Effect of Precursor Structures on Arylcarbene Processes in Low-Temperature Matrices. Importance of Topochemically Controlled Processes

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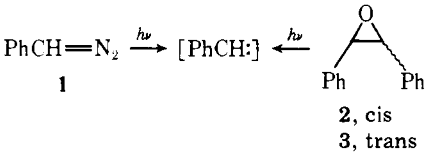
Abstract: C–H insertion selectivities of [PhCH:] generated from diverse sources, i.e., $PhCHN_2$ and *cis-* and *trans*-2,3-diphenyloxiranes, in 2-propanol and 2,3-dimethylbutane matrices at −196 °C showed considerable dependence on the structure of precursors, while liquid-phase experiments showed that insertion selectivities were essentially invariant regardless of source. [Ph_2C:] generated from Ph_2CN_2, tetraphenyloxirane, and 2,2,4,4-tetraphenyloxetan-3-one showed precursor dependences of C–H insertion selectivities as well as singlet/triplet product ratio even in the liquid phase and more dramatically in the solid phase. Possible effects of precursors on the angle and energy of nascent carbene and sensitization by photofragment (Ph_2CO) were excluded based on control experiments and EPR studies. Topochemical factors, i.e., contact of carbene center with the host molecules, are considered to play an important role especially in the matrix reactions and hence it has been suggested that attempts to extrapolate singlet/triplet carbene ratios from product compositions in matrices could prove unreliable since the fate of carbenes generated in a matrix may be predestined by site preference imposed upon the precursor.

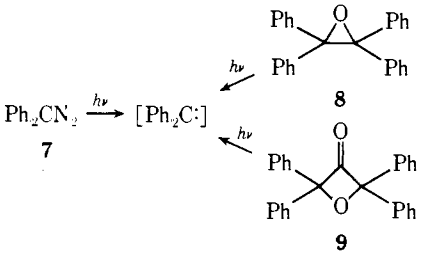
In recent years interest has increased in the low-temperature photolysis of aryldiazoalkyl compounds in reactive organic matrices.[2-4] The reactions observed for carbenes generated photolytically in a matrix environment at −196 °C are primarily triplet in character, which is attributed to differential temperature and/or matrix effects imposed on the kinetics of the competitive singlet and triplet carbene processes. As a consequence, matrix product ratios have been utilized as a means of diagnosing those processes characteristic of triplet arylcarbenes. Recently, however, we have demonstrated[5] that the reactions of carbenes generated in a matrix are not controlled solely by differences in carbene multiplicity and that topochemical factors may play an important role. For example, the nature of the interactions imposed on a carbene center by a host matrix is a function of the relative structure, size, and shape of the host and guest molecules, and such factors may exert a dominant effect on the course of reactions. We wish to report here our preliminary results on a dependency of arylcarbene processes within a matrix on precursor structures and to show that selected arylcarbene processes occurring within a matrix are indeed affected by precursor structure whose influence is presumably exerted through topochemical interactions.

Results and Discussion

Photolysis of the isomeric 2,3-diphenyloxiranes (**2** and/or **3**)[6] in 2-propanol solution at a temperature of 0 °C gives mainly benzyl 2-propyl ether (**4**) accompanied by lesser amounts of C–H insertion products (**5** and **6**). The insertion product ratios were found to be practically identical (within experimental error) with those obtained under similar photolytic conditions from the alternate precursor **1**.[3] In contrast, a dramatic increase in the yield of the C–H insertion products is obtained upon photolysis of the oxiranes in a matrix of 2-propanol at −196 °C. This effect may be attributed to an increase in triplet insertion or abstraction–recombination reactions,[3] at the expense of singlet O–H "insertion process" (Table I), and is in accord with the results observed upon photolysis of **1** under similar conditions. Singlet/triplet product ratios (i.e., **4**/(**5** + **6**)) are shown to be essentially invariant, with respect to source, indicating that "free" carbene is generated from the oxiranes even in a rigid matrix;[7] however, the C–H insertion selectivities (i.e., **5**/**6**) are more sensitive to the precursor structure. For example, [PhCH:] generated from the oxiranes shows greater selectivity than that produced from **1**. A similar dependence of C–H insertion selectivity on precursor structure is also observed in 2,3-dimethylbutane matrix at −196 °C (Table II), while insertion selectivities, for all practical purposes, are insensitive to source structure in such experiments conducted in fluid media.[8]



An impressive example of precursor structure–selectivity variations is displayed by diphenylcarbene [Ph_2C:] generated from different sources, e.g., **7**, **8**,[6] and **9**.[9] In contrast to the results compiled for the [PhCH:] system, [Ph_2C:] generated from three such widely diverse sources shows a detectable dependence of singlet/triplet product ratios on precursor structure even in liquid-phase photolyses performed at 0 °C in 2-propanol (Table III). In rigid matrices, the precursor dependency of the singlet/triplet ratio becomes more prominent and relative to **7** a significant increase in selectivity is observed in the C–H abstraction–recombination (insertion) processes exhibited by [Ph_2C:] produced from **8** and **9**. It is significant that a marked increase in diphenylmethane, a double hydrogen abstraction product, also occurs upon photolysis of **8** and **9**, i.e., relative to **7**. The consequences of variations in precursor structure are also evident from insertion selectivity data obtained in ethyl ether and displayed in Table IV.



The results indicate that triplet carbene is implicated in those reactions performed at least in 2-propanol, where insertion selectivity is clearly sensitive to precursor structure. It has been demonstrated that triplet ground state arylcarbenes generated in organic matrices at −196 °C are relatively stable, and react

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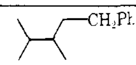
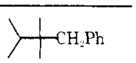
Table I. Product Distributions. [PhCH:] Generated from Diverse Sources in 2-Propanol[a]

precursor	t, °C	$PhCH_2O$-*i*-Pr (**4**)	$PhCH_2C(OH)Me_2$ (**5**)	$PhCH_2CH_2CH(OH)Me$ (**6**)	**4**/(**5** + **6**)	**5**/**6**
1	0	84.8	14.2	1	5.6	
	−196	15.7	68.5	15.8	0.19	4.3
2	0	83.2	15.8	1	5.0	
	−196	14.3	79.5	6.2	0.17	12.8
3	0	83.6	15.4	1	5.1	
	−196	15.9	76.4	7.7	0.18	9.9

[a] Data are expressed as percentages (based on the average of triplicate runs) of products **4-5**, normalized to 100%. The reproducibility achieved was <±4%. Toluene was detected in each run, but not quantitatively because of difficulties encountered in separation. The total yields of products are essentially invariant regardless of source (70-80%).

Table II. Product Distributions. [PhCH:] Generated from Diverse Sources in 2,3-Dimethylbutane[a]

precursor	t, °C		
1	0	8.2	91.8
	−196	48.1	51.9
2	0	9.3	90.7
	−196	36.5	63.5
3	0	9.0	91.0
	−196	40.3	59.7

[a] Data cited are expressed in percent of C-H insertion product, normalized to 100%. See also footnote *a*, Table I.

slowly with the host molecules even in the dark under these conditions.[10] Furthermore, it has been established that triplet ground state [Ph_2C:] generated from such diverse sources as **7**, **8**, and a *geminal* diazide at −196 °C achieves the same final geometry.[11] Consequently, it is not unreasonable to assume that a common isoenergetic ground state, triplet carbene of identical geometry is involved in each system studied despite the differences in reactivity observed. It has been postulated[12] based on spectroscopic data that certain products observed in the photolysis of **7** in rigid hydrocarbon matrices might result from the reactions of photoexcited [Ph_2C:] or by photolysis of products formed by reaction of photoexcited [Ph_2C:] with the matrix. However, the product distributions at low temperature are essentially independent of the wavelength employed (253-366 nm) in the photolysis of **1** and **7**. Such changes in wavelength of the incident light should certainly affect the product distribution if photoexcited carbene intervenes.

The marked decrease in the singlet/triplet ratio of carbenes obtained in the photocycloelimination reactions of **8** and **9**, however, might be attributed to the accompanying formation of benzophenone in each case, which conceivably could play a role as a photosensitizer and thus alter the carbene reaction course.[9] However, no appreciable change is observed in the product ratios (singlet/triplet as well as α-/β-CH insertion ratios) upon inclusion of excess benzophenone in control runs conducted with diphenyldiazomethane (**7**) in both fluid and rigid media, which provides evidence that the disparate results observed cannot be attributed to sensitization.

Although triplet sensitiziation in rigid matrices at 77 K is unfavorable and short range in character, we could not dismiss the possibility here in view of the extended lifetime of triplet benzophenone at low temperature.[13] For example, triplet sensitization by benzophenone does occur on photolysis of diazoacetate even at much lower temperatures.[14] That benzophenone does indeed serve as a photosensitizer for decomposition of **7** to [Ph_2C:], despite the product ratio studies, is clear from the acceleration in rates observed as the concentration of this ketone is increased not only in fluid, but in rigid media as well. It is not unreasonable that the course of the reaction remains unaltered in the sensitized reactions of **7** in light of the facile singlet/triplet equilibration mechanism available for arylcarbenes.[4]

A plausible explanation may be advanced to rationalize (1) the C-H insertion selectivity data and (2) the variations in singlet/triplet ratios observed with [Ph_2C:] which apparently arise as a consequence of variations in the precursor structures. The relevant energies and bond angles are obvious features of the precursor structure which could exert an effect on the chemical characteristics of the nascent carbene. Furthermore, those substrates which participate in a matrix reaction occupy a space with unique geometrical requirements which must certainly reflect the size and shape of both guest and host molecules. Sufficient freedom may exist within a matrix cell, however, to accommodate precursors whose spatial requirements differ and yet impose no restrictions on the final carbene geometry.[11] On the other hand, it has been shown that molecular motion, including diffusion of large molecules (PhCHO or Ph_2CO), is severely restricted within the matrix cage.[15] On this basis it is reasonable to assume that the course of reactions of nascent carbenes within such a cage will be influenced by the particular contact surface of the host encountered by the guest carbene precursor. Consider, for example, that Figure 1 constitutes a typical cell site configuration within the 2-propanol matrix host. Assume that molecules of the oxetane **9**, for example, are so disposed within the cage that they are in close contact with face (a), or that the nascent [Ph_2C:] is generated in such a manner that it is in proximity with this face. This would provide an explanation for the dramatic differences observed in O-H "insertion" product ratios, since the carbene generated under such circumstances would be constrained and blocked to a greater or lesser extent from reaction with the shielded/distal hydroxy group. A carbene molecule oriented in juxtaposition with face (a) is also favorably disposed to encounter and abstract hydrogen atoms from the α and β positions of 2-propanol via a concerted or sequential overall process, perhaps more favorable than formal insertion into C-H bonds. The relative increase in the O-H insertion and β-CH insertion products observed with [Ph_2C:] generated from **7** is explained in like manner, although a shift of the trapping site to face (b) must be assumed. Such a shift in a guest site could be not only related to the relative size of host and guest molecules, but also be induced in the fluid phase by weak solute-host interactions.[16]

The fact that carbonyl ylides are photolabile and have been characterized as intermediates which may intervene wholly or in part in the photolytic conversion of oxiranes (**2**, **3**, and **8**) and the oxetanone **9** to arylcarbenes in fluid and matrix solutions does not materially alter the topological arguments advanced to reconcile the data presented.[6] For example, even if [Ph_2C:] were formed from **8** solely in a two-step process involving initial C-C bond photocleavage to give an ylide, topological interactions should still be manifest in the organized medium and exert influence on the course of the ensuing photocleavage reaction to carbene. In other words, one would anticipate that those matrix environmental factors operative

Table III. Product Distributions. [Ph_2C:] Generated from Diverse Sources in 2-Propanol[a]

precursor	t, °C	Ph_2CHO-*i*-Pr (**10**)	Ph_2CH_2	$Ph_2CHC(OH)Me_2$ (**11**)	$Ph_2CHCH_2CH(OH)Me$ (**12**)	α/β[b]
7	0	88.5	11.5	0	0	
	−196	30.1	5.3	49.9	14.7	3.4
8[c]	0	81.8	16.6	1.6	0	
	−196	9.9	13.6	68.7	7.8	8.8
9[d]	0	70.2	26.6	3.2	0	
	−196	9.8	30.0	55.1	5.1	10.8

[a] Data tabulated represent the percent of products formed and are normalized to 100%. The reproducibility achieved was $<\pm 4\%$. [b] Product ratios for α- to β-CH insertion products. [c] Ph_2CO was detected. [d] Ph_2CO and Ph_2CHCO_2-*i*-Pr were produced.

Table IV. Product Distributions. [Ph_2C:] Generated from Diverse Sources in Ethyl Ether[a]

precursor	*t*, °C	Ph_2CHOEt[b] (**13**)	Ph_2CH_2	$Ph_2CHCH(CH_3)OEt$ (**14**)	$Ph_2CHCH_2CH_2OEt$ (**15**)	α/β[c]
7	0	15.7	12.1	69.9	2.3	30.4
	−196	2.1	1.4	84.3	12.2	6.9
8[d]	0	23.0	14.6	61.1	1.3	47.0
	−196	3.4	1.3	89.0	6.3	14.1
9[d]	0	16.3	14.6	67.5	1.6	42.2
	−196	3.1	7.4	84.4	5.1	16.5

[a] See footnote *a*, Table III. [b] A displacement product assumed to arise via initial nucleophilic attack of the ether on the diphenylcarbene: H. Iwamura, Y. Imahashi, K. Kushida, K. Aoki, and S. Satoh, *Bull. Chem. Soc. Jpn.*, **49**, 1690 (1976); G. K. Agopian, D. W. Brown, and M. Jones, Jr., *Tetrahedron Lett.*, 2931 (1976). [c] Product ratios for α- to β-CH insertion products. [d] Ph_2CO was detected.

upon such divergent precursors as **8** and **9** should be imposed on the photogenerated ylide as well.

Although definite proof for the interpretations proposed herein is lacking and thus they remain tenuous, certainly topochemical control of photoproduct stereochemistry in the more ordered solid state is a widely documented phenomenon at ambient temperature[17] and further work is required to prove that such control extends to the matrix experiments described herein.

In conclusion, it is suggested that the results presented reveal that the fate of carbenes generated in a matrix from various substrates may be predestined by site preferences (topochemical factors) imposed upon the precursor. Thus assessments of singlet/triplet carbene ratios from observed product distributions are of questionable validity insofar as such control extends to rigid matrix systems, although insertion of the singlet in a C–H bond of an alcohol is of low energy and more probable[16,18] than insertion of the triplet into a high-energy O–H bond of the same substrate. Expanded studies in this area using other precursors have been initiated in these laboratories and the viability of our mechanistic hypotheses will be discussed in terms of related systems later in a more extensive form.

Experimental Section

Materials. The aryldiazo compounds **1** and **7** were prepared according to literature procedures.[19] Prior to use, the diazo compounds were dissolved in cold pentane and decanted from any solid azine that may have formed. The syntheses of oxiranes **2**, **3**, and **8** and oxetanone **9** have been published elsewhere.[8] The alcohol **11** was prepared by the Grignard reaction[20] and **12** by the reduction of the corresponding imidolactone with sodium-*i*-PrOH.[21] Ethers **4**, **10**, and **13** were prepared by the Williamson synthesis while **14** and **15** were obtained by treatment of the corresponding alcohols **11** and **12** with ethyl iodide in the presence of silver oxide. The hydrocarbons displayed in Table II were prepared by the Friedel–Crafts acylation reaction and subsequent Clemmensen reduction of the resulting ketones. Satisfactory spectroscopic and mass spectral data have been obtained on all compounds. Commercial 2,3-dimethylbutane, 2-propanol, and ethyl ether were purified prior to use.

Photochemical Reactions and Analyses. All irradiations were conducted using a Halos 300-W high-pressure mercury lamp with a water-cooled quartz jacket. In a typical procedure, 0.005 mmol of the precursor compound was added to 2.0 mL of the appropriate solvent in Pyrex and/or quartz tubes 13.0 mm in external diameter, into which a second Pyrex tube of 8.0 mm external diameter was inserted in order to maximize exposure and utilization of radiation, particularly in matrices where this presents a problem. The tube was suspended in a transparent quartz Dewar filled with coolant and irradiated until consumption of the precursor was complete. Irradiations performed in the solid phase were conducted over 4-h intervals without thawing the matrix in the dark, since control experiments confirmed that insertion ratios were relatively sensitive to the period of irradiation-thaw cycles. Sensitized experiments were performed under conditions similar to those described above. In the sensitized runs a 50-molar excess of benzophenone was added to ensure that >95% of the incident light was absorbed by the sensitizer. That addition of benzophenone greatly accelerates the rates of decomposition of **7** was noted. Control experiments exclude possible photoconversions of the product during the irradiation period and also demonstrate that no reaction occurs in the absence of light over the temperature range studied. Product identification and relative yields were conveniently determined by standard GC and/or GC-MS techniques.

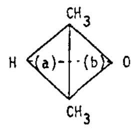


Figure 1.

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Electrochemically Induced Aromatic Nucleophilic Substitution in Liquid Ammonia. Competition with Electron Transfer

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Abstract: Electrochemical inducement of aromatic nucleophilic substitution of ArX compounds is investigated for a number of substrate and nucleophile systems in liquid ammonia. Electron transfer to the Ar·radical resulting from the initial reductive cleavage is essentially the only reaction competing with substitution. The competition occurs under two different regimes involving either homogeneous or heterogeneous electron transfer leading to different kinds of kinetic control. Cyclic voltammetry is used both for a rapid estimate of the nucleophile reactivity and for a quantitative determination of the rate constants of the nucleophile addition on Ar·. The method is also applied to the determination of the kinetic stabilities of the substrate anion radicals which is not possible through the standard application of electrochemical techniques. The agreement of the predicted kinetics with the experimental data both under homogeneous and heterogeneous electron transfer conditions provides further support for the $S_{RN}1$ mechanism.

It has been shown recently that $S_{RN}1$ nucleophilic substitution (see ref 2 and references cited therein) of aromatic halides can be induced electrochemically involving the reaction sequence

$$\mathrm{ArX} + 1\mathrm{e}\ (\text{electrode}) \rightleftarrows \mathrm{ArX}^{-\cdot}\ (\text{standard potential: } E_1^\circ) \tag{0}$$

$$\mathrm{ArX}^{-\cdot} \xrightarrow{k_1} \mathrm{Ar}\cdot + \mathrm{X}^- \tag{1}$$

$$\mathrm{Ar}\cdot + \mathrm{Nu}^- \xrightarrow{k_2} \mathrm{ArNu}^{-\cdot} \tag{2}$$

$$\mathrm{ArNu}^{-\cdot} - 1\mathrm{e}\ (\text{electrode}) \rightleftarrows \mathrm{ArNu}\ (\text{standard potential: } E_2^\circ) \tag{3}$$

and/or

$$\mathrm{ArNu}^{-\cdot} + \mathrm{ArX} \overset{k_4}{\rightleftarrows} \mathrm{ArNu} + \mathrm{ArX}^{-\cdot} \tag{4}$$

(equilibrium constant: $K_4 = \exp[(F/RT)(E_1^\circ - E_2^\circ)]$)

The reaction is initiated by setting up the electrode potential at the level of the reduction wave of the substrate. When the substrate is easier to reduce than the substitution product ($E_1^\circ > E_2^\circ$), the electrochemical injection of electrons is catalytic since reaction 3 is in favor of the right-hand side at the working potential and reaction 4 is spontaneously in favor of the right-hand side as well. In the reverse case the $\mathrm{ArNu}^{-\cdot}$ anion radical may have to be reoxidized independently in order to complete the reaction.

So far, the electrochemical inducement of such aromatic nucleophilic substitution reactions has been carried out in organic solvents such as acetonitrile and dimethyl sulfoxide with tetraalkylammonium salts as supporting electrolyte.[3,4] In these media a competing reaction that may lower the substitution yield is then H-atom abstraction from the solvent by Ar·.

$$\mathrm{Ar}\cdot + \mathrm{SH} \rightarrow \mathrm{ArH} + \mathrm{S}\cdot \tag{5}$$

with further electron transfer to S· leading to S^-.[4,5]

Another competing reaction that may occur in any solvent is the reduction of Ar· through electrode and/or solution electron transfer.

$$\mathrm{Ar}\cdot + 1\mathrm{e}\ (\text{electrode}) \rightarrow \mathrm{Ar}^- \tag{6}$$

$$\mathrm{Ar}\cdot + \mathrm{ArX}^{-\cdot} \xrightarrow{k_7} \mathrm{Ar}^- + \mathrm{ArX} \tag{7}$$

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