THE MATRIX EFFECT ON STEREOSELECTIVITY OF OLEFIN CYCLOPROPANATION BY ARYLCARBENE

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Summary: Temperature studies of addition of phenylcarbene to styrene showed that stereoselectivity changed rather dramatically as the reaction phase changed.

It has been shown that the reactivity of arylcarbenes dramatically changes in rigid matrix at low temperature. The C-H insertion products generally formed in rigid matrices of alcohol¹⁻⁴ and olefin⁵⁻⁸ are believed to be derived from triplet carbenes via abstraction-recombination mechanism. Recent kinetic studies of $Platz^{9-11}$ et al have shown that the predominant decay pathway of the triplet carbene in matrix is hydrogen atom tunneling. From non-exponential decay of triplet carbene observed in rigid matrix, it has been suggested that the carbenes are immobilized relative to the host molecules with which they react, and that the reactivity in matrix will depend on its fixed orientation relative to the host. Chemical evidence for such effect of matrix has been obtained in the temperature study^{12,13} on insertion selectivities of arylcarbene into C-H bonds of isobutane : primary C-H insertion gains over tertiary once matrix is formed. No information is now available of the matrix effect on the stereoselectivity of addition of carbene to C-C double bond, since olefins thusfar employed⁵⁻⁸ for matrix study have allylic C-H bonds which efficiently trap most triplet carbenes in matrix. We have examined the effect of reaction phase on stereoselectivity of cyclopropanation by use of styrene, which does not undergo CH insertion of carbene even in rigid matrix.

Photolysis¹⁴ of methyl phenyldiazoacetate (la, X=H, Y=CO₂Me) in styrene at 0°C gave cyclopropanes (3) as a 10:1 mixture of cis and trans isomers. In contrast, irradiation of la in frozen styrene matrix at -78 and -196°C resulted in a dramatic increase in the yield of the trans isomer with the ratio of cis:trans being 2.8:1 and 1.5:1, respectively. Similar increase in trans cyclopropane at lower temperature was observed in the photolysis of p-Br and p-H phenyldiazomethane in styrene (entries 2-5 in Table). However, the trends are reversed as the combination of reagents is changed. For example, low-temperature irradiation of phenyldiazomethane in p-substituted styrenes resulted in increase in cis-cyclopropane (entries 6 and 7; see also 8 and 9).

It is quite important to know the origin of the effect on stereoselectivity. One may suppose that the observed change in stereoselectivity is attributable to the simple temperature effect, <u>i.e.</u>, activation energy difference between cis and trans cyclopropanation. This possibility is reduced by the findings that photolysis of 1 in ethereal solution of styrene at -78° C (liquid phase) did not resulted in dominant increase in trans isomer (c/t = 0.68) compared with that observed (c/t = 0.33) in similar photolysis in acetonitrile crystalline matrix (-78° C). Moreover,

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$\frac{Table^{a}}{p-X-C_{6}H_{4}-C-Y} + p-Z-C_{6}H_{4}CH=CH_{2} \xrightarrow{hv}{T, \circ C} p-X-C_{6}H_{4} \xrightarrow{V} C_{6}H_{4}-Z-p$								
Entries	x	Y	Z	Solvent ^b	T,°C	State ^C	3,% ^d	(cis/trans)
1	Н	CO ₂ Me	Н	- - -	0 -78 -196	L C C	75 65 60	(10) (2.8) (1.5)
2	Η	Н	н	- -	0 -78 -196	L C C	73 62 54	(0.71) (0.33) (0.20)
3	Н	Н	H	Et ₂ 0 Et ₂ 0 Et ₂ 0	0 -78 -196	L L G	67 76 26	(0.89) (0.68) (0.66)
4	н	Η	Η	MeCN MeCN MeCN	0 -78 -196	L C C	88 85 58	(0.95) (0.33) (0.12)
5	Br	Н	H	-	0 -78 -196	L C C	50 46 35	(0.95) (0.48) (0.19)
6	Η	н	C1	- - -	0 -78 -196	L C C	78 66 50	(0.43) (0.64) (0.71)
7	H	Н	Br	- -	0 -78 -196	L C C	67 37 41	(0.42) (0.72) (0.89)
8	Me	Н	Н	- -	0 -78 -196	L C C	58 57 56	(0.46) (0.82) (1.0)
9	Н	C1	Н	-	0 -196	L C	65 60	(1.4) (4.2)

a) Irradiations were performed on a 5 mM solution of 1 in Pyrex tubes.

b) About 5-fold of solvent to styrene was used.

c) L: liquid phase, C: crystalline, G: glass. d) Determined by GC.

photolysis in ethereal glass at $-196^{\circ}C$ did not result in prominent increase trans isomer (c/t = 0.66) whereas the increase in trans isomer was much more striking (c/t = 0.12) in acetonitrile crystalline matrix (-196°C). These facts indicate that crystal environments play an important role in the stereochemical course of the cyclopropanation. Since there is accumulating spectro $scopic^{9-11,15}$ and chemical ¹⁻⁸ evidence for the intervention of triplet arylcarbene in the low temperature photolysis of 1 in matrix, triplet arylcarbene is an intermediate for cyclopropanes at low temperature. Kinetic studies indicated that absolute rates of decay of triplet arylcarbenes is faster in cyclohexene matrix than in styrene matrix, suggesting that the triplet carbene reacts with olefins by hydrogen-atom abstraction rather than by addition to double bond when both pathways are allowed.⁹ Neverthless, the kinetics of triplet diphenylcarbene ESR signal in single crystals of Ph₂C=CH₂ shows that addition is rapid in this case.¹⁶ Since no C-H insertion products, <u>e.g.</u>, $PhCH_2$ -CH=CHPh, were detected in the photolysis of PhCH=N₂ in PhCH=CH₂ matrix, decay pathway of triplet carbene is also a stepwise addition involving a 1,3-diradical. Styrene is known¹⁷ as an excellent triplet trap. It is then important to examine the behavior of 1,3diradicals in rigid matrix at low temperature. Thus, we examined the effect of temperature and phase on the stereochemical course in the photolysis of cis and trans-1,3-diarylpyrazolines (4) leading to cyclopropane (5) since the reaction has been shown to proceed via similar 1,3-diradicals (Scheme).¹⁸ The findings that retention of configuration was better in solid phase than in

Scheme



solution indicated that the rotation of 1,3-diradical becomes severely restricted in matrix environment. This is quite reasonable in the light of limited mobility of large molecule or group ($\underline{e}.\underline{g}.$, phenyl) in rigid matrix.¹⁹ It is very tempting to assume that the mode of reaction of arylcarbenes in matrix is predetermined by the location of carbene precursor in the styrene crystal lattice. Carbenes generated under such circumstances were forced to react with styrene without changing initial geometry and orientation of two molecules which are involved in the reaction. Presumably orientation might be dependent upon the relative size and shape of both guest and host molecules. A carbene precursor molecule will be favorably disposed in trans orientation in some styrene crystallattice, while the trapping site will be shifted to cis orientation in other styrene crystals. Although definite proof for the interpretations proposed herein is lacking, certainly topochemical control of photoproduct stereochemistry in the more ordered solid state is a widely documented phenomenon at ambient temperature.²⁰

Finally, it is to be noted that the stereoselectivity of phenylchlorocarbene addition to styrene is also affected by the reaction phase (entry 9). It has been shown²¹ that the reaction patterns of phenylchlorocarbene with alcohol, butene and isobutane are not altered by reaction temperature as well as phase, suggesting that it reacts in its singlet ground state even in matrix environment. The present observation indicates that singlet carbene reaction can be affected by matrix only in its stereochemical course of styrene cyclopropanation.

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