Effects of Solvent and Additives on the Rearrangement Pathway of the Seyferth Reaction

Joseph B. Lambert,*[1] Richard J. Bosch, and Eric G. Larson

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received December 27, 1984

The Seyferth reagent has dual reactivity with electron-deficient alkenes. *trans*-1,2-Dichloroethene reacts both with the free carbene to give cyclopropane stereospecifically and with a complex between carbene and a second molecule of Seyferth reagent (homogeneous catalysis) to give a rearranged propene. The addition of other materials to the reaction mixture can have a profound effect on the ratio of the two pathways. Good π donors such as *p*-xylene decrease the pathway to rearranged propene via the complexed carbene. Such materials thus serve as inhibitors to the process of homogeneous catalysis by forming a competing complex that does not go on to propene but instead reverts to free carbene. The existence of the inhibitor–carbene complex is supported by concentration studies. The presence of insoluble materials such as zinc chloride, on the other hand, serves to decrease the pathway that leads through free carbene to the cyclopropane. Free carbene may react with the surface of the additive and be removed as a reactive species. This latter process would have no effect on carbene previously complexed with the homogeneous catalyst, the Seyferth reagent, which could still proceed to rearranged propene.

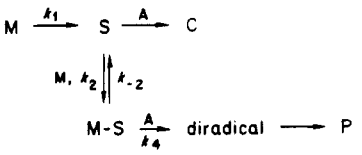
The Seyferth reaction produces singlet carbenes by the decomposition of organomercurials under mild conditions (eq 1). The carbenes may be trapped in the traditional

$$PhHgCBr_3 \xrightarrow{70\ ^\circ C} PhHgBr + :CBr_2 \qquad (1)$$

fashion by reaction with alkenes to produce cyclopropanes with the retained stereochemistry expected for singlet spin states.[2] Such a mechanism predominates with electron-rich alkenes. We have found [3-5] that with electron-deficient alkenes a more complex mechanism becomes important (Scheme I, in which M is $PhHgCBr_3$, S is singlet $:CBr_2$, C is the normal cyclopropane product, A is the alkene, and P is a rearranged propene). Under these circumstances the singlet carbene has poor reactivity with the alkene and competitively forms a complex with Seyferth reagent, $M–CBr_2$. We demonstrated that the second mole of Seyferth reagent serves as a Lewis base.[5] As a result, the complexed carbene possesses more negative charge and hence is more nucleophilic than the normally electrophilic singlet carbene. The complexed carbene then reacts more readily with electron-deficient alkenes such as dichloroethene, dibromoethene, fumaronitrile, and styrene. Loss of the catalytic molecule of $PhHgCBr_3$ produces the diradical $\cdot CBr_2CHClCHCl\cdot$ (in the case of dichloroethene), or its dipolar equivalent, which can undergo rapid 1,2-chlorine shift to the propene product $CBr_2{=}CHCHCl_2$, referred to by the letter P in Scheme I. Although the exact structure of the complex between carbene and Seyferth reagent is not certain, we have presented evidence in favor of a π or σ complex between the phenyl ring of the organomercurial and the empty p orbital of the carbene.[5]

If the function of the additional mole of Seyferth reagent in the k_2 step of Scheme I is to heighten the nucleophilicity of the carbene through reversible complexation, then it is reasonable that other materials should be able to serve in a like role. These materials may be present as additives to the reaction mixture or they may replace benzene as solvent. They may increase the propene pathway at the expense of the cyclopropane pathway if their predominant effect is to enhance k_4. On the other hand they may reduce k_4 or enhance k_{-2}, decreasing the propene pathway so that they serve as a competitive inhibitor. We have studied and report herein the effects of a wide range of solvents and additives on the proportions of the two pathways and on the overall yield. These results are interpreted in terms of an expanded mechanism that includes competing catalysis both by Seyferth reagent M and by the additive (I, for inhibitor).

Scheme I



Results

The products of the decomposition of $PhHgCBr_3$ (2.5 mol %) in the presence of 25 mol % of *trans*-1,2-dichloroethene for 24 h at 70 °C were determined as a function of solvent. The primary products were the stereospecifically formed *trans*-1,1-dibromo-2,3-dichlorocyclopropane (C) and the rearranged 1,1-dibromo-3,3-dichloropropene (P). Minor amounts of bromobenzene, bromoform, and tetrabromoethene were formed in either the presence or the absence of dichloroalkene and hence are not of direct interest. The small amount of nonstereospecifically formed *cis*-cyclopropane is in agreement with earlier results with furmaronitrile[4] and will be discussed elsewhere in greater detail.[6] The amounts of these products are given in Table I for 10 solvents.

Although benzene is the most commonly used solvent for the Seyferth reaction, it also can serve as a Lewis base and hence might be involved as a catalyst or an inhibitor. Consequently, we measured the relative proportions of reaction products with variable amounts of benzene. Table II lists the products of reactions with X mol % of

(1) This work was supported by the National Science Foundation (Grant CHE83-12885).

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

(3) Lambert, J. B.; Mueller, P. H.; Gaspar, P. P. *J. Am. Chem. Soc.* **1980**, *102*, 6615-6616.

(4) Lambert, J. B.; Larson, E. G.; Bosch, R. J. *Tetrahedron Lett.* **1983**, *24*, 3799-3802.

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

(6) Lambert, J. B.; Larson, E. G.; Bosch, R. J.; TeVrucht, M. L. E. *J. Am. Chem. Soc.*, in press.

0022-3263/85/1950-3054$01.50/0

Table I. Products[a] from Reaction of $PhHgCBr_3$ and *trans*-1,2-Dichloroethene in Various Solvents[b]

solvent	P[c]	C[d]	PhBr	$CHBr_3$	$Br_2C{=}CBr_2$	N[e]	P/C
C_6H_6	0.95	2.87	0.40	0.24	0.19	0.18	0.33
CCl_4	1.47	2.78	0.44	0.10	0.15	0.30	0.53
$CHCl_3$	1.05	2.87	0.44	0.26	0.26	0.22	0.37
CH_2Cl_2	1.00	3.03	0.71	0.11	0.22	0.33	0.37
cyclohexane	0.33	2.80	0.31	0.40	0.44	0.20	0.12
CH_3CN	0.16	0.33	0.13	2.78			1.48
THF	0.17	0.14	0.093	1.06	0.023		1.21
CH_3OH			0.054	4.46			
$PhNO_2$	0.94	2.37	0.88	2.02	0.19		0.40
$PhCH_3$	0.14	1.08	0.049	0.71	0.24		0.13

[a] Relative to internal $Br(CH_2)_6Br$ at 1.00. [b] $PhHgCBr_3$ at 2.5 mol %, alkene at 25 mol %, 24 h at 70 °C. [c] $Br_2C{=}CHCHCl_2$. [d] *trans*-1,1-Dibromo-2,3-dichlorocyclopropane. [e] *cis*-1,1-Dibromo-2,3-dichlorocyclopropane.

Table II. Products[a] from Reaction of $PhHgCBr_3$ and *trans*-1,2-Dichloroethene in Benzene[b]

X[b]	P[c]	C[d]	PhBr	$CHBr_3$	$Br_2C{=}CBr_2$	N[e]	P/C
0.50	0.16	1.13	0.069	0.54	0.16	tr	0.14
1.0	0.41	2.05	0.18	0.51	0.15	tr	0.20
2.0	0.65	2.39	0.32	0.49	0.16	tr	0.27
2.5	0.73	2.53	0.32	0.41	0.19	0.17	0.29
5.0	1.16	2.94	0.44	0.13	0.21	0.24	0.39
9.1	1.47	2.84	0.55	0.11	0.15	0.28	0.52

[a] Relative to internal $Br(CH_2)_6Br$ at 1.00. [b] $PhHgCBr_3$ at X mol %, alkene to 10X mol %, benzene at $(100 - 11X)$ mol %, 24 h at 70 °C. [c] $Br_2C{=}CHCHCl_2$. [d] *trans*-1,1-Dibromo-2,3-dichlorocyclopropane. [e] *cis*-1,1-Dibromo-2,3-dichlorocyclopropane.

Table III. Products[a] from Reaction of $PhHgCBr_3$ and *trans*-1,2-Dichloroethene in CCl_4 with Additives[b]

additive	P[c]	C[d]	PhBr	$CHBr_3$	$CBr_2{=}CBr_2$	N[e]	IP[f]	P/C
none	1.66	2.57	0.47	0.12	0.24	0.26		0.65
$PhNO_2$	1.81	2.29	0.47	0.33	0.21	0.30	9.92	0.79
C_6H_6	1.72	2.37	0.43	0.090	0.26	0.26	9.24	0.73
PhCl	1.56	2.34	0.41	0.074	0.22	0.24	9.07	0.67
$PhCH_3$	1.14	2.54	0.30	0.14	0.24	0.20	8.82	0.45
PhOMe	1.12	1.76	0.26	0.21	0.19	0.13	8.27	0.64
p-xylene[g]	0.48	3.02	0.14	0.27	0.26	0.13	8.44	0.16
mesitylene[g]	0.10	0.99	0.037	0.20	0.20		8.40	0.10
durene[g]	0.12	1.52	0.053	*h*	0.24		8.03	0.075
Me_6C_6[g]	0.051	0.31	0.042	0.25	0.18		7.85	0.16

[a] Relative to internal $Br(CH_2)_6Br$. Some additives, however, had the same retention time as $Br(CH_2)_6Br$. Thus for all additives except as indicated internal $Br(CH_2)_8Br$ was used. The results are presented as if $Br(CH_2)_6Br$ were the internal standard by dividing the data by 0.86. This factor compensates for the differences between the thermal conductivities of $Br(CH_2)_6Br$ and $Br(CH_2)_8Br$. This change in conditions may cause a systematic difference between these data and those based on internal $Br(CH_2)_6Br$, e.g., those in Tables I and II. [b] $PhHgCBr_3$ at 2.5 mol %, alkene at 25 mol %, additive at 2.5 mol %, 24 h at 70 °C. [c] $Br_2C{=}CH{-}CHCl_2$. [d] *trans*-1,1-Dibromo-2,3-dichlorocyclopropane. [e] *cis*-1,1-Dibromo-2,3-dichlorocyclopropane. [f] Ionization potential in eV. [g] Internal $Br(CH_2)_6Br$ was used directly (see footnote *a*). [h] Obscured by the durene peak.

Table IV. Products[a] from Reaction of $PhHgCBr_3$ and *trans*-1,2-Dichloroethene in CCl_4 with Additives[a]

additive	P[a]	C[a]	PhBr	$CHBr_3$	$CBr_2{=}CBr_2$	N[a]	P/C
$PhNO_2$[a]	1.57	1.91	0.59	0.49	0.21	*b*	0.82
C_6H_6	1.79	2.25	0.45	0.11	0.25	0.22	0.79
PhCl	1.81	2.37	0.47	0.088	0.47	0.24	0.80
$PhCH_3$	0.77	2.24	0.20	0.24	0.36	0.13	0.34
PhOMe	0.56	0.95	*c*	*c*	0.17	0.047	0.59

[a] See analogous footnote in Table III. Concentrations are the same, except the additive is at 10.0 mol %. [b] Obscured by the $PhNO_2$ peak. [c] Obscured by the PhOMe peak.

Table V. Products[a] from Reaction of $PhHgCBr_3$ and *trans*-1,2-Dichloroethene in Benzene[b] with Added Diphenylmercury

X[b]	P[c]	C[d]	$CBr_2{=}CBr_2$	N[e]	Σ[f]	P/C
0.00	0.95	2.87	0.19	0.18	4.00	0.33
0.12	0.79	2.98	0.14	0.15	3.91	0.27
0.17	0.72	3.17	0.17	0.12	4.06	0.23
0.25	0.52	3.56	0.095	0.086	4.17	0.15
0.50	0.23	3.91		0.082	4.22	0.059
1.00	0.15	3.94			4.09	0.038

[a] Relative to internal $Br(CH_2)_6Br$. [b] $PhHgCBr_3$ at 2.5 mol %, alkene at 25 mol %, Ph_2Hg at X mol %, 24 h at 70 °C. [c] $Br_2C{=}CH{-}CHCl_2$. [d] *trans*-1,1-Dibromo-2,3-dichlorocyclopropane. [e] *cis*-1,1-Dibromo-2,3-dichlorocyclopropane. [f] Sum of products P, C, and N.

$PhHgCBr_3$ and $10X$ mol % of *trans*-1,2-dichloroethene in $(100 - 11X)$ mol % of benzene. The final entry, for X = 9.1 (0 mol % benzene) in essence uses the alkene as the solvent.

Experiments were carried out in which various aromatic compounds were present as additives, with noninteracting CCl_4 as the solvent. In all experiments, the Seyferth reagent, $PhHgCBr_3$, was present at 2.5 mol % and

Table VI. Rates of Product Appearance[a]

[M]	[A]	[I]	k(P)	r	k(C)	r
1.49	25.01	0.0	7.0×10^{-6}	0.940	2.9×10^{-5}	0.998
2.50	24.99	0.0	3.5×10^{-5}	0.984	5.5×10^{-5}	0.998
4.49	25.02	0.0	8.4×10^{-5}	0.999	8.4×10^{-5}	0.999
1.50	24.99	0.1	4.6×10^{-6}	0.982	3.0×10^{5}	0.997
2.50	24.96	0.1	1.8×10^{-5}	0.998	5.7×10^{-5}	0.991
4.50	25.04	0.1	7.4×10^{-5}	0.997	7.7×10^{-5}	0.996

[a] M is $PhHgCBr_3$, A is *trans*-CHCl=CHCl, I is Ph_2Hg, concentrations are in mol %, and rates are in mol % s^{-1} at 69 °C.

trans-1,2-dichloroethene at 25 mol %. The additives were present either at 2.5 mol % (Table III) or at 10.0 mol % (Table IV).

Extensive experiments were carried out with diphenylmercury as the additive. Variation of the concentration of Seyferth reagent ($PhHgCBr_3$), alkene (*trans*-1,2-dichloroethene), and diphenylmercury required a host of experiments. The complete results for five concentrations of diphenylmercury, with $PhHgCBr_3$ at 2.5 mol % and alkene at 25 mol %, are given in Table V. For the sake of brevity, we will give only the [P]/[C] ratios for independent variation of Seyferth reagent and of alkene. At 2.5 mol % diphenylmercury and 25 mol % alkene, Seyferth reagent was varied over the range 0.50, 0.99, 2.01, 2.99, and 4.01 mol %, to give [P]/[C] respectively of 0.0046, 0.014, 0.060, 0.13, and 0.23. At 2.5 mol % Seyferth reagent and 0.25 mol % diphenylmercury, the alkene was varied over the range 10.7, 13.4, 20.4, 30.3, and 41.4 mol % to give [P]/[C] of 0.30, 0.26, 0.19, 0.15, and 0.10, respectively (only large molar percentages of alkene are permitted, in order to maintain pseudo-zero order).

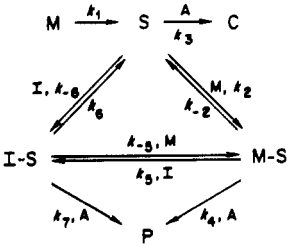
Numerous other materials also were studied as homogeneous (soluble) additives, including p-X-$C_6H_4HgCCl_3$ (X = CH_3, Cl, H, Me_2N, MeO, and NO_2), (p-$MeOC_6H_4)_2Hg$, (p-$MeC_6H_4)_2Hg$, $(PhCH_2CH_2)_2Hg$, Ph_2Zn, and $Ph_2C{=}O$. In addition, numerous insoluble materials were studied as additives, including PhHgCl, PhHgBr, H_2O, Hg, $HgCl_2$, $HgBr_2$, Cu_2Cl_2, Cu_2Br_2, Cu_2I_2, Cu(bronze), $CuSO_4{\cdot}5H_2O$, $CuCl_2$, $Hg(OAc)_2$, $SnCl_4$, $ZnCl_2$, ZnI_2, $AlCl_3$, $AlBr_3$, and $FeCl_3$. These somewhat tedious compilations have been given elsewhere.[7] Pertinent results will be mentioned in the Discussion section.

Absolute kinetics were carried out by following the appearance of the stereospecifically formed cyclopropane C and of the rearranged propene P over time by VPC. Table VI collects the kinetic results. The concentration of Seyferth reagent was varied to determine the kinetic dependence of both P and C on this material. The complete set of experiments was then repeated with added diphenylmercury in order to determine the effect of the additive on the absolute rates. Variation of alkene concentration also was carried out, but the range of variation was too small to reveal any significant changes.

Discussion

Diphenylmercury. All experiments served to demonstrate that diphenylmercury is an inhibitor in the formation of the propene from the complexed carbene. As the diphenylmercury concentration was increased from 0.00 to 1.00 mol %, the amount of propene decreased from 0.95 to 0.15 (relative amounts compared with the internal standard at 1.00), i.e., the additive served to quench the product from the complexed carbene pathway almost entirely even at relatively low concentrations (Table V)). At the same time, the amount of stereospecifically formed cyclopropane rose from 2.87 to 3.94, so that total product formation was nearly constant at about 3.9–4.0 (4.0–4.1 if nonstereospecifically formed cyclopropane is included). Thus, diphenylmercury was not causing side reactions that were responsible for the decreased amounts of propene. Instead, it was acting as a classical inhibitor, halting the propene-forming pathway and enhancing the singlet carbene pathway. The kinetic data in Table VI support these results. The addition of inhibitor depressed the rate of formation of P and possibly had a slightly enhancing effect on the rate of formation of C.

Scheme II



There are at least two possible explanations for these observations, which will be considered in terms of the expanded mechanism in Scheme II. In this scheme, complexes from both Seyferth reagent (M–S) and additive/inhibitor (I–S) are included. (1) M–S is unstable with respect to I–S ($k_5 > k_{-5}$), and I–S does not go on to product (k_7 small). (2) I–S is formed much more rapidly than M–S ($k_{-6} > k_2$ or $k_{-2} > k_6$), but I–S does not go on to product (k_7 small) and there is no interconversion of the two complexes (k_5, k_{-5} very small). Both scenarios require that I–S not go on to product. If k_7 is small, the ratio of products is given by eq 2.

$$\frac{[P]}{[C]} = [k_4/k_3][(k_2k_6[M] + k_2k_{-5}[M]^2 + k_{-5}k_{-6}[I]\cdot[M])/(k_{-2}k_{-5}[M] + k_{-2}k_6 + k_4k_{-5}[A][M] + k_4k_6[A] + k_5k_6[I])] \quad (2)$$

The data presented earlier gave the results of changing the concentrations of M, A, and I. These results may be summarized by eq 3–5. When M and I are held constant, constant I and M:

$$\frac{[P]}{[C]} = \frac{0.0461}{0.0465 + [A]} \quad (3)$$

constant M and A:

$$\frac{[P]}{[C]} = \frac{0.0465}{0.0248 + [I]} \quad (4)$$

constant I and A:

$$\frac{[P]}{[C]} = 0.014[M]^2 + 0.00083[M] \quad (5)$$

the ratio varies with $[A]^{-1}$ (eq 3), as expected from constant

(7) Bosch, R. J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1983.

I and M: eq 2. When M and A are held constant, the ratio varies with $[I]^{-1}$ (eq 4). This result follows from eq 2 only if the term in I in the numerator is small, i.e., if k_{-5} or k_{-6} is small. When I and A are held constant, the ratio varies with M as a quadratic (eq 5). The second power in M occurs only if the k_2k_{-5} term in the numerator is quite large and is not offset by terms in M in the denominator. Thus k_{-5} cannot be particularly small, and consequently the inverse [I] dependence requires that k_{-6} be small. If there is any validity to these conclusions, then explanation (1) is more likely than explanation (2), which requires both that k_{-6} be large and that k_{-5} be small. The inverse [I] dependence suggests that the k_5k_6[I] term in the denominator is large and that the inhibitor serves to replace M–S with I–S (k_5), which returns rapidly to S (k_6). Under these circumstances, C builds up at the expense of P.

Phenyl(trichloromethyl)mercury. This material acts in a fashion analogous to diphenylmercury, although somewhat less effectively. The [P]/[C] ratio varied only from 0.31 to 0.17 as the additive was increased from 0.0 to 1.0 mol %. The dependence on concentration of $PhHgCBr_3$ was still a quadratic, but the term in $[M]^2$ was much smaller than that in [M]. The dependence of the ratio on alkene concentration was still inverse first power. Thus the basic mechanism of Scheme II appears still to hold, but relative values of rate constants differ.

Solvents and Aromatic Additives. The Seyferth reaction was successful in a wide range of solvents (Table I). Of those tried, the only ones that failed contain an active hydrogen. Thus acetonitrile, THF, and methanol gave low yields of P and C; the singlet carbene may insert in CH or OH, ultimately to give high yields of bromoform. Toluene had a similar tendency, although not so extreme. The remaining solvents all gave high yields, in terms of the sum of P, C, and N. The highest yields of rearranged propene were found with carbon tetrachloride. This solvent is sufficiently polarizable to stabilize the complex (M–S) between singlet carbene and $PhHgCBr_3$, and also it does not serve as an inhibitor by forming its own complex as in Scheme II. The best yields of stereospecific cyclopropane, coupled with a low yield of propene, were found in cyclohexane. This nonpolar, poorly polarizable solvent cannot stabilize the M–S complex nor can it form its own complex with the carbene. The poor solubility of the Seyferth reagent in cyclohexane also may contribute to the low yield of propene. Thus in terms of the [P]/[C] ratio, the highest value (most rearranged propene via the complexed carbene) was found with carbon tetrachloride, and the lowest value (most product from singlet carbene pathway) was found with cyclohexane (low yield solvents such as THF are disregarded).

The somewhat lower value for propene production in the commonest Seyferth solvent, benzene, suggests that this solvent may form its own complex, in competition with $PhHgCBr_3$, leading to the mechanism of Scheme II, in which the inhibitor I is benzene. Consequently, we carried out studies in which the benzene concentration was varied (Table II). At $X = 0.5$, the mol % of benzene was very high, about 95%; at $X = 9.1$ mol %, there was no benzene. The ratio of alkene to Seyferth reagent was kept constant at 10. As the benzene concentration increased (X decreased), the [P]/[C] ratio decreased from 0.52 to 0.14. Thus benzene appears to act as an inhibitor much in the same way that diphenylmercury does. *As a solvent, it is an active participator in the pathway that produces rearranged propene.* Again it is possible that benzene can form a carbene complex more stable than the one with $PhHgCBr_3$, that this complex cannot go on to propene, and that it returns to singlet carbene, thereby promoting formation of C over P. Carbon tetrachloride in Table I cannot perform in this way, so it gave a high yield of P.

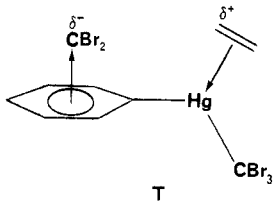
If benzene can complex with carbene and inhibit the formation of propene, a better aromatic donor might serve as a more effective inhibitor. Indeed toluene gave a vastly reduced yield of propene (Table I), so that the [P]/[C] ratio was 0.13, compared with 0.33 for benzene. The lower yield of cyclopropane was caused by the presence of the activated benzylic hydrogens, which brought about a higher yield of the byproduct bromoform.

Further experiments on aromatic materials as additives were carried out in the noncomplexing solvent carbon tetrachloride, in which the best yield of rearranged propene was obtained (Tables III and IV). We have used ionization potential as a means of measuring the complexing ability of the additive. Nitrobenzene has the highest IP and hence should be the worse inhibitor. Indeed, it gave the highest yield of propene and the highest [P]/[C] ratio (0.79). The yield of rearranged propene in fact was a monotonic function of IP throughout the monosubstituted series nitrobenzene, benzene, chlorobenzene, toluene, anisole, and on to the polymethylated series with even lower IP's, *p*-xylene, mesitylene, durene, and hexamethylbenzene. Exceptions occurred at anisole and the highly methylated benzenes primarily because of reduced amounts of cyclopropane formed in the presence of active hydrogens. The results depended on concentration (compare Tables III and IV), with higher concentrations exaggerating a given effect. The amount of propene and the product ratio were increased further for nitrobenzene and decreased further for toluene.

Why do good electron donors give poor yields of rearranged propene? In terms of Scheme II, it appears that a good donor such as *p*-xylene can inhibit propene formation by converting all the M–S complex to I–S. If this complex cannot go to product (k_7 small), its only available pathway is return to singlet carbene, eventually leading to cyclopropane.

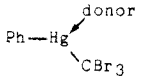
Why then do the I–S complexes not lead to product? On this issue we can only provide a hypothesis. We have already argued[5] that an integral part of the formation of rearranged propene is the use of the catalytic molecule of Seyferth's reagent as a template for gathering together the two electron-deficient species, dibromomethylene (CBr_2) and 1,2-dichloroethene. We showed[5] that the most likely site for complexation of the carbene with $PhHgCBr_3$ is the aromatic ring. Thus the ability of other aromatic compounds to form similar complexes is not surprising. We further argued[5] that the alkene may react initially at mercury, so that eventually a double complex of the type T (as shown in Chart I) is formed. Within this double complex, the carbene is more nucleophilic and the alkene is more electrophilic than when it is uncomplexed, so that reaction between them should be dramatically enhanced both enthalpically by alteration of electron demand and entropically by positioning of the reactants close together. The presence of good electron donors could reduce the concentration of T by two factors (shown in Chart II). (1) The added donors can complex directly with mercury, preventing the alkene from reaching the "active site", as in **1**. (2) The added donors can form their own complexes I–S, as in **2** for *p*-xylene. If the template model is correct, the I–S complex is poorly equipped to react with alkene, since it must do so intermolecularly. Consequently, its most likely pathway is return to uncomplexed carbene, eventually leading to C. In this way a better electron donor leads to less rearranged propene.

Chart I

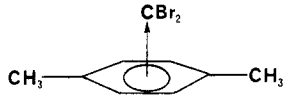


T

Chart II



1



2

Comparison of $PhHgCBr_3$ with Ph_2Hg is very difficult. Both should be able to act as a template, unless other electronic factors intervene. We have seen that Ph_2Hg acts as an inhibitor in the formation of propene. It is possible that Ph_2Hg forms a good carbene complex I–S but that replacement of CBr_3 by Ph makes mercury less electrophilic. Complexation with alkene then, as in T and 1, occurs less readily, and k_7 is reduced.

The effect of $(PhCH_2CH_2)_2Hg$ as an additive is interesting in this context, as it serves as an excellent quencher of the rearrangement pathway. Introduction of only 0.25 mol % of $(PhCH_2CH_2)_2Hg$ with 2.5 mol % $PhHgCBr_3$ and 25 mol % *trans*-CHCl=CHCl in benzene at 70 °C for 25 h decreases [P] from 0.70 to 0.15, increases [C] from 2.24 to 2.90, and hence decreases [P]/[C] from 0.31 to 0.05. This molecule appears to be a very effective competitive inhibitor. The I–S complex may react with alkene to form a double complex like T (A–I–S), but the large distance between the carbene and alkene moieties, because of the CH_2CH_2 spacer, prevents reaction between them. Reversion to free singlet carbene, leading to C, then becomes the major pathway.

Inhomogeneous Materials. None of the numerous insoluble materials we examined raised the amount of rearranged propene substantially, but many raised the [P]/[C] ratio by decreasing the yield of cyclopropane. This effect has no major bearing on the mechanism under discussion but may be of interest in its own right. The product of the Seyferth reaction PhHgBr, the analogous PhHgCl, and water had little or no effect on the product distribution, even at concentrations as additives of 1 mol % (at the bottom of the vessel, not in solution). Those materials that had little effect on production of P but inhibited the production of C included cuprous chloride ([P]/[C] = 0.90), cuprous bromide (1.11), cuprous iodide (3.21), cupric chloride (5.8), mercuric acetate (8.5), tin tetrachloride (9.9), and zinc iodide (9.5). Concentrations of the additives were always about 1 mol %. The absolute concentrations respectively of P and C (compared with 1,6-dibromohexane at 1.00) were 0.86 and 0.087 for $SnCl_4$ and 1.22 and 0.12 for ZnI_2, compared with 0.91 and 2.76 for no additive. The effect is surface-area related, since the [P]/[C] ratio increased (2.5, 5.8, 9.5) as the amount of ZnI_2 for example was increased (0.24, 0.50, 0.99 mol %). Tests were run with ZnI_2 and $HgBr_2$ to learn whether the cyclopropane decomposed in the presence of additive, but under reaction conditions with these additives cyclopropane remained unchanged. It is possible that free carbene is being adsorbed and chemically attached to the surface of the heterogeneous additive, so that the normal singlet reaction to give cyclopropane is quenched. Complexed carbenes, however, are not available for reaction with the surface, so they proceed as usual to rearranged propene.

Summary

A number of Lewis bases serve as inhibitors of the Seyferth pathway that involves complexed carbene. Diphenylmercury and various aromatic materials as additives (Tables III–V) decrease the amount of rearranged propene. The effect is related to the ionization potential of the aromatic. Good electron donors such as *p*-xylene (IP = 8.44 eV) are most effective in reducing the yield of rearranged propene. In terms of kinetics, the addition of diphenylmercury decreases the rate of formation of propene and slightly raises the rate of formation of stereospecifically formed cyclopropane (Table VI). Electron donors as solvents (Tables I and II) also reduce the amount of propene. For maximization of propene, a noncomplexing solvent like CCl_4 is most effective.

These effects are best understood in terms of the mechanism of Scheme II, in which both Seyferth reagent and the additive or solvent can form a complex with carbene. The free carbene produces cyclopropane. Analysis of the product ratios as a function of inhibitor, alkene, and Seyferth reagent concentrations shows that the inhibitor complex (I–S) is unable to proceed to product (k_7 small). One possible explanation of the inhibitory effects is that the additive forms a more stable complex with carbene (2), as would be expected as the ionization potential decreases. Unable to go to product propene, the inhibitor complex returns to free carbene (k_6), eventually leading to cyclopropane rather than propene. The large values of k_5 (conversion of M–S to I–S) and k_6 (return of I–S to singlet carbene) are substantiated by the inverse relationship between [P]/[C] and the concentration of additive (I) (compare the theoretical expression of eq 2 with the observed expression of eq 4).

One possible explanation for the failure of the I–S complex to go to propene is that the catalytic molecule of Seyferth reagent serves as a template T, reacting both with carbene and with alkene. Whereas such a double complex can proceed to propene, a complex with an aromatic additive (2) does not have the nearby and more electrophilic alkene, as in T, so it proceeds poorly to propene via an intermolecular reaction.

Experimental Section

Procedures for the Seyferth reaction have been described elsewhere.[5] Organic additives were obtained from Aldrich. Mercury (D. F. Goldsmith Chemical and Metal Corp.), $SnCl_4$ (Baker), $AlBr_3$ (Aldrich), $AlCl_3$ (Aldrich), and $CuSO_4 \cdot 5H_2O$ (Mallinckrodt) were used without further purification. Copper bronze (BHD Chemicals Ltd.), $HgCl_2$ (Merck), $HgBr_2$ (Aldrich), $Hg(OAc)_2$ (Aldrich), ZnI_2 (Aldrich), $FeCl_3$ (Fisher), and Hg_2Cl_2 (Sargent) were dried at 0.01 mm for 1 h. Cuprous chloride (Aldrich), cuprous bromide (Fisher), and cuprous iodide (Alfa) were washed with dilute HX (X = Cl, Br, I, respectively) and dried at 0.10 mm for at least 1 h. Zinc chloride (Mallinckrodt) was recrystallized in 1,4-dioxane and dried at 0.10 mm for 6 h. Cupric chloride (Allied) was recrystallized in dilute HCl and dried for 6 h at 0.10 mm.

Kinetics. The reaction of 24.99 mol % of *trans*-1,2-dichloroethene with 2.49 mol % of $PhHgCBr_3$ is given as an example. A solution of 2.01 g (0.0208 mol) of alkene, 0.103 g (4.23×10^{-4} mol) of 1,6-dibromohexane (internal standard), and 4.68 g (0.0599 mol) of benzene was prepared. Into a tube containing 0.110 g (2.08×10^{-4} mol) of $PhHgCBr_3$ was quickly weighed 0.683 g of the 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 2.5×10^{-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 (10–12 tubes) had been prepared and sealed. The tubes were firmly inserted into a wire cage and immersed in a Haake constant-temperature bath at 69.0 ± 0.2 °C. After 5 min, the wire cage was removed and inverted several times until each solution was thoroughly mixed. Tubes were removed at intervals, quickly frozen in a 2-propanol/dry ice bath, and labeled. Analysis of each tube was performed by GC on the opened reaction tube. A 1 m × $^1/_8$ in. 25% DEGS on NAW Chromosorb W 60/80 column was used for analysis of the products. At a column temperature of 105 °C, retention times were 3.7 min for the propene and 5.8 min for the cyclopropane at a flow rate of 35 mL/min. Response factors were calibrated by comparing peak integration in the ^{1}H NMR spectrum with the values obtained from the GC integrator. The response factors were 4.1 for the propene and 1.7 for the cyclopropane by using the flame ionization detector. The corrected product ratios are based on averages of three to four injections.

Registry No. *trans*-CHCl=CHCl, 156-60-5; $PhHgCBr_3$, 3294-60-8; $PhNO_2$, 98-95-3; C_6H_6, 71-43-2; PhCl, 108-90-7; $PhCH_3$, 108-88-3; PhOMe, 100-66-3; *p*-$Me_2C_6H_4$, 106-42-3; Me_6C_6, 87-85-4; Ph_2Hg, 587-85-9; *p*-$MeC_6H_4HgCCl_3$, 6782-08-7; *p*-$ClC_6H_4HgCCl_3$, 96964-95-3; $PhHgCCl_3$, 3294-57-3; *p*-$Me_2NC_6H_4HgCCl_3$, 21511-17-1; *p*-$MeOC_6H_4HgCCl_3$, 89938-87-4; *p*-$NO_2C_6H_4HgCCl_3$, 89640-91-5; $(p\text{-}MeOC_6H_4)_2Hg$, 2097-72-5; $(p\text{-}MeC_6H_4)_2Hg$, 537-64-4; $(PhCH_2CH_2)_2Hg$, 956-73-0; Ph_2Zn, 1078-58-6; Ph_2CO, 119-61-9; PhHgCl, 100-56-1; PhHgBr, 1192-89-8; H_2O, 7732-18-5; Hg, 7439-97-6; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; Cu_2Cl_2, 75763-85-8; Cu_2Br_2, 63310-83-8; Cu_2I_2, 12527-63-8; Cu (bronze), 12597-70-5; $CuSO_4$, 7758-98-7; $CuCl_2$, 7447-39-4; $Hg(OAc)_2$, 1600-27-7; $SnCl_4$, 7646-78-8; $ZnCl_2$, 7646-85-7; ZnI_2, 10139-47-6; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3; $FeCl_3$, 7705-08-0; mesitylene, 108-67-8; durene, 95-93-2.

Substituent Effects on One-Bond ^{13}C–^{13}C NMR Coupling Constants in Aromatic Carbonyl Compounds

Pradeep S. Iyer, V. V. Krishnamurthy, and George A. Olah*

The Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received December 11, 1984

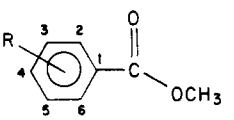
The one-bond ^{13}C–^{13}C NMR coupling constants ($^1J_{C,C}$) in a series of substituted methyl benzoates, benzoyl chlorides, and benzophenones were measured at natural abundance by using the INADEQUATE pulse sequence. These results when evaluated and compared with the $^1J_{C,C}$ values obtained from the study of substituted acetophenones, benzaldehydes, and benzoyl cations reveal their sensitivity to both mesomeric and inductive substituent effects. Within a given series, the changes in $^1J_{C_1,CO}$ values, as a function of the remote substituent on C_4 carbon, reflect the magnitude of the mesomeric interaction. The inductive effect of an α-substituent, on the other hand, is best portrayed by the consistency observed in the $\Delta J_{C_1\text{-}CO}$ ($J_{CHO} - J_{COX}$) values. Such consistency of these effects is also seen in the J_{C_3,C_4} or J_{C_4,C_5} values.

^{13}C NMR spectroscopy has proved to be a powerful tool in providing detailed information about structure, bonding, and electron distribution in organic molecules.[1] The focus has been predominantly on the study of chemical shifts (δ_C), together with the complimentary use of spin–spin interactions with relatively sensitive, high abundant nuclei such as ^1H, ^{19}F, ^{31}P, etc. One particular interaction which is of considerable interest is that between directly bonded ^{13}C nuclei. However, the low natural abundance of these nuclei, have, in the past, severely restricted their study and utility[2,3] generally necessitating difficult and often costly ^{13}C labeling.

Using Freeman's INADEQUATE pulse sequence,[4] we studied the one-bond ^{13}C–^{13}C coupling constants, at natural abundance, in a series of adamantane[5] and diamantane[6] derivatives and analyzed the substituent effect on these $^1J_{C,C}$ values (SCC) in terms of electronic and stereochemical effects. We, subsequently, extended our study to electron-deficient carbocationic systems and reported such results in a series of substituted acetophenones, benzaldehydes, their corresponding *O*-protonated carboxonium ions,[7] and benzoyl cations.[8]

As an extension of this study we have determined the one-bond ^{13}C–^{13}C coupling constants in a series of sub-

Table I. One-Bond ^{13}C–^{13}C Coupling Constants[a] in Substituted Methyl Benzoates (1R)



R	J_{CO,C_1}	J_{C_1,C_2} or J_{C_1,C_6}	J_{C_2,C_3} or J_{C_5,C_6}	J_{C_3,C_4} or J_{C_4,C_5}
4-OCH_3	77.1	59.3	58.5	66.5
4-CH_3[c]	76.0	*b*	*b*	56.5
H	74.8	*b*	56.6	55.5
4-F	76.6	59.6	57.3	70.7
4-Cl	76.0	59.1	56.5	64.8
4-Br	76.1	59.6	*b*	63.4
4-CF_3	74.6	59.3	57.6	59.9

[a] All coupling constants are in hertz. [b] Could not be measured accurately. [c] J_{C_4,CH_3} = 43.6 Hz.

(1) (a) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972. (b) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", Wiley Interscience: New York, 1980.

(2) For recent reviews and data compilations, see: (a) Marshall, J. L. In "Methods in Stereochemical Analysis"; Marchand, A. P., Ed.; Verlag Chemie International: Deefield Beach, FL, 1983; Vol. 2, pp 1–241. (b) Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc. 13*, 177. (c) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1981**, *11A* 65. Wray, V.; Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1981**, *11A*, 99.

(3) Pomerantz, M.; Bittner, S. *Tetrahedron Lett.* **1983**, *24*, 7. Stocker, M. *Monatsh. Chem.* **1982**, *113*, 1415. Kamienskatrela, *J. Mol. Struct.* **1982**, *78*, 121. London, R. E. *Org. Magn. Reson.* **1981**, *17*, 134.

(4) (a) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849. (b) Bax, A.; Freeman, R.; Kempsell, S. P. *J. Magn. Reson.* **1980**, *41*, 349. (c) Bax, A.; Freeman, R. *J. Magn. Reson.* **1980**, *41*, 507.

(5) Krishnamurthy, V. V.; Iyer, P. S.; Olah, G. A. *J. Org. Chem.* **1983**, *48*, 3373.

(6) Krishnamurthy, V. V.; Shih, J. G.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 1161.

(7) Krishnamurthy, V. V.; Prakash, G. K. S.; Iyer, P. S.; Olah, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 7068.

(8) Olah, G. A.; Iyer, P. S.; Krishnamurthy, V. V.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1984**, *106*, 7073.

0022-3263/85/1950-3059$01.50/0