March, 1980] *Bull. Chem. Soc. Jpn.*, ***53***, *753—756 (1980)* 753

The Low-temperature Photolysis of Diazo Compounds. The Utility of Tertiary Alcohol in Matrix Studies of Carbene Chemistry

Hideo Tomioka,* Takaaki Miwa, Shinji Suzuki, and Yasuji Izawa

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514

(Received August 20, 1979)

Carbene processes within the *t*-BuOH matrix at −196 °C were investigated in order to show the utility of the matrix as a tool for the study of carbene chemistry. The photolysis of several aryldiazomethane derivatives in the *t*-BuOH matrix gave the olefinic dimer as the main product, probably arising from a combination of two triplet arylcarbenes in the aggregate of molecules. The similar photolysis of other diazo compounds (*e.g.*, N_2CHCOR, $R=OR'$, NEt_2, and Ph) resulted in no detection of the olefinic dimer. This was explained in terms of the structural effect on the ground-state multiplicity of carbene. The photolysis of Ph_2CN_2 in *t*-BuOH containing 5% EtOH at −196 °C gave almost exclusively O–H and C–H insertion products with the solute alcohol at the expense of the O–H insertion product with the host, *i.e.*, Ph_2CHOBu^t, which was the major product in the liquid-phase photolysis. This is ascribable to the co-aggregation of the carbene precursor with the solute alcohol because of the relatively large guest hole provided by the bulky tertiary alcohol matrix. A more general utility of this matrix was shown in the reaction of Ph_2C with Ph_2CO to give oxirane, in which the intervention of carbonyl ylide was demonstrated at low temperatures.

The low-temperature photolysis of organic compounds has attracted much attention from the standpoint of physical as well as organic chemistry because of its usefulness in detecting reaction intermediates which are suspected to be involved in processes carried out at much higher temperatures. It has been noted, however, that some of the photochemical processes at low temperatures are highly sensitive to matrix properties, *e.g.*, polarity. For example, Kolc has reported[1)] that the photolysis of benzocyclobutene-1,2-dione in the EPA matrix at −196 °C underwent bisdecarbonylation to give benzyne, whereas a similar photolysis in the 3-methylpentane matrix gave no sign of benzyne being formed. A similar striking effect of matrix properties on the course of low-temperature photochemical reactions has been suggested[2)] to account for some of the reported discrepancies between the results of different authors.[3,4)]

In the course of our study of the low-temperature photolysis of diazo compounds, we also found[5)] a striking host effect; arylcarbenes generated in the *t*-BuOH matrix at −196 °C give almost exclusively coupling products, *e.g.*, $Ph_2C{=}CPh_2$ and $Ph_2C{=}N{-}N{=}CPh_2$, despite the fact that they give mainly C–H and O–H insertion products with host molecules in other alcoholic matrices (*i.e.*, MeOH—*i*-PrOH). This striking effect of the host on the course of carbene reactions in the matrix is especially noteworthy from the viewpoint of recent growing interest in the behavior of carbene in a rigid matrix.[5–7)] We wish now to report developments in the application of the method in synthetic and mechanistic studies of carbene chemistry and, more generally, in synthetic photochemistry at low temperatures.

Results and Discussion

In order to examine the general utility of the low-temperature synthesis of olefin *via* the dimerization of carbene within crystalline matrices, we have irradiated several diazo compounds in a *t*-BuOH matrix and found that olefinic dimer formation is extremely sensitive to the structure of the carbenes (Table 1). Thus, the formation of the olefinic dimer was observed in the low-temperature photolysis of the aryldiazomethane derivatives (**1a**—**c**), which are known[8)] to yield carbenes with triplet ground states. A similar photolysis of **2** also gave ethylene tetracarboxylate. Markedly to the contrary, however, no trace of olefin was detected in the photolysis of **3a**—**c**, even after all the diazo compounds had been destroyed. The main products detected were Wolff rearrangement products[9)] in the cases of **3a** and **b**, and intramolecular C–H insertion products[9,10)] in the case of **3c**. It is very interesting to note that some of the carbenes derived from **3** have been frequently postulated[11)] as having singlet ground states. One would not expect triplet carbene chemistry to occur in the low-temperature direct-photolytic method if one assumes that the carbene has a singlet ground state separated by somewhat more than 5 kcal mol^{-1} from an upper triplet state, and that the

Table 1. Detection of olefinic dimer in the photolysis of some diazo compounds in *t*-butyl alcohol matrix at −196 °C

R and R′ in $RR'C{=}N_2$	$RR'C{=}CR'R$ yield/%[a)]
1a: $R=R'=Ph$	48.1
1b: $R=Ph$, $R'=H$	17.0
1c: $R=Ph$, $R'=CO_2Me$	25.1
2: $R=R'=CO_2Me$	13.2
3a: $R=H$, $R'=CO_2Me$	n.d.[b,c)]
3b: $R=H$, $R'=CONEt_2$	n.d.[b,d)]
3c: $R=H$, $R'=COPh$	n.d.[b,e)]

a) Based on the $RR'C{=}N_2$ used. b) Not detected. c) The main products were O–H insertion and Wolff rearrangement products. d) The main products were *β*- and *γ*-lactam. See Ref. 10. e) The main product was a Wolff rearrangement product.

$PhCN_2R$	$N_2C(CO_2Me)_2$	N_2CHCOR
1	**2**	**3**
a, $R=H$		**a**, $R=OMe$
b, $R=Ph$		**b**, $R=Ph$
c, $R=CO_2Me$		**c**, $R=NEt_2$

Table 2. Product distributions[a] as a function of temperature. Photolysis of $\mathrm{Ph_2CN_2}$ in t-BuOH containing EtOH

T °C	[EtOH] mol %	$\mathrm{Ph_2CH_2}$	$\mathrm{Ph_2CHOBu}^t$	$\mathrm{Ph_2CHOEt}$	$\mathrm{Ph_2CH\overset{CH_3}{C}HOH}$	$\mathrm{Ph_2CHCH_2CH_2OH}$	Yield[b] %
24	1	0.7	96.7	2.6	0	0	98.2
	5	1.9	88.4	9.7	0	0	87.5
	10	3.0	78.9	18.1	0	0	84.9
−77	1	7.2	29.9	62.9	0	0	29.7
	5	6.3	22.5	71.2	0	0	54.7
	10	6.6	18.6	74.8	0	0	58.6
−196	1	4.0	16.5	45.0	34.5	trace	15.0
	5	2.6	8.2	44.6	44.6	trace	35.9
	10	3.2	5.8	42.0	45.4	3.6	68.5

a) Data are percentages of total products listed above normalized to 100%. The other products were benzophenone, the azine, and tetraphenylethylene. b) Total yields based on $\mathrm{Ph_2CN_2}$ used.

Table 3. Product distribution as a function of temperature. Photolysis of $\mathrm{Ph_2CN_2}$ in EtOH-i-PrOH mixture[a]

T	[EtOH]	$\mathrm{Ph_2CH_2}$	EtOH			i-PrOH			Yield[b]
°C	mol %		O-H	α-CH	β-CH	O-H	α-CH	β-CH	%
24	5	7.0	7.1	0	0	85.9	0	0	≈100
	95	2.3	95.0	0	0	2.7	0	0	≈100
−196	5	4.0	5.6	8.2	0	27.2	45.0	10.0	87.0
	95	3.1	32.2	63.1	0	0.4	1.2	0	89.7

a) See footnote a in Table 2. The O-H, α-CH, and β-CH terms refer to the OH, α-CH, and β-CH insertion products into alcohols respetively. b) Total yield.

intersystem crossing process of the diazo compound does not compete with the dissociation.[12] Furthermore, although it is highly improbable that a reactive carbene can meet with another carbene to form olefin in the liquid phase before it attacks the substrate, evidence has been accumulating which shows that olefin could be formed by the combination of two triplet carbenes in the case where the carbenes are highly stabilized by structural[13] and/or environmental[5] effects. Recently, the flash photolysis of **1b** in benzene at 25 °C has been shown[14] to give tetraphenylethylene as the major product; this substance has not been observed in the steady-state photolysis. The fact that there is no spectroscopic evidence for any significant concentration of another transient except the triplet diphenylmethylene indicates that tetraphenylethylene is formed *via* the dimerization of the triplet carbene. Theoretical consideration also shows[15] that the least-motion formation of ethylene from triplet methylenes is an allowed process. Thus, it is reasonable to assume that the dimerization of the carbenes within a crystalline matrix would be affected by the ground-state multiplicity. The present method may, then, be expected to give us important information on the reactivity and multiplicity of the ground-state carbene,[16] although, as with most negative results, there might be several possible explanations for the failure to observe the olefinic dimer. Quite recently, for example, Roth *et al.* have shown,[17] by EPR study, that **3a** has a ground-state triplet or a triplet state that lies a maximum of 10 cal above the singlet state. Interestingly, its EPR signals follow the Curie law in the temperature range of 10—40 K, but vanish at higher temperatures, presumably by means of the reaction of the triplet with a matrix or by the conversion of the triplet state to a more reactive state capable of undergoing intra- and intermolecular reactions.[9] This is in marked contrast with that phenomenon observed in arylcarbene systems, in which the triplet state has been shown[8] to be fairly stable even at 77 K. Our results for **3a** might indicate, then, that the 77 K matrix is not cool enough to populate the triplet **3a** by quenching the singlet reaction; hence, more extensive temperature experiments would be desirable to form a more widely applicable method.

The photolysis of $\mathrm{Ph_2CN_2}$ in t-BuOH containing a small amount of EtOH (up to 10%) at 25 °C gave $\mathrm{Ph_2CHOBu}^t$ almost exclusively. Surprisingly, however, when photolysis was performed in the solid phase at −77 °C, O–H insertion with the solute alcohol increased dramatically at the expense of the product formed from the host alcohol (Table 2). t-Butyl ether was almost completely suppressed in −196 °C photolysis, with a concomitant formation of C–H and O–H insertion products of the solute alcohol. The coupling products were also greatly reduced with an increase in the concentration of EtOH in the −196 °C photolytic runs. Similar phenomena were also observed with other solute alcohols (*e.g.*, MeOH, i-PrOH) in other tertiary alcohols (*e.g.*, t-$\mathrm{C_5H_{11}OH}$).

A parallel series of irradiations in the EtOH–i-PrOH mixed matrix (Table 3) showed, however, that no selective reaction of carbene with the solute alcohol was observed in this system. This implies that tertiary alcohols provide a special environment for carbene reactions.

Several possible explanations may be offered for the selective reaction of carbene with solute alcohol in a *t*-BuOH matrix. First, it may be that the Ph_2C generated in a matrix at −196 °C migrates through the host matrix and reacts with the more reactive solute alcohol molecules, as has been proposed[18)] in the tunnelling effect in the selective H-abstraction by an H atom in a crystalline alkane mixture at −196 °C. This is less likely, however, since it has been shown[19)] that the cage about the precursor severely restricts the molecular motion of such large molecules. Further, phenyl migration has been shown to be highly unfavorable in a rigid matrix, even in intramolecular 1,2-shifts, while the 1,2-H shift was relatively easy under the same conditions.[20)] Secondly, one may propose that most of the Ph_2C reacts when the matrix is thawed in the dark with the more reactive, and more rapidly melting, solute alcohol. There has been accumulating evidence,[6,7)] however, which demonstrates that most of the reaction of the carbene in the matrix occurs while the reaction mixtures are still frozen (see below). A more probable explanation would be that the co-aggregation of the carbene precursor and the solute alcohol is occurring in the crystalline matrix. Similar striking effects of the host on the course of low-temperature photochemical reactions have been explained[1,2)] in terms of such aggregation. Such co-aggregation might be attributable, at least in part, to the limited solubility of the solute molecules in the *t*-BuOH crystal at low temperatures. However, this is by no means unavoidable, since similar selective reactions between solute molecules has been noted in a 10% EtOH-*t*-$C_5H_{11}OH$ mixed matrix which does not crystallize, but which forms a glass at −196 °C. Also noteworthy is that all crystalline matrices were not unreactive to carbene at −196 °C. C–H insertion products were obtained[6b)] in reasonable yields (40—50%) in the low-temperature photolysis of $PhCH{=}N_2$ in a crystalline matrix, *e.g.*, pentane, butane, and isobutane. The interpretation of these results we favor is that the guest cavity provided by bulky tertiary alcohol has enough space to bind a molecular aggregate inside it.

Finally, an example to show the more general utility of the *t*-BuOH matrix was obtained in the reaction of Ph_2C with Ph_2CO. The irradiation (>300 nm) of Ph_2CN_2 in a 5% Ph_2CO-*t*-BuOH mixture at −196 °C resulted in a rapid and splendid change in the original wine-red color of the reaction mixture to a deep blue, which rapidly faded to a light yellow solution when the matrix was then thawed in the dark. The GC analysis of the resulting mixture showed the presence of oxirane (**5**) as the main product (Table 4). The transient formation of a blue-colored species is very reminescent of the carbonyl ylide (**4**) which has been detected[21)] in the low-temperature photolysis (253 nm) of the oxirane (**5**), although our attempt at the spectroscopic identification of **4** was not successful because of the extremely low transmission of the matrix. This strongly indicates the intervention of carbonyl ylide in the reaction of Ph_2C with the Ph_2CO, probably formed by the initial attack of carbene on carbonyl oxygen. Such an intermediate had been postulated[22)] in the addition of carbene to a carbonyl compound, but it had not been detected before. It should be noted again that neither blue-colored species nor oxirane can be observed in similar photolyses within other alcoholic matrices, which form glass. The main products in this case are those formed from the host alcohol. The spin multiplicity of the attacking carbene poses a very interesting question. The attack by the triplet, followed by electron demotion, could explain the formation of ylide. However, the one-step formation of the electrophilic attack of the singlet could equally well be applied, since it has been shown that the presence of Ph_2CO as a sensitizer does not change the singlet/triplet ratio of carbene at −196 °C. This is ascribable to the rapid and reversible singlet-triplet equillibrium involved[9)] in this carbene system. Note that the experimental[14)] value for $E_S - E_T$ is ≤ 3 kcal/mol. Further studies to show the general usefulness of this matrix are in progress.

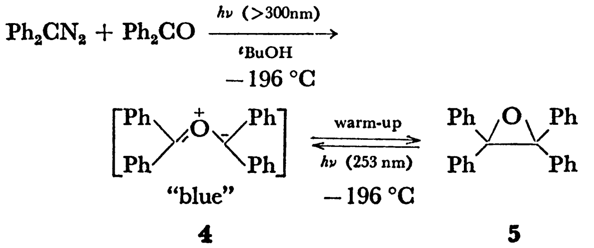

Table 4. Product distributions in the photolysis[a)] of diphenyldiazomethane in the presence of benzophenone in *t*-butyl alcohol matrix at −196 °C

$[Ph_2CO]$ mol %	Yield/%			
	$Ph_2C{=}CPh_2$	$\overset{O}{Ph_2C{-}CPh_2}$	$(Ph_2CH)_2$	$(Ph_2C{=}N)_2$
5	9.8	31.5	2.1	3.6
10	5.5	32.9	2.3	5.3

a) The yields were determined by GC and are based on the Ph_2CN_2 used.

Experimental

The IR spectra were determined on a JASCO IR-G recording spectrometer. The H^1 NMR spectra were determined on a JEOL JNM-MH-100 NMR spectrometer. The GC-MS spectra were obtained on a Shimadzu GC-MS 1000 spectrometer using a column consisting OV-17 on Shimalite (5.0 mm×2.0 m). The GC analyses were performed on a Yanagimoto instrument, Model G-180, with a flame ionization detector. The following columns were used: A, 5.0 mm×2.0 m 10% OV-17 on 60—80 mesh Diasolid L; B, 5.0 mm×2.0 m 5% PEG 20 M on 60—80 mesh Diasolid L.

Materials. All the diazo compounds employed (**1a**,[23)] **1b**,[23)] **1c**,[24)] **2**,[25)] **3a**,[26)] **3b**,[27)] and **3c**,[28)]) were prepared according to the literature procedures and were purified just prior to use. The *trans*-dibenzoylethylene was prepared by means of the Friedel-Crafts reaction[29] with fumaryl chloride. The dimethyl α,β-diphenylmaleate was obtained by the reaction[30] of methyl α-bromophenylacetate with $NaNH_2$. The *N,N,N′,N′*-tetraethylfumaramide was prepared by the treatment of fumaryl chloride with diethylamine. The preparations of the other authentic specimens have been reported elsewhere.[6c] Satisfactory spectroscopic data have been obtained for all authentic compounds. The commercial alcohols were purified prior to use.

Photochemical Reactions and Analyses. All the irradiations were conducted using a Halos 300 W high-pressure mercury lamp with a water-cooled quartz jacket. In the general procedure, 0.06 mmol of Ph_2CN_2 was added to 2 ml of *t*-butyl alcohol with or without a second alcohol or Ph_2CO in a Pyrex tube with a capacity of 5 ml. The tube was suspended in a transparent Pyrex Dewar flask filled with coolant and irradiated until all of the precursor molecules had been destroyed. The coolants were water (24 °C), solid CO_2–EtOH (−77 °C), and liquid nitrogen (−196 °C). For solid-phase irradiations, the mixture was periodically warmed in the dark until the rigid glass or solid melted, so that mixing could occur. Control experiments ruled out the interconversion of the product during the irradiations and also showed that no reaction occurred in the absence of light in the range of temperatures studied.

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

The authors wish to express their thanks to Professor Gary W. Griffin, University of New Orleans, for the supply of tetraphenyloxirane.

References

1) J. Kolc, *Tetrahedron Lett.*, **1972**, 5321.

2) V. Dvorak, J. Kolc, and J. Michl, *Tetrahedron Lett.*, **1972**, 3443.

3) O. L. Chapman and C. L. McIntosh, *J. Am. Chem. Soc.*, **92**, 7001 (1970).

4) A. O. Pederson, S.-O. Lawesson, P. O. Klemmensen, and J. Kolc, *Tetrahedron*, **26**, 1157 (1970).

5) H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977).

6) (a) H. Tomioka, T. Inagaki, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, **1976**, 1023; *J. Chem. Soc., Perkin Trans. 1*, **1979**, 130; (b) H. Tomioka, *J. Am. Chem. Soc.*, **101**, 256 (1979); (c) H. Tomioka, G. W. Griffin, and K. Nishiyama, *ibid.*, **101**, 6009 (1979).

7) (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**, 1315 (1978); (d) R. A. Moss and M. A. Joyce, *ibid.*, **100**, 4475 (1078).

8) A. M. Trozzolo, *Acc. Chem. Res.*, **1**, 329 (1968), and references cited therein.

9) For reviews, see (a) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y. (1971); (b) "Carbenes," ed by R. A. Moss and M. Jones, Jr., Wiley, New York (1974), Vol. 1.

10) (a) R. Rando, *J. Am. Chem. Soc.*, **92**, 6706 (1977); **94**, 1629 (1972); (b) H. Tomioka, H. Kitagawa, and Y. Izawa, *J. Org. Chem.*, **44**, 3072 (1979).

11) (a) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973); (b) I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and P. O. Strausz, *ibid.*, **95**, 133 (1973); (c) M. Tanaka, T. Nagai, and N. Tokura, *J. Org. Chem.*, **37**, 4106 (1972); (d) M. Tanaka, T. Nagai, and N. Tokura, *ibid.*, **38**, 1602 (1973); (e) P. S. Skell, S. J. Valenty, and P. W. Humer, *J. Am. Chem. Soc.*, **95**, 5041 (1973).

12) For a discussion of this point, see P. P. Gasper and G. S. Hammond, "Carbenes," ed by M. Jones, Jr., and R. A. Moss, Wiley, New York (1975), Vol II, p. 327.

13) (a) H. E. Zimmerman and D. H. Paskovich, *J. Am. Chem. Soc.*, **86**, 2149 (1964); (b) P. A. S. Smith and E. M. Bruckman, *J. Org. Chem.*, **39**, 1047 (1974).

14) G. L. Closs and B. E. Rabinow, *J. Am. Chem. Soc.*, **98**, 8190 (1976).

15) R. Hoffman, R. Gleiter, and F. B. Mallory, *J. Am. Chem. Soc.*, **92**, 1460 (1970).

16) See, for example, (a) P. J. Stang and M. G. Mangum, *J. Am. Chem. Soc.*, **97**, 1459 (1975). (b) R. J. Norstrom, H. E. Gunning, and O. P. Strausz, *ibid.*, **98**, 1454 (1976).

17) R. S. Hutton and H. D. Roth, *J. Am. Chem. Soc.*, **100**, 4324 (1978).

18) (a) T. Wakayama, T. Miyazaki, K. Fueki, and Z. Kuri, *J. Phys. Chem.*, **77**, 2365 (1973); (b) T. Miyazaki and T. Hirayama, *ibid.*, **79**, 566 (1975); (c) T. Miyazaki, K. Kinugawa, M. Eguchi, and M. L. Guedes, *Bull. Chem. Soc. Jpn.*, **49**, 2970 (1976).

19) E. Wasserman and W. A. Yager, *J. Phys. Chem.*, **71**, 201 (1967).

20) H. Tomioka, H. Ueda, and Y. Izawa, submitted for publication.

21) (a) T. Do-Mihn, A. M. Trozzolo, and G. W. Griffin, *J. Am. Chem. Soc.*, **92**, 1402 (1970); (b) R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *ibid.*, **92**, 1302 (1970).

22) (a) R. H. Huisgen, *Angew. Chem. Int. Ed. Engl.*, **2**, 565 (1963); (b) Recently, it has been demonstrated that diazoalkanes add to penta- and hexafluoroacetone to give 2,5-dihydro-1,3,4-oxadiazoles, which subsequently decompose to oxidrane *via* carbonyl ylides; N. Shimidzu and P. D. Bartlett, *J. Am. Chem. Soc.*, **100**, 4260 (1978).

23) W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Am. Chem. Soc.*, **95**, 826 (1973).

24) M. Regitz and F. Menz, *Chem. Ber.*, **101**, 2622 (1968).

25) M. Regitz and A. Liedhegener, *Chem. Ber.*, **99**, 3128 (1966).

26) M. Regitz, J. Hocker, and A. Liehegener, *Org. Synth.*, Coll. Vol. V, 179 (1973).

27) R. A. Franich, G. Lowe, and J. Parker, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 2034.

28) M. S. Newman and P. Beal, *J. Am. Chem. Soc.*, **71**, 1506 (1949).

29) R. E. Lutz, *Org. Synth.*, Coll Vol. III. 248 (1955).

30) M. Ramort-Lucas and M. J. Hoch, *Ann. Chim.*, **14**, 395 (1930).