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MECHANISM OF C-H INSERTION OF CARBENE IN RIGID MATRIX

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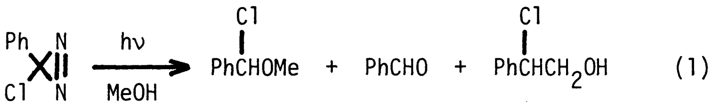
C-H insertion process of phenylchlorocarbene, a ground state singlet carbene, is not affected by matrix which generally exerts its effect in C-H insertion of most arylcarbenes. This reveals the origin of the matrix effects on carbene reactions.

Recent reports from this[1-4] and other[5-8] laboratories have shown that the reactivity of arylcarbenes changes dramatically as the reaction temperature is lowered. For example, we have found that O-H insertion product observed in the photolysis of aryldiazo compounds in alcohol solution becomes less important when the photolysis is carried out in frozen alcoholic matrix at -196 °C. Instead, large amounts of C-H insertion products are formed, which are shown to be arising by abstraction-recombination reaction of the triplet arylcarbene (eq. 2).[1-4] Moss et al. have found in the reaction of arylcarbene with olefin that the C-H insertion products increase significantly at the expense of cyclopropane as the temperature is lowered (eq. 4).[5-8] Thus, the reactions observed for carbenes generated in a matrix environment at -196 °C are primarily triplet in character. Nevertheless, temperature studies on insertion selectivities of arylcarbene into C-H bonds of iso-butane have shown that primary C-H insertion gains over tertiary once the matrix is formed (eq. 6).[9-10] Since triplet carbenes are generally more selective intermediates in the C-H insertion reaction,[11] this is explained by assuming that the reaction patterns of arylcarbene in matrix are not soley controlled by differences in carbene multiplicity but that fixed orientation of carbenes relative to the host exerts a dramatic effect (matrix effects) on the course of reactions. It is of immediate interest to know which multiplicity undergoes matrix effects in the C-H insertion. It is quite important in this connection to examine the chemical behaviors of singlet carbene in matrix. Phenylchlorocarbene (PCC) is suitable for this purpose since it has been shown to have ground state singlet (i.e., no ESR signal[12] and no tendency to react with oxygen[13]).

Photolysis[14] of phenylchlorodiazirine (1)[15] in methanol at 0 °C gave phenyl chloromethyl ether (2) along with benzaldehyde (3). The latter was shown to be a decomposition product of the



$$\mathbf{1} \xrightarrow[\text{MeOH}]{h\nu} \text{Ph}\overset{\text{Cl}}{\text{C}}\text{HOMe} + \text{PhCHO} + \text{Ph}\overset{\text{Cl}}{\text{C}}\text{HCH}_2\text{OH} \qquad (1)$$

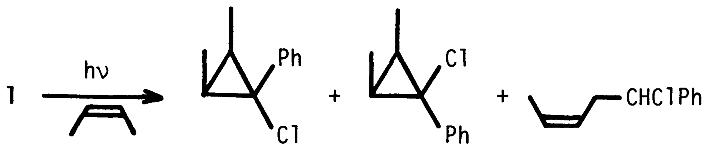
1 2 3 4

	2	3	4
0 °C	65%	25%	<1%
-196 °C	40%	10%	<1%

$$\underset{\mathbf{5}}{PhCH{=}N_2} \xrightarrow[MeOH]{h\nu} \underset{\mathbf{6}}{PhCH_2OMe} + \underset{\mathbf{7}}{PhCH_2CH_2OH} \qquad (2)^{2}$$

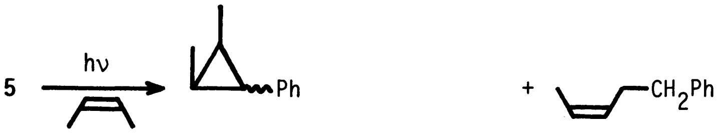
	6	**7**
0 °C	93%	1%
-196 °C	53%	40%

ether **2**. Low temperature photolysis[16] of **1** in methanolic matrix only resulted in a slight change in the ratio of **2** to **3**. No prominent increase in the C-H insertion product (**4**) was observed. Photolysis of **1** in cis-2-butene gave similar results.[17] Thus, irradiation of **1** in cis-2-butene solution afforded cyclopropanes (**8** and **9**). Again low temperature photolysis[16] of **1** in the olefinic matrix did not result in increase in C-H insertion (**10**). These results (eq. 1 and 3) are in sharp



(3)

	8 **9**	**10**
0 °C	>98% (8:9 = 1.9)	<1%
-196 °C	>98% (8:9 = 1.8)	<1%

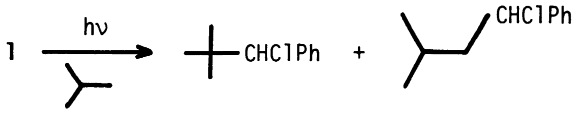


+ others (4)[5]

	11	**12**
0 °C	94.4% (syn:anti = 1.1)	2.2%
-196 °C	45.0% (syn:anti = 1.1)	30.2%

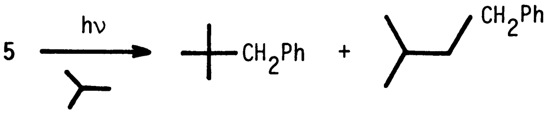
contrast with that observed for phenylcarbene (PC) (eq. 2 and 4) which has ground state triplet and shows dramatic increase in C-H insertion when generated in alcoholic[1-4] or olefinic[5-8] matrices at -196 °C. Accepting that it is ground state triplet that undergoes hydrogen atom abstraction-recombination reaction to give C-H insertion products, the observations suggest that PCC reacts in its singlet state even in rigid matrix since it has no lower-lying triplet state to decay.

Now it is possible to examine what kind of matrix effects are operating on C-H insertion of singlet carbene at low temperature. Since carbene center of PCC is sterically much more crowded than that of PC, one may expect that more primary C-H insertion product will be formed in the reaction of PCC with rigid iso-butane matrix if singlet carbene insertion into C-H bonds is affected by the matrix effects. Photolysis of **1** in iso-butane either at 0 °C or at -196 °C, however, yielded experimentally indistinguishable product distributions (eq. 5), indicating singlet carbene reaction is insensitive to the matrix effect. Again the results are in sharp contrast with that observed for PC which shows a marked increase in primary C-H insertion once matrix is formed (eq. 6).



(5)

	13	14
0 °C	>99%	<1%
-196 °C	>99%	<1%



(6)[9]

	15	16
0 °C	61%	14%
-196 °C	33%	47%

It is now clear that the carbene multiplicity which undergoes the matrix effect in the C-H insertion process is the triplet. What is the origin of the matrix effects, then? Platz[18,19] and Gasper[20] have recently measured the absolute decay rate of triplet arylcarbene in rigid matrix and demonstrated that the hydrogen atom abstraction from matrix is not a classical process but quantum mechanical tunneling in nature. The rate of a hydrogen atom tunneling process is dependent upon the barrier height and width: the barrier height is the classical activation energy and the barrier width is the distance which the hydrogen atom must tunnel from matrix molecule to the arylcarbene. From nonexponential decay of triplet carbene it has been suggested that the carbenes are immobilized relative to the host molecules with which they react and that different fixed orientation of the carbene produces different products. In rigid butane matrix, for example, triplet carbene abstracts the closest hydrogens, which are primary one in some reactive sites. Thus, the primary C-H insertion increases as the reaction temperature is decreased since the tunneling becomes relatively important at lower matrix temperature. Such site problems imposed by matrix seem not important for singlet carbene insertion. This is somewhat surprising in view of the fact[11] that the singlet carbene insertion into C-H bond is generally considered to be more sensitive to the steric effect due to its concerted nature than the abstraction-recombination process of the triplet in gas and liquid phase. The present result might support the Hoffman[21] and Dewar[22] pictures of the insertion process in which initial approach of carbene is along the axis of the C-H bond, since this mechanism is much less sensitive to the steric factor than perpendicular attack[23] on C-H bond.

In summary, it can be said that, while in gas and liquid phase singlet carbenes are generally less selective intermediate in C-H insertion owing to the concerted nature than triplet carbene, the triplet becomes less selective in matrix as a result of hydrogen atom tunneling.

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17) Since syn-isomer of cyclopropane (8) has been shown to decompose quantitatively on GC, relative yields were determined by NMR: G. L. Closs and J. J. Coyle, J. Org. Chem., 31, 2759 (1966). See also R. A. Moss, J. R. Whittle, and P. Freidenreich, J. Org. Chem., 34, 2220 (1969).
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