J. Am. Chem. Soc. 1984, 106, 4175–4180

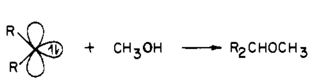
Chemistry and Kinetics of Aryl Carbenes in Methanol at Low Temperatures

Bradford B. Wright and Matthew S. Platz*[1]

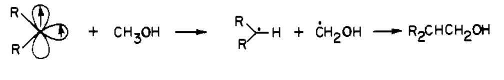
Contribution from the Department of Chemistry, Ohio State University, Columbus, Ohio 43210.
Received November 25, 1983

Abstract: The chemistry and kinetics of six aryl carbenes in polycrystalline methanol are reported. The kinetics were monitored by triplet ESR spectroscopy. Isotope effects were used heavily to probe reaction mechanisms. Several analogues to solution chemistry and kinetics were found. It is concluded that the singlet–triplet energy separation decreases as DBS > DPC > DBT > NC > Fl > DMA.

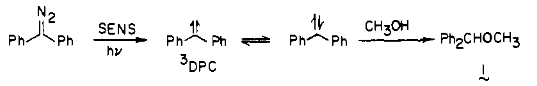
Simple hydrocarbon aryl carbenes are known to have ground-state triplet multiplicities.[2] However, the chemistry of aryl carbenes in methanolic solution is predominantly if not exclusively derived from the low-lying singlet state.[3] The singlet carbene reacts analogously to a cation with methanol to give an ether.



The triplet ground state is expected to display reactivity analogous to that of a radical to ultimately give products derived from radical–radical disproportionation or coupling.

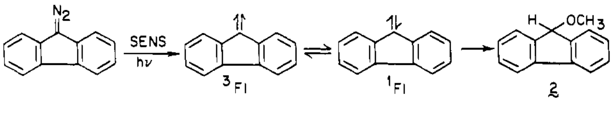


Photolysis of dilute solutions of aryl diazomethanes in methanol gives nearly quantitative yields of ethers. Bethell has demonstrated that sensitized photolysis of diphenyldiazomethane in methanol to presumably generate triplet diphenylcarbene (DPC) directly



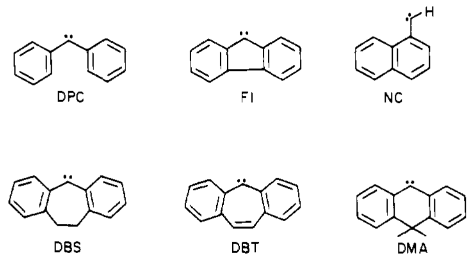
leads only to the singlet, OH insertion product[4] **1**. Bethell interpreted this to mean that singlet ⇄ triplet equilibration in DPC is much faster than chemical reaction of either spin state. Subsequently, Closs came to the same conclusion concerning fast equilibration in the reaction of DPC with olefins.[5]

Schuster and co-workers have examined the photochemistry of 9-diazofluorene in the presence in methanol.[6] Direct and photosensitized irradiation of 9-diazofluorene leads to loss of nitrogen and fluorenylidene (Fl) and ultimately exclusive formation of the product **2**.

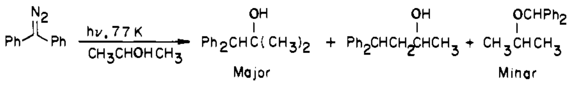


It was assumed that in this case the initially formed ^{3}Fl forms the low-lying singlet ^{1}Fl; the singlet carbene then forms product **2**, more rapidly than ^{3}Fl reacts with methanol.

Chart I



The unusual chemistry of carbenes generated in low-temperature matrices was discovered by Moss.[7] Moss' studies focused on carbenes in polycrystalline olefins. Subsequently, Tomioka studied the chemistry of carbenes in polycrystalline alcohols at low temperature.[8] Under these conditions the major products observed were those of formal CH insertion. Changing the temperature and phase of the reaction apparently enhanced the yield of triplet-derived products.



This effect has at least two origins. First, lowering the temperature will dramatically increase the equilibrium ratio of the triplet to the singlet carbene, and second, there may be a "matrix effect". Some carbenes may be generated distant from the OH bond of the alcohol. Due to the carbene's immobility in the amorphous solid, it will react only with the bonds which are nearby such as a primary CH rather than an OH bond.

Results

We have investigated the chemistry of a series of triplet carbenes in methanol at 77 K. We have also investigated their reaction kinetics under these conditions by ESR. Methanol was employed as the matrix as the solution chemistry and kinetics of aryl carbenes with methanol are well developed. It was also hoped that "matrix effects" would be minimized by using a small host molecule such as methanol. We specifically hoped to minimize the formation of sites in which only one reaction mode (formal CH or OH insertion) was sterically permitted.

---

[1] A. P. Sloan Foundation Fellow and Camille and Henry Dreyfuss Fellow.

[2] Trozzolo, A. M.; Wasserman, E. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2.

[3] (a) Closs, G. L. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. 2. (b) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. (c) Turro, N. J. *Tetrahedron* **1982**, *38*, 809.

[4] Bethell, D.; Stevens, G.; Tickele, P. *Chem. Commun.* **1970**, 792.

[5] Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193.

[6] (a) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958. (b) *Ibid.* **1981**, *103*, 944. (c) *Ibid.* **1981**, *103*, 2423.

[7] (a) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475–4480. (b) Moss, R. A.f Huselton, J. K. *Ibid.* **1978**, *100*, 1314–1315. (c) Moss, R. A.; Joyce, M. A. *Ibid.* **1977**, *99*, 1262–126j. (d) Moss, R. A.; Dolling, U. H. *Ibid.* **1971**, *93*, 954–960.

[8] (a) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *Ibid.* **1979**, *101*, 6009–6012. (b) Tomioka, H.; Inagaki, T.; Nakamura, S.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 130–134. (c) Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128–6129. (d) Tomioka, H. *Ibid.* **1979**, *101*, 256–257. (e) Tomioka, H.; Suzuki, H.; Izawa, Y. *Chem. Lett.* **1980**, 293. (f) Moss, R. A.; Wetter, W. P. *Tetrahedron Lett.* **1981**, *22*, 997. (g) Tomioka, H.; Ueda, H.; Kondo, S.; Izawa, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7817.

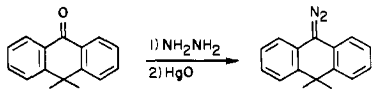
0002-7863/84/1506-4175$01.50/0

Table I. Carbene Rate Data in Isotopically Labeled Methanols[a]

carbene	solvent	temp, K	10^4k_{obsd}, s^{-1}	concn, M
DBS	MeOH	77	9.57 ± 0.16	0.010
	MeOD	77	8.47 ± 0.64	
	MeOH-d_4	77	0.0713 ± 0.0020	
		102	0.241 ± 0.031	
		106	0.238 ± 0.049	
		116	1.46 ± 0.08	
		126.5	3.61 ± 0.03	
		138	3.52 ± 0.63	
DBT	MeOH	77	64.5 ± 1.8	0.10
	MeOD	77	66.6 ± 1.5	
	MeOH-d_4	77	1.14 ± 0.03	0.10
		85.4	106 ± 0.04	
		88	162 ± 0.02	
		90	217 ± 15	
		93	299 ± 22	
Fl	MeOH	77	129 ± 11	0.10
	MeOD	77	125 ± 9	
	MeOH-d_4	77	80.5 ± 5.1	
DPC	MeOH	77	22.9 ± 1.6	0.10
	MeOD	77	22.2 ± 0.1	
	MeOH-d_4	77	6.74 ± 0.21	
		94	36.1 ± 2.4	
		98	81.2 ± 4.4	
		102	130 ± 10	
DMA		77	*d*	0.10

[a] 100-s photolysis time. [b] Immeasurably slow. [c] 40-s photolysis time. [d] Not detected.

All of the diazo compounds used in this study were known at the outset of this work with the exception of **4**. This material was prepared from the parent ketone[9] **3** by conventional procedures.



3 **4**

Photolysis of **4** in methanol, methanol-d_4, CCl_4, or perfluorinated alkanes at 77 K failed to produce a detectable ESR signal at 77 K. Photolysis of neat polycrystalline **4** at 6 K did produce a strong ESR signal. The zero-field parameters $D/hc = 0.4523$ cm^{-1} and $E/hc = 0.02396$ cm^{-1} are very similar to those of DPC which supports the spectral assignment. The spectral intensities followed the Curie law between 6 and 50 K.[10] This proves that DMA is a ground-state triplet carbene. The lack of a triplet signal from **4** in methanol or its deuterated modifications precluded an ESR kinetic study of DMA. Photolysis of 1-naphthyldiazomethane in methanol gave rise to the known ESR signals of syn and anti 1-NC; however, the signals were too weak for kinetic study. All of the other carbenes used gave signals sufficiently intense for ESR kinetic studies.

The ESR kinetics were performed in the following manner. A 0.1 M solution of aryldiazo compound was sealed under vacuum following 3 freeze–pump–thaw cycles. The sample was immersed in liquid nitrogen in a quartz dewar positioned in the cavity of an ESR spectrometer. The sample was irradiated for a brief timed interval (usually 40–100 s) to produce a measurable signal. The decay of this signal was monitored following shuttering of the light source. As is typical in amorphous solids, nonexponential kinetics were observed.[11] Thus only the initial 20% of the decay was analyzed as a pseudo-first-order process to give the data of Table I.

Table II. OH/CH Bond Insertion Product Ratios for Various Aryl Carbenes in Isotopically Labeled Methanolic Matrices at 77 K[a]

carbene	solvent	OH[b,d]	CH[b–d]
DBS	MeOH	31.7 (6)	68.3 (6)
	MeOD	23.7 (12)	76.3 (12)
	MeOH-d_4	60.7 (10)	39.3 (10)
DBT	MeOH	75.8 (25)	24.2 (25)
	MeOD	64.2 (14)	35.8 (14)
	MeOH-d_4	93.3 (9)	6.7 (9)
1-NC	MeOH	82.6 (2)	17.4 (2)
	MeOD	63.0 (8)	37.0 (8)
	MeOH-d_4	100	0
Fl	MeOH	95.8 (5)	4.2 (5)
	MeOH	90.8 (16)	9.2 (16)
	MeOH-d_4	100	0
DPC	MeOH	52.8 (9)	47.2 (9)
	MeOD	43.2 (11)	56.8 (11)
	MeOH-d_4	88.7 (15)	11.3 (15)
DMA	MeOH	100	0
	MeOD	94.5 (11)	5.5 (11)
	MeOH-d_4	100	0

[a] Products reported normalized to 100%; acrylonitrile was added after samples had annealed for 40 h to remove any remaining diazo compound. [b] Products identified by GC/MS and assayed by GC and adjusted for response factors. [c] Trace amounts of double hydrogen abstraction products were also observed in each case. [d] The figures in parentheses are the errors in the last significant figure.

Table III. Isotope Effects at 77 K

		chemical	kinetic
DPC	OH/OD	1.5	1.03
	CH/CD	10.7	3.29
DBS	OH/OD	1.49	1.13
	CH/CD	5.0	118.7
DBT	OH/OD	1.75	0.97
	CH/CD	7.76	58.4
NC	OH/OD	2.78	
	CH/CD	58	
Fl	OH/OD	2.3	1.03
	CH/CD	10.0	1.55
DMA	OH/OD	5.76	
	CH/CD	5.76	

Samples of aryldiazo compounds in methanol were exhaustively photolyzed at 77 K (λ 350 nm). The samples were allowed to sit in the dark at 77 K for 24 h following photolysis to ensure complete carbene consumption prior to thawing the matrix. Unreacted diazo compound was consumed by the addition of acrylonitrile prior to product analysis by gas–liquid chromatography. The product data are given in Table II.

The product OH/OD isotope effects were determined by comparison of the OH/CH insertion ratios obtained in CH_3OH and CH_3OD

$$\frac{k_{OH}}{k_{OD}} = \frac{\text{OH/CH insertion}}{\text{OD/CH insertion}}$$

and assuming that there was no secondary isotope effect. The CH/CD product isotope effects were determined by comparison of the OH/CH insertion ratios obtained in CD_3OD and CH_3OD

$$\frac{k_{CH}}{k_{CD}} = \frac{\text{OD/CD insertion}}{\text{OD/CH insertion}}$$

and assuming no secondary isotope effect.

The kinetic isotope effects were determined by direct comparison of the rates in CH_3OH/CH_3OD and in CH_3OD/CD_3OD. The chemical and kinetic isotope effects are listed in Table III.

The chemical and kinetic isotope effects are in qualitative but not quantitative agreement. The chemical and kinetic OH/OD isotope effects are both quite small while the chemical and kinetic CH/CD isotope effects are moderate. The isotope data obtained from the two approaches are in substantial numerical disagree-

---

(9) Davis, M. A.; Winthrop, S. O.; Thomas, R. A.; Herr, F.; Charest, M.-P.; Gaudry, R. *J. Med. Chem.* **1964**, *7*, 88.

(10) Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.

(11) (a) Platz, M. S.; Senthilnathan, V. P.; Wright, B. B.; McCurdy, C. W., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 6494. (b) Wright, B. B.; Senthilnathan, V. P.; McCurdy, C. W., Jr.; Platz, M. S. *Tetrahedron Lett.* **1982**, *23*, 833. (c) Lin, C.-T.; Gaspar, P. P. *Tetrahedron Lett.* **1980**, *21*, 3553.

Scheme I

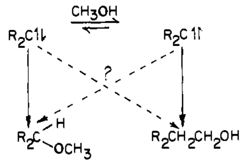


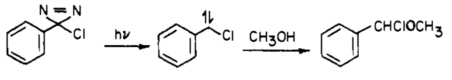
Table IV. Isotope Effects Expected at 77 K from the Value at 300 K Assuming the Arrhenius Equation and No Tunneling

k_H/k_D (300 K)	ΔE, cal/mol	k_H/k_D (77 K)
1.5	243	4.85
2	416	14.8
3	659	72.2
4	832	222
5	966	529
6	1075	1076
7	1168	1961

ment. Photolysis of an aryldiazo compound in an amorphous solid produces carbenes in a multitude of differing local environments or sites. These sites display different absolute reactivities, hence nonexponential kinetic rate laws are observed. The chemical isotope effect data are integrated over all of the sites in the matrix. The kinetic data focuses in on a small number of the total sites. The isotope effect for a given site may vary throughout the matrix. Furthermore, the sites measured in the methanol matrices probably do not even correspond to the same sites in the deuterated matrix. Hence there is no reason to expect a convergence of the chemical and kinetic isotope data. The fact that there is some qualitative agreement between the chemical and kinetic data does give us some hope that the sensitive ESR technique is not focusing on a chemically insignificant process.

It has usually been assumed that the matrix reaction of a singlet carbene with an alcohol gives exclusively formal OH insertion and ethers and that triplet carbenes give formal CH insertion adducts and alcohols (by abstraction–recombination) (Scheme I). It appears to us that this assumption is based mainly on analogy to solution chemistry and that there is no compelling evidence to demand it. There is some circumstantial evidence in favor of this view. The triplet carbene will react with the matrix by hydrogen-atom abstraction in the absence of surface crossings. The OH hydrogen of an alcohol is not easily abstracted due to the large bond dissociation energy (≅103 kcal/mol).[12] Thus this process is expected to be insignificantly slow. We have shown that the rate of the matrix reaction of triplet diphenylcarbene with another poor H-atom donor, benzene, is vanishingly small at 77 K.[11] Second, the very small OH/OD isotope effect argues against an abstraction–recombination mechanism. Our data are consistent with triplet CH abstraction from methanol in matrices but not OH abstraction. The ether products are purely singlet derived.

Do singlet aryl carbenes undergo CH insertion reactions with alcohols in matrices at 77 K? Tomioka has studied the matrix chemistry of phenylchlorocarbene **5** in alcohols.[13] This carbene is known to have a singlet ground state,[14] thus its matrix chemistry should be purely singlet in nature. Tomioka has found that carbene **6** does not undergo CH insertion in alcohols at 77 K; OH insertion is the only reaction path of singlet **6** in the matrix. Thus by analogy the low-lying singlet of aryl carbenes such as DPC and Fl may also react by exclusive OH insertion in matrices. We assume (for simplicity) that the singlet aryl carbenes of this work do not insert methanol, and in CH bond of methanol. The alcohol products are then purely triplet derived.



5 6 7

Table V. Solution Rate Constants for Triplet Carbene with Methanol at Ambient Temperatures

carbene	k, M^{-1} s^{-1}
DBS	1.9×10^{6} [43]
DPC	6.9×10^{7} [44]
NC	3.2×10^{7} [44]
Fl	6.3×10^{8} [6,45]
DMA	4.0×10^{9} [46]

The CH/CD isotope effects are smaller than expected for an abstraction reaction at 77 K. Hadel has measured an isotope effect of 2.6 in cyclohexane and of 6.5 in toluene for hydrogen abstraction by triplet diphenylcarbene at 300 K.[15] This would extrapolate to very large isotope effects at 77 K (Table IV) assuming the Arrhenius equation holds over this interval and that the preexponential factors $A_H = A_D$. Unfortunately, one cannot measure the rate of triplet diphenylcarbene abstracting hydrogen from the CH bond of methanol in solution because in solution the only reaction is OH insertion of singlet DPC. A quantum mechanical tunneling mechanism of matrix atom abstraction also predicts larger isotope effects than those observed.[11,16]

In the interests of simplicity, we will assume that all formal CH insertion adducts are triplet derived and that all formal OH insertion adducts are singlet derived. We recognize that this assumption may require revision in light of new experiments. This assumption allows us to readily dissect the observed product ratios into a percentage of singlet and triplet chemistry. By this reasoning the smallest amount of singlet chemistry occurs in DBS, followed by DPC, DBT, NC, Fl, and DMA. In the latter carbene the matrix chemistry appears to be purely singlet in nature. This trend is consistent with the kinetics of the same triplet carbenes in solutions containing methanol, and in low-temperature polycrystals. Increasing singlet chemistry of the carbene in the matrix is accompanied by increasing absolute reactivity of the carbene toward methanol in solution and in the matrix. The correlation between matrix and solution data encourages us to believe that the matrix chemistry is not dominated by obscure local environmental factors but is influenced by molecular structure.

The reaction of a triplet carbene with methanol to give a singlet ether is formally spin forbidden

$$R_2C\uparrow\uparrow + CH_3OH \rightarrow R_2CHOCH_3$$

The exact mechanism of this process is not known at present and is the subject of speculation. One viewpoint is that triplet–singlet equilibration is rapid and that the small population of singlet present at equilibrium leads to ether formation.

$$R_2C\uparrow\uparrow \underset{K}{\overset{\text{fast}}{\rightleftharpoons}} R_2C\downarrow\uparrow \underset{k_s}{\overset{CH_3OH}{\rightarrow}} R_2CHOCH_3$$

Thus the observed rate constant (k_{obsd}) is

$$k_{obsd} = k_s K$$

As the upper limit of k_s is the diffusion-controlled rate constant, one can calculate the lower limit of the equilibrium constant and the upper limit of the singlet–triplet splitting from k_{obsd}. This approach was first taken by Closs and Rabinow, who obtained an energy gap of 2.4–3 kcal/mol for diphenylcarbene.[17] Eisenthal and Turro have recently confirmed the Closs experiment and obtained an energy gap of 3–5 kcal/mol.[18] The higher number results from the choice of a somewhat larger value of a diffusion-controlled rate favored by Eisenthal and Turro. Triplet fluorenylidene is much more reactive than triplet diphenylcarbene toward methanol.[19] This has been interpreted to mean that the singlet–triplet gap in fluorenylidene is smaller than that of di-

---

(12) Benson, S. W., "Thermochemical Kinetics"; Wiley: New York, 1968.

(13) Tomioka, H.; Suzuki, S.; Izawa, Y. *Chem. Lett.* **1980**, 293.

(14) (a) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R.; Fedorynski, M. *J. Am. Chem. Soc.* **1982**, *104*, 1754; **1980**, *102*, 7576. (b) Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. *Tetrahedron Lett.* **1983**, *24*, 685.

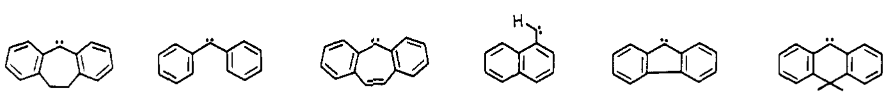
(15) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.*, in press.

(16) Williams, F.; Spague, E. D. *Acc. Chem. Res.* **1982**, *12*, 408.

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

(18) Turro, N. J. *Tetrahedron* **1982**, *38*, 809.

(19) Griller, D.; Mongtomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813.



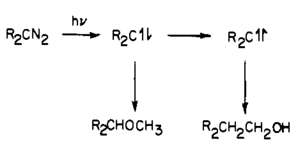
% OH Matrix insertion	31.7	52.8	75.8	82.6	95.8	100
Matrix rate constant 77%	1 :	2.39 :	6.74 :	—	13.4	—
Solution rate constant	1 :	3.6	— :	16.8 :	332 :	2105

Figure 1. Trends in solution and low-temperature solids.

phenylcarbene, approximately 1 kcal/mol. Although this analysis has been criticized by Griller, Nazran, and Scaiano,[20] it is generally accepted that k_{obsd} is inversely related to the size of the singlet–triplet gap. By this reasoning DBS has the largest singlet–triplet gap, followed by DPC, DBT, NC, Fl, and DMA which has the lowest lying singlet (Table V).

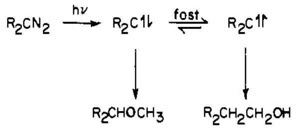
There are at least two distinct kinetic regimes describing the matrix chemistry of carbenes with methanol within the context of Scheme I. In case 1, photolysis of diazo precursor leads to loss of nitrogen and singlet carbene. The singlet partitions between intersystem crossing (ISC) to the triplet and reaction with matrix to give an ether via OH insertion. In this case the ISC process is unidirectional. The ISC lifetimes of singlet DPC and Fl are 110 and 241 ps, respectively, in solution at room temperature.[21,22] One would not expect this process to be highly temperature dependent. Indeed the ISC lifetime of singlet 1-nitrenopyrene increases from only 22 to 34 ns on cooling from room temperature to 77 K.[23] Doettschmann has shown that triplet DPC is formed faster than 100 ns even at 1 K.[24] As it appears unlikely that bimolecular reactions of singlet DPC will proceed on a picosecond timescale at 77 K in a polycrystal we do not feel that the conditions of case 1 are likely. Furthermore, the case 1 scenario cannot explain the correlation between matrix chemistry and kinetics and the solution kinetics.

Case I



A second alternative is described in case 2. In this kinetic regime singlet ⇄ triplet ISC is fast in both directions relative to matrix reactions of the singlet or triplet carbene. This scenario is frequently postulated in the solution phase. In this case the product ratio is

Case 2



$$\frac{\text{yield of ether}}{\text{yield of alcohol}} = \frac{k_S}{k_T}K$$

where k_S and k_T are the respective rate constants of the singlet and triplet carbenes with the matrix and K is the equilibrium constant at 77 K. We expect that K will show perhaps more variation between different carbenes than will k_S or k_T. Case 2 kinetics are consistent with the observed OH and CH isotope effects. The correlation of matrix chemistry and kinetics in methanol with the solution rate constants with methanol is consistent with rapid equilibration at 77 K with K increasing as DBS < DPC < DBT < NC < Fl < DMA.

There are a range of kinetic possibilities intermediate between cases 1 and 2. The finite chemical OH/OD isotope effects at 77 K argue against the following mechanism There is no reason

$$R_2C{\uparrow\uparrow} \overset{\text{slow}}{\rightleftharpoons} R_2C{\uparrow\downarrow} \xrightarrow{\text{fast}} R_2CHOCH_3$$

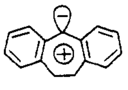
to assume that case 2 holds strictly for all carbenes studied. It is assumed here on the basis of simplicity and the absence of compelling counter evidence.

The observed trend in the magnitude of the singlet–triplet gap with carbene can be readily understood by consideration of bond angles and electronic factors. Singlet methylene has an HCH bond angle of 102°.[25] The energy of this state climbs rapidly as the angle is increased due to the loss of s character in the doubly occupied, in-plane orbital. On the other hand, triplet methylene has a larger HCH angle of 138°,[26] and the energy of this state does not climb as steeply as does the singlet with variation in angle.

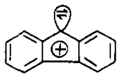
Triplet DPC is known to have a large bond angle of 140–148° by ENDOR[27] due to steric interactions between the two aryl rings. DBS must also have a large angle due to the ethano linkage. Clearly singlets DPC and DBS cannot have the desired small central angle. This raises the singlet energy relative to the triplet resulting in a relatively large energy gap.

Carbene DBT also has a large central angle, but apparently it has a smaller S–T gap than DBS or DPC. This can be rationalized by considering the electronic structure of singlet DBT which benefits from the aromatic character of dibenzotropylium. The 1-naphthylcarbene can assume any central carbene angle desired in both the singlet and triplet forms and consequently has a smaller energy gap than DBS or DPC.

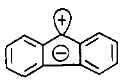
The solution and matrix data indicate that Fl and DMA have extremely low lying singlets. These carbenes necessarily have small central angles which stabilize the singlet relative to the triplet. In the case of fluorenylidene this stabilization is sufficient to overcome unfavorable electronic interactions in the singlet state.



A



B



Structure A contains the antiaromatic cyclopentadienyl cation.

---

[20] Scaiano, J. C., National Meeting of the American Chemical Society, Washington, D.C., September 1983.

[21] Eisenthal, K. B.; Turro, N. J.; Ikawa, N. A.; Butcher, J. A., Jr.; Dupuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. H. *J. Am. Chem. Soc.* **1980**, *102*, 6563.

[22] Brauer, B. E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6814.

[23] Sumitani, M.; Nagakura, S.; Yoshihana, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2995.

[24] Doetschmann, D. C. *J. Phys. Chem.* **1976**, *80*, 2167.

[25] (a) Pople, J. A.; Binkley, J. S.; Seegen, R. *Int. J. Quantum Chem.* **1976**, *104*, 1. (b) Harding, L. B.; Goddard, W. A., III *Chem. Phys. Lett.* **1978**, *55*, 217. (c) Shih, S.-K.; Peyerimhoff, S. D.; Buenker, R. J.; Peric, M. *Chem. Phys. Lett.* **1978**, *55*, 206. (d) Bauschlicher, C. W., Jr.; Shavitt, I. *J. Am. Chem. Soc.* **1978**, *100*, 739. (e) Lucchese, R. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1977**, *99*, 6765. (f) For earlier theoretical treatments of methylene see: Harrison, J. F. *Acc. Chem. Res.* **1974**, *7*, 378. (g) Zittel, P. F.; Ellison, G. B.; O'Neill, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731.

[26] (a) Wasserman, E.; Yager, W. A.; Kuck, V. J. *Chem. Phys. Lett.* **1970**, *7*, 409. (b) Zittel, P. F.; Ellison, G. B.; O'Neill, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731.

[27] Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1969**, *51*, 3327.

Form B has an empty orbital rich in s character reminiscent of phenyl and vinyl cation. Apparently the angle effect dominates the electronic factor in Fl resulting in a smaller gap than DPC. DMA also has a small angle, but singlet DMA lacks the antiaromatic character of ^{1}Fl. Thus DMA appears to have the smallest ST gap encountered in this work.

Experimental Section

ESR measurements were made with a Varian E-112 X-band ESR spectrometer equipped with a modified microwave cavity which admitted light through a series of louvres on one side. Carbene spectra were obtained at 10 mW of microwave power. All samples were prepared in 4-mm Suprasil quartz sample tubes. Samples were sealed under vacuum after 3 freeze–pump–thaw cycles to remove traces of oxygen. Samples were stored in liquid nitrogen between experiments.

Kinetics measurements were obtained by one of two methods.

(a) The field was swept through the signal and the time at which the signal maximum was obtained was noted. The signal intensity was obtained by drawing in the base line in the absence of signal and measuring the vertical height between the base line and the signal maximum.

(b) The field was positioned exactly on the derivative signal maximum in a trial run. With the field sweep width at 0 G a short trace was made to establish the background level. The light was turned on for the allotted time interval and then shuttered. Coincident with shuttering the lamp, the pen sweep was started. Time was determined from a knowledge of the horizontal pen position and the sweep time. Further details can be found elsewhere.[11]

All kinetic measurements were obtained as a minimum of two and typically three trials.

ESR measurements at 77 K were obtained with the sample immersed in a dewar of liquid nitrogen inside the microwave cavity.

ESR measurements at higher temperatures were obtained with use of a Varian nitrogen gas flow system. Temperature was measured by an Omega Trendicator digital thermometer positioned just below the sample tube.

Measurements at lower temperatures were obtained by using a helium gas flow system (the transfer line and glass dewar were supplied by Air Products).

Irradiation of ESR samples was accomplished with use of a Schoeffel 1000-W high-pressure Hg-Xe lamp. A water-cooled aqueous $CuSO_4$ filter (Pyrex, 0.1 M, 2 cm path length) was used to remove ultraviolet and infrared radiation. In filtered light experiments, an additional water-cooled filter containing 1,4-diphenyl-1,3-butadiene in *p*-dioxane (Pyrex, 5 mg/100 mL, 2 cm path length) was used.

Time was measured with use of timer mechanisms from Precision Scientific.

Product studies were performed as follows:

Solutions of diazo compound (0.010 M, 0.300 mL) were placed in 4-mm Pyrex tubing which had been thoroughly washed with ammonium hydroxide and dried prior to use. The samples were sealed under vacuum after 3 freeze–thaw cycles and photolyzed for 90 min at 77 K with two Rayonet RPR-3500 lamps (3500 A).

After photolysis was complete the sample tubes were rapidly transferred to a storage dewar containing liquid nitrogen where they were stored for 40–50 h. The samples were then thawed, and 0.100 mL of acrylonitrile (distilled over CaH_2) was added to remove residual diazo compound. The samples were allowed to stand in the dark 2 h prior to analysis to allow for complete reaction. Solvents used in the samples were purchased from Aldrich Chemical (99+%) and were used without further purification. Deuterated solvents were 99.5+ atom % purity.

GC analysis of product mixtures was accomplished on a Hewlett-Packard 5830A gas chromatograph equipped with a flame ionization detector, and a 12-ft × $^1/_8$-in. column (10% SE-30, 80/100 mesh Chromasorb W). Typical run times were 2.5–3.5 h/injection over a temperature range of 160–230 °C. Product assignments were made on the basis of GC/MS spectra obtained on a Finnegan 4021 mass spectrometer using a 6-ft × $^1/_8$-in. glass column (10% SE-30, 80/100 mesh Supel). The assignments were confirmed by comparison with the mass spectra of authentic samples described below and by coinjection.

In the cases of DBT and DMA methanol adducts relative response factors were not determined. The relative response factors of DBS adducts were used for both systems due to synthetic difficulties in obtaining some of the compounds in these series. The results which are given are the average of three separate sample tubes, each of which was injected twice.

The appropriate benzylic alcohol (15 mM, Aldrich) was placed in 30 mL of dry THF under N_2. Sodium hydride (1.1 equiv) was added with stirring. After addition was complete the mixture was allowed to stir overnight. The mixture was cooled to room temperature and 10 mL of methyl iodide was added causing formation of a tan precipitate. After being stirred for 3 h the mixture was poured cautiously into 200 mL of water. The aqueous layer was extracted with 3 × 100 mL portions of ether. The ether layers were combined, dried, and evaporated to give the product. Typical yields are 65–85% depending on the compound.

1-Methoxy-1,1-diphenylmethane: bp 94–5 °C (0.03 mmHg) (lit.[28] bp 150–154 °C 20 mmHg); NMR (CCl_4, 90 MHz) δ 7.0–7.3 (m, 10 H), 5.0 (s, 1 H), 2.9 (s, 3 H); IR (neat film) 1100 cm^{-1} (C–O stretch); MS 198 (M$^+$, base peak), 183 (loss of methyl), 167 (loss of methoxy); exact mass of $C_{14}H_{14}O$ calcd 198.104459, found 198.104918, difference 0.000459.

9-Methoxyfluorene: mp 43–44 °C, bp 106–108 °C (0.03 mmHg) (lit.[29] mp 43.5 °C); NMR (CCl_4, 90 MHz) δ 7.1–7.8 (m, 8 H), 5.5 (s, 1 H), 2.9 (s, 3 H); IR (neat film) 1070 cm^{-1} (C–O stretch); MS 196 (M$^+$), 195 (loss of H), 181 (loss of methoxy, base peak); exact mass of $C_{14}H_{12}O$ calcd 196.088809, found 196.089388, difference 0.000579.

5-Methoxy-5*H*-dibenzo[*a*,*d*]cycloheptene: bp 124 °C (0.05 mmHg) (lit.[30] oily residue); NMR ($CDCl_3$, 90 MHz) two conformers A and B were observable in the ratio of 5:1, A δ 7.0–7.8 (m, 10 H), 5.2 (s, 1 H), 3.3 (s, 3 H), B δ 7.0–7.8 (m, 10 H), 4.8 (s, 1 H), 3.4 (s, 3 H), (lit.[30] 7.1 (m, 10 H), 3.3 (s, 3 H)); IR (neat film) 1080 cm^{-1} (C–O stretch); MS 222 (M$^+$), 207 (loss of methyl), 191 (loss of methoxy, base peak); exact mass of $C_{16}H_{14}O$ calcd 222.104459, found 222.105070, difference 0.000612.

10,11-Dihydro-5-methoxy-5*H*-dibenzo[*a*,*d*]cycloheptene: bp 122–124 °C (0.01 mmHg) (lit.[31] bp 142–143 °C (0.35 mmHg); NMR (CCl_4, 90 MHz) δ 7.0–7.5 (m, 8 H), 5.2 (s, 1 H), 2.9–3.8 (m, 4 H, AA BB), 3.4 (s, 3 H); IR (neat film) 1080 cm^{-1} (C–O stretch); MS 224 (M$^+$), 192 (loss of methanol, base peak); exact mass of $C_{16}H_{16}O$ calcd 224.1198, found 224.1198, difference 0.0003.

1-(Methoxymethyl)naphthalene: 1-(Chloromethyl)naphthalene (5.0 g, 28.3 mM, Aldrich) was dissolved in 50 mL of dry methanol. Sodium methoxide (45 g) was added, and the mixture was stirred overnight. The reaction mixture was poured into water, extracted into CCl_4, dried, and evaporated to give 4.9 g of a clear colorless liquid which was distilled to give 4.03 g of product as a clear colorless free-flowing liquid: 83% yield; bp 78–80 °C (0.05 mmHg) (lit.[32] bp 133 (10 mmHg); NMR (CCl_4, 90 MHz) 7.9–8.1 (m, 1 H), 7.6–7.8 (m, 2 H), 7.2–7.5 (m, 4 H), 5.8 (s, 2 H), 3.3 (s, 3 H); IR (neat film) 1110 cm^{-1} (C–O stretch); MS 172 (M$^+$, base peak), 141 (loss of methoxy); exact mass of $C_{12}H_{12}O$ calcd 172.088809, found 172.089427, difference 0.000618.

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-carboxylic Acid. 10,11-Dibenzosuberone (5.0 g, 25.7 mM, Aldrich) was dissolved in 50 mL of dry THF. Methyllithium/ether solution (22 mL, 1.5 N, 33.4 mM) was added and the mixture was stirred overnight under N_2. The mixture was then poured onto crushed dry ice and extracted into 200 mL of 5% aqueous KOH solution. This solution was washed with 3 × 100 mL portions of CH_2Cl_2. Acidification of the aqueous layer gave a white solid which was filtered and dried for 2 days in a vacuum oven to give a 4.2 g of the desired acid as a white powder: 69% yield; mp 235–236 C (lit.[33] mp 237–238 °C); NMR (acetone-d_6, 90 MHz) δ 6.9–7.3 (m, 8 H), 4.8 (s, 1 H), 4.3 (s, 1 H, exchanges with D_2O), 3.2–3.6, 2.6–3.0 (m, 4 H, AA BB).

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene-5-methanol. The acid prepared above (2.0 g, 8.4 mM) was dissolved in 50 mL of dry THF. $LiAlH_4$ (0.7 g) was added slowly with stirring under N_2. The mixture was heated to reflux and stirred overnight. The reaction was cooled and ethanol was added to quench excess $LiAlH_4$. The mixture was poured into 5% aqueous KOH (150 mL) and extracted with 3 × 50 mL portions of ether. The ether layers were combined, dried, and evaporated to give 2.3 g of an oily residue. Kugelrohr distillation at 125 °C (0.3 mmHg) gave 1.1 g of product as a white solid: 58% yield; mp 65–66 °C (lit.[34] mp 56–59 °C); NMR ($CDCl_3$, 60 MHz) δ 7.0–7.3 (m, 8 H), 4.1 (t, 2 H, *J* = 7 Hz), 2.5–3.6 (m, 5 H, symmetric), 1.6 (s, 1 H, exchanges); MS 224 (M$^+$), 206 (loss of water), 193 (loss of hydroxymethyl, base peak); exact mass of $C_{16}H_{16}O$ calcd 224.1202, found 224.1230, difference 0.0028.

---

(28) Kirmse, W.; Horner, L.f Hoffmann, H. *Ann.* **1958**, *614*, 19.

(29) Guthrie, R. D.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 587.

(30) Nally, J.; Nazareno, J.; Polensk, J.; Maulding, H. V. *J. Pharm. Sci.* **1975**, *64*, 437.

(31) Seidlova, V.; Protiva, M. *Collect. Czech. Chem. Commun.* **1967**, *32*, 2836; c. *Chem. Abstr.* **1967**, *67*, 90575b.

(32) Kruyt, W.; Veldstra, H. *Landbouwk. Tijdschr.* **1951**, *63*, 398; cf. *Chem. Abstr.* **1967**, *67*, 7287c.

(33) Hoening, D. E.; Muchowski, J. M. *Can. J. Chem.* **1968**, *46*, 3665.

(34) Cioranescu, E.; Bucu, A.; Banciu, M.; Nenitzescu, C. D. *Rev. Roum. Chim.* **1965**, *10*, 141; cf. *Chem. Abstr.* **1965**, *63*, 11459a.

2-Propyl Diphenylmethyl Ether. Sodium (2.2 g, 97 mM) was placed in 55 mL of dry 2-propanol and stirred under dry N_2 until dissolved. Bromodiphenylmethane (10 g, 40.5 mM, Aldrich) was added to the mixture at reflux. The mixture was refluxed overnight and quenched with water. The mixture was poured into 100 mL of water and extracted with 3 × 100 mL portions of ether. The ether layers were combined, dried, and filtered to give a yellow oil from which the desired product was obtained by vacuum distillation: 5.96 g (66% yield; bp 80–82 °C (0.03 mmHg) (lit.[35] bp 155–158 °C (14 mmHg); NMR ($CDCl_3$, 90 MHz) δ 7.1–7.5 (m, 10 H), 5.5 (s, 1 H), 3.7 (septet, 1 H, $J = 6$ Hz), 1.2 (d, 6 H, $J = 6$ Hz); IR (neat film) 1115 (C–O stretch), 1385 cm^{-1} (isopropyl symmetric bend).

Diphenylmethyllithium.[36] Dry ether (100 mL) was placed in a 500-mL flask under N_2. Diphenylmethane (27.0 g, Aldrich) was added followed by slow addition of 87 mL of 1.65 N *n*-butyllithium. The mixture was refluxed with stirring for 20 h resulting in a dark red solution which was transferred to a dry storage bottle. Titration indicated that the concentration of diphenylmethyllithium was 0.46 N.

1,1-Diphenyl-2-methyl-2-propanol. The solution prepared above (38 mL) was placed in a dry 100-mL flask under Ar at −78 °C. Acetone (3.0 mL) was added dropwise resulting in a total discharge of color. After 5 min the mixture had formed a white precipitate making stirring impossible. The mixture was warmed to room temperature and 50 mL of water was added. The ether layer was separated, and the aqueous layer was extracted with 3 × 50 mL portions of ether. The ether layers were combined, dried, and evaporated to give 5.8 g of a thick liquid which was vacuum distilled to give 1.76 g of the desired alcohol as a clear colorless viscous liquid: 44% yield; bp 110–114 °C (0.02 mmHg) (lit.[37] bp 151–152 °C (5.5 mmHg); NMR ($CDCl_3$, 90 MHz) δ 7.0–7.7 (m, 10 H), 3.8 (s, 1 H), 1.8 (br s, 1 H, exchanges with D_2O), 1.2 (s, 6 H); IR (neat film) 3580, 3460 (OH stretch).

4,4-Diphenyl-2-butanol. The diphenylmethyllithium solution prepared above (38 mL) was cooled to −78 °C in a dry 100-mL round-bottomed flask under Ar with stirring. Propylene oxide (3.0 mL, Aldrich) was added, and the mixture was warmed slowly to room temperature with continued stirring for 20 min. After 20 min 3 mL of water was added and stirring was continued for 20 min. The mixture was washed twice with water, dried, and evaporated to give 5.8 g of an opaque white liquid which was vacuum distilled to give the product as a clear colorless liquid: 2.6 g, 65% yield; bp 118–119 °C (0.04 mmHg) (lit.[38] bp 107–109 °C (0.1 mmHg); NMR ($CDCl_3$, 90 MHz) δ 7.1–7.4 (br s, 10 H), 4.2 (t, 1 H, $J = 8$ Hz), 3.6 (sextet, 1 H, $J = 7$ Hz), 2.1–2.3 (m, 2 H), 1.9 (s, 1 H, exchanges with D_2O), 1.1 (d, 3 H, $J = 7$ Hz); IR (neat film) 3560, 3360 (OH stretch).

***5H*-Dibenzo[*a*,*d*]cycloheptene** was obtained as a side product in the preparation of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one hydrazone: mp 128.5 °C (lit.[39] mp 130–131 °C); NMR (CCl_4, 90 MHz) δ 7.2 (s, 8 H), 6.9 (s, 2 H), 3.7 (s, 2 H).

10,11-Dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene, 2,2-diphenylethanol, 9-fluorenemethanol, 2-(1-naphthyl)ethanol, 1-methylnaphthalene, diphenylmethane, and fluorene were obtained from Aldrich Chemical and were used without further purification.

10,10-Dimethylanthrone was prepared by the method of Davis et al.[9] from 2-benzylbenzoic acid (Aldrich) in 50% overall yield: mp 102.5–104 °C (lit.[39] mp 103–104 °C); NMR ($CDCl_3$, 90 MHz) 8.4 (d, 2 H, $J = 8$ Hz), 7.2–7.8 (m, 6 H), 1.7 (s, 6 H); MS 222 (M^+), 207 (loss of methyl, base peak); exact mass of $C_{16}H_{14}O$ calcd 222.1045, found 222.1045, difference 0.0000.

Benzophenone hydrazone and fluorenone hydrazone were purchased from Aldrich Chemical. Other hydrazones were prepared according to the following general procedure:

Ketone (10 g) is placed in 20 mL of anhydrous hydrazine and 10 g of hydrazine sulfate. The stirred mixture is heated to reflux and monitored by TLC (20% ethylacetate/hexane) until complete. The mixture is then poured onto 150 g of crushed ice and extracted with 3 × 100 mL portions of ether. The ether layers are combined, washed with water, dried, and evaporated to give the hydrazone. Purification was achieved by Kugelrohr sublimation. Yields range from 70 to 90%.

***5H*-Dibenzo[*a*,*d*]cyclohepten-5-one hydrazone**: yellow glassy resin; NMR (CCl_4, 90 MHz) δ 7.1–7.7 (m, 8 H), 6.8 (s, 2 H), 5.2–5.8 (br s, 2 H, exchanges with D_2O); IR (neat film) 3380, 3280, 3200 (hydrazone NH_2 stretching modes), 1620 cm^{-1} (C=N stretching).

10,11-Dihydro-*5H*-dibenzo[*a*,*d*]cyclohepten-5-one hydrazone: yellow oil; NMR (CCl_4, 90 MHz) δ 6.9–7.8 (m, 8 H), 5.3–5.7 (br s, 2 H, exchanges with D_2O), 2.7–3.3 (br s, 4 H, does not exchange with D_2O); IR (neat film) 3400, 3280, 3200 (NH_2 stretching modes), 1635 cm^{-1} (C=N stretch).

10,10-Dimethylanthrone hydrazone: yellow oil; NMR (CCl_4, 90 MHz) δ 7.9–8.1 (m, 1 H), 7.0–7.8 (m, 7 H), 5.3–5.7 (br s, 2 H, exchanges with D_2O), 1.5 (s, 6 H); IR (neat film) 3470, 3260, 3200 (hydrazone NH_2 stretching modes), 1615 cm^{-1} (C=N stretch).

Diphenyldiazomethane, diazofluorene, 1-naphthyldiazomethane, 5-diazo-5*H*-dibenzo[*a*,*d*]cycloheptene, and 10,11-dihydro-5-diazo-5*H*-dibenzo[*a*,*d*]cycloheptene were prepared from the corresponding hydrazones by mercuric oxide oxidation as described below:

Hydrazone (1.0 g) was dissolved in 200 mL of ether, and 20 g of yellow mercuric oxide (Baker) was added. Three drops of 40% aqueous KOH were added, and the mixture was stirred until TLC showed complete consumption of the starting hydrazone. The mixture was filtered and evaporated, and the residue was dissolved in petroleum ether (low boiling). The solution was dried and evaporated to give usable diazo compound. Typical yields by this method ranged from 50 to 80%. Samples of higher purity were obtained by either sublimation or recrystallization from methanol.

Diphenyldiazomethane (25): purple solid; mp 30 °C (lit.[40] mp 30 °C); NMR ($CDCl_3$, 90 MHz) 7.2–7.6 (m); IR (neat film) 2030 cm^{-1} (diazo N=N stretch).

Diazofluorene (53): red needles from methanol; mp 99 °C dec (lit.[40] mp 99 °C dec).

9-Diazo-10,10-dimethyl-9,10-dihydroanthracene (74): purple prisms from methanol; NMR (CCl_4, 90 MHz) δ 6.8–7.5 (m, 8 H), 1.7 (s, 6 H); IR (CCl_4) 2060 cm^{-1} (diazo N=N stretch). Carbene (DMA): $|D/hc| = 0.4253$ cm^{-1}, $|E/hc| = 0.02396$ cm^{-1}. A Curie plot of signal intensity vs. $1/T$ showed this to be a ground-state triplet; however, some deviation from linearity was observed indicating the possible presence of a very low lying singlet state.

1-Naphthyldiazomethane:[41] red needles from methanol; mp 41 °C dec.

10,11-Dihydro-5-diazo-*5H*-dibenzo[*a*,*d*]cycloheptene: Purple plates from methanol; mp 78.5 °C dec (lit.[42] mp 71 °C dec); NMR (CCl_4, 90 MHz) δ 6.9–7.3 (m, 8 H), 3.0 (s, 4 H, sharp); IR (CCl_4) 2020 cm^{-1} (diazo N=N stretch).

5-Diazo-*5H*-dibenzo[*a*,*d*]cycloheptene: dark red plates; mp 62.5 °C dec (lit.[42] mp 62 °C dec); NMR (CCl_4, 90 MHz) δ 6.9–7.4 (m, 8 H), 6.4 (s, 2 H); IR (CCl_4) 2025 cm^{-1} (diazo N=N stretch).

Acknowledgment. B.B.W. is indebted to the Phillips Petroleum Company for a graduate fellowship. Support of this work by the National Science Foundation is gratefully acknowledged.

---

(35) Schering, A. G. German Patent 1 213 856, 1966; cf. *Chem. Abstr.* **1966**, *64*, P19632b.

(36) Zieger, H. E.; Angres, I.; Mathisen, D. *J. Am. Chem. Soc.* **1976**, *98*, 2580.

(37) Bornstein, J.; Nunes, F. *J. Org. Chem.* **1965**, *30*, 3324.

(38) Walborsky, H. M.; Pitt, C. G. *J. Am. Chem. Soc.* **1962**, *84*, 4832.

(39) Amiel, Y.; Ginsburg, D. *Tetrahedron* **1957**, *1*, 19.

(40) Baltzly, R.; Mehta, N. B.; Russell, P. B.; Brooks, R. E.; Grivsky, E. M.; Steinberg, A. M. *J. Org. Chem.* **1961**, *26*, 3699.

(41) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5503.

(42) Moritani, I.; Murahashi, S.-I.; Nishino, M.; Kimura, K.; Tsubomura, H. *Tetrahedron Lett.* **1966**, *4*, 373.

(43) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *Chem. Phys. Lett.*, submitted.

(44) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *Chem. Phys. Lett.* **1983**, *97*, 446.

(45) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813.

(46) Hadel, L. M., unpublished research.