

TEMPERATURE AND MATRIX EFFECTS ON COMPETITIVE INTERMOLECULAR AND INTRAMOLECULAR
REACTION OF BENZYLCHLOROCARBENES IN ETHANOL

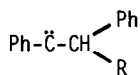
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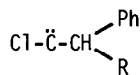
Summary: Benzylchlorocarbenes generated photolytically from diazirines in EtOH afford chlorostyrenes and acetals, whose distributions are sensitive to the reaction temperature.

In the past few years several research groups have studied the chemistry of carbenes in rigid matrix at low temperature.¹⁻⁴ In the case of carbenes with triplet ground states there are profound differences between the chemistry observed in fluid solution at ambient temperature and that obtaining in matrix at -196°C. For example, arylcarbene generated in alcoholic solution at ambient temperature gives O-H insertion product almost exclusively which is mostly derived from the singlet state, whereas arylcarbene generated in alcoholic matrices at -196°C resulted in a dramatic increase in C-H insertion products at the expense of the ether. These C-H insertion products are proposed to be formed via a H atom abstraction of the triplet carbene. More recently, it has been brought to our attention that the migratory aptitude and stereochemistry in 1,2 migration of arylcarbene system were also dependent upon temperature.⁵ Thus, the migratory aptitude trends observed for arylcarbene (A) changed from H>Ph>>Me to Ph>H>>Me as the temperature is lowered. In contrast to these intensive studies lavished upon the matrix reactions of arylcarbene with triplet ground state, only scant information⁶ is available on the effect of temperature on the chemistry of carbene with singlet ground state. In this work we have examined the effect of temperature on the reaction patterns of benzyl-



(A)

R=H, Me



(B)

chlorocarbene (B), a potent singlet ground state carbene, in order to learn more about the carbene chemistry in matrices.

Irradiation of 3-benzyl-3-chlorodiazirine (1a)⁷ in cyclohexane was carried out with a 300-W high-pressure Hg lamp at 0°C until all of the diazirine was destroyed. A Corning CS-052 filter cutoff at 350 nm was used in order to avoid product isomerization. The photolysis products were exclusively E- and Z-β-chlorostyrenes (3a), which are apparently arising from

a 1,2 H shift in the photolytically generated chlorocarbene (**2a**). Similar irradiation of other diazirine (**1b-d**) also resulted in the exclusive formation of β -chlorostyrene (**3b-d**).⁸ The behaviors are in sharp contrast with that observed^{5,9} for the corresponding arylcarbenes (**A**), where appreciable amount of Ph migration products are formed. It has been proposed^{5,9} that, while H migration occurs from the singlet state of the carbene, a Ph group can migrate in the triplet state. In the light of the fact that most of chlorocarbene have the ground state singlet,¹⁰ the present results indicate that Ph migration does not occur in the singlet manifold at least in chlorocarbene.

When irradiation of **1a** was carried out in EtOH, 1,2 H migration was appreciably suppressed concomitant with the formation of acetal (**5a**). The formation of **5** is rationalized¹¹ in terms of O-H insertion of the chlorocarbene to give the reactive chloro ether (**4a**), followed by its spontaneous ethanolysis. Similar irradiation of other diazirines (**1b-d**) in EtOH also resulted in the formation of acetal (**5b-d**) at the expense of **3** (Table 1). Two intriguing trends are seen in Table 1.

(i) The ratio of intramolecular to intermolecular reaction products (**3/5**) increased gradually as aryl substituent (X) was changed from Cl to H to Me (0.41→0.43→0.45). In other

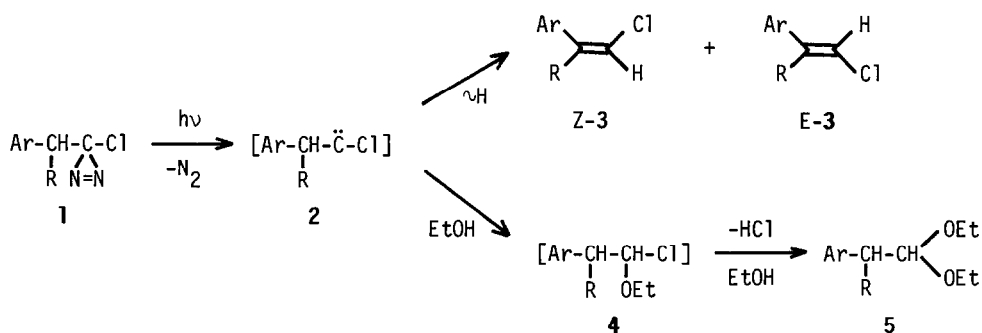


Table 1. Photolysis of **1** at 0°C

1	R	Ar	Solv	yield, %			E/Z	3/5
				Z-3	E-3	5		
a	H	C ₆ H ₅	c-C ₆ H ₁₂	10.9	62.3	-	5.7	-
			EtOH	9.5	20.0	69.1	2.1	0.43
b	H	p-MeC ₆ H ₄	c-C ₆ H ₁₂	5.2	79.2	-	15.2	-
			EtOH	8.4	21.8	67.5	2.6	0.45
c	H	p-ClC ₆ H ₄	c-C ₆ H ₁₂	10.6	56.5	-	5.3	-
			EtOH	8.3	20.3	70.4	2.4	0.41
d	Me	C ₆ H ₅	c-C ₆ H ₁₂	20.7	73.2	-	3.5	-
			EtOH	23.2	37.1	32.0	1.6	1.88

words, the intermolecular interceptions compete less efficiently against 1,2 H shift for the carbene bearing electron-releasing group at the migrating origin. This supports the idea^{8,12} that there is substantial hydride character associated with the migrating hydrogen. Much more dramatic increase in 3/5 was observed when R was changed from H to Me (0.43→1.88). This increase involves not only the electronic effect but also a steric effect and product alkene stability acting in the same direction.

(ii) The intermolecular interception caused a significant change in the stereochemistry of 1,2 H shift as reflected on a considerable decrease in E/Z ratio. The reason for this change probably partly due to the difference in the reactivity of the carbene conformers leading to E and Z-3 towards alcohols.⁸

Irradiations of 1a and 1d in EtOH were then carried out at various temperatures ranging from 0 to -196°C (Table 2). Inspection of the results in Table 2 indicates immediately that reaction patterns are markedly influenced by temperature. Several important trends are noted.

Table 2. Photolysis of 1a (1d) in EtOH at Various Temperatures

Temp (°C)	yield, %				
	Z-3	E-3	5	E/Z	3/5
0	9.5(23.2)	20.0(37.1)	69.1(32.0)	2.1(1.6)	0.43(1.9)
-45	6.7(20.5)	10.4(25.0)	67.4(42.9)	1.6(1.2)	0.25(1.1)
-78	6.5(20.6)	9.3(23.2)	68.1(43.8)	1.4(1.1)	0.23(1.0)
-110	5.2(19.6)	7.1(20.9)	67.1(45.8)	1.4(1.1)	0.18(0.9)
-150	5.7(24.8)	6.0(21.8)	68.3(41.1)	1.1(0.9)	0.17(1.1)
-196	32.4(67.0)	35.4(19.7)	25.8(10.4)	1.1(0.3)	2.6(8.3)

(i) The yields of 3 decrease as reaction temperatures are lowered (0°C→-110°C). Analysis of the 3/5 ratios reveals a satisfactory Arrhenius relation between 1,2 H shift and O-H insertion with slope (ΔE_a) = ~ 0.7 kcal/mol. This suggests that E_a for 1,2 H shift exceeds E_a for O-H insertion by ~ 0.7 kcal/mol. Since it has often been assumed¹³ that 1,2 H shift occurs with essentially zero activation energies, E_a for O-H insertion should be nearly zero and/or negative. It is quite important to note here that negative activation energies are observed for the reaction of phenylchlorocarbenes with alkene by laser photolysis experiments.¹⁴ This is interpreted in terms of the intervention of a carbene-alkene complex. The present results indicate, then, that a carbene-alcohol complex may intervene in the reaction of the chlorocarbene with alcohol.

(ii) These trends are reversed, however, once the environment becomes solid (-150°C→-196°C), with 3 again dominant. In matrix, the carbene is trapped in cage of EtOH matrix framework and hence mobility of the carbene is severely restricted.¹ Thus, intermolecular insertion is reduced relative to intramolecular rearrangement. Similar phenomena have been observed¹⁵ in the competitive ring expansion and intermolecular interception of cyclopropylcarbene by alkene.

(iii) No C-H insertion products into EtOH were observed even in the -196°C matrix reactions, indicating chlorocarbene (B) differs markedly from arylcarbene (A) which affords considerable amount of C-H insertion products (20%) in addition to O-H insertion (7%) and H shift products (56%) in -196°C EtOH matrices. This supports the idea that the triplet state undergoes C-H insertion presumably via H atom abstraction from the matrix.

(iv) Finally, stereochemistry of 1,2 H migration was also subjected to the temperature effect. Thus, the E/Z ratio decreased rather sharply as the reaction phase was changed from liquid to solid. Similar decrease has also been observed⁵ in arylcarbene system and is explained by assuming that, in a matrix environment, the nascent carbene is forcibly paired with the leaving N₂ due to the limited diffusibility. Apparently, this would reduce the population of carbene conformer leading to E alkene as a result of steric repulsion between N₂ and Ph group.

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