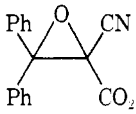
the synthetic utility of the method. After 9 h of simultaneous visible and ultraviolet irradiation of **8** in 2-methyl-2-butene (25°) the isomeric methyl 1-cyano-2,2,3-trimethylcyclopropane carboxylates (**9**) (20%) and the oxetane (**10**) are formed and separated by repeated short-path distillation.[11] In the absence of the visible source the extent of reaction under otherwise identical conditions was barely detectable within limits of NMR techniques.



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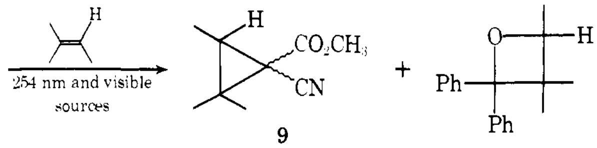

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The rate of carbene formation from vicinal diaryloxiranes which also exhibit photochromic properties[4] may also be enhanced utilizing the procedure described. For example, the extent of conversion of *trans*-stilbene oxide to 1-phenyl-2,2,3,3-tetramethylcyclopropane (21%) and the oxetane **4a** (31%) increases by a factor of ~2.0 in 2 h when visible as well as ultraviolet sources are used concurrently rather than the ultraviolet source alone.

In summary it appears from the data accumulated to date that while ylides such as **6** and symmetrical counterparts are photolabile and give carbenes, recyclization competes effectively. Furthermore, photocleavage of ylides cannot account completely for fragmentation and concerted or sequential processes perhaps involving initial C–O bond cleavage have not been excluded.[12]

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(3) I. J. Lev, K. Ishikawa, N. S. Bhacca, and G. W. Griffin, *J. Org. Chem.*, in press.

(4) In contrast carbonyl ylides derived photochemically from 2,3-diaryloxiranes also may be trapped although electron deficient alkenes such as dimethyl fumarate and fumaronitrile are required as dipolarophiles. Similar results have been observed by Dr. G. A. Lee, Dow Chemical, Wayland, Mass.

(5) H. Hamberger and R. Huisgen, *Chem. Commun.*, 1190 (1971); A. Dahmen, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, 1192 (1971).

(6) A. Robert, J. J. Pommeret, E. Marchand, and A. Foucaud, *Tetrahedron*, **29,** 463 (1973), and references cited therein.

(7) Irradiations were conducted in serum-capped Vycor test tubes employing a Rayonet chamber reactor equipped with 16 8-W 254-nm lamps unless otherwise indicated.

(8) J. P. Wasacz, M. M. Joullié, U. Mende, I. Fuss, and G. W. Griffin, *J. Org. Chem.*, **41,** 572 (1976).

(9) E. Ciganek, *J. Am. Chem. Soc.*, **88,** 1979 (1966). We are indebted to Dr. Ciganek for authentic samples of the dinitriles **2** and **3.**

(10) Similar double-irradiation studies of the photoequilibration of *cis*- and *trans*-methyl 2-cyano-3-phenylglycidates in rigid matrices at 77 K have been conducted and will be described in a future communication.

(11) It is evident from NMR data obtained on the crude photolysate that an isomeric pair of cyclopropanes **9** is formed. Difficulty was encountered in resolving the mixture of epimers by TLC due to decomposition of these sensitive cyclopropanes. Furthermore separation by GLC proved futile perhaps because of thermal equilibration and/or losses incurred by other reaction modes such as ring opening or elimination of hydrogen cyanide. Thus extreme care must be exercized in the distillation of the mixed isomers (<100°) in order to achieve the results reported, maintain the observed isomer ratio (~3:1; δ 3.72 and 3.81, $-OCH_3$, respectively), and avoid undue decomposition.

(12) Examples of carbene formation from phosphorus ylides upon photolysis are known: A. Ritter and B. Kim, *Tetrahedron Lett.*, 3449 (1968); Y. Nagao, K. Shima, and H. Sakurai, *Ibid.*, 2221 (1970).

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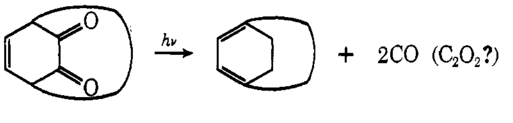
Photochemical Reactions of Cyclic, Unsaturated Diketones

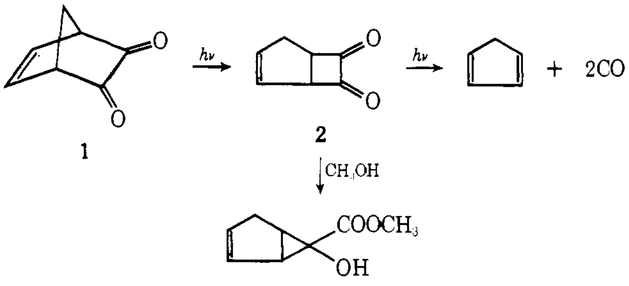
Sir:

A number of examples of photochemical bis decarbonylation of unsaturated, bicyclic α-diketones to dienes or aromatic compounds and carbon monoxide have been reported.[1] The



possibility that elimination of carbon monoxide could occur by a concerted mechanism to form the oxycumulene ethylenedione (C_2O_2) as a primary product has prompted several theoretical studies[2] of this interesting but elusive[3] species. We report a more careful examination of some of these photochemical reactions which establishes that they do not, in fact, involve decarbonylation at all but instead rearrangement via a 1,3-shift to cyclobutanediones. It is the latter compounds which decarbonylate photochemically and are responsible for the results previously ascribed to their bridged presursors.

The detailed course of these reactions can be observed by choosing an appropriate wavelength for irradiation and monitoring the progress of reaction so that the initially formed cyclobutanedione is not destroyed in situ. A typical result is shown in Figure 1 for photolysis of 8×10^{-3} M bicyclo[2.2.1]-heptene-2,3-dione[1e] (**1**) in benzene at 404 (preferred) or 436 nm. Disappearance of the maximum of **1** at 460 nm is accompanied by increase in intensity of absorption at longer wavelengths and a new maximum, typical of cyclobutanediones,[4] appears at 503 nm (ϵ 93) due to the product, bicyclo[3.2.0]heptene-6,7-dione[5] (**2** ir max (Chf) 1760, 1790 cm^{-1}; NMR, multiplets at δ 6.2–6.45 (1 H), 5.7–6.0 (1 H), 4.6–5.0 (1 H), 3.7–4.2 (1 H), 2.4–3.6 (2 H) ppm; MS, *m/e* 122 (M^+), 94 ($M^+ - CO$), 66 ($M^+ - 2CO$), 56)). In methanol solution at room temperature, **2** underwent facile ring contraction[6] to the unsaturated hydroxy ester **3**.[5] Both spectroscopic and gas chromatographic analyses established that **1** is converted *exclusively* into **2** during the early stages of reaction when the concentration of **2** is sufficiently low that its light absorption at the irradiating wavelength is negligible. This



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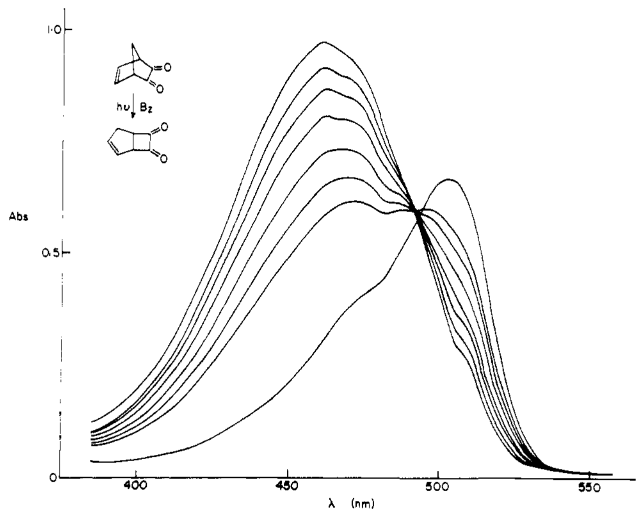


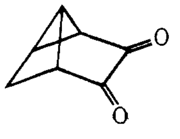
Figure 1. Irradiation of 8×10^{-3} M **1** in benzene at 404 nm.

is also apparent in Figure 1 where an isosbestic point is observed[7] at 492 nm for the initial 25–35% of the reaction. An analogous rearrangement has been observed[8] in some attempts to prepare the radical anion of **1** from compounds having the bicyclo[2.2.1] skeleton; the ESR spectrum of the radical anion of **2** was observed.

The initial quantum yield at 404 or 436 nm for disappearance of **1** or formation of **2** was 0.21 ± 0.02. This value was observed in the presence of air or in carefully degassed solutions in benzene or toluene; rearrangement also occurred cleanly in methylene chloride and deuteriochloroform solutions and in the solid state. No quenching by anthracene was observed even at concentrations as high as 10^{-2} M. Further indications that the reactive excited state of **1** might be its singlet state were provided by observations that the reaction was sensitized by anthracene, that **1** quenched the fluorescence of anthracene in benzene solution at 25 °C with a rate constant[9] of 1×10^{10} M^{-1} s^{-1}, and that **1** quenched all the emission of biacetyl. However, comparable quantum yields for disappearance of **1** were obtained when *m*-methoxyacetophenone, benzil, or acetone (50% in benzene) were used as sensitizers. These compounds also sensitized the further reaction **2** → cyclopentadiene but no products of the oxadi-π-methane type,[10] such as **4**, could be detected.

The results above indicate that the photorearrangement **1** → **2** proceeds via a short-lived excited state(s) but do not permit a decision as to whether the singlet state, the triplet state, or both are reactive. We were unable to detect either fluorescence or phosphorescence from **1**. It is also not possible to distinguish between concerted and stepwise mechanisms[11] at this stage.

Rearrangements to cyclobutanediones were also observed with bicyclo[2.2.2]octene-2,3-dione[12] (**5**), benzobicyclo[2.2.2]octadiene-2,3-dione (**6**), and the tetrachlorodione **7**. Thus all of these unsaturated diones, even **6** which could bisdecarbonylate to naphthalene, yield products of 1,3-migration upon direct irradiation as is observed with β,γ-unsaturated monoketones[10] but differ from the monoketones in their reaction with triplet sensitizers. An acyclic unsaturated dione underwent intramolecular Paterno–Buchi reaction upon irradiation.[13]



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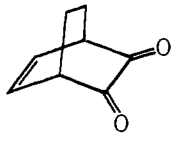

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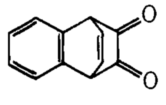

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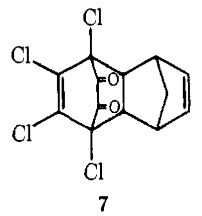

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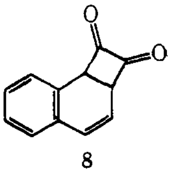

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The cyclobutanediones obtained in this work were stable thermally[14] with the exception of the dione **8** derived from **6** which gave naphthalene with a half-life of about 16 h at room temperature in the dark. Upon irradiation they lost carbon monoxide and were converted to the dienes (or naphthalene) previously reported.[1] Conversion of **2** to cyclopentadiene was effected by irradiation at 546 or 436 nm or by the full spectrum (through Pyrex) of a high pressure mercury vapor lamp. The reverse process, **2** → **1**, was not observed in any of these experiments.

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(6) Cf. J. M. Conia and M. J. Robson, *Angew Chem., Int. Ed. Engl.*, **14**, 473 (1975), and references contained therein.

(7) A second isosbestic point, not shown in the figure, was observed at 374 nm.

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(10) For a review see W. G. Dauben, G. Lodder, and J. Ipaktschi, *Top. Curr. Chem.*, **54**, 73 (1975).

(11) Since triplet energies of **1** and **2** probably do not differ greatly, a mechanism involving the triplet state of 1 need not necessarily occur in stepwise fashion.

(12) Experiment performed by Mr. A. Blank.

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(14) **2** survived gas chromatographic analysis at 100 °C without measurable decomposition.

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Ion Cyclotron Resonance Investigation of the Decarbonylation of Aldehydes by $(\eta^5\text{-}C_5H_5)Ni^+$

Sir:

Ion cyclotron resonance spectroscopy (ICR) is proving to be a valuable tool for investigating the reactions,[1-6] thermochemical properties,[4-6] and photochemistry[7] of metal ions in the gas phase.[8] The most significant results to date have involved the determination of metal–ligand bond dissociation