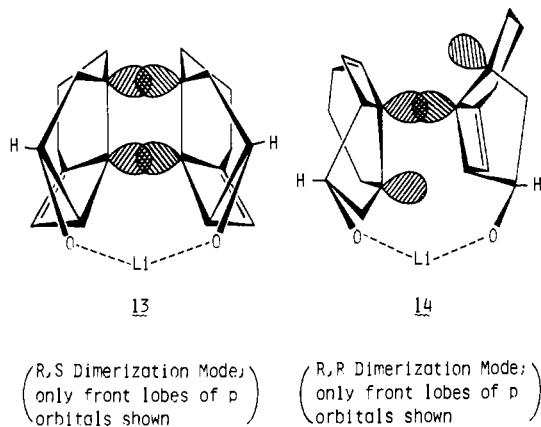


are held together by lithium bridging prior to the onset of dimerization. If this is so, an *R-S* pair can only dimerize in a strongly disallowed [2 + 2] fashion (see 13), in which the transition



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; ¹³C 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 again¹¹ indicate the strong preference for trans-1,4 biradical formation in [2 + 2] dimerizations.

Supplementary Material Available: A listing of final positional and thermal parameters, bond distances, bond angles, and structure factors for 5-(OPP)₂, 7a-OPBB, and 7b-OPBB (Tables II-XI; 57 pages). Ordering information is given on any current masthead page.

(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.

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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 processes¹ 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 tetraphenyl-oxirane (TPO) which are not detected in the conventional "lamp"

(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.

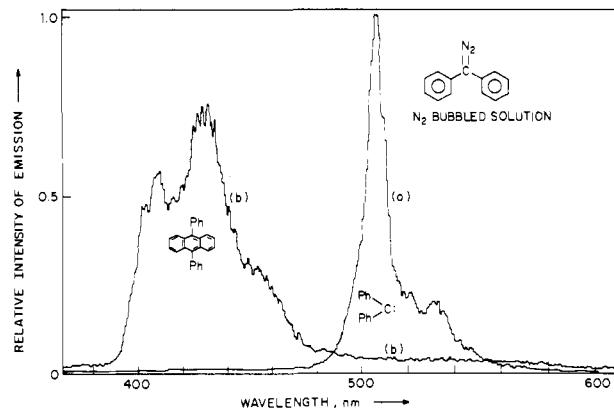


Figure 1. Emission spectra obtained by OMA analysis for DDM (1.0×10^{-4} M) of N_2 -bubbled isooctane solution: (a) Emission spectrum for first pulse and (b) after 13-pulse irradiation. The species responsible for the various emissions is indicated by the structure drawn beneath the bands of interest. Pulse intensity is 180 mJ/pulse at 249 nm.

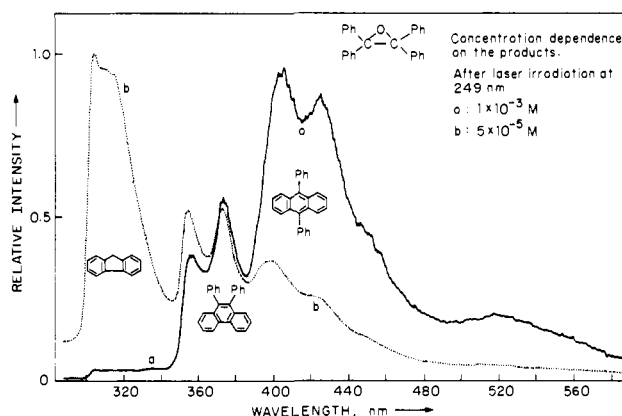


Figure 2. Concentration dependence of products. Emission spectra were obtained by using a standard spectrophotometer for TPO (1.0×10^{-4} M) solution after 30-pulse irradiation of a N_2 -bubbled sample (excitation wavelength 255 nm). See also ref 8.

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.

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 spectrum³ 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

(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.

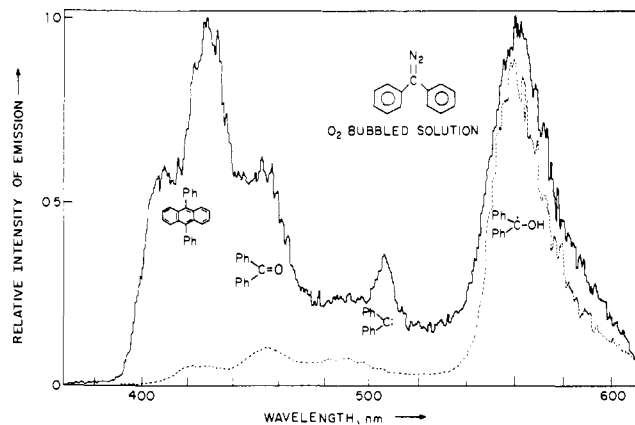


Figure 3. Emission spectra of transients and products for DDM obtained by OMA analysis. The spectra were recorded after N_2 purging the isooctane solution of a sample (1.0×10^{-4} M) which had previously been irradiated with 30 pulses at room temperature while saturated with O_2 . The dotted spectrum was obtained for benzophenone in N_2 -bubbled isooctane solution. The emission of benzophenone ketyl radical ($\lambda_{max} \approx 560$ nm) was observed in addition to benzophenone phosphorescence ($\lambda_{max} \approx 455$ nm).

Lamp photolysis of TPO under identical conditions does not lead to formation of TPE, DPA, or FL [undetectable by VPC and fluorescence analysis]. TPE is a product formed in flash- and low-temperature work; however, DPA, DPP, and FL are not reported.⁵

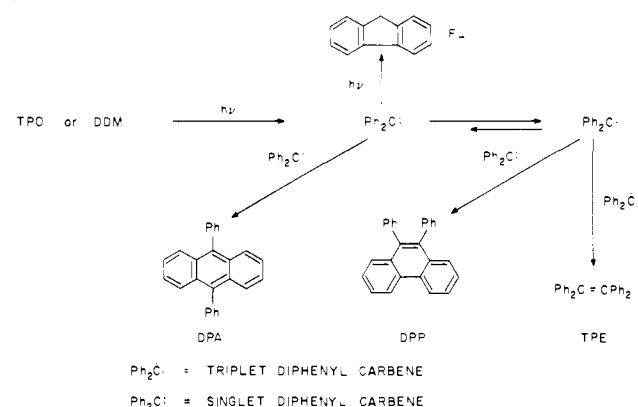
The yield of both DPA and FL increased markedly with increased laser power. Furthermore, the relative yield of DPA increased with increased concentration of carbene precursor while FL showed a contrasting behavior (Figure 2). The relative yield of DPP did not undergo a substantial change when either the substrate concentration or the laser intensity was varied.

The results of laser photolysis of O_2 -purged isooctane solutions of DDM (or TPO) are strikingly different (Figure 3) from those observed in N_2 -purged solution. Two new emissions that are virtually absent in samples which were N_2 purged during laser photolysis appear and are readily assigned to phosphorescence from benzophenone⁶ and to fluorescence from the diphenylketyl radical.⁷ Furthermore, the fluorescences of DPA and FL are now absent.

Although the chemical yields of these new products are low (as determined by VPC analyses of photolysis solutions⁸), they are of unique and unusual structure, and their production derives from the laser intensity; these products are absent in lamp photolysis. Work directed toward optimizing the conditions leading to their formation is now in progress.

Firm establishment of the details of the mechanism of formation of DPA, DPP, and FL must await the results of further experiments. However, we propose Scheme I at this time as a working, if somewhat speculative, mechanism that is consistent with our findings so far. First, the formation of TPE appears to occur predominately from dimerization of two triplet carbenes. This is consistent with the second-order decay of the DPC transient and the formation of TPE as a major product under flash-photolysis conditions. Second, the observation that the relative yield of FL decreases with respect to DPA as the number of absorbed laser photons increases (Figure 3) is consistent with production of FL from a first-order carbene reaction whereas DPA is produced from a path that is second order. Since formation of FL

Scheme I



is observed in the thermolysis of DDM and is typical of *singlet* carbene rearrangements, we propose that FL is produced from DPC singlet. Finally, since the response of DPP to the intensity of absorbed photons is different from both DPA and FL, we propose that DPP arises from either a triplet-singlet carbene dimerization or a triplet-triplet carbene dimerization. Control experiments suggest that the major portion of DPP formed does not arise from secondary photolysis of initially produced TPE.

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Direct Lanthanide-Induced-Shift NMR Determination of Conformer Populations in Substituted Cyclohexanones

Sir:

Shift reagents offer the possibility for the determination of conformer geometries and energies in solution¹ which would be difficult, if not impossible, by any other technique. Nevertheless, despite this promise, examples of the use of the lanthanide-induced shift (LIS) approach to the estimation of conformer energies are invariably either questionable in their analyses² or rely on other associated data³ (e.g., comparison of the LIS's in conformationally mobile molecules with the corresponding shifts in "rigid" systems).^{4,5}

(1) O. Hofer, *Top. Stereochem.* **9**, 111 (1976).

(2) For example, rotational isomerism in 2- and 3-carboxaldehydes of furan, pyrrole, and thiophene has been repeatedly investigated with LIS's. In none of these investigations were both the 1H and ^{13}C nuclei used, giving poorly determined systems (three equations in four unknowns). G. Gacel, M. C. Fournie-Zaluski, and B. P. Roques, *Org. Magn. Reson.*, **8**, 525 (1976); S. Nagata, T. Yanabe, K. Y. Yoshikawa, and H. Kato, *Tetrahedron*, **29**, 2545 (1973); G. Montaudo, S. Caccamese, V. Librando, and P. Maravigna, *ibid.*, **29**, 3915 (1973).

(3) J. A. Peters, J. D. Renijnse, A. V. D. Wiele, and H. V. Bekkum, *Tetrahedron Lett.*, 3065 (1971).

(4) K. L. Servis and D. J. Bowler, *J. Am. Chem. Soc.*, **95**, 3392 (1973).

(5) R. E. Davis and M. R. Wilcott, *J. Am. Chem. Soc.*, **94**, 1744 (1972).

(5) (a) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.
(b) Becker, R.; Bost, R. O.; Kolk, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *Ibid.* **1970**, *92*, 1302.

(6) Wolf, M. W.; Legg, K. D.; Brown, R. E.; Singer, L. A.; Parks, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 4490.

(7) Topp, M. R. *Chem. Phys. Lett.* **1976**, *39*, 423.

(8) After 100 pulses at 100 mJ, a 10^{-3} M N_2 -purged isooctane solution of precursor yielded 13.5% TPE, trace FL, and 0.2% TPA, and after 66 pulses at 100 mJ, a 10^{-5} M solution yielded 45.0% TPE, 0.8% FL, and trace TPA. The percent yield is 100 times the mole fraction of potential DPC present initially.