by $\geq E_g$ light followed by reduction of the surface-confined reagent, PQ^{2+} to $PQ^{+\cdot}$, that then in turn reduces A^+, regenerating surface-confined PQ^{2+}. Kinetics and energetics for A^+ reduction therefore depend on the reducing power and reducing rate of $PQ^{+\cdot}$. Proof for the mediated reduction of solution species comes from cyclic voltammetry experiments in the presence of A^+. Representative data are given in Figure 2 for $A^+ = [Fe(\eta^5\text{-}C_5H_5)_2]^+$. The key is that the positive sweep reveals the amount of surface $PQ^{+\cdot}$; in the absence of A^+, the anodic wave corresponding to $PQ^{+\cdot} \rightarrow PQ^{2+}$ is equal in area to the photocathodic wave corresponding to $PQ^{2+} \rightarrow PQ^{+\cdot}$. But when solutions of A^+ are used, the photocathodic current increases, since it is no longer only limited by the surface concentration of the PQ^{2+}. Upon turning off the light at the negative limit and scanning in the positive direction at 100 mV/s, we find only a small $PQ^{+\cdot} \rightarrow PQ^{2+}$ oxidation wave. An even smaller wave is observed upon stirring the solution to bring more A^+ to the surface. Apparently, chemistry according to eq 2 is sufficiently fast that A^+ regenerates PQ^{2+}. Fast $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ reduction by $PQ^{+\cdot}$ is expected, since $E^\circ[PQ^{2+}/PQ^{+\cdot}] = -0.45$[10] and $E^\circ([Fe(\eta^5\text{-}C_5H_5)_2]^{+/0}) = +0.45$ V vs. SCE.[17] Additional data suggest that this mediated photoreduction of the $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ is the only mechanism for its reduction, i.e., there are no pinholes in the coverage precluding direct reduction of the $[Fe(\eta^5\text{-}C_5H_5)_2]^+$ as at the naked surface.[4b]

Functionalized p-type Si is also durable in $H_2O/NaClO_4$ electrolyte solution for the first one-electron reduction. Potentials sufficiently negative to yield the second reduction generally result in irreversible chemical change to yield a new surface species that has not yet been identified. Mediated reduction of $Ru(NH_3)_6{}^{3+}$ in aqueous solution has been demonstrated with p-type Si derivatized with I. Again, $Ru(NH_3)_6{}^{3+}$ should be rapidly reducible with $PQ^{+\cdot}$, since the formal potentials indicate an ~0.5-V driving force for reaction.[11,18] Experiments directed toward mediating H_2O reduction are in progress.

Acknowledgments. We thank the Department of Energy, Office of Basic Energy Sciences, and the M.I.T. Laboratory for Computer Science I.B.M. Fund for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980.

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[17] Janz, G. J.; Tomkins, R. P. T. "Nonaqueous Electrolytes Handbook", Vol. II, Academic Press: New York, 1972.

[18] Koval, C. A.; Anson, F. C. *Anal. Chem.* **1978**, *50*, 223.

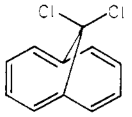
Dana C. Bookbinder, Mark S. Wrighton*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received March 12, 1980

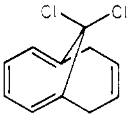
Dimerization of Bridgehead Olefins Formed from Tricyclic Cyclopropylidenes[1]

Sir:

In two recent papers, Levin[2,3] has reported the formation of dimer(s) from the treatment of 1 and 2 with MeLi. We have reported[4] that 3 affords only one dimer, which evidently is of the [2 + 2] type (presence of four olefinic carbons in the ^{13}C NMR). However, no detailed structural information regarding any of these dimers has been published. We now wish to report on some of the dimers formed from the related system, **4**.[5]



1



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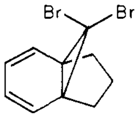

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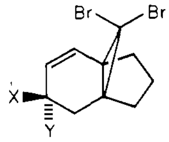
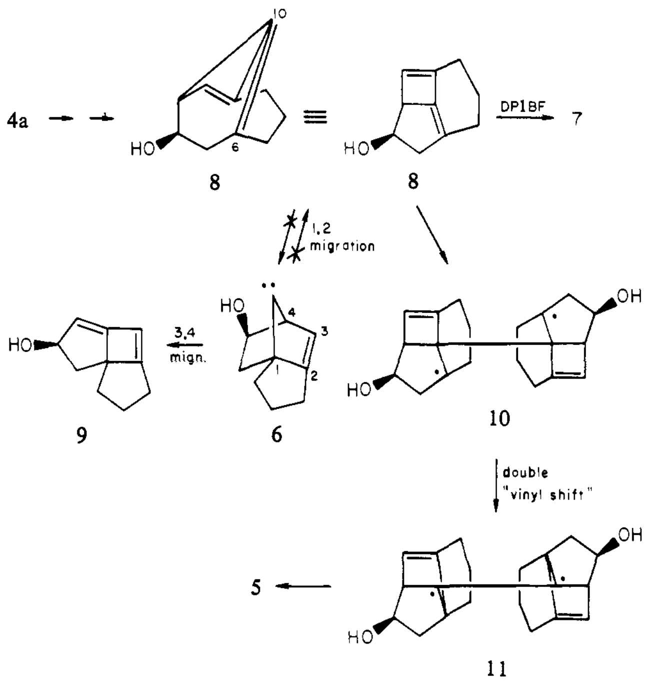


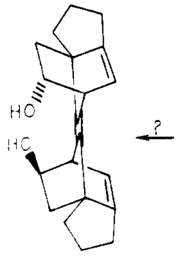
4

a, X = OH; Y = H
b, X = OMe; Y = H
c, X = H; Y = OH
d, X = H; Y = OMe

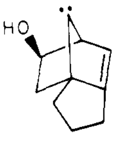
Scheme I



Treatment of **4a**[6] with MeLi at either −78 °C or room temperature affords, in addition to rearranged product,[5] only one dimer (^1H NMR, GLC analysis, 19% isolated). While the ^1H NMR spectrum is unexceptional, the ^{13}C NMR spectrum shows three *olefinic carbons*, rather than the expected two. Single-crystal X-ray analysis (see Table I) of the derived bis(*p*-bromobenzoate) (Figure 1) revealed the structure of the dimer as **5**. Stereochemically, **5** is a chiral dimer resulting from the dimerization of two *R* (or *S*) monomers to give an *E* olefin.[7] At first glance, it might appear that **5** comes from the dimerization of **6**. If this is true, the chemistry of **4a** would be quite different than previously supposed.[4,5] It thus became critical to be sure of the structures of the trapping products formed from **4a** in the presence of diphenylisobenzofuran (DPIBF). In fact, the only previous really solid structural work in this whole area is the X-ray structural analysis of but one of the two DPIBF adducts obtained from **1**.[2] As occurred previously,[4,5] reaction of **4a** with MeLi in the presence of DPIBF led to two adducts (24 and 21%). The single-crystal X-ray analysis of the derived *p*-bromobenzoate (Figures 2 and



5



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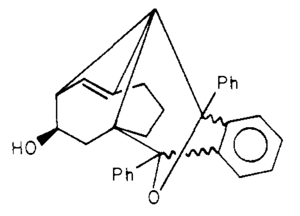

7

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[1] We gratefully acknowledge partial support of this work by National Science Foundation Grant CHE-7618701.

[2] Carlton, J. B.; Levin, R. H.; Clardy, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 6068.

[3] Carlton, J. B.; Levin, R. H. *Tetrahedron Lett.* **1976**, 3761.

[4] Warner, P.; Chang, S.-C. *Tetrahedron Lett.* **1979**, 4141.

[5] Warner, P.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 3981.

[6] Warner, P.; Boulanger, W.; Schleis, T.; Lu, S.; Le, Z.; Chang, S.-C. *J. Org. Chem.* **1978**, *43*, 4388.

[7] The tetrasubstituted double bond of **5** is actually twisted some 8.3 ± 2.4° out of planarity.

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Table I. X-ray Data for *p*-Bromobenzoates of 5, 7a, and 7b

	$(C_{17}H_{14}O_2Br)_2$	$C_{37}H_{29}O_3Br$	$C_{37}H_{29}O_3Br$
structural picture	Figure 1	Figure 2	Figure 3
space group	*P*1	$P2_1/c$	$P2_1/a$
a, Å	12.562 (3)	14.651 (2)	20.747 (4)
b, Å	14.596 (4)	15.885 (2)	7.775 (2)
c, Å	8.308 (2)	12.186 (2)	18.965 (3)
α, deg	102.60 (3)		
β, deg	95.15 (3)	90.83 (2)	113.05 (1)
γ, deg	82.49 (3)		
radiation used	Mo, $\lambda = 0.71002$ Å[a]	Mo, $\lambda = 0.71002$ Å[a]	Cu, $\lambda = 1.5418$ Å[b]
no. of obsd reflections ($F > 3\sigma_f$)	2944	3179	2343
solution method	heavy-atom	heavy-atom	heavy-atom
refinement method	block-matrix least-squares	block-matrix least-squares	block-matrix least-squares
final *R*	0.063	0.066	0.070
R_w	0.075	0.077	0.060

[a] Graphite-monochromated Mo radiation. [b] Ni-filtered Cu radiation.

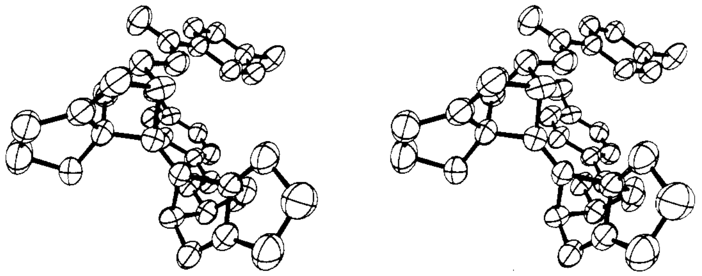

Figure 1. Stereoscopic computer-generated drawing of the bis(*p*-bromobenzoate) derived from dimer **5**.

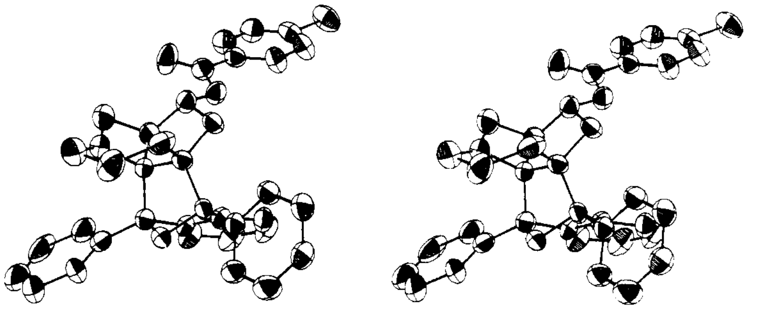

Figure 2. Stereoscopic computer-generated drawing of the *p*-bromobenzoate derived from DPIBF adduct **7a**.

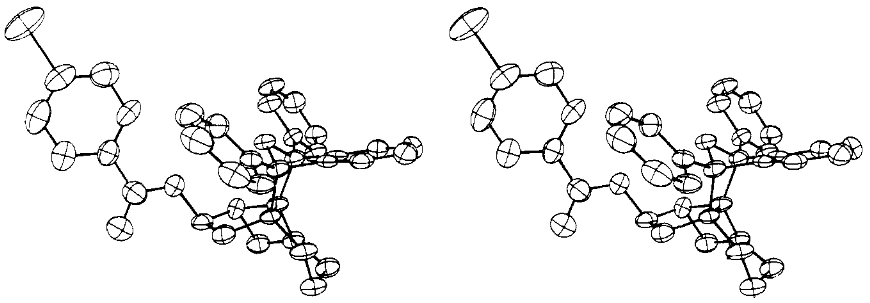

Figure 3. Stereoscopic computer-generated drawing of the *p*-bromobenzoate derived from DPIBF adduct **7b**.

3) of each (Table I) showed both have structure **7**, differing only in whether the bridging oxygen points toward the hydroxyl group or away from it.

These results firmly support previous[2-5] conclusions and exclude trapping of **6**. Scheme I summarizes our explanation for the chemistry observed. Thus, **4a** somehow gives rise to **8**, the 6,10 double bond of which is highly strained. Trapping of **8** by DPIBF affords **7**. In the absence of DPIBF, dimerization is initiated by C_{10}–C_{10}' bonding to give a diradical. In this instance (see below), rotation and closure to give cyclobutane are impossible, and (precedented[8]) vinyl migration occurs to give a new ditertiary diradical. However, after double-vinyl migration, the radical centers find themselves adjacent, whereby a new double bond forms. The alternate postulate that **8** rearranges to **6**, which then dimerizes, is felt to be untenable. The reasons are that such a rearrangement is quite endothermic (the dimerization occurs equally well at −78 °C or at room temperature) and, were **6** to be formed, rapid rearrangement to the relatively less strained **9** would be expected,[9] whereas re-formation of **8** would not be. Since some dimerization does occur in the presence of DPIBF, we feel **9** would have been trapped had it been formed.

There remains to be explained why **4a** affords only one dimer (**5**). We believe the reason is that two molecules of monomer (**8**)

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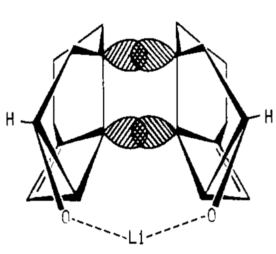
(8) Boyle, P. H.; Cocker, W.; Crayson, D. H.; Shannon, P. V. R. *J. Chem. Soc. C* **1971**, 1073.

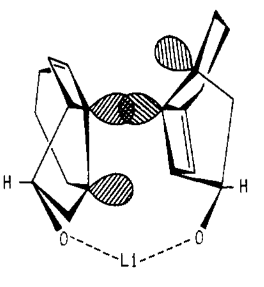
(9) Moss, R. A.; Ho, C.-T. *Tetrahedron Lett.* **1976**, 3397.

are held together by lithium bridging prior to the onset of dimerization. If this is so, an *R–S* pair can only dimerize in a strongly disallowed [2 + 2] fashion (see **13**), in which the transition state is crowded, bringing the oxygens close to or within van der Waals radii of each other. Contrariwise, an *R–R* (*S–S*) pair can give only a trans-1,4 biradical (see **14**). Due to the bridging, **14** cannot rotate around and close to a cyclobutane dimer. In support of the above explanation, we have found that **4c** (in which the OH is endo) gives four dimers; ^{13}C NMR spectra indicate that two of these are of the cyclobutane type, and two of the norbornenyl type.[10] Thus, in the absence of Li bridging, dimerization does not favor the *R–R* (*S–S*) combination over the *R–S* pairing. We feel these results again[11] indicate the strong preference for trans-1,4 biradical formation in [2 + 2] dimerizations.



13

(R,S Dimerization Mode; only front lobes of p orbitals shown)



14

(R,R Dimerization Mode; only front lobes of p orbitals shown)

Supplementary Material Available: A listing of final positional and thermal parameters, bond distances, bond angles, and structure factors for **5-(OPPB)$_2$**, **7a-OPBB**, and **7b-OPBB** (Tables II–XI; 57 pages). Ordering information is given on any current masthead page.

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(10) Details to be published after X-ray analyses are complete.

(11) Warner, P.; LaRose, R.; Lee, C.; Clardy, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 5507.

Philip Warner,* Suae-Chen Chang
Douglas R. Powell, Robert A. Jacobson*
Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received December 6, 1979

Organic Photochemistry: The Laser vs. the Lamp. The Behavior of Diphenylcarbene Generated at High Light Intensities

Sir:

The use of UV–vis lasers to initiate photochemical processes has established itself as an important technique for investigating electronically excited states in solution. Although numerous reports of intensity dependences of dynamic processes and spectroscopic processes[1] have been noted, reports of "novel" or "specific" solution photochemistry induced by UV–vis lasers are almost nonexistent.[2] We report here the observation that certain photoproducts are produced by a pulsed-excimer laser-induced excitation of diphenyldiazomethane (DDM) and tetraphenyloxirane (TPO) which are not detected in the conventional "lamp" induced excitation of the same substrates in fluid solution. We also describe the detection of products by an analytical method that simultaneously employs the laser pulse for photolysis and interrogation by exciting the luminescence of products generated during the early portion of the pulse.

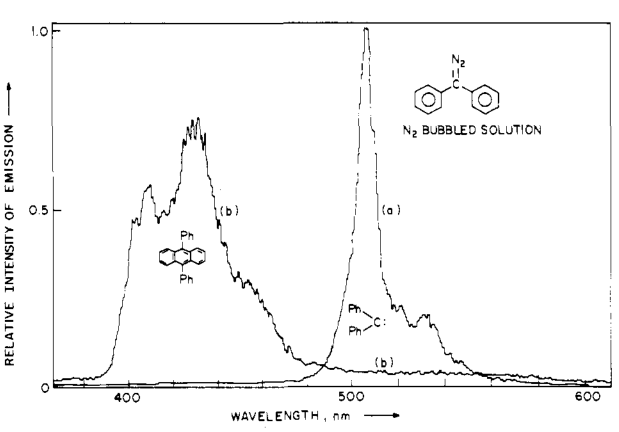

Figure 1. Emission spectra obtained by OMA analysis for DDM (1.0 × 10^{-4} M) of N$_2$-bubbled isooctane solution: (a) Emission spectrum for first pulse and (b) after 13-pulse irradiation. The species responsible for the various emissions is indicated by the structure drawn beneath the bands of interest. Pulse intensity is 180 mJ/pulse at 249 nm.

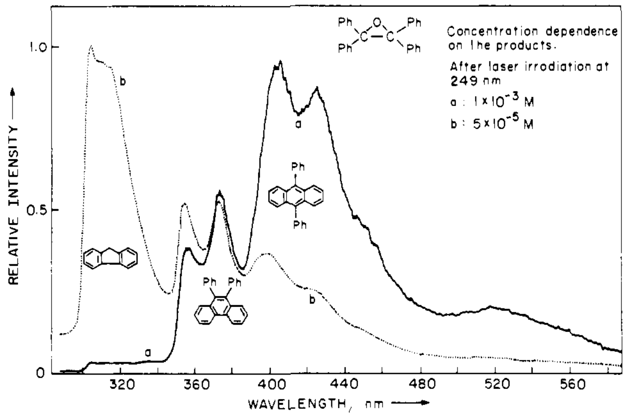

Figure 2. Concentration dependence of products. Emission spectra were obtained by using a standard spectrophotometer for TPO (1.0 × 10^{-4} M) solution after 30-pulse irradiation of a N$_2$-bubbled sample (excitation wavelength 255 nm). See also ref 8.

Excitation of a nitrogen-purged isooctane solution of DDM (or TPO) with a single pulse (~180 mJ/15 ns) of the 249-nm line (KrF) from a Lamda Physik excimer laser (Model EMG500) and monitoring of the emission of the sample with a PAR optical multichannel analyzer (OMA) result in the spectrum shown in Figure 1. The emission maximizing at 507 nm is assigned to the fluorescence of diphenylcarbene (DPC), on the basis of comparison with a standard spectrum[3] taken at 77 K. After ten or more shots, the emission of DPC is no longer detectable and is replaced by several emissions of stable products. Conventional fluorescence analysis (Figure 2) allowed identification of these emissions as arising from 9,10-diphenylanthracene (DPA), 9,10-diphenylphenanthrene (DPP), and fluorene (FL). The occurrence of these products was also confirmed by TLC and vapor chromatographic analyses. In addition to the above products, tetraphenylethylene (TPE) was formed as a major product of laser photolysis. Conventional lamp excitation of DDM in fluid solution at ambient temperature results in the formation of benzophenone azine as a major product; DPA, DPP, and FL are not produced in amounts detectable by fluorescence or vapor chromatographic analyses.[4]

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(1) For a general discussion of dynamic and spectroscopic processes induced by lasers, see: Moore, C. B. "Chemical and Biochemical Applications of Lasers", Academic Press: New York, 1974.

(2) (a) Gardner, E. J.; Squire, R. H.; Elder, R. C.; Wilson, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 1693. (b) Wilson, R. M.; Gardner, E. J.; Elder, R. C.; Squire, R. H.; Florian, L. R. *Ibid.* **1974**, *96*, 2955.

(3) (a) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239. (b) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

(4) (a) Reimlinger, H. *Chem. Ber.* **1964**, *97*, 339. (b) Dürr, H. *Top. Curr. Chem.* **1975**, *55*, 87. (c) Tomioka, H.; Griffin, G. W.; Nishiyama, K. *J. Am. Chem. Soc.* **1979**, *101*, 6009.

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