot is given elsewhere[6]). Thus a singlet-only source for both cyclopropanes, N and C, is not possible. After communication of our preliminary results,[7] an additional example of stereomutation in a carbene reaction was reported,[8] with a mechanism analogous to ours.

Just as the [P]/[C] ratio for dichloroethene was found to be directly proportional to the concentration of Seyferth reagent, the ratio of nonstereospecific to stereospecific products, [N]/[C] or in the corrected form 2[N]/([C] − [N]), also was found to be directly proportional to the concentration of Seyferth reagent for fumaronitrile and styrene (Figure 2 and elsewhere[6]). Reexamination of the data for *trans*-dichloroethene revealed a small amount of stereomutated (cis) cyclopropane. The [N]/[C] ratio for this material also was found to be directly proportional to the concentration of the Seyferth reagent (Figure 3). Moreover, the ratio of stereomutated to rearranged product, [N]/[P], did not vary with Seyferth concentration, indicating that the two products (N and P) came from a common intermediate. We interpret the common intermediate to be a complex between singlet carbene and Seyferth reagent, as exemplified in Scheme I for dichloroethene and in an abbreviated form with rate constants added in Scheme II for fumaronitrile or styrene. The structure of the complex M–S has been discussed extensively by us.[2]

Preequilibration between carbene and alkene may occur to form a charge-transfer complex.[5] Such a complex, however, does not lead to the stereomutation observed in the present study, because [N]/[C] depends on [M] (Figures 2 and 3). The dependence of stereomutation on [M] requires that the carbene become complexed with the Seyferth reagent, as in Scheme II.

In order to explore the effect of electron demand in the alkene, we prepared a series of para-substituted styrenes to serve as substrates. The plots of [N]/[C] vs. [M] were linear for all these compounds. Interpretation of the slopes of these plots requires further examination of the kinetic expression. As derived previously,[2] the ratio of the products from the two intermediates is given by eq 2, provided that the diradical forms equal amounts

$$\frac{2[N]}{[C] - [N]} = \frac{k_4}{k_3}\frac{k_2[M]}{k_4[A] + k_{-2}} \qquad (2)$$

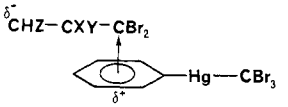
of N and C. If [N] (the stereomutated product) is small compared with [C], as is certainly the case for dichloroethene, dibromoethene, and styrene, then plots using [N]/[C] as well as 2[N]/([C] − [N]) will be linear in [M] (Figure 3, for example). In the [A]$^{-1}$ plots, the concentration of alkene is held artifically high in order to make it pseudo first order and hence not vary for a given starting value of [A]. Under these circumstances, k_4[A] appears to be much greater than k_{-2}, and linearity of [P]/[C] or of [N]/[C]

(3) Skell, P. S.; Valenty, S. J.; Humer, P. W. *J. Am. Chem. Soc.* **1973**, *95*, 5041–5042.
(4) Jones, M., Jr.; Tortorelli, V. J.; Gaspar, P. P.; Lambert, J. B. *Tetrahedron Lett.* **1978**, 4257–4260.
(5) Dehmlow, E. V.; Kramer, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 706–707. Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685–688. Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H *J. Am. Chem. Soc.* **1984**, *106*, 454–456, and references therein.
(6) Larson, E. G. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1984.
(7) Lambert, J. B.; Larson, E. G.; Bosch, R. J. *Tetrahedron Lett.* **1983**, *24*, 3799–3802.
(8) Doyle, M. P.; Terpstra, J. W.; Winter, C. H. *Tetrahedron Lett.* **1984**, *25*, 901–904.

in $[A]^{-1}$ is observed. For the analogous plots vs. [M] rather than $[A]^{-1}$, it is not clear whether $k_4[A]$ or k_{-2} is larger, since the concentration of alkene is kept constant and relatively small. If the k_4 term dominates, the slope of the [M] plots is k_2/k_3. If the k_{-2} term dominates, the slope is K_2k_4/k_3, in which K_2 is the equilibrium constant for complex formation, k_2/k_{-2}.

At reasonably high concentrations of M, the stereomutated product is clearly favored by electron donation in the alkene (Table II). Thus at [M] ~ 4 mol %, [N]/[C] is 0.17 for p-CH_3, 0.13 for H, 0.13 for p-F, 0.05 for p-Cl, and 0.0 for p-CF_3. The slopes of these plots, which correspond to K_2k_4/k_3 if [A] is low, confirm these results. The Hammett plot for the logarithm of the slope vs. σ^+ gives a ρ of −2.0. The ρ for the singlet reaction, k_3, has already been determined by Seyferth to be −0.4.[9] Therefore, the ρ for K_2k_4 is −2.4. Since alkene does not enter into the K_2 step, ρ for K_2 should be zero, so that the ρ of −2.4 corresponds to k_4. Thus the large negative value indicates that reaction between the complex and the alkene (k_4) is strongly promoted by electron donation in the alkene.

We have already shown by similar studies that formation of the rearranged propene is favored by electron donation in the aryl group of the Seyferth reagent.[2] At first glance, these two studies of electron demand seem paradoxical. How can electron donation from both Seyferth reagent and alkene promote the diradical pathway? One possibility is that the alkene reacts initially not with carbenoid to form **2** but with the electrophilic mercury site to form **3**. We suggested this intermediate previously on the basis



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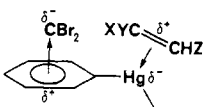

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of other data.[2] Formation of the donor complex **3** would clearly be favored by electron donation from the phenyl ring (Z) on the alkene. Thus electron donation in the Seyferth reagent promotes formation of the complex **1**. The second step is addition of the alkene (favored by electron donation in the alkene) to a second site on the catalytic molecule of Seyferth reagent (**3**). Reaction between the carbene and alkene moieties within **3** is then favored entropically by their nearness and enthalpically by higher negative charge density on the carbenoid piece and lower electron density on the alkene piece (after complexation). Complex **2** is not supported because the partial negative charge on CHZ (Z is the aryl ring for styrene) would be stabilized by electron withdrawal, contrary to observation.

The observations of Table III are in agreement with these conclusions. Benzene as solvent (no additive) can also serve as complexing agent with the carbene. This complex cannot lead to propene P or stereomutated cyclopropane N because it lacks the Lewis acid site on mercury with which the alkene can complex. The result is lower proportions of P and N. The solvent CCl_4 does not sidetrack the carbene as a nonproductive complex, so the amounts of P and N are much larger. If toluene, a good π donor, is added to the reaction when CCl_4 is solvent, another nonproductive complex is formed, resulting in smaller amounts of P and N. Diphenylmercury as an additive forms a similarly nonproductive complex, again lowering P and N. The ratio of N to P is constant in the vicinity of 0.17–0.20 throughout all these experiments, whereas the ratio of N to C ranges from 0.02 (benzene and diphenylmercury, both forming nonproductive complexes) to 0.11 (noncomplexing CCl_4 as solvent). A more complete discussion of additives appears elsewhere.[10]

Summary and Conclusions

Cyclopropanes are formed nonstereospecifically from the addition of dibromomethylene to electron-deficient alkenes via the Seyferth reaction. The ratio of the nonstereospecific and the stereospecific pathways is directly proportional to the concentration of the Seyferth reagent. Thus the nonstereospecific product is not the result of triplet carbene or of a stereolabile charge-transfer complex between CBr_2 and alkene. Instead, a molecule of Seyferth reagent must be interjected between the carbene-forming step and the product-forming step. These results require the intermediacy of a complex between carbene and Seyferth reagent.

The nonstereospecific reaction was observed for fumaronitrile, styrene, 1,2-dichloroethene, and 1,2-dibromoethene. The major pathway in the reaction of the last two compounds with the carbene–Seyferth complex is rearrangement via a 1,2-halogen shift. The plot of the relative amounts of rearranged and stereomutated products for dichloroethene (Figure 3) suggests that they derive from the same intermediate.

Reaction of para-substituted styrenes with Seyferth-generated dibromomethylene provides information regarding electron demand in the step in which the carbene–Seyferth complex reacts with alkene. The amount of nonstereospecific product is enhanced by electron donation in the alkene. This result is best explained by initial reaction of the alkene with mercury (**3**), followed by intramolecular reaction between the complexed, nucleophilic carbene and the complexed, electrophilic alkene. Stereomutation or rearrangement then occurs in the product of this reaction, in which the ·CBr_2–CXY–CHZ· moiety may or may not still be attached to the catalytic and template molecule of Seyferth reagent.

Experimental Section

Boiling points and melting points are uncorrected. Proton NMR spectra were obtained at 60 MHz on a Varian EM360 or a Perkin-Elmer R20B spectrometer, at 90 MHz on a Varian EM390 spectrometer, or at 270 MHz on a JEOL FX270 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield of Me_4Si (δ = 0.00). Mass spectra were obtained on a Hewlett-Packard Model 5985A GC-MS system. Gas chromatography was performed on Varian Vista 6000 and Hewlett-Packard series 700 gas chromatographs with $^1/_8$ and $^1/_4$ in. packed columns respectively for analytical and preparative purposes. Peak areas were measured by electronic integration on a Hewlett-Packard 3390A reporting integrator. Values shown in the tables were obtained by averaging the results from three or four injections.

(4-X-Phenyl)ethyne.[11] The p-Cl, p-F, and p-CH_3 systems were prepared by a common procedure, illustrated for (4-chlorophenyl)ethyne. Into a flask equipped with a reflux condenser and N_2 inlet were weighed p-chloroacetophenone (Aldrich, 14.8 g, 0.096 mol) and PCl_5 (24 g, 0.114 mol). The flask was heated to 70 °C in an oil bath. Rapid evolution of HCl began when the p-chloroacetophenone melted. The reaction was over in 10 min. The clear yellow liquid was distilled under reduced pressure. $POCl_3$ was distilled off under water aspirator vacuum. The products were distilled at a pressure of 0.01 mm. The fraction collected from 45 to 56 °C contained 14.2 g of a mixture of 1-(4-chlorophenyl)-1-chloroethene and 1-(4-chlorophenyl)-1,1-dichloroethane. After the mixture of chlorides was dissolved in 90 mL of Me_2SO, 12 g of KOH dissolved in 10 mL of H_2O was added. The reaction mixture was heated in an 80 °C oil bath for 2 h. The mixture was then poured into 300 mL of ice water and extracted with hexane. The combined organic extracts were washed with H_2O and brine and were dried over K_2CO_3. The volatiles were removed and the residue was crystallized from ethanol–water to give yellow crystals, which were sublimed (70 °C oil bath (15 mm)) to give 3.4 g (26% from p-chloroacetophenone) of (4-chlorophenyl)ethyne, bp 79–82 °C (23 mm) (lit.[11] 84 °C (25 mm)). The following compounds were prepared by analogous procedures: (4-methylphenyl)ethyne (48%), bp 75–81 °C (20 mm) (lit.[11] 60 °C (12 mm)); (4-fluorophenyl)ethyne (36%), bp 28–41 °C (13 mm) (lit.[11] 45–46 °C (20 mm)).

1-(4-Trifluoromethylphenyl)ethanol was prepared by the method of Mesnard in 49% yield, bp 103 °C (14 mm) (lit.[11] 95 °C (10 mm)).

4-Trifluoromethylstyrene was prepared by the method of Mesnard in 50% yield, bp 50–52 °C (14 mm) (lit.[11] 56 °C (18 mm)).

(4-Trifluoromethylphenyl)ethyne was prepared by the method of Mesnard in 55% yield, bp 46–48 °C (12 mm) (lit.[11] 59 °C (35 mm)) from 4-$CF_3C_6H_4CHBrCH_2Br$, which was prepared from 4-$CF_3C_6H_4CH{=}CH_2$ by the method of Mesnard.[11]

(4-X-Phenyl)ethyne-*2-d*. The p-Cl, p-F, p-H, and p-CH_3 compounds were all prepared by the same procedure, illustrated for (4-methyl-

(9) Kostikov, R. R.; Molochanov, A. P.; Folovanova, G. V.; Zenkevich, J. G. *J. Org. Chem. USSR* **1977**, *13*, 1712–1721.

(10) Lambert, J. B.; Bosch, R. J.; Larson, E. G., *J. Org. Chem.*, in press.

(11) Mesnard, D.; Bernadore, F.; Migniac, L. *J. Chem. Res.* **1981**, *3216*–3245.

phenyl)ethyne-*2-d*. Into a dry three-necked flask, equipped with an addition funnel and a reflux condenser with N_2 inlet, were placed Mg turnings (3.2 g, 0.132 mol) with a crystal of I_2 and enough anhydrous diethyl ether to cover them. The addition funnel was charged with a solution of bromoethane (13.5 g, 0.124 mol) in 40 mL of ether. This solution was added dropwise as a vigorously exothermic reaction commenced. After addition was complete, the reaction mixture was heated under reflux for 3 h. Then a solution of (4-methylphenyl)ethyne (8.47 g, 0.073 mol) in 10 mL of ether was transferred to the addition funnel. The solution was added dropwise to the reaction mixture and then stirred for 5 h. Deuterium oxide (D_2O, 5 mL, 0.25 mol) was then added dropwise, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was then poured into an ice-cooled flask, and 50 mL of saturated aqueous NH_4Cl was added. The two phases were filtered and separated. Distillation of the organic portion gave 6.18 g (73%) of product. The absence of any resonance at δ 3.0 in the proton NMR spectrum indicated complete (>99%) deuteration.

***p*-X-Styrene-*cis*-β-*d*.** The general procedure of Brown and Gupta[12] was followed for every derivative (X = Cl, F, H, CH_3, CF_3). The yields varied from 20 to 70%.

Phenyl(tribromomethyl)mercury was prepared by the method of Seyferth in 60–70% yield, mp 117–118 °C (lit.[13] 118–120 °C).

General Procedures. Vessels for the Seyferth reaction were made from 11-mm Pyrex tubing cut into 14-in. lengths and divided into two tubes. All tubes were washed in an Alconox water solution, rinsed thoroughly with water and methanol, and dried at 110 °C for at least 14 h prior to use. The $PhHgCBr_3$, alkene, and benzene were weighed directly into the tubes on a Mettler balance. The reaction of $PhHgCBr_3$ with diethyl fumarate is given as an example. Into a tube containing 0.5331 g (0.001 mol) of $PhHgCBr_3$ were weighed 0.3438 g of diethyl fumarate (0.002 mol) and 1.58 g of benzene. 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 1–5 × 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. 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 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 ether (2 mL), and removing the solvents at reduced pressure. Analysis of the residue by gas chromatography, NMR, and GC–MS identified and gave the yields of the products. Diethyl *trans*-1,1-dibromo-2,3-cyclopropanedicarboxylate: ^{1}H NMR ($CDCl_3$) δ 1.1–1.4 (t, 6, CH_3), 2.95 (s, 2, cyclopropyl), 4.0–4.45 (q, 4, CH_2); MS (70 eV) (M^+) 338, 340, 342, 344 (1/3/3/1), ($M^+ - CO_2CH_2CH_3$) 269, 271, 273 (1/2/1), (M^+ – Br) 259, 261, 263 (1/2/1), ($M^+ - Br_2$) 180, 182 (1/1). The following products were characterized from other substrates. *trans*-1,1-Dibromo-2,3-diiodocyclopropane: ^{1}H NMR ($CDCl_3$) δ 3.25 (s, 2). 1,1-Dibromo-3,3-diiodopropene: ^{1}H NMR ($CDCl_3$) δ 6.15 (d (J = 8 Hz), 1, H3), 7.05 (d (J = 8 Hz), 1, H2). *trans*-1,1-Dibromo-2,3-cyclopropanedicarbonitrile: ^{1}H NMR ($CDCl_3$) δ 2.84 (s, 2); MS (70 eV) (M^+) 248, 250, 252 (8.1, 14.3, 10.6), ($M^+ - C_2H_2 - (CN)_2$) 170, 172, 174 (30.4, 44.1, 23.0), (M^+ – Br) 169, 171 (98.1, 100.0), ($M^+ - C_3HNBr$) 118, 120 (28.0, 31.1), ($M^+ - Br_2H$) 89 (35.4). *cis*-1,1-Dibromo-2,3-cyclopropanedicarbonitrile: ^{1}H NMR ($CDCl_3$) δ 3.45 (s, 2); MS (70 eV) (M^+) 248, 250, 252 (33.7, 55.4, 27.7), ($M^+ - C_2H_2 - (CN)_2$) 170, 172, 174 (31.3, 37.3, 9.6), (M^+ – Br) 169, 171 (100.0, 80.7), ($M^+ - CH_2BrCl$) 129, 131 (22.9, 20.5), ($M^+ - C_3HNBr$) 118, 120 (44.6, 34.9), ($M^+ - C_4H_2BrN_2$) 91, 93 (19.3, 30.1), ($M^+ - Br_2H$) 89 (53.0). *trans*-1,1-Dibromo-2,3-diphenylcyclopropane:[14] ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 2), 7.0 (s, 10). *cis*-1,1-Dibromo-2,3-diphenylcyclopropane:[14] ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 2), 6.9–7.4 (m, 10). *trans*-1,1-Dibromo-3-methyl-2-cycloproapnecarbonitrile: ^{1}H NMR ($CDCl_3$) δ 1.38–1.41 (d (J = 6.2 Hz), 3), 1.86–1.89 (d (J = 7.6 Hz), 1), 2.0–2.15 (m, 1). *cis*-1,1-Dibromo-3-methyl-2-cyclopropanecarbonitrile: ^{1}H NMR ($CDCl_3$) δ 1.40–1.42 (d (J = 6.6 Hz), 3), 2.05–2.15 (m, 1), 2.40–2.45 (d (J = 9.9 Hz), 1). *cis*-1,1-Dibromo-3-methyl-2-phenylcyclopropane:[15] ^{1}H NMR ($CDCl_3$) δ 1.15–1.18 (d (J = 6.6 Hz), 3), 2.05–2.17 (m, 1), 2.88–2.92 (d (J = 10.2 Hz), 1), 7.2–7.45 (m, 5). Methyl *trans*-1,1-dibromo-3-methyl-2-cyclopropanecarboxylate:[16] ^{1}H NMR ($CDCl_3$) δ 1.30–1.45 (m, 3), 1.8–1.95 (m, 1), 2.05–2.22 (m, 1); MS (70 eV) ($M^+ - OCH_3$) 239, 241, 243 (9.1, 18.4, 9.7), ($M^+ - CO_2CH_3$) 211, 213, 215 (49.9, 100.0, 49.1), (M^+ – Br) 191, 193 (96.5, 98.7), (M^+ – COBr) 163, 165 (90.5, 87.4), ($M^+ - CH_4O_2Br$) 131, 133 (45, 47). *trans*-1,1-Dibromo-3-phenylcyclopropanecarbonitrile: ^{1}H NMR ($CDCl_3$) δ 2.6–2.7 (d (J = 7.5 Hz), 1), 3.3–3.4 (d (J = 7.5 Hz), 1), 7.3 (s, 5); MS (70 eV) (M^+ – Br) 220, 222 (25, 24), ($M^+ - Br_2$) 141 (100), ($M^+ - HBr_2$) 140 (70), ($M^+ - CBr_2N$) 114 (18), ($M^+ - CHBr_2N$) 113 (10). 1,1-Dibromo-2-phenylcyclopropane-*cis*-3-*d*:[17] ^{1}H NMR ($CDCl_3$) δ 2.90–2.13 (d (J = 10.5 Hz), 1), 2.93–2.97 (d (J = 10.5 Hz), 1), 7.24–7.36 (m, 5). The nonstereospecific proton resonated at δ 2.0 (d (J = 8.2 Hz)). 1,1-Dibromo-2-(4-chlorophenyl)cyclopropane-*cis*-3-*d*:[9] ^{1}H NMR ($CDCl_3$) δ 2.09–2.13 (d (J = 10.2 Hz), 1), 2.88–2.92 (d (J = 10.2 Hz), 1), 7.21, 7.38 (ABq, 4). The nonstereospecific proton resonated at δ 1.93 (d (J = 7.9 Hz)). 1,1-Dibromo-2-(4-fluorophenyl)cyclopropane-*cis*-3-*d*: ^{1}H NMR ($CDCl_3$) δ 2.12–2.16 (d (J = 10.5 Hz), 1), 2.92–2.96 (d (J = 10.5 Hz), 1) 7.04–7.4 (m, 4). The nonstereospecific proton resonated at δ 1.94 (d (J = 7.6 Hz)). 1,1-Dibromo-2-(4-methylphenyl)cyclopropane-*cis*-3-*d*: ^{1}H NMR ($CDCl_3$) δ 2.05–2.09 (d (J = 10.5 Hz), 1), 2.33 (s, 3), 2.88–2.92 (d (J = 10.5 Hz), 1), 7.10–7.22 (ABq, 4). The nonstereospecific proton resonated at δ 1.95 (d (J = 7.3 Hz)). 1,1-Dibromo-2-(4-trifluoromethylphenyl)cyclopropane-*cis*-3-*d*: ^{1}H NMR ($CDCl_3$) δ 2.18–2.22 (d (J = 10.5 Hz), 1), 3.00–3.04 (d (J = 10.5 Hz), 1), 7.40, 7.66 (ABq, 4). The nonstereospecific proton resonated at δ 2.05 (d (J = 7.9 Hz)).

Registry No. *p*-$ClC_6H_4COCH_3$, 99-91-2; *p*-$FC_6H_4COCH_3$, 403-42-9; *p*-$CH_3C_6H_4COCH_3$, 122-00-9; *p*-$ClC_6H_4C{\equiv}CH$, 873-73-4; *p*-$FC_6H_4C{\equiv}CH$, 766-98-3; *p*-$CH_3C_6H_4C{\equiv}CH$, 766-97-2; *p*-$ClC_6H_4CCl{=}CH_2$, 51738-09-1; *p*-$ClC_6H_4CCl_2CH_3$, 49711-26-4; *p*-$F_3CC_6H_4C{\equiv}CH$, 705-31-7; *p*-$CH_3C_6H_4C{\equiv}CD$, 97552-19-7; *cis*-*p*-$ClC_6H_4CH{=}CHD$, 97552-15-3; *cis*-*p*-$FC_6H_4CH{=}CHD$, 97552-16-4; *cis*-$C_6H_5CH{=}CHD$, 21370-59-2; *cis*-*p*-$CH_3C_6H_4CH{=}CHD$, 89039-10-1; *cis*-*p*-$F_3CC_6H_4CH{=}CHD$, 97552-17-5; *trans*-*p*-$F_3CC_6H_4CH{=}CHD$, 97552-18-6; *trans*-$C_6H_5CH{=}CHC_6H_5$, 103-30-0; *trans*-$C_6H_5CH{=}CHCH_3$, 873-66-5; *trans*-$CH_3CH{=}CHCN$, 627-26-9; *cis*-$CH_3CH{=}CHCN$, 1190-76-7; *trans*-$CH_3CH{=}CHCO_2Me$, 623-43-8; *trans*-$ICH{=}CHI$, 590-27-2; *trans*-$NCCH{=}CHCN$, 764-42-1; *trans*-$ClCH{=}CHCl$, 156-60-5; *trans*-$EtO_2CCH{=}CHCO_2Et$, 623-91-6; $PhHgCBr_3$, 3294-60-8; $Br_2C{=}CHCHI_2$, 97552-06-2; diethyl *trans*-1,1-dibromo-2,3-cycloproponedicarboxylate, 97552-04-0; *trans*-1,1-dibromo-2,3-diiodocyclopropane, 97552-05-1; *trans*-1,1-dibromo-2,3-cyclopropanedicarbonitrile, 88710-59-2; *cis*-1,1-dibromo-2,3-cyclopropanedicarbonitrile, 88710-60-5; *trans*-1,1-dibromo-2,3-diphenylcyclopropane, 33044-88-1; *cis*-1,1-dibromo-2,3-diphenylcyclopropane, 67437-46-1; *trans*-1,1-dibromo-3-methyl-2-cyclopropanecarbonitrile, 97552-07-3; *cis*-1,1-dibromo-3-methyl-2-cyclopropanecarbonitrile, 97552-08-4; *cis*-1,1-dibromo-3-methyl-2-phenylcyclopropane, 97552-09-5; methyl *trans*-1,1-dibromo-3-methyl-2-cyclopropanecarboxylate, 97570-04-2; *trans*-1,1-dibromo-3-phenyl-2-cyclopropanecarbonitrile, 97552-10-8; 1,1-dibromo-2-phenylcyclopropane-*cis*-3-*d*, 77249-50-4; 1,1-dibromo-2-(4-chlorophenyl)cyclopropane-*cis*-3-*d*, 97552-11-9; 1,1-dibromo-2-(4-fluorophenyl)cyclopropane-*cis*-3-*d*, 97552-12-0; 1,1-dibromo-2-(4-methylphenyl)cyclopropane-*cis*-3-*d*, 97552-13-1; 1,1-dibromo-2-[4-(trifluoromethyl)phenyl]cyclopropane-*cis*-3-*d*, 97552-14-2.

(12) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 5249–5255.
(13) Seyferth, D.; Lambert, R. L. *J. Organomet. Chem.* **1969**, *16*, 21–26.
(14) Bache, G.; Buckl, K.; Martens, D.; Schneider, D. R.; Wagner, H.-U. *Chem. Ber.* **1979**, *112*, 2961–2996.
(15) Kostikov, R. R.; Molchanov, A. P. *J. Org. Chem. USSR* **1978**, *14*, 323–327.
(16) Joshi, G. C.; Devaprabhakara, D. *Indian J. Chem.* **1967**, *5*, 653–654.
(17) Pinhas, A. R.; Samuelson, A. G.; Risenberg, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668–1675.