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(12) The weaker polarization of diethylaniline compared to pyrene arises, at least in part, from more effective exchange which leads to cancellation of geminate and escape polarization.

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Received May 2, 1977

Photolysis of Aryldiazomethanes in Alcoholic Matrices. Temperature and Host Dependences of Phenylcarbene Processes in Alcohols

Sir:

It is generally accepted that carbene generated in alcohols inserts into the O–H bond rather than the C–H bonds of the alcohol to give ether,[1] and hence the detection of the ether in an alcoholic reaction system in which carbene seems to be involved has been strong evidence[2] for the intervention of carbene intermediate. In the present communication we wish to report, however, that the O–H insertion reaction of carbene is highly temperature dependent and the C–H insertion products become dominant at the expense of the O–H insertion product in low temperature alcoholic matrices. Interestingly, we also found that carbene processes in low temperature matrix are highly sensitive to host effects.

Irradiation[3] of phenyldiazomethane **1** in degassed 2-propanol in a quartz tube at 20 °C gave 2-propyl benzyl ether (77%) as a main product. In contrast, irradiation[3] of **1** in frozen 2-propanol matrix at −196 °C resulted in the C–H insertion products (**5α** and **5β**) in high yield (78%) and the yield of the ether was greatly reduced (15%). Toluene **3** and bibenzyl **4** were also formed as minor products in each experimental condition.

Table I. Temperature Dependence of Product Distributions in the Photolysis[a] of **1** in Alcohols

ROH	*T*, °C	Relative product yields,[b] %				
		2	**3**	**4**	**5α**	**5β**
MeOH	0	92.6	3.4	2.8	1.1	
	−72	90.3	2.3	3.5	3.9	
	−110	74.0	4.3	1.0	20.7	
	−196	52.9	6.0	0.8	40.3	
EtOH	0	87.1	5.0	3.3	4.6	Trace
	−72	82.7	4.6	2.0	10.7	Trace
	−110	74.1	5.0	1.9	17.8	1.2
	−196	20.8	9.8	0.4	64.2	4.8
i-PrOH	0	72.4	3.8	6.7	16.6	0.5
	−72	51.6	5.8	13.7	28.1	0.9
	−110	35.7	5.2	2.0	46.3	10.8
	−196	14.7	5.6	1.3	63.8	14.7

[a] All products were identified by gas chromatography (2.5 m × 5 mm 5% OV-17 column) comparisons with authentic samples and by GC–mass spectroscopy techniques. Control experiments demonstrated that product distributions were essentially independent of irradiation time as well as wavelength of light. [b] Total product yields are ~70–80%. Other products (<5%) were benzaldehyde, the azine, and stilbenes derived from **1**.

$$\underset{\mathbf{1}}{PhCH{=}N_2} \xrightarrow[ROH]{h\nu} \underset{\mathbf{2}}{PhCH_2OR} + \underset{\mathbf{3}}{PhCH_3} + \underset{\mathbf{4}}{(PhCH_2)_2}$$

$$+ \underset{\mathbf{5\alpha}}{PhCH_2CR_1R_2(OH)} + \underset{\mathbf{5\beta}}{PhCH_2CH_2CHR_3(OH)}$$

a, R = Me; $R_1 = R_2 = H$
b, R = Et; R_1 = Me; $R_2 = R_3 = H$
c, R = *i*-Pr; $R_1 = R_2 = R_3$ = Me

The product distributions in other alcohols (i.e., methanol and ethanol) were also examined as a function of temperature in more detail and the results shown in Table I demonstrated that the temperature dependence of regioselectivity of carbene insertion reactions is quite general in each system studied. Diphenyldiazomethane (**6**) showed analogous behavior. A parallel series of irradiations[3] with 1-phenyldiazoethane in 2-propanol, however, showed that the C–H insertion products were also formed only in solid run at −196 °C, but as minor components (20%), and a main product was styrene (72%). From Table I it can be seen that the ethers decrease monotonously as the temperature is lowered in solution phase and drastic alterations in product distributions are observed when the reaction phase is changed from liquid to solid. Also striking is the significant increase in the C–H insertion product (**5**) yield in solid-phase experiments as temperature is lowered to −196 °C, although these reaction mixtures (in methanol and 2-propanol) appear solid at −110 °C.[4]

It has been proposed[1a] that the O–H insertion is the characteristic reaction of singlet phenylcarbene. There are ample examples,[1,5] on the other hand, that triplet phenylcarbene abstracts hydrogen in hydrocarbon solution to give toluene and bibenzyl via free benzyl radical. We suggest here that the key intermediate leading to the C–H insertion products in the solid-phase experiments is also triplet phenylcarbene since there have been spectroscopic[6] and chemical[5] evidences for the presence of the ground-state triplet carbene in the low temperature matrix photolysis of **1** at −196 °C.[7,8] The presence of triplet carbene also accounts for the observed selective[9] insertion into the secondary and tertiary C–H bonds compared with the primary. Thus we suggest the abstraction-recombination mechanism rather than the direct insertion to rationalize formation of **5** in the matrix experiments. The observed difference in the chemical behavior of triplet carbenes generated in the liquid and solid phases, then, reflects, at least in part, on the mobility of members of radical pairs. It is possible that the triplet carbene formed in the solid-phase abstracts hydrogen from C–H bonds of alcohols to form radical pairs (e.g., $PhCH_2\cdot + \cdot CH_2OH$) which would recombine with high efficiency to give the C–H "insertion" products in the matrix environment, whereas in the liquid phase the members of the pairs would diffuse apart to yield **2** and **3**. The facts that the yield of bibenzyl drops markedly as the reaction phase is changed from liquid to solid and **5** increases significantly in colder and presumably harder −196 °C matrix[10] are apparently related to the relative diffusibility of radicals.

The reason for the marked reduction in the ether yields at lower temperature is uncertain. A rapid decay of the initially formed singlet carbene to the triplet in rigid matrix seems unlikely since styrene, an intramolecular product of singlet PhCMe,[11] was formed in high yield even in −196 °C matrix and, further, rapid and reversible singlet–triplet equilibrium has been assumed[1,5] to be involved in phenylcarbene reactions. There is a possibility, however, that the O–H insertion reaction could be more significantly assisted by solvation, which might become less important in solid phase, compared with the other radical processes, since ionic species,[1a] i.e., benzyl cation and/or ylide, have been proposed to be involved in the reaction. Thus, matrix might affect the kinetics of the competitive intermolecular singlet and triplet carbene processes occurring within it.[5]

The low temperature photolysis[3] of diphenyldiazomethane in *tert*-butyl alcohol matrix gave a completely different picture than irradiation in other alcoholic matrices. There was no sign of the C–H insertion product being formed; instead, there was formed azine (**8**), ethylene (**9**), and ethane (**10**)

$$\underset{\mathbf{6}}{Ph_2CN_2} \xrightarrow[\substack{t\text{-BuOH} \\ 70\text{-}80\%}]{h\nu} \underset{\mathbf{7}}{Ph_2CHO\text{-}t\text{-}Bu} + \underset{\mathbf{8}}{Ph_2C{=}NN{=}CPh_2}$$

$$+ \underset{\mathbf{9}}{Ph_2C{=}CPh_2} + \underset{\mathbf{10}}{Ph_2CHCHPh_2}$$

T, °C	Relative yields, % 7	8	9	10
27	97.5	2.5	0	0
−72	3.0	56.6	26.9	13.5
−196	0.8	26.6	72.6	0

all of which were only minor products (<5%) in the photolysis in other alcohols.[12] The high yield formation of the olefinic dimer (**9**) in *tert*-butyl alcohol matrix is especially noteworthy since solution-phase photolysis of **6** in inert solvent gave[13] predominantly azine but no trace of ethylene. Presumably, molecules are not matrix isolated but coherent with large dislocation in matrix of *tert*-butyl alcohol which does not form glass but crystallizes upon cooling,[14] and, hence, carbenes or radicals derived from them in the solid would dimerize or attack the neighboring diazo compound inside the molecular aggregates of **6**. Whether the olefinic dimer arises from combination of two triplet carbenes[15] or an action of a carbene on a diazo compound[16] is an interesting question.[17] There is particularly sound precedence for the former in this special condition since triplet phenylcarbenes are known[18] to have enough lifetime to encounter each other at this temperature. Drastic decrease in the azine yield at lower temperature would suggest that the azine could be formed via electrophilic attack by singlet carbene on the terminal nitrogen of the diazo linkage as has been suggested[15] previously, if one assumes that the temperature dependence of intermolecular singlet carbene processes is general.[5]

In conclusion the present results provide a carbene route to the C–H insertion products into alcohols as well as important informations on chemical behaviors of carbenes in rigid matrix and the relationship between the multiplicities and the reaction pathways of carbenes. Further we hope the observed matrix effect would be extended to a unique low temperature synthesis of unstable ethylenes (e.g., tetra-*tert*-butylethylene) via carbenes.

References and Notes

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(2) See, for example, D. R. Morton and N. J. Turro, *Adv. Photochem.*, **9**, 197–309 (1974).

(3) The degassed and sealed quartz tubes containing alcohol solution of diazo compounds were suspended in a transparent quartz Dewar flask filled with coolant and irradiated with a Halos 300-W high-pressure mercury lamp. When the irradiation was performed in solid phase, the mixture was periodically warmed in the dark until the rigid glass or solid melted so that mixing could occur.

(4) The melting points of pure methanol, ethanol, and 2-propanol are −97.8, −114.1, and −88.5 °C, respectively: "The Merck Index", 9th ed, M. Windholz, Ed., Merck and Co., Rahway, N.J., 1976.

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(7) The emission spectrum of **6** in ethanol glass at −196 °C was identical with that of triplet diphenylmethylene.[6]

(8) A possible alternative source[1b] of **5** might involve the intervention of the $Ph\dot{C}N_2$ radical, since photolysis of diazomethane in an Argon matrix at 8 K is reported to yield substantial amounts of the corresponding diazo radical: J. F. Ogilvie, *Photochem. Photobiol.*, **9**, 65 (1969). This may seem less likely since the comparative chemistry in different matrix at different temperature would considerably differ.

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(12) (a) Although photolysis of **1** in *tert*-butyl alcohol matrix at −196 °C also yielded *trans*-stilbene and benzalazine, quantitative studies have not been made since the control experiments showed that some of the azine was formed on thawing the matrix at 25 °C (melting point of *tert*-butyl alcohol). (b) Moss et al.[5] have also observed that *trans*-stilbene became the more important product in the irradiation of **1** in *crystalline* olefinic matrices at −196 °C than in solution. (c) Absence of *cis*-stilbene in low temperature matrix experiments is reminiscent of the almost exclusive formation of trans isomer in the photoisomerization of stilbene at low temperature: D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 3907–3918 (1968).

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(17) **9** was not formed in the photolysis of **8** in methanol: J. Gorse, III, and R. W. Binkley, *J. Org. Chem.*, **37**, 575–578 (1972).

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Received April 29, 1977

Binuclear Rhodium(I) Complexes. Molecular A Frames

Sir:

The design, synthesis and characterization of binuclear complexes in which d^8 metal centers are held in close, fixed proximity, represents an important objective in the systematic study of multicentered reagents and catalysts.[1] The primary approach to this objective involves the use of bridging ligands to achieve the desired structure and orientation of the metal centers.[2-7] The bridging ligands can also serve to introduce additional functionality into the complex which can be utilized in the binding and activation of substrates. The binuclear Rh(I)