Acknowledgment. This work was supported by the National Science Foundation under Grant No. BN5-8705777 (A.G.E.) and the U.S. Army Research Office, Grant no. 4528 (H.R.A.). A.G.E. is a recipient of an N.S.F. Presidential Young Investigator Award (CHE-8657193).

Laser-Jet Photochemistry: The Photofragmentation of Triplet 1,1,3,3-Tetraarylpropane-1,3-diyls and Their Role in the Photometathesis between Diarylcarbenes and 1,1-Diarylethylenes

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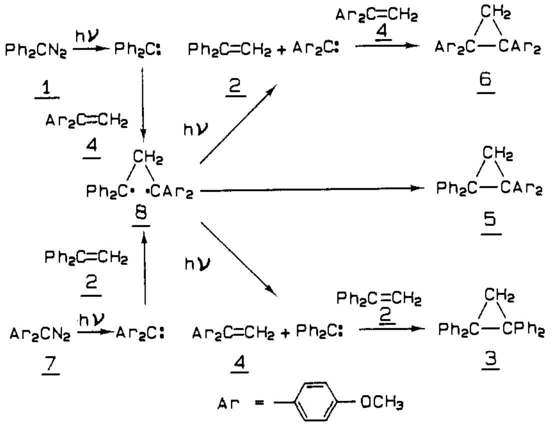
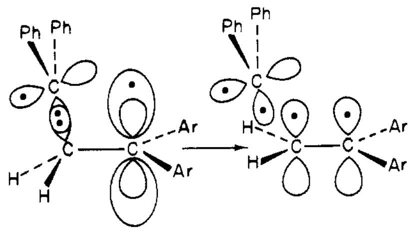
Until recently the only method available for studying the photochemistry of transient photochemical intermediates was to stabilize them in low-temperature matrices where their lifetimes are increased to the point where conventional low intensity light sources can induce photochemistry.[1] During the past several years, pulsed excimer laser sources have made it possible to study the photochemistry of transient intermediates under ambient conditions.[2] We have recently developed a laser-jet technique for the study of transient intermediate photochemistry with a CW argon ion laser.[3] This technique consists of irradiating a high velocity solution microjet (~4.5 m/s, ~100 μm in diameter) with the focused output of an argon ion laser (all UV lines, 333-364 nm, ~3W). Since microjet self-focusing and waveguide properties greatly enhance the light intensity within the jet,[4] and since relatively large quantities of material can be processed by this method, multiphoton products can often be isolated from these jet reactions and characterized by conventional spectroscopic methods. In this report we describe the application of this laser-jet technique to the photochemistry of triplet 1,1,3,3-tetraarylpropane-1,3-diyls generated through the irradiation of diaryldiazomethanes in the presence of 1,1-diarylethylenes.

As a control for the biradical photochemical studies to be reported below and in an effort to compare the argon laser-jet technique with high intensity excimer laser irradiation, we have repeated the photolysis of diphenyldiazomethane (**1**) described by Turro and co-workers.[2b] They observed the formation of tetraphenylethylene (TPE), 9,10-diphenylphenanthrene (DPP), 9,10-diphenylanthracene (DPA), and fluorene (FL). Under laser-jet conditions TPE also was observed to be the predominant product along with DPP and DPA. However, no FL could be detected even by GLC-mass spectrometry. These results are in accord with the earlier observations, since FL formation was ascribed to the further excitation of the very short-lived ^{1}DPC ($\tau \sim 95$ ps in isooctane),[5] while either DPP or DPA may arise from the much longer lived ^{3}DPC. Apparently under laser-jet conditions there is insufficient light intensity or photon energy to affect cyclization of ^{1}DPC to FL.

Scheme I



Scheme II



When **1** is irradiated under low intensity conditions (Rayonet Photochemical Reactor, 350 nm) in the presence of **2**, the predominant product is 1,1,2,2-tetraphenylcyclopropane (**3**)[6] along with small amounts of benzophenone azine. Under jet conditions, this same reaction also gives **3** in addition to TPE, DPP, DPA as well as trace amounts of 1,1,3,3-tetraphenylpropene.[6,7] Michl has observed a similar 1,2-H shift upon irradiation of matrix-isolated 1,3-biradicals.[1g] If **2** is replaced by 1,1-bis(*p*-methoxyphenyl)ethylene (**4** in Scheme I), low intensity irradiation yields the expected unsymmetrical cyclopropane, 1,1-diphenyl-2,2-bis(*p*-methoxyphenyl)cyclopropane (**5**). However, under jet conditions two products not observed in the low intensity reactions are formed as well. These were shown to be **2** and 1,1,2,2-tetrakis(*p*-methoxyphenyl)cyclopropane (**6**).[6,7] In a complementary set of experiments, bis(*p*-methoxyphenyl)diazomethane (**7**)[8] was irradiated in the presence of **2**. Again low intensity irradiation resulted in the unsymmetrical tetraarylcyclopropane **5** as the predominant product, and jet irradiation yielded the intensity dependent products **4** and the symmetrical cyclopropane **3**.[6,7]

The results of these two carbene addition reactions which should both lead to the unsymmetrical biradical ^{3}**8** are most easily correlated by the mechanism outlined in Scheme I.[9] If ^{3}**8** has

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(1) (a) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251. (b) Dunkin, I. R.; MacDonald, J. G. *Tetrahedron Lett.* **1982**, *23*, 5201. (c) Schmidt, S. P.; Pinhas, A. R.; Hammons, J. H.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 6822. (d) Nakanishi, H.; Yabe, A.; Honda, K. *Chem. Commun.* **1982**, 86. (e) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597. (f) Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537. (g) Muller, J. F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629.

(2) (a) Scaiano, J. C.; Wagner, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 4626. (b) Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 5127. (c) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (d) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2349.

(3) Wilson, R. M.; Hannemann, K.; Peters, K.; Peters, E.-M. *J. Am. Chem. Soc.* **1987**, *109*, 4741. Wilson, R. M.; Hannemann, K.; Heineman, W. R.; Kirchhoff, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 4743.

(4) Simple calculations indicate that intensities within the jet should be about 10^{22}–10^{23} photons cm^{-2} s^{-1}. However, laser beams become trapped within microbodies, and the light intensities to which the sample is exposed in this work will be at least several orders of magnitude higher than that indicated above: Qian, S.-X.; Snow, J. B.; Tzeng, H.-M.; Chang, R. K. *Science* (*Washington, D.C.*) **1986**, *231*, 486. Owen, J. F.; Chang, R. K.; Barber, P. W. *Optics Letters* **1981**, *6*, 540.

(5) Eisenthal, K. B.; Moss, R. A.; Turro, N. J. *Science* (*Washington, D.C.*) **1984**, *225*, 1439.

(6) Authentic samples of the photoproducts were prepared by the following procedures: **3**, Hodgkins, J. E.; Hughes, M. P. *J. Org. Chem.* **1962**, *27*, 4187. **4**, Aldercreutz, P.; Magnusson, G. *Acta Chem. Scand.* **1980**, *B34*, 647. Pfeiffer, P.; Wizinger, R. *Ann.* **1928**, *461*, 144. **5** and **6**, Arnold, D. R.; Wayner, D. D. M.; Yoshida, M. *Can. J. Chem.* **1982**, *60*, 2313. 1,1,3,3-Tetraphenylpropene, Tadros, W.; Sakla, A. B.; Helmy, A. A. A. *J. Chem. Soc.* **1961**, 2687.

(7) All multiple photon reaction products were compared with authentic samples by HPLC, GLC-mass spectrometry, high resolution mass spectrometry, and, in the case of 1,1-diphenylethylene, NMR analysis and found to be identical.

(8) Humphreys, R. W. R.; Arnold, D. R. *Can. J. Chem.* **1977**, *55*, 2286. Miller, J. B. *J. Org. Chem.* **1959**, *24*, 560.

a lifetime of >100 ns, then it should be possible to excite ^{3}**8** under jet conditions, since the diphenylmethyl radical is known to absorb strongly with a λ_{max} of 325–335 nm.[10] Apparently, ^{3}**8** does absorb to a significant degree and ^{3}**8*** extrudes either bis(*p*-methoxyphenyl)carbene or DPC as its primary mode of decay. However, in each of these unsymmetrical carbene additions only one of the two possible carbene extrusion processes will be observed, as the complementary extrusion process will be "invisible", since it constitutes a reversal of the reaction leading to **8**.

The mechanistic details of these carbene extrusion processes are uncertain at present. However, it seems quite likely that these carbene extrusions are β-cleavage reactions as shown in Scheme II. The photochemical β-cleavage of carbonyl-generated biradicals has been observed.[2a] Thus, β-cleavage may be emerging as a general pattern for biradical photochemistry. Furthermore, the observation of these carbene extrusions and the associated olefin metatheses adds a new dimension to triplet biradical chemistry and clearly demonstrates the utility of the laser-jet technique in the study of the photochemistry of moderately short-lived transient intermediates.

Acknowledgment. We thank the National Science Foundation (NSF CHE-8409628) for support of this research and for a grant used to assist in the purchase of high resolution mass spectrometry facilities used in this work (PCM-8219912).

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(9) In control experiments the unsymmetrical cyclopropane **5** proved to be inert upon jet irradiation, thus, excluding the possibility that the aforementioned carbene extrusions were due to the photolytic or even thermal cleavage of **5**. McNesby, J. R.; Okabe, H. *Advances in Photochemistry* **1963**, *3*, 157. Srinivasan, R.; Ors, J. A. *J. Org. Chem.* **1979**, *44*, 3426. Srinivasan, R.; Baum, T.; Ors, J. A. *Tetrahedron Lett.* **1981**, *22*, 4795. Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 537. Hodgkins, J. E. and Hughes, M. P., in ref 6.

(10) Caldwell, R. A.; Dhawan, S. N.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 6454. Barton, D. H. R.; Charpiot, B.; Ingold, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607.

Convergent Functional Groups: Catalysis of Hemiacetal Cleavage in a Synthetic Molecular Cleft

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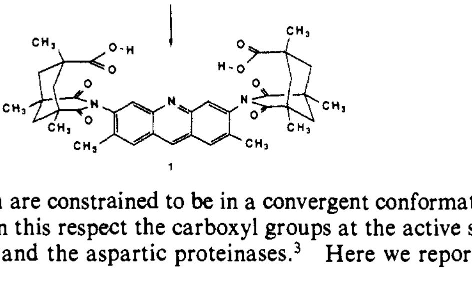
We recently reported the synthesis of diacid **1** and demonstrated its utility as a probe in molecular recognition studies.[1] The substance is readily made by the condensation of the Kemp triacid[2] and acridine yellow (eq 1). The new structure features carboxyl



1

(1)

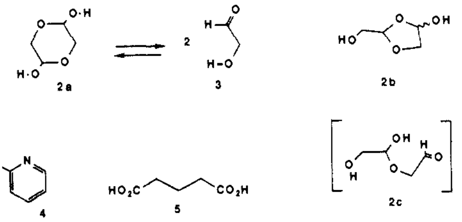
groups which are constrained to be in a convergent conformation, resembling in this respect the carboxyl groups at the active sites of lysozyme and the aspartic proteinases.[3] Here we report on some of the catalytic advantages that attend such structural constraints.

Table I. Dissociation (Eq 2) in $CDCl_3$ 25 °C

catalyst	[catalyst]	k_{obsd}	approx half-life[a,b]	k_{obsd}/[cat]
none		2.7×10^{-6}	72.1[a]	–
benzoic acid	2×10^{-4}	6.3×10^{-6}	30.8[a]	3.1×10^{-2}
glutaric acid, **5**	4.8×10^{-5}	8.6×10^{-6}	22[a]	1.8×10^{-1}
2-hydroxypyridine, **4**	5×10^{-5}	1.6×10^{-5}	12[a]	3.2×10^{-1}
7	6×10^{-5}	1.6×10^{-5}	12[a]	2.7×10^{-1}
1	2.5×10^{-6}	9.8×10^{-4}	12[b]	3.9×10^{2}

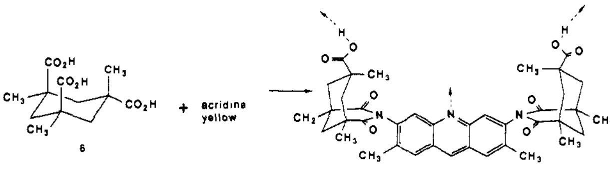
[a] Time is in hours. [b] Time is in minutes.

The dissociation of glycoaldehyde dimer **2a** to the monomer **3** (eq 2) has been studied by a number of workers[4] in various media. In $CDCl_3$ dissociation in the absence of catalysts is very slow ($\tau_{1/2}$ = 3 days). The reaction involves the rapid buildup[5] and then somewhat slower disappearance of the dioxolane isomer **2b** which remains at a steady-state concentration over most of the reaction. Substances such as 2-hydroxypyridine (**4**) and simple monocarboxylic acids, much admired for their catalysis of glucose mutarotation,[6] are quite modest in their effects on this dissociaton reaction (Table I). Dicarboxylic acids such as glutaric show little activity in this regard, and even acid–base mixtures fail to catalyze the dissociation.[7]



(2)

The convergent diacid **1** is a remarkably effective catalyst for this reaction: less than 0.5 mol% suffices to convert 2 → 3 within minutes! In contrast, the *divergent* diacid[8] **7** (eq 3) shows poor efficiency. This latter structure bears all of the functional groups of **1**, but its divergent structure does not permit these functional groups to act in a concerted manner.



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(3)

The open-chained dimer **2c** is a necessary intermediate for both forward and reverse reactions but has eluded detection.[4] In acetone, where the reverse reaction of eq 2 is favored, **1** acts as

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(1) Rebek, J., Jr. *Science (Washington, D.C.)* **1987**, *235*, 1478–1484, and references therein.

(2) (a) Kemp, D. S.; Petrakis, K. S. *J. Org. Chem.* **1981**, *46*, 5140–5143. (b) Rebek, J., Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426–2431.

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(4) For other studies of the dissociation, see: Bell, R. P.; Hirst, J. P. H. *J. Chem. Soc.* **1939**, 1777–1780. Wertz, P. W.; Garver, J. C.; Anderson, L. *J. Am. Chem. Soc.* **1981**, *103*, 3916–3922, and references therein. Stassinopoulou, C. I.; Zioudrou, C. *Tetrahedron* **1972**, *28*, 1257–1263.

(5) The equilibrium constant [**2b**/**2a**] was determined by NMR to be ca. 1.6 ± 0.4 after 2–3 h, and the initial, uncatalyzed rate of **2b** formation from **2a** was 5.4×10^{-5} s^{-1}. The initial concentration of **2a** was 10^{-3} M in all reactions.

(6) (a) Swain, C. G.; Brown, J. F., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 2534–2537. (b) Engdahl, K. A.; Bivehed, H.; Bohman, O.; Obenius, U.; Ahlberg, P. *Chem. Scr.* **1981**, *18*, 176–183. Engdahl, K.-A.; Bivehed, H.; Ahlberg, P.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 4767–4774. (c) Rony, P. R.; Nef, R. O. *Ibid.* **1973**, *95*, 2896–2905, and earlier work by these authors.

(7) For example 2:1 mixtures of acetic acid and pyridine (several molar equivalents) were no more effective than benzoic acid. These experiments are not recorded in the table because of the difficulty in comparing systems of different molecularities.

(8) Compound **7** (dec ~ 300 °C) showed all the expected spectroscopic features. The cis/trans isomer **6** of the triacid showed mp 205–215 °C; it is obtained as a byproduct of the alkylation reaction[2b] used in the synthesis of the Kemp triacid.

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