J = 6.41 Hz, 1), 3.637 (q, J = 6.41 Hz, 1), 4.123 (t, J = 6 Hz, 2), 4.94–5.07 (m, 2), 5.60–5.80 (m, 1), 7.299 (s, 5).

Stereochemistry of 32. Iodolactonization To Form 33. The iodolactonization was carried out as described above. **33**: ^{1}H NMR (CDCl$_3$, 400 MHz) δ 0.978 (d, J = 6.71 Hz, 3), 1.339 (d, J = 6.41 Hz, 3), 2.321 (m, 1), 2.601 (ddd, J = 10.37, 1.16, 1.00 Hz, 1), 3.019 (d, J = 0.80 Hz, 1), 3.365 (q, J = 6.41 Hz, 1), 3.451 (dd, J = 7.02, 1.16 Hz, 1), 3.486 (dd, J = 7.02, 1.00 Hz, 1), 7.344 (s, 5); IR (CCl$_4$) 690, 750, 780, 890, 900, 960, 1070, 1140, 1450, 1490, 1785, 2920, 2960 cm^{-1}. When the reaction product in the ratio 93:3:3:1 was converted into the five-membered ring, **33** was accompanied with small amounts of the isomeric lactones. Although this isomer could not be isolated in pure form, its H-2 peak appeared at δ 3.060 (d, J = 9.77 Hz, 1).

Stereochemistry of 32. Hydrogenation to 34. The hydrogenation was carried out as described above, and an authentic sample was prepared from L-alloisoleucine. **34**: ^{1}H NMR (CCl$_4$) δ 0.91 (t, J = 6 Hz, 3), 0.94 (t, J = 6 Hz, 3), 0.96 (d, J = 6 Hz, 3), 1.2–1.7 (m, 9), 3.51 (d, J = 6 Hz, 1), 4.07 (t, J = 6 Hz, 2); IR (CCl$_4$) 780, 840, 950, 1020, 1070, 1170, 1210, 1380, 1460, 1600, 1730, 2860, 2920, 2960, 3360 cm^{-1}.

Supplementary Material Available: Complete listings of positional parameters, bond angles, and bond distances and structures for **25** (Cram-trans-cis) and **25** (anti-Cram-trans-cis) (13 pages). Ordering information is given on any current masthead page.

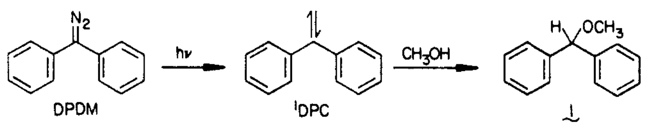
Reinvestigation of the Chemistry of Arylcarbenes in Polycrystalline Alcohols at 77 K. Secondary Photochemistry of Matrix-Isolated Carbenes

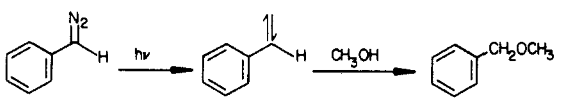
Elisa Leyva, Robert L. Barcus, and Matthew S. Platz*[1]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 23, 1986*

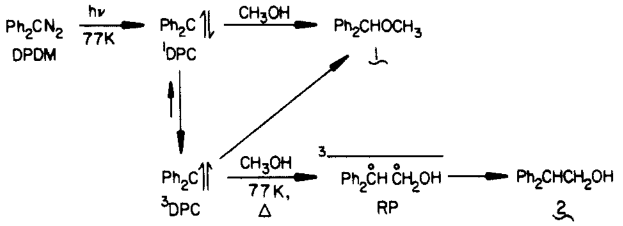
Abstract: Photolysis of diphenyldiazomethane (DPDM) in frozen alcoholic matrices gives ground-state triplet diphenylcarbene (DPC). At 77 K ^{3}DPC reacts primarily with alcohols by OH insertion to give ethers. Photolysis of ^{3}DPC produces an excited carbene ^{3}DPC* which reacts with the matrix by H-atom abstraction to ultimately give alcohol-type products. Secondary photolysis of triplet fluorenylidene at 77 K is not as prevalent as that of ^{3}DPC.

Photolysis of diphenyldiazomethane (DPDM) in simple alcohols gives near quantitative yields of ethers by formal OH insertion. This reaction is generally believed to proceed via the low-lying singlet state of ^{1}DPC.[2] Sensitized photolysis of DPDM in methanol generates the triplet ground state (^{3}DPC) directly and yields ether **1** in quantitative yields.[3] Very similar results are observed on photolysis of phenyldiazomethane.[4] Several research groups have explained this result by postulating a rapid triplet-singlet equilibration.[5-7] It has also been proposed that ^{3}DPC can react directly with methanol to give **1** by a surface crossing mechanism.[8]





Scheme I



A near quantitative yield of **1** is observed over a wide temperature interval in fluid solution. Tomioka discovered, however, that photolysis of aryldiazo compounds in alcohols frozen to just below their melting points leads to a dramatic change in the product distribution.[4] High yields of formal CH insertion products were observed under these conditions in addition to the OH insertion product. Tomioka attributed the change in product distribution to an exaltation in triplet carbene–hydrogen atom abstraction–recombination chemistry. Tomioka's findings and conclusions were consistent with earlier studies of Moss who studied the chemistry of carbenes in olefinic matrices.[9] It was recognized that the equilibrium population of the low-lying singlet state of the carbene is vanishingly small at very low temperature

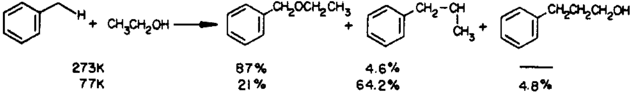


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Table I. Distribution of Products Formed on Photolysis of 0.01 M DPDM in Methanol at 77 K for 30 min as a Function of Light Intensity[a]

light intensity	**1**	**2**	alcohol/ether
1.0[a]	9.5	13.7	1.44
0.525[a]	6.3	7.2	1.14
0.39[a]	5.4	7.0	1.29
0.30[a]	3.7	2.3	0.62
Tomioka[b]	62.	35.0	0.56
Wright[c]	52.8	47.2	0.89
Zayas[d]	59	18	0.31

[a] All yields in this work are absolute; principal irradiating wavelengths were 365, 405, and 435 nm. [b] Reference 4. [c] Reference 10, relative yields. [d] Reference 17, relative yields.

Table II. Distribution of Products Formed on Photolysis of 0.01 M DPDM in Methanol at 77 K as a Function of Photolysis Time[a]

time, min	**1**	**2**	alcohol/ether
60	22	29	1.3
30	15	15	1
15	14	5	0.36
5	9	2	0.22

[a] All yields are absolute; principal irradiating wavelengths are 365, 405, and 435 nm.

Table III. Distribution of Products Formed on Photolysis of 0.01 M DPDM in 2-Propanol at 77 K as a Function of Light Intensity[a]

rel light intensity	**3**	**4**	**5**	alcohol/ether
1.0	3.2	3.2	1.2	1.38
0.52	2.2	1.4	1.2	1.18
0.39	2.1	1.4	0.6	0.95
0.30	2.0	1.8	0.4	1.10

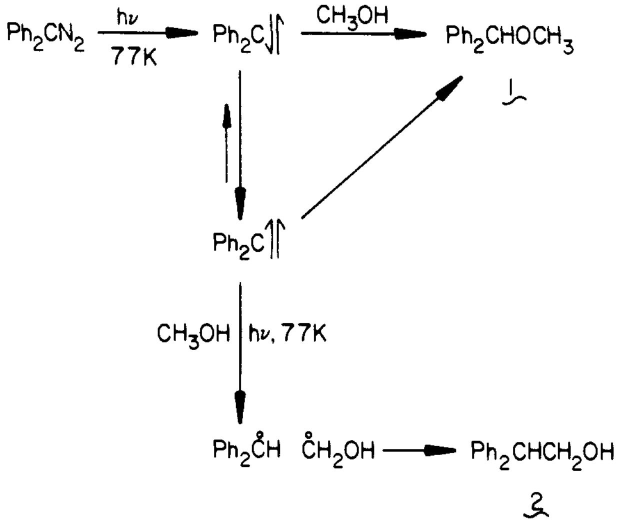
[a] All yields are absolute; the samples were irradiated at 365, 405, and 436 nm.

Table IV. Distribution of Products Formed on Photolysis of 0.01 M DPDM in 2-Propanol as a Function of Photolysis Time[a]

time, min	**3**	**4**	**5**	alcohol/ether
30	2.9	2.3	0.9	1.1
15	2.4	1.1	0.4	0.63
5	2.3	0.4	0.2	0.26
2	1.9	0.0	0.0	0.0
Tomioka[4]	36.2	49.7	8.5	1.61
Platz[10]	24.6	54.5	20.9	3.07

[a] All yields are absolute; the samples were irradiated at 365, 405, and 436 nm.

Scheme II



which would thereby favor chemistry of the ground-state triplet (Scheme I).[10] However the fact that the change in product distribution occurs within a range of a few degrees at the melting point of the alcohol host pointed to a "matrix effect". In this paper we report that with certain carbenes under certain conditions, the matrix functions merely to prolong the lifetime of triplet carbenes which allows for their subsequent photolysis. The photochemistry of the carbene can be different from its thermal chemistry, leading to a change in product distribution.

Experimental Section

Diphenyldiazomethane and 9-diazofluorene were prepared by known methods.[5,11] All of the alcohol and ether products derived from DPC and fluorenylidene (Fl) reactions with simple alcohols have been described previously.[4,6,10,19] The product mixtures were analyzed on a Hewlett-Packard 5840A GC using a 6-ft × $^1/_8$-in. 10% SE-30 column. All peaks were identified by GC/MS (using a Finnegan GC/MS) and by coinjection with authentic samples. Solutions were sealed in Pyrex tubes after three freeze-thaw-pump cycles. The Pyrex tubes (4 mm) had been previously soaked with ammonium hydroxide and oven dried. Samples were exposed to the output of a 1000-W Hg-Xe lamp filtered through $CuSO_4$ and a 350-nm Oriel long-pass filter. This filter combination transmits only the 365-, 405-, and 435-nm Hg lines. After photolysis samples were stored in the dark at 77 K for 40-50 h to ensure complete reaction of the carbene with the matrix before thawing. After thawing to room temperature, the sample tubes were opened and treated with acrylonitrile to consume excess diazo compound. Samples were analyzed 2 h after the addition of acrylonitrile. The light produced by the 1000-W Hg-Xe lamp was attenuated by means of neutral density filter purchased from the Oriel Corporation. Yields were calculated relative to naphthalene as internal standard.

Results

Samples of 0.01 M DPDM in polycrystalline methanol were photolyzed at 77 K. The principal radiations were at 365, 405, and 436 nm. Two types of experiments were conducted. In one approach four identical samples were photolyzed for 30 min with varying light intensities. Light attenuation was achieved by means of neutral density filters. It is clearly evident that increased light intensity increases the ratio of alcohol/ether (or CH/OH insertion). The same trend is apparent on photolysis of identical tubes for varying time periods; the alcohol/ether ratio increases on prolonged irradiation (Table II). At short photolysis time (or at low light levels), ether **1** is the major product; at long photolysis times (or at high light levels) alcohol **2** predominates. These trends are also evident on photolysis of DPDM in 2-propanol at 77 K (Tables III and IV). At very short photolysis times, the OH insertion product (**3**) is the only compound formed. At long photolysis times or at high light intensity, alcohols **4** and **5** predominate. Control experiments demonstrated that **1**–**5** are stable to prolonged photolysis at 77 K.

Photolysis of 9-diazofluorene (DAF) in ethanol at 77 K gave somewhat different results from that observed with DPDM; only small changes in product ratios were observed as a function of photolysis time. It was not possible to reverse the major and minor products in the case of diazofluorene by variation of light intensity or length of light exposure.

Discussion

It is known that ^{1}DPC reacts with methanol at a diffusion-controlled rate.[7] It is equally well appreciated that ^{3}DPC reacts with methanol in solution to give the same product **1** of formal OH insertion. The mechanism of this spin-forbidden reaction is somewhat controversial; Bethell,[5] Closs[6] and Turro[7] have postulated a conventional preequilibrium model in which ^{3}DPC serves as a reservoir of the more reactive ^{1}DPC. Griller et al.[8] have postulated that ^{3}DPC can react directly with methanol to give

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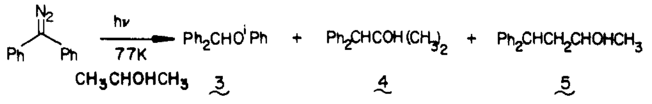
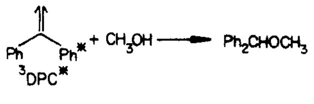
1 via a surface crossing. The present work adds no new insight to this problem. We have incorporated both pathways into Schemes I and II, recognizing that further work is needed to resolve the issue. It is not our purpose to distinguish between ^{1}DPC and ^{3}DPC processes in alcohols at 77 K but to differentiate thermal from photochemical processes of spin-equilibrated carbenes immobilized in frozen polycrystals. It is important to note that ^{3}DPC and ^{3}Fl are relatively long lived at 77 K (minutes to hours). They cannot be considered to be fleeting reactive intermediates generated during the photolysis of DPDM and 9-diazofluorene (DAF) under matrix conditions. Instead they accumulate during the photolysis of the diazo precursor and may inadvertently suffer secondary photolysis. This is a real concern because the absorption spectra of the diazo precursor and triplet carbene are very similar.[6] One cannot find an excitation wavelength which will be absorbed only by DPDM.

The validity of these concerns is amply demonstrated in Tables I-IV. At low light intensity or at short photolysis times in methanol at 77 K, ether **1** is the major product and alcohol **2** is formed in only minor amounts. The product ratios are reversed upon increasing the light intensity or the length of sample photolysis. Upon brief photolysis of DPDM in 2-propanol at 77 K, the only carbene product observed is ether **3**; alcohols **4** and **5** are not found in the reaction mixture. The alcoholic products **4** and **5** are only observed upon extended photolysis of the sample at 77 K at which point they become the dominant products. It is obvious that **4** and **5** are formed by secondary photolysis. Control experiments have shown that **3**, **4**, and **5** are stable under the conditions of the photolysis (λ = 365, 405, 436 nm; 77 K). This leaves ^{3}DPC as the likely photochemical precursor to **4** and **5** as shown in Scheme II. It appears as if matrix-isolated DPC reacts thermally with alcoholic matrices at 77 K to give the same product of OH insertion as in fluid solution. All of the apparent triplet-derived products of formal CH insertion are photochemical reaction products of the carbene. With hindsight it is clear that the previous matrix product studies reported by Tomioka[4] and Platz[10,13] were influenced by secondary photolysis and that alcoholic products were incorrectly assigned as products of thermal reaction of ^{3}DPC.



It is very reasonable to expect secondary matrix photolysis of ^{3}DPC. The similarity in the absorption spectrum of DPDM and ^{3}DPC prevents selective irradiation of the diazo precursor. In fact Trozzolo and Gibbons have reported that extended photolysis of ^{3}DPC in 2-MTHF produces fluorescence due to the benzhydryl radical. Very recently Horn,[14] Scaiano,[15] and Eisenthal[16] have observed photochemistry of DPC in solution phase by laser flash photolysis techniques. Eisenthal reported that ^{3}DPC* reacts with methanol by formal OH insertion in solution at room temperature rather that by H-atom abstraction as we have observed in the matrix.



Somewhat different results were observed on photolysis of 9-diazofluorene (DAF) in ethanol glass at 77 K. It has been reported that solution phase photolysis of DAF in ethanol gives a near quantitative yield of OH insertion product **6** although care must be taken to account for the secondary photolysis of this ether.[19] Matrix photolysis of DAF gives fluorene **7** and ether **6** in addition to alcohol **8**. The product distribution (Tables V and VI) varies only slightly with light intensity and photolysis time.

Table V. Distribution of Products Formed on Photolysis of 0.01 M DAF in Ethanol at 77 K as a Function of Photolysis Time[a]

time, min	6	8	alcohol/ether
75	4.9	11.4	2.3
60	5.1	11.2	2.1
45	4.3	9.2	2.1
30	2.9	4.8	1.7
15	1.9	3.2	1.7

[a] All yields are absolute; the samples were irradiated at 365, 405, and 436 nm.

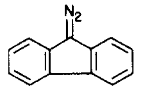
Table VI. Distribution of Products Formed on Photolysis of 0.01 M DAF in Ethanol for 30 min at 77 K as a Function of Light Intensity[a]

light intensity	6	8	alcohol/ether
1.00	4.9	16.7	3.41
0.52	4.6	14.9	3.24
0.39	3.2	8.0	2.50
0.30	2.5	7.7	3.08

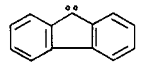
[a] All yields are absolute; the samples were irradiated at 365, 405, and 436 nm.

There is no reversal in the major product of the matrix reaction with varying either the photolysis time or the light intensity. The data are permissive of some secondary photolysis of triplet fluorenylidene (^{3}Fl), but we feel that the substantial amounts of CH insertion product **8** are formed by thermal reaction of Fl with ethanol at 77 K. The apparent lack of fluorenylidene photochemistry is not due to a poor overlap between the output of the lamp and the absorption spectrum of ^{3}Fl. Matrix-isolated ^{3}Fl is absorbing light under these conditions as ^{3}Fl has λ_{max} = 470 nm with a shoulder at 440 nm,[20] and the sample is being exposed to 436-nm mercury arc lamp radiation.

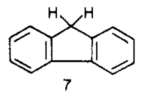
We can think of two reasons why ^{3}DPC shows more photochemistry than ^{3}Fl at 77 K. First, the lifetime of ^{3}DPC in methanol is more than 5 times longer than that of ^{3}Fl in the same matrix at 77 K. This means that ^{3}Fl will not accumulate as much as ^{3}DPC during the course of the photolysis of the diazo precursor. Second, the excited-state energy of ^{3}Fl (λ_{max} = 470 nm)[20] must be much lower than that of ^{3}DPC (λ_{max} = 300 nm);[12-16] thus ^{3}Fl* may be inherently much less reactive than ^{3}DPC*.



DAF



Fl



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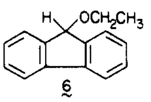
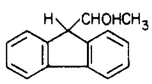


6



8

Conclusions

Photolysis of diphenyldiazomethane in polycrystalline alcohol matrices generates triplet diphenylcarbene. Under these conditions the long-lived carbene is prone to secondary photolysis. Formal CH insertion reaction products formed with diphenylcarbene and the alcohol host are now recognized as photochemical rather than thermal reaction products at 77 K. Triplet fluorenylidene is much less sensitive than triplet diphenylcarbene to secondary photochemistry in alcohol matrices.

Registry No. DPDM, 883-40-9; DPC, 3129-17-7; Fl, 2762-16-5; DAF, 832-80-4; CH_3OH, 67-56-1; $H_3CCH(OH)CH_3$, 67-63-0; H_3CCH_2OH, 64-17-5; H_2, 1333-74-0.

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