CHEMISTRY LETTERS, pp. 695-698, 1986.

CHEMICAL EVIDENCE FOR STABILIZATION OF ELECTRICALLY NEUTRAL DIVALENT CARBON BY POLAR SOLVENTS

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Benzylhalocarbene generated in non-polar solvent is trapped readily by alkene, but the intermolecular process comes to compete poorly with the intramolecular process as the solvent polarity is increased.

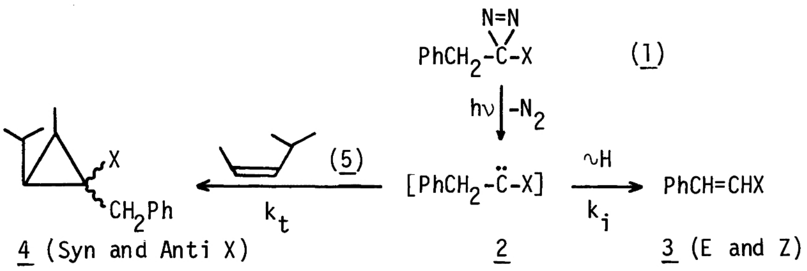
It is well recognized that reactivity of neutral reactive intermediates such as free radicals and carbenes is generally insensitive to the nature of solvent. However, it has been shown[1)] that regio-selectivity of radical chlorination of hydrocarbons is considerably enhanced in aromatic solvents and carbon disulfide. This is interpreted as indicating that chlorine radical is stabilized by the complexation with these solvents. Although a considerable number of studies have been reported[2)] on the effect of solvent in carbene chemistry, they are mainly focussed[2,3)] upon so-called "dilution effect", namely collisional deactivation of singlet carbene to the triplet by inert solvent such as C_6F_6. Recent laser-flash photolytic studies,[4,5)] however, provided kinetic evidence which demonstrates that singlet state of carbene is considerably stabilized by polar solvent such as acetonitrile or ethers. These findings prompted us to disclose our data indicating that stabilization of singlet carbene by solvent changes its chemical reactivity.

The carbenes which we utilize to probe the stabilization by solvents are benzylhalocarbenes which undergo rapid 1,2-H migration to give β-halostyrene. Thus, 3-benzyl-3-halodiazirines (1)[6)] were irradiated in various solvents with a 300 W Hg lamp filtered by Corning CS-052 (> 350 nm) at 0 °C afforded E- and Z-β-halostyrenes (3), which are apparently arising from a 1,2-H shift in the photolytically generated singlet halocarbenes (2). E/Z ratios of 3 were somewhat sensitive to the solvents employed, but no obvious trends are seen as a function of solvent polarity (Table 1).

When the photolysis of 1 (0.01 M) was carried out in the presence of cis-4-methyl-2-pentene (1.0 M), the singlet halocarbenes (2) were trapped by the alkene to give cyclopropanes (4) at the expense of the β-halostyrenes (see Scheme 1 and Table 2). Addition of 2 to 5 was stereospecific[7)] within the limit of GC detection. This is consistent with the earlier observation[8)] that the singlet carbene is involved in the cyclopropanation. The product distributions in this case are highly dependent upon the solvents as reflected on the ratio of

Table 1. Effect of Solvent on Stereochemistry of 1,2-H Migration of 2

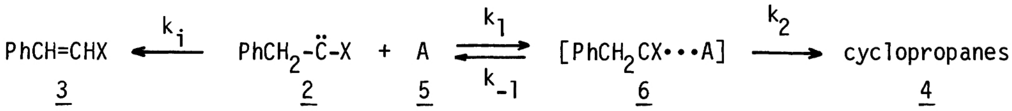
Solvents	X=Cl yield/% 3E	X=Cl yield/% 3Z	X=Cl E/Z	X=Br yield/% 3E	X=Br yield/% 3Z	X=Br E/Z
Cyclohexane	71.1	10.5	5.88	64.6	17.4	3.70
Benzene	82.6	12.6	5.55	79.7	9.1	9.09
Acetonitrile	65.9	17.5	3.23	64.1	24.0	2.70
1,4-Dioxane	82.1	13.1	5.26	75.5	15.0	5.00



Scheme 1.

3 to 4. For example, the chlorocarbene (2, X=Cl) generated in non-polar solvent, e.g., cyclohexane, is trapped by the alkene, but as the polarity of the solvent was increased, the intermolecular process became less important than 1,2-H migration and comes to compete poorly with the intramolecular process. Similar trends were observed for the bromocarbene (2, X=Br).

Recently, we have shown[7)] that the intermolecular/intramolecular product ratio (4/3) does not exactly reflect the ratio of the intermolecular (k_i)/intramolecular (k_t) rate constants since a plot of the product ratio (4/3) as a function of alkene concentration showed pronounced curvature. The results can be better interpreted in terms of a kinetic model recently suggested[9)] by Turro and Moss for the reaction of phenylchlorocarbene and an alkene, which is represented by Scheme 2, where [$PhCH_2CX\cdots A$] is a reversibly formed intermediate.



$$\underset{3}{PhCH{=}CHX} \xleftarrow{k_i} \underset{2}{PhCH_2\text{-}\ddot{C}\text{-}X} + \underset{5}{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{6}{[PhCH_2CX\cdots A]} \xrightarrow{k_2} \underset{4}{\text{cyclopropanes}}$$

Scheme 2.

It follows from Scheme 2 that

$$\frac{3}{4} = \frac{k_i}{k_2} + \frac{k_i}{k_t}\frac{1}{[5]} \qquad (1)$$

where the overall rate constant (k_t) equals to $k_1k_2/(k_{-1}+k_2)$. The dependency of the product ratio on the concentration of alkene completely agrees with eq 1. Thus, the plots of 3/4 vs. the reciprocal of alkene concentration give fairly linear correlation coefficients r > 0.99. From the slopes of such plots, real reactivity ratios, k_i/k_t's, are determined by least-squares linear regression analysis and are listed in Table 2.

Table 2. Effect of Solvent on Intermolecular Interception of Halocarbenes

X in 1	Solvents	Yield/%		3/4	k_i/k_t(rel)
		3 (E/Z)	4 (Syn/Anti)		
Cl	Cyclohexane	24.9(3.37)	71.9(15.3)	0.35	0.17 (1.00)
	Benzene	52.3(5.15)	44.0(12.8)	1.19	1.01 (5.9)
	Acetonitrile	72.6(3.81)	15.2(11.7)	4.78	3.34(19.6)
	1,4-Dioxane	84.3(6.08)	13.1(15.4)	6.44	5.36(31.5)
Br	Cyclohexane	59.9(3.02)	29.3 (0.20)	2.04	1.42 (1.00)
	Benzene	80.3(3.16)	9.2 (0.33)	8.73	9.42 (6.6)
	Acetonitrile	86.7(2.67)	2.7 (0.42)	32.1	32.0 (22.5)
	1,4-Dioxane	87.2(3.19)	2.3 (0.53)	37.9	41.5 (29.2)

The results summarized in Table 2 clearly indicate that k_i/k_t is increased as more polar solvents are employed. Recent laser-flash photolytic studies showed that the singlet to triplet intersystem crossing rate (k_{ST}) of carbene depends strongly on the choice of solvent. Thus, Platz$^{5)}$ showed that intersystem crossing from singlet naphthylcarbene is at least five times faster in a non-polar solvent relative to that in acetonitrile. Eisenthal$^{4)}$ also showed that k_{ST} of diphenylcarbene decreases as the solvent polarity is decreased and that a linear correlation exists between the logarithm of k_{ST} and the emprical solvent polarity parameter (E_T). These results are interpreted$^{5)}$ as indicating that the singlet state being highly polar will be strongly stabilized in polar solvents whereas the less polar triplet will only experience a weak stabilization. Stabilization by the complexation will be important especially for the electron-pair donor solvents, e.g., ether or acetonitrile, since a transient absorption assignable to ylide has been often detected by laser flash photolytic studies$^{10)}$ when carbene is generated in these solvents. In the present reaction systems, however, both intermolecular and intramolecular products are shown$^{7)}$ to be derived from the singlet state of halocarbenes. Moreover, most halocarbenes have the singlet ground state.$^{9a,11)}$ Thus, the observed effect of solvent on the product distributions is not explicable by invoking the effect on the singlet-triplet equilibrium. A plausible expalnation, then, is that a highly stabilized or complexed singlet carbene generated in polar solvent is much less reactive than the singlet carbene presumably free in non polar solvent. This is presumably attributable to a change in the ease with which carbene forms the intermediate 6 in its addition to alkene. Thus, a singlet carbene in a polar solvent is already solvated or even complexed by the solvent and therefore is less susceptible to the formation of the complex with the external alkene than the free carbene which is naked and hence is more easily attacked by the alkene.

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(Received January 21, 1986)