J. Am. Chem. Soc. **1984**, *106*, 1867–1868 1867

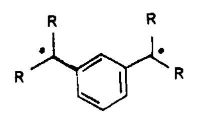
Formation and Intermolecular Capture of *m*-Quinodimethane

Joshua L. Goodman and Jerome A. Berson*

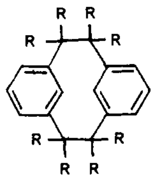
Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received December 8, 1983

The *m*-quinodimethane biradical **1**[1,2] has been characterized by fluorescence[3] and electron paramagnetic resonance (EPR)[4] spectroscopy, and its tetramethyl derivative, **2**, probably is the precursor of the octamethylmetacyclophane **3** formed[5] in the reaction of 6,6-dimethylfulvene with dimethylvinylidene. The present paper reports a new synthetic method for the generation of **1**, which permits the first observations of its intermolecular capture by olefins.



1: R = H
2: R = CH_3



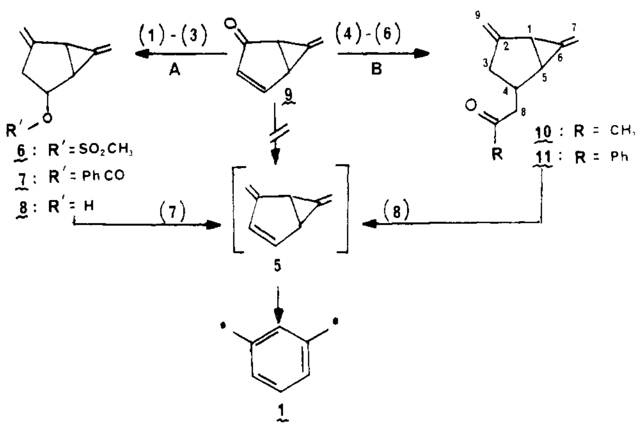
3: R = CH_3
4: R = H

The synthesis is aimed at the unknown hydrocarbon **5**, which is expected[1a,c] to be thermally unstable with respect to **1**. Although all attempts to convert the known ketone **9** directly to **5** by methylenation so far have led to intractable products,[6] two indirect methods are feasible (Scheme I).[7] Both involve protection of the endocyclic double bond of **9** before methylenation. In method A, the endocyclic double bond is restored by, respectively, a base or Norrish type II[8] photoinduced β-elimination of an ester moiety from **6** or **7**. Method B employs the Norrish type II photoreaction to eliminate the enol of acetone or acetophenone, respectively, from the ketones **10** or **11**.

That method A leads to **5** and ultimately to **1** is suggested by the formation (in 8–16% yields) of the known[9] metacyclophane **4** from **6** and **7** in solution reactions. Moreover, irradiations of glassy or polycrystalline samples of **7** (unfiltered Oriel high-pressure Hg arc, 77 K) in EtOH or *i*-PrOH in the cavity of a Varian E-9 EPR spectrometer give rise to a spectrum of a randomly oriented triplet species, which (except for different doublet impurity lines near $g = 2$) is identical with the one obtained by Wright and Platz[4] from α,α′-didiazo-*m*-xylene in hydrogenic matrices and assigned to *m*-quinodimethane.

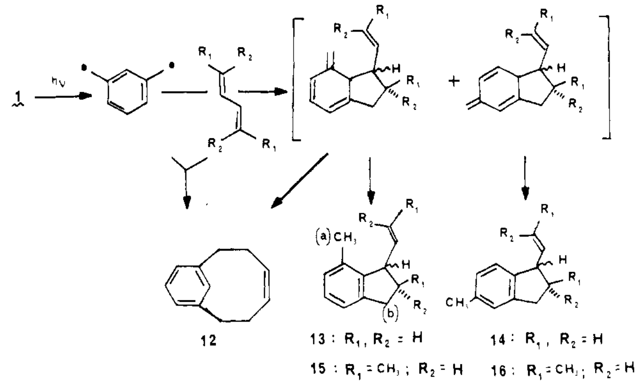
Method B is more suitable for a study of the reactions of **1**. Irradiation of **10** in 4:1 EtOH/MeOH, propyleneglycol, or *i*-PrOH with an unfiltered Hg arc at 77 K gives a triplet EPR spectrum indistinguishable from the previous one. Warming of the *i*-PrOH matrix again gives metacyclophane **4**. In the presence of large excesses of olefins (see below), irradiation (300 nm) of solutions of **10** at 25 °C gives adducts empirically derived from 1 mol each of **1** and olefin. That these reactions initially generate the bicyclic hydrocarbon **5** is suggested (i) by the observation that the known[10] acetophenone enol can be observed by low-temperature NMR spectroscopy of a $CDCl_3$ or acetone-d_6 solution of **11** that had been photolyzed at −78 °C and (ii) by the intramolecular kinetic isotope effect $\phi_H/\phi_D \sim 2.2$ (determined by competition experiments) in the photolysis of **10**-*3,3*-d_2 in the presence of a large excess of 2,3-dimethylbutadiene. Under these conditions the Norrish type II photocleavage very probably occurs in the singlet manifold, since the triplet Norrish type II photocleavage is strongly suppressed by dienes.[11] The isotope effect observed here is similar in magnitude to that in other Norrish type II singlet processes.[12]

Scheme I[a]



[a] Methods: (1) NaOH, aqueous THF; (2) Ph_3PCH_2, THF; (3) esterify; (4) NaOMe, MeOH, $RCOCH_2CO_2R'$ (R = CH_3 or Ph, R′ = CH_3 or Et, respectively); (5) Ph_3PCH_2, THF; (6) NaOH, aqueous THF; (7) from 6, KO-*t*-Bu/Me_2SO; from 7, *hν*; (8) *hν*.

Scheme II



Conjugated dienes (butadiene, 2,3-dimethylbutadiene, 2,4-hexadiene, and isoprene) are efficient traps for the reactive intermediate **1** generated by photolysis of **10**. Yields of adducts with these dienes are 40–60%. Conjugated esters and nitriles also serve as fair to good traps, but butyl vinyl ether and methanol fail to capture **1**.

From butadiene, the major products are the cyclophane **12** and an approximately equal amount of a 13:1 mixture of the ortho and para substituted indans **13** and **14** (Scheme II).[13] Compound **12** is converted to the known[14] [6]metacyclophane by catalytic hydrogenation. The indans **13** and **14** are identified by spectroscopic data and independent syntheses of hydrogenated adducts. Similar products are obtained from 2,3-dimethylbutadiene and

---

(1) For studies of related non-Kekulé systems, see: (a) Rule, M.; Martin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098 and references cited therein. (b) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *Ibid.* **1981**, *103*, 720. (c) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. (d) Matlin, A. R.; Inglin, T. A.; Berson, J. A. *J. Am. Chem. Soc.*, **1982**, *104*, 4954. (e) Seeger, D. E.; Berson, J. A. *Ibid.* **1983**, *105*, 5144, 5146.

(2) For a review of *m*-quinone chemistry, see: Platz, M. S. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; p 195.

(3) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400.

(4) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628.

(5) Gajewski, J. J.; Chang, M. J.; Stang, P. J.; Fisk, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 2096.

(6) Matlin, A. R. Ph.D. Dissertation, Yale University, New Haven, CT, 1982.

(7) New substances were characterized by elemental composition and spectroscopic properties.

(8) (a) Barltrop, J. A.; Coyle, J. D. *J. Chem. Soc. B* **1971**, 251. (b) Pacifici, J. G.; Hyatt, J. A. *Mol. Photochem.* **1971**, *3*, 267. (c) Borkowski, R.; Ausloos, P. *J. Am. Chem. Soc.* **1961**, *83*, 1053. (d) Gano, J. E.; Eizenberg, L. *Ibid.* **1973**, *95*, 974 and references cited therein. (e) For a review, see: Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(9) (a) Vögtle, F.; Neumann, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 73 and references cited therein. (b) Flammang, R.; Figeys, H. P.; Martin, R. H. *Tetrahedron* **1968**, *24*, 1171.

(10) (a) Rosenfeld, S. M.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1973**, *95*, 946. (b) Rosenfeld, S. M. *Tetrahedron Lett.* **1978**, 2655.

(11) Casey, C. P.; Boggs, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 6457.

(12) Coulson, D. R.; Yang, N. C. *J. Am. Chem. Soc.* **1966**, *88*, 4511.

(13) A third product is bicyclo[6.4.0]dodeca-1(12),4,9,11-tetraene obtained by secondary photolysis of **12**.

(14) Hirano, S.; Hara, H.; Fujita, S.; Nozaki, H. *Tetrahedron* **1975**, *31*, 2219.

0002-7863/84/1506-1867$01.50/0

from 2,4-hexadienes. In these cases, we have found that the product composition is virtually unaffected by dilution or O_2. This behavior contrasts with that of trimethylenemethane cycloadditions, where capture of *two* sequentially formed intermediates, a singlet and a triplet, permits the product composition to be manipulated by such perturbations.[15]

The cycloadditions to *cis,cis*- and *trans,trans*-2,4-hexadiene preserve the stereochemistry about the propenyl side chain in the indan product, but the relative configuration (assigned by NMR) of the new pair of asymmetric centers of the indan ring is predominantly trans, regardless of the starting diene. Thus, the indan products from *cis,cis*- and *trans,trans*-2,4-hexadiene, respectively, are 5.4:1 and 6.9:1 trans/cis mixtures. The major components differ only in the stereochemistry of the propenyl side chain, and upon diimide reduction to propyl derivatives, they each give the *same* product.

These results are consistent with capture of only one type of intermediate, which reacts in a two-step cycloaddition mechanism through a long-lived adduct biradical. That the true reactive intermediate has static or time-averaged bilateral symmetry is shown by the equal amounts of deuterium at positions a and b in product **13** from butadiene and **10**-9,9-d_2 (^{2}H NMR). Although direct evidence on the spin state of the intermediate is not available, the observed symmetry properties and cycloaddition stereochemistry are those expected of the triplet state of biradical **1**.

Acknowledgment. We thank the National Science Foundation for partial support of this research (CHE 8011399) and for support of the NSF Northeast Regional NMR Facility at Yale University. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(15) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

Intermolecular Effects on Intersystem Crossing Studied on the Picosecond Time Scale: The Solvent Polarity Effect on the Rate of Singlet to Triplet Intersystem Crossing of Diphenylcarbene

E. V. Sitzmann, J. Langan, and K. B. Eisenthal*

Department of Chemistry, Columbia University
New York, New York 10027

Received December 27, 1983

Intersystem crossing plays a critical role in defining the intramolecular dynamics of diphenylcarbene (DPC) and thereby directly affects its spin state depdent chemistry.[1,2] For example, the chemistry of DPC depends on the rapid thermal equilibration that takes place between its ground triplet state and its low-lying singlet state.[3,4] In fluid solution, at room temperature, the singlet to triplet conversion step has been found[4,5] to proceed at a rate on the order of 10^{10} s^{-1}, while the reverse triplet to singlet conversion step is roughly 3 orders of magnitude slower. Beyond this information little is actually known about the intersystem crossing rates associated with the carbene system. The problem of characterizing the factors, which include both intermolecular and intramolecular effects on the intersystem crossing dynamics of the carbene, remains an outstanding issue. In particular, an extremely important question is the extent to which the environment can affect the intramolecular spin conversion dynamics of the carbene. In this communication we wish to report the observation of a novel solvent polarity effect on the singlet to triplet intersystem crossing rate of DPC. A similar observation on the ground triplet formation rate of another carbene, fluorenyledine, in two solvents has been reported recently.[6]

Table I. Intersystem Crossing Rate of Diphenylcarbene in Various Solvents

solvent[a]	$10^{-9}k_{ST}$, s^{-1}	$E_T(30)$,[b] kcal/mol
isooctane	10.52 ± 0.95	30.9
3-methylpentane	10.52 ± 0.93	30.9
diethyl ether	7.69 ± 0.65	34.6
tetrahydrofuran	5.5 ± 0.45	37.4
butyronitrile	3.57 ± 0.26	43.1
acetonitrile	3.23 ± 0.19	46.0
acetonitrile, 274 K	2.90 ± 0.25	46.9[c]
acetonitrile, 253 K	2.60 ± 0.26	47.9[c]

[a] Temperature at 300 K unless specified otherwise. [b] Reference 7a; $E_T(30)$ values of isooctane and 3-methylpentane were assumed equal to those of *n*-hexane. [c] This work.

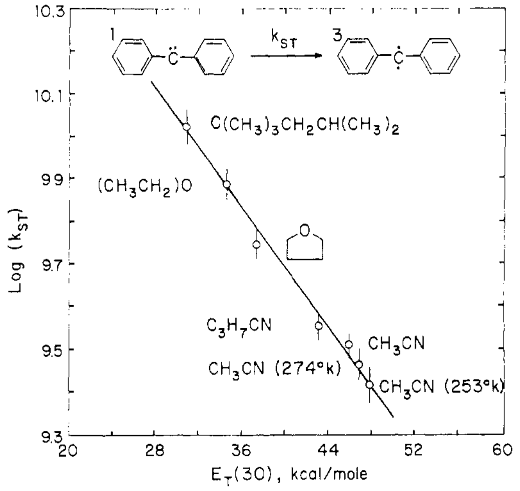


Figure 1. Plot of log (k_{ST}) as a function of the solvent polarity parameter $E_T(30)$ for various solvents.

In the studies reported here the diphenylcarbene is generated by photoexcitation of diphenyldiazomethane in the ultraviolet, which yields ^{1}DPC upon loss of nitrogen from the excited singlet state of the diazo compound. Once formed, ^{1}DPC will undergo energy relaxation via intersystem crossing to produce the ground triplet, ^{3}DPC (eq 1). The rate of ^{3}DPC formation (k_{ST}) was

$$^{1*}Ph_2C{=}N_2 \xrightarrow[-N_2]{} {}^1Ph_2C \xrightarrow{k_{ST}} {}^3Ph_2C \qquad (1)$$

measured by means of a laser-induced fluorescence experiment.[5] The experiment consisted of the irradiation of a vacuum degassed solution of diphenyldiazomethane (8×10^{-4} M) with a picosecond laser pulse at 266 nm using a passively mode-locked Nd/YAG laser (25–30-ps fwhm, < 0.02 mJ). The formation rate of ^{3}DPC was monitored by its laser-induced fluorescence using a weak probe pulse at 266 nm at variable time delays.

The results given in Table I show that the intersystem crossing rate constant depends strongly on the choice of solvent. A key

---

(1) (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (b) Moss, R. A., Jones, M., Jr., Eds. "Carbenes"; Wiley Interscience: New York, 1975; Vol. 1, 2. (c) Durr, H. *Top. Curr. Chem.* **1975**, *55*, 87–135.

(2) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed., Engl.* **1972**, *11*, 92–111.

(3) (a) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190–8198. (b) Bethell, D.; Whittaker, D.; Callister, J. D. *J. Chem. Soc.* **1965**, 2466–2476. (c) Bethell, D.; Stevens, G.; Tickel, P. *Chem. Commun.* **1970**, 792–794. (d) Gasper, P. P.; Whitsel, B. L.; Jones, M., Jr.; Lambert, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6108–6113.

(4) (a) Eisenthal, K. B.; Turro, N. J.; Aikawa, J. A.; Butcher, J. A., Jr.; Dupuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6563–6565, (b) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I.; Hefferon, G.; Langan, J.; Cha, Y. *Ibid.*, submitted for publication.

(5) Dupuy, C.; Korenowski, G. M.; McAuliffe, M.; Hetherington, W.; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *778*, 272–274.

(6) Grasse, P. B.; Brauer, B.-E.; Zupanic, J. J.; Kaufman, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833–6845.

0002-7863/84/1506-1868$01.50/0