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Carbene in Rigid Matrix. XI.[1] Temperature and Matrix Effect on Phenylcarbene Processes in Ether and Amine

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Product distributions from reactions of phenylcarbene with diethyl or diisopropyl ether or diethylamine were found to be highly dependent on reaction temperature. As temperature decreases, the C–O displacement reaction and N–H insertion are decreased. Concomitantly, primary C–H insertion products markedly increase especially at lower matrix temperatures.

In recent years the importance of the method of generation of a carbene for its chemical behavior has become evident. Among examples which may be cited, the low temperature photolysis of aryldiazomethanes in rigid matrices has been shown[2,3] to be a unique method for looking into the triplet arylcarbene chemistry, especially in systems in which competitive singlet and triplet reactions occur. Photolysis of aryldiazomethane in olefin matrices at −196 °C, for example, results[2] in a dramatic increase in the yield of C–H insertion products at the expense of cyclopropane, which is a dominant product in a liquid phase photolytic run. A similar dramatic yield increase of C–H insertion products is also observable[3] in the photolysis of aryldiazomethanes in alcoholic matrices, whereas O–H insertion is generally a major reaction pathway of arylcarbene generated at ambient temperature. These C–H insertion products are proposed[2,3] to be formed *via* an abstraction-recombination (*a-r*) of the triplet carbene on the basis of ample spectroscopic[4] and chemical[4a] evidence for the presence of the ground-state triplet carbene in the low temperature matrix photolysis of most aryldiazomethanes at −196 °C. The method is thus expected to serve as a useful adjunct in the investigation of the relationship between the multiplicity and reaction pattern of carbene. However, since there is still some ambiguity as to the exact mechanism by which the matrix controls C–H insertion processes within itself, we have investigated temperature effects on carbene reactions with other reactive substrates involving hetero atoms, *i.e.*, ether and amine. Temperature effect studies of reactions of carbene with these substrates are intriguing in the following points in connection with results in alcohols. First, one can expect to get information on the temperature dependence of C–H insertion selectivity in both the liquid and solid phases, since C–H insertion is a major pathway[5] for these substrates; in contrast, C–H insertion scarcely proceeds[2] in reactions with alcohol, especially in the liquid phase. Second, it is quite important to examine the temperature effect on characteristic reactions[5] of the singlet carbene in these solvents, *i.e.*, the successive sequence of two reactions: the electrophilic attack on the lone pair of electrons on the hetero atom (X) to form an ylidic intermediate; and the Stevens rearrangement and/or the Hoffman type β-elimination, leading to C–X insertion and C–X displacement. The N–H insertion process of carbene will especially be informative because, unlike its reaction with alcohols[2] involving, if possible, abstraction of a hydrogen atom from the α-carbon atom, the triplet carbene may be expected to abstract[5b] hydrogen from the N–H bond in view of the bond energy and hence will take part also in the N–H insertion together with the singlet-state carbene. Thus, the present systems are expected to throw additional light not only on the applicability of the technique to looking into the triplet carbene chemistry but also on the mechanism of reactions of arylcarbene with ether or amine.

Reaction of Phenylcarbene with Ethers. A solution of phenyldiazomethane (**1**) in ether (**2**, R=H, CH_3) was irradiated at 0 °C and analysed by GC. This analysis revealed formation of the C–O displacement product (**3**), the C–O insertion product (**4**), and two C–H insertion products (**5** and **6**) (Table 1). The product distributions are found to be sensitive to the structure of ethers. Thus, either **3** or **4**, presumably resulting *via* an oxygen ylide intermediate, is formed in more suppressed yield as the ether changes from ethyl ether to isopropyl ether. This is apparently due to the steric hindrance on the accessibility to the central oxygen. A similar steric hindrance on the ylide formation has been noted with a photolysis[6] of dimethyl diazomalonate in allyl ethers, where the yield of the ylidic product decreases from 31 to 0% as the ether changes from allyl methyl ether to allyl *t*-butyl ether. Since it is quite important here to examine the exact intermediates leading to each insertion product, we have examined effects of precursor, triplet sensitizer, and singlet carbene quencher on product distributions (Table 1). First, photolysis of *cis*- and *trans*-1,2-diphenyloxiranes, a nitrogen-free precursor[7] of phenylcarbene, in ethyl ether gave a comparable result with that observed in similar photolysis of **1**. This eliminates the possible intervention of the diazomethane as an intermediate in the reaction and thus indicates involvement of free carbene. Second, product distributions were not altered by the addition of a large excess of benzophenone as a triplet sensitizer so as to assure absorption of 99% of the incident light by the sensitizer. This is often observed[8] in the arylcarbene system and can be interpreted as indicating that singlet-triplet equilibrium is faster than reactions with ether. Third, the examination of effect of 2-propanol, an efficient quencher for singlet carbene,[2,9] on the product distribution indicated that both the ylidic products and the C–H insertion products were quenched but with different degrees of efficiency. Thus, the ratio of the C–H insertion products to the ylidic products increased as the concentration of alcohol increased. This implies

Table 1. Product distribution in photolysis of **1** in ethers at 0 °C$^{a)}$

R_2O	Additive (mmol dm^{-1})	Relative yield/%$^{b)}$			
		3	**4**	**5**	**6**
Et_2O	None	13.7	18.1	68.2	Trace
	None$^{c)}$	11.3	19.3	69.4	Trace
	Ph_2CO (25)	12.5	17.3	70.2	Trace
	i-PrOH (25)$^{d)}$	8.0	12.6	65.2	Trace
	i-PrOH (75)$^{d)}$	5.9	9.6	59.2	Trace
	i-PrOH (125)$^{d)}$	4.5	8.3	54.4	Trace
i-Pr_2O	None	≈1	≈1	95.1	2.9
	None$^{c)}$	≈1	≈1	96.8	1.2

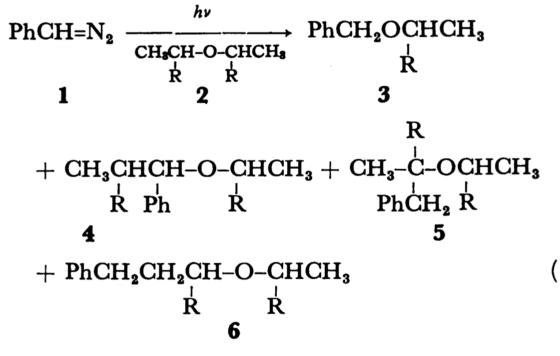
a) Irradiations were performed on a 2.5 mmol dm^{-3} solution of **1** in Pyrex tubes. b) Yields were determined by GC and normarized to 100%. Total yields (*ca.* 50—60%) did not vary appreciably under these conditions. c) Diphenyloxiranes used as a carbene precursor. d) OH insertion product, $PhCH_2OCH(CH_3)_2$, formed was included in numerator.

Table 2. Product distribution as a function of temperature. Photolysis of **1** in ethers

R_2O	*T*/°C	Relative yield/%$^{a)}$			
		3	**4**	**5**	**6**
Et_2O	0$^{b)}$	13.7	18.1	68.2	Trace
	−50$^{b)}$	6.3	5.3	84.7	3.7
	−78$^{b)}$	2.6	1.3	94.8	1.3
	−110$^{b)}$	1.9	Trace	94.2	3.9
	−150$^{c)}$	1.6	Trace	92.5	5.9
	−196$^{c)}$	1.1	Trace	89.2	9.7
	−196$^{c,d)}$	≈1	Trace	88.3	10.4
i-Pr_2O	0$^{b)}$	≈1	≈1	95.1	2.9
	−50$^{b)}$	≈1	≈1	96.5	1.5
	−78$^{b)}$	≈1	≈1	97.0	1.0
	−110$^{c)}$	Trace	Trace	66.4	33.6
	−150$^{c)}$	Trace	Trace	25.9	74.1
	−196$^{c)}$	Trace	Trace	14.6	85.4
	−196$^{c,d)}$	Trace	Trace	12.3	87.7

a) Normarized to 100%. Total yields were *ca.* 50—60%. Other minor products detected in each run were toluene, bibenzyl, stilbenes, and aldehyde azine. Control experiments ruled out the interconversion of products during irradiation. b) Liquid phase. d) Solid phase. d) Diphenyloxiranes used as a carbene precursor.

that singlet carbene takes part in the ylidic products but that not only singlet but also triplet carbenes are involved in the C–H insertion reaction.



$$\underset{\mathbf{1}}{\mathrm{PhCH{=}N_2}} \xrightarrow[\underset{\mathbf{2}}{\mathrm{CH_3\underset{R}{C}H\text{-}O\text{-}\underset{R}{C}HCH_3}}]{h\nu} \underset{\mathbf{3}}{\mathrm{PhCH_2O\underset{R}{C}HCH_3}}$$

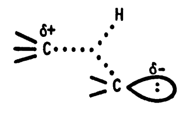
$$+\ \underset{\mathbf{4}}{\mathrm{CH_3\underset{R}{C}H\underset{Ph}{C}H\text{-}O\text{-}\underset{R}{C}HCH_3}} +\ \underset{\mathbf{5}}{\mathrm{CH_3\text{-}\overset{R}{\underset{PhCH_2}{C}}\text{-}O\underset{R}{C}HCH_3}}$$

$$+\ \underset{\mathbf{6}}{\mathrm{PhCH_2CH_2\underset{R}{C}H\text{-}O\text{-}\underset{R}{C}HCH_3}} \qquad (1)$$

a, R = H; **b**, R = Me

The effect of temperature on the product distribution was next examined and the results are summerized in Table 2. Two apparent trends of temperature dependence can be seen from an inspection of Table 2. First, as the photolysis temperature was lowered, yields of the displacement product (**3**) and C–O insertion product (**4**) decreased continuously, especially in the reaction with ethyl ether, and they were almost completely suppressed at −196 °C, whereas the C–H insertion product increased. Similar phenomena have been observed[2)] in the O–H/C–H insertion ratio in the reaction of phenylcarbene with alcohols as temperature is lowered. This can be interpreted as indicating that triplet reactions gain over singlet reactions since it has been demonstrated[4)] that a photolysis of aryldiazomethanes in organic matrices at −196 °C results in an almost exclusive formation of triplet carbenes. Thus the present results indicate that the characteristic reaction of singlet carbene with ethers is also suppressed at lower temperature. This suggests that the process has a higher activation energy than the competitive C–H insertion process. Alternatively, the reason for suppression of **3** and **4** at lower temperature probably lies partly in the ramification of stabilization by solvation. Thus, the transition state for the formation of **3** and **4** might be more polar than that leading to the C–H insertion and hence is more stabilized by solvation. Such solvation becomes less important as temperature decreases and hence yields of **3** and **4** decrease.

One more interesting feature of the present reaction is that C–H insertion selectivity is also highly temperature dependent; the selectivity increases as temperature is lowered as far as the reaction phase is liquid, but it dramatically decreases when the reaction phase changes from liquid to solid. Similar phenomena have been observed[10)] in the C–H insertion selectivity of phenylcarbene in hydrocarbons with various types of C–H bonds and can be explained in terms of competitive temperature and matrix effects. Thus, as temperature decreases, the tertiary C–H insertion gains over the primary one because the tertiary C–H insertion is favored by lower activation energy. It has been suggested that both singlet and triplet carbenes take part in the C–H insertion at least in liquid phase, but if the C–H "insertion" takes place *via* the *a-r* reaction of the triplet, apparently tertiary abstraction is favored over primary one in view of bond energy, and if, on the other hand, the concerted insertion of the singlet is assumed, the transition state (**7**) proposed[11)] for the insertion predicts that tertiary insertion is favored by an electronic factor. In the matrix photolysis, however, triplet carbene is thought to be a dominant intermediate for the C–H insertion product since recent studies[4b)]



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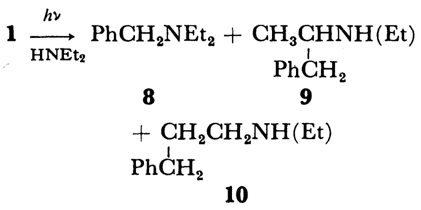
on decay rates of triplet arylcarbenes in various organic matrices have shown that the predominant decay pathway of the triplet is hydrogen atom tunneling to give C–H "insertion." Intervention of free carbene was again verified by the finding that the photolysis of the diphenyloxirane in rigid matrix gave a comparable trend in the product distribution. The decrease in the C–H insertion selectivity observed in rigid matrix is, however, a completely unexpected behavior for triplet carbenes since triplet carbenes have been shown[12] to be much more selective intermediates in the C–H insertion reaction than the corresponding singlet in gas- as well as liquid-phase experiments. The reason for the marked increase in the primary C–H insertion in a rigid matrix then probably lies partly in that a matrix imposes steric demand on the C–H insertion process. It is not unreasonable to assume that the size and shape provided by the host molecule and its rigidity impose severe steric hindrance on the guest molecule (PhCH:) in the accessibility to tertiary C–H bonds. A similar argument can be applied to explain that a much less dramatic change in the C–H insertion selectivity was observed even at −196 °C in the reaction with ethyl ether matrix which has less sterically-hindered secondary C–H bonds.

Reactions of Phenylcarbene with Diethylamine. Photolysis of **1** in diethylamine resulted in formation of the N–H insertion product (**8**) and two C–H insertion products (**9** and **10**). Temperature dependence of the product distribution (**8**—**10**) is summerized in Table 3. From the Table, it is evident that the N–H insertion product decreases steadily concomitant with the increase in the C–H insertion product, as temperature is lowered. Accepting that triplet arylcarbene is generated also in the amine matrix, it is somewhat surprising to note that **8** is not appreciably formed even at −196 °C, because the energy for N–H bond must be less by some 3 kcal mol^{-1} than that for the α-CH bond[5b] in the amine and hence the abstraction of hydrogen by triplet carbene should occur from the N–H bond more easily than from C–H bonds especially at lower temperature, resulting in the production of **8** *via a-r* mechanism. It is worth noting that, in gas-phase reactions of methyl radical with methylamine, the N–H bond is more than twice as reactive as the C–H bond.[13] Moreover, CIDNP studies of thermal (80 °C) decomposition of diphenyldiazomethane in butylamines have shown[5b] that triplet diphenylcarbene actually abstracts hydrogen from the N–H bond to form the radical pair $\overline{Ph_2CH\cdot\ \cdot NHR}$, which however separates to each component to give radical dimeric products at this temperature. The kinetics of the reaction have indicated,[5b] on the other hand, that the N–H insertion product is formed *via* an initial attack of the singlet carbene on nitrogen atom of the amine followed by rearrangement of the resulting ylide. The present results support this mechanism. Since the recombination of the radical pair is shown[2] to be favored in rigid media due to the increased viscosity, a decrease in the formation of **8** even in rigid amine matrix suggests that the triplet carbene generated in rigid matrix does not abstract hydrogen from the N–H bond in spite of the energetic advantage. Exact reason for this interesting phenomena is not known at present. It might partly lie in that the interaction of solvent molecules themselves comes to predominate over interactions between guest and amine molecules as temperature is lowered.[14]



$$\mathbf{1} \xrightarrow[\text{HNEt}_2]{h\nu} \underset{\mathbf{8}}{PhCH_2NEt_2} + \underset{\mathbf{9}}{\underset{PhCH_2}{CH_3CHNH(Et)}} + \underset{\mathbf{10}}{\underset{PhCH_2}{CH_2CH_2NH(Et)}} \qquad (2)$$

TABLE 3. PRODUCT DISTRIBUTION AS A FUNCTION OF TEMPERATURE. PHOTOLYSIS OF **1** IN DIETHYLAMINE

T/°C	Relative yield/%[a]		
	8	**9**	**10**
0[b]	62.5	37.5	0
−50[b]	59.9	38.5	1.6
−78[c]	35.1	59.8	5.1
−110[c]	25.5	69.6	4.9
−150[c]	18.1	80.8	1.1
−196[c]	17.0	80.8	1.2

a) See footnote a in Table 2. b) Liquid phase. c) Solid phase.

Concluding Remarks. The present results have suggested that the low temperature photolysis of aryldiazomethanes in a rigid matrix is a very useful technique to suppress characteristic reactions of singlet carbene and to increase C–H insertions presumably resulting *via a-r* reaction of triplet arylcarbenes. The method has its merits in that (i) it generates the triplet arylcarbene which is usually in a rapid equilibrium with the upper-lying singlet states and hence is not populated generally in liquid phase to the extent which permits the prominent formation of the product derived from it in the sensitized experiment and (ii) it also makes the triplet arylcarbene a synthetically more useful intermediate, while the triplet arylcarbene generated in the liquid phase usually leads to a complex mixture of radical-derived products.

Experimental

The infrared, ^{1}H NMR, and GC-MS spectra were recorded on a JASCO IR-G spectrometer, a JEOL JNM-MH-100 NMR spectrometer, and a Shimadzu GC-MS 1000 spectrometer, respectively. The GC analyses performed on a Yanagimoto instrument, Model G-180, with a flame ionization detector. The following columns were used: A, 4.0 mm×2.0 m 10% PEG 20 M on 60—80 mesh Diasolid L; B, 4.0 mm×2.0 m 10% OV-17 on 60—80 mesh Diasolid L.

Materials. Diazomethane **1** was prepared from the corresponding tosylhydrazone immediately before use. All authentic ethers (**3**—**6**) in Eq. 1 were prepared by treatment of the corresponding aromatic alcohols with either ethyl bromide or isopropyl bromide in the presence of silver oxide according to the literature procedure.[5c] Authentic amines (**8**—**10**) were prepared by the reaction of appropriate bromide with excess diethylamine or ethylamine. Their boiling points were 101—103 °C/23 mmHg†(**8**), 103—105 °C/24 mmHg (**9**),

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† 1 mmHg≈133.3 Pa.

and 117—119 °C/21 mmHg (**10**), respectively. Preparations of commercially unavailable alcohols were reported elsewhere.[2a,e] Satisfactory spectroscopic and mass spectral data have been obtained on all compounds.

Irradiations 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 diazomethane was added to 2.0 cm^3 of the appropriate solvent in Pyrex tubes. The sample was then degassed using three freeze-thaw cycles, and the sample tube was sealed in vacuum. The tube was suspended in a transparent Pyrex Dewar flask filled with coolant and irradiated until all diazomethane was destroyed. Photolysis of diphenyloxirane was carried out in quartz tubes in a transparent quartz Dewar. Control experiments ruled out the interconversion of the product during irradiations and also showed that no reaction occurred in the absence of light in the range of temperature studied.

The product identification and relative yields were conveniently determined by standard GC and/or GC-MS techniques.

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References

1) Part X: H. Tomioka, H. Ueda, S. Kondo, and Y. Izawa, *J. Am. Chem. Soc.*, **102**, 7817 (1980).

2) a) H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977); b) H. Tomioka, T. Inagaki, S. Nakamura, and Y. Izawa, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 130; c) H. Tomioka, T. Miwa, S. Suzuki, and Y. Izawa, *Bull. Chem. Jpn.*, **53**, 753 (1980); d) Tomioka, H. Okuno, and Y. Izawa, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 1636; e) H. Tomioka, S. Suzuki, and Y. Izawa, *J. Am. Chem. Soc.*, in press.

3) a) R. A. Moss and U.-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954 (1971); b) R. A. Moss and M. A. Joyce, *ibid.*, **99**, 1262 (1977); c) R. A. Moss and J. K. Huselton, *ibid.*, **100**, 1314 1978); d) R. A. Moss and M. A. Joyce, *ibid.*, **100**, 4475 (1978).

4) a) A. M. Trozzolo, *Acc. Chem. Res.*, **1**, 329 (1968) and references cited therein; b) V. P. Senthilnathan and M. S. Platz, *J. Am. Chem., Soc.* **102**, 7637 (1980).

5) a) See for review, W. Kimse, "Carbene Chemistry," 2nd ed, Academic Press, New York (1971), p. 407; b) D. Bethell, J. Hayes, and A. R. Newall, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 1307: c) H. Iwamura, Y. Imahashi, K. Kushida, K. Aoki, and S. Satoh, *Bull. Chem. Soc. Jpn.*, **49**, 1690 (1976); d) G. K. Agopian, D. W. Brown, and M. Jones, Jr., *Tetrahedron Lett.*, **1976**, 2931.

6) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, *J. Am. Chem. Soc.*, **94**, 3870 (1972).

7) A comprehensive review of carbene formation from oxiranes by cycloelimination is presented, N. R. Bertoniere and G. W. Griffin, "Carbenes," ed by M. Jones and R. A. Moss, Wiley-Interscience, New York (1973), Vol. I.

8) See for example, G. L. Closs and B. E. Rabinow, *J. Am. Chem. Soc.*, **98**, 8190 (1976).

9) J. J. Zupancic and G. B. Suchuster, *J. Am. Chem. Soc.*, **102**, 5958 (1980).

10) H. Tomioka, *J. Am. Chem. Soc.*, **99**, 6128 (1977).

11) D. Seyferth and Y.-M. Cheng, *J. Am. Chem. Soc.*, **95**, 6763 (1973).

12) a) M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Am. Chem. Soc.*, **94**, 7469 (1972); b) B. M. Herzog and R. W. Carr, Jr., *J. Phys. Chem.*, **70**, 1971 (1966).

13) P. Gray and J. C. J. Tynne, *Trans. Faraday Soc.*, **59**, 2275 (1963).

14) S. Hirayama, *Bull. Chem. Soc. Jpn.*, **48**, 2653 (1975).