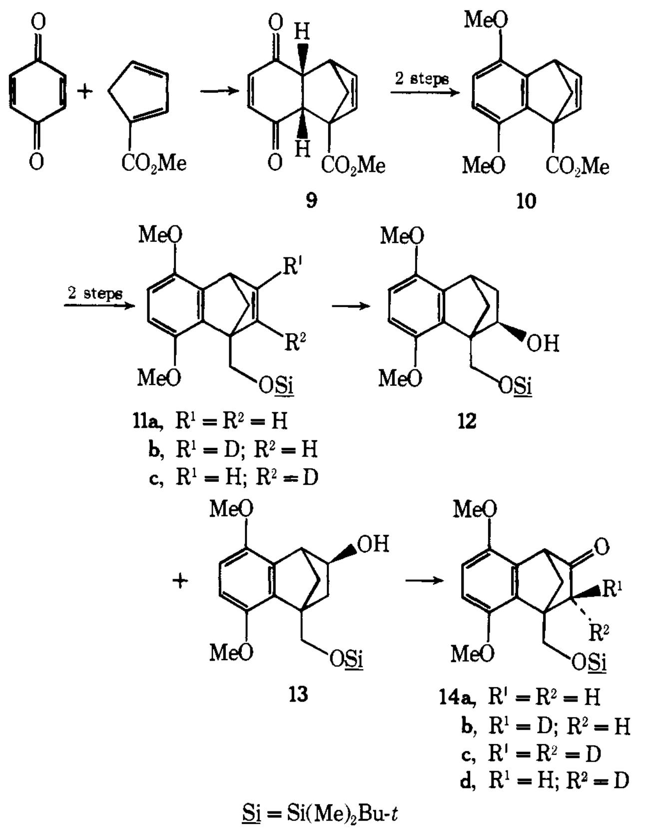

9

10

11a, $R^1 = R^2 = H$
b, $R^1 = D$; $R^2 = H$
c, $R^1 = H$; $R^2 = D$

12

13

14a, $R^1 = R^2 = H$
b, $R^1 = D$; $R^2 = H$
c, $R^1 = R^2 = D$
d, $R^1 = H$; $R^2 = D$

$\underline{Si} = Si(Me)_2Bu\text{-}t$

of these olefins derived from **14b** and **14d** gave the following migratory ratios: $D_x/H_n = 7.7$; $H_x/D_n = 23$. These results lead to a deuterium isotope effect of 1.7 and thus to the migratory ratio $H_x/H_n = 13$. At 190°, this ratio corresponds to a substantial activation energy difference, $E_a{}^n - E_a{}^x \simeq 2.4$ kcal/mol, assuming similar preexponential factors for exo and endo migration.

The difference in H^x/H^n migratory ratios between our system and that of Nickon and co-workers (13 cf. 140) might be rationalized a number of ways,[4b,16] but no unambiguous explanation is possible, based on present data. We have demonstrated, however, that carbene migratory preferences in a bicyclo[2.2.1] system (albeit in a benzo analogue[17]) may be unique and subject to various interpretations, as they are in the corresponding carbonium ion analogues. We are currently investigating a system which we hope will provide an unambiguous demonstration of the theoretical predictions discussed above.

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(6) All new compounds gave satisfactory spectroscopic and analytical data.

(7) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.*, **94,** 6190 (1972).

(8) At room temperature the ratio **13/12** was ca. 2/1.

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(10) (a) By MS analysis, **14b** had $d_0:d_1:d_2 = 0:93:7$. By ^1H NMR, no exo-H was evident <2%. (b) By MS analysis, **14c** had $d_0:d_1:d_2 = {<}1:{<}1:{>}99$. (c) By MS analysis, **14d** had $d_0:d_1:d_2 \approx 8:81:11$. By ^1H NMR no endo-H was evident in the d_1 material (<3–4%).

(11) T. T. Tidwell, *J. Am. Chem. Soc.*, **92,** 1448 (1970).

(12) Although the lithium salts of the tosylhydrazones were insoluble in cyclohexane at room temperature, at elevated temperatures (>120°) the reaction mixture was homogeneous until decomposition set in, depositing TsLi.

(13) By MS analysis, it was found that the conversion of **14b** or **14d** → **11** resulted in ≤3% H–D exchange.

(14) These analyses were corrected for the amount of d_0 (**11a**) material present. The results presented are averages of duplicate runs which gave essentially identical results.

(15) Assuming the same kinetic isotope effect (kie) for both exo and endo migration, the kie is then obtained from the equations $y/x = 7.7$ and $yx = 23$, where x = the kie and y = the migratory ratio H_x/H_n.

(16) H. Tanida, *Acc. Chem. Res.*, **1,** 239 (1968), and references contained therein.

(17) We feel that interaction of the benzo group (endo-side) with the carbene center should be minimal, since any resonance interaction must involve charge separation. In fact, it has been found that substituent effects are quite minor in rearrangements of *o*- and *p*-X-$C_6H_4(Ph)_2\ddot{C}H$ (using σ^+, $\rho = -0.28$); see P. B. Sargeant and H. Schecter, *Tetrahedron Lett.*, 3957 (1964).

Evan P. Kyba,* Carl W. Hudson
Department of Chemistry, The University of Texas
Austin, Texas 78712

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Photolysis of Carbonyl Ylides. Double-Irradiation Studies

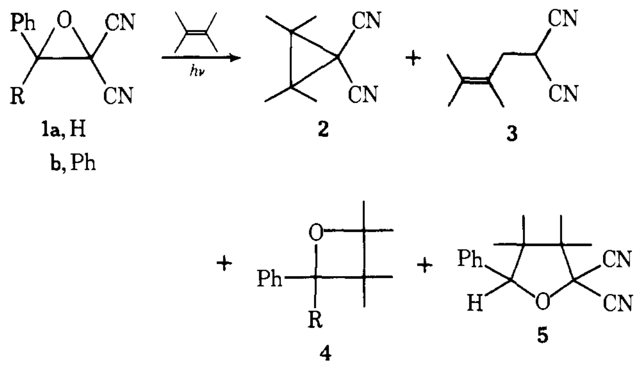
Sir:

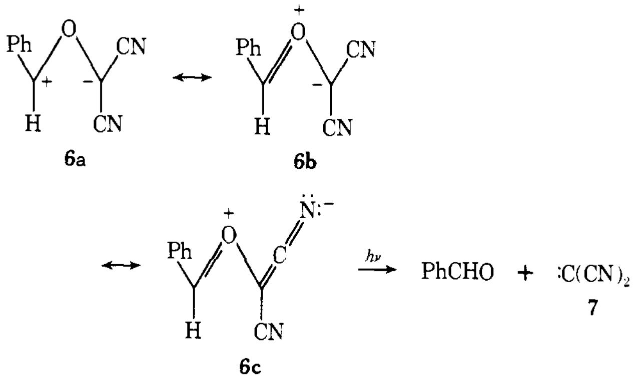
Photochromism is a phenomenon characteristic of vicinal diaryl and other suitably substituted oxiranes. In many cases the color associated with oxirane photolysis is apparent only in matrices at 77 K.[1] Color formation is attributed to C-C bond cleavage with formation of carbonyl ylides which may fragment to carbenes and carbonyl compounds.[1,2] In fact several such photogenerated carbonyl ylides, including that derived from 3,3-dicyanostyrene oxide (**1a**) have been intercepted at ambient temperature in solution with common dipolarophiles.[2-4]

The mechanism for the potential conversion of carbonyl ylides to carbenes has been the subject of interest in connection with the photofragmentation of oxiranes to carbenes.[1] It has been recognized that carbene formation is *not* associated with the thermal generation of carbonyl ylides from styrene and stilbene oxides including 2,3-dicyanostilbene oxide[5] as well as ethyl *trans*-2-cyano-3-phenylglycidate.[6] Furthermore, photodecarbonylation of 2,2,4,4-tetraphenyloxetanone may be accomplished in solution (25°; 350 nm)[7] to give tetraphenyloxirane presumably through an ylide intermediate without fragmentation to diphenylcarbene.[8] It is clear from these observations that thermal carbene formation from those ground state ylides studied is at best inefficient.

The possibility that carbonyl ylide fragmentation may be photoinduced remained to be tested since concerted oxirane fragmentation to carbene and/or sequential process(es) involving initial C-O bond photocleavage also provide viable mechanistic alternatives. The transformation of 3,3-dicyanostyrene oxide (**1a**) in 2,3-dimethyl-2-butene was selected for study since the [3 → 2 + 1] photocycloelimination reaction to dicyanocarbene is suppressed to the point where [3 + 2] cycloaddition becomes competitive.[3] Irradiation[7] of **1a** in the presence of 2,3-dimethyl-2-butene produces the spectrum of products **2–5** whose relative yields provide a reference for comparison of levels of cycloelimination and [3 + 2] cycloaddition.[9]

Experiments were designed using **1a** to test the validity of the assumption that products **2**, **3**, and **4a** derived from [3 →





2 + 1] cycloelimination to dicyanocarbene (**7**) and benzaldehyde are produced in fluid solution by photolysis of the carbonyl ylide **6** formed in turn from **1a.** In rigid matrices (77 K) ylide formation is restricted to the region of the cell-surface exposed to ultraviolet light. Although the origin of this phenomenon remains to be defined in detail shielding certainly occurs which may extend to fluid solution. In order to maximize exposure and utilization of radiation, particularly in matrices where the problem is magnified, an apparatus was constructed which consists of a quartz reaction vessel fitted with a jacketed probe which in turn accommodates a 500-W tungsten-iodine visible light source. With a unit of this configuration, simultaneous irradiation may be accomplished from both the interior and exterior regions of the sample. A Dewar with a quartz end required for cooling the entire assemblage was fabricated by interfacing a large Pyrex reservoir (capable of retaining a liquid nitrogen supply) with the quartz tip using concentric graded seals. Irradiation of the substrates contained in the sample compartment from the exterior through the Dewar with ultraviolet radiation from a chamber reactor may then be accomplished over a wide temperature range.[7] The temperature of the solution was monitored by means of a thermocouple inserted through a side arm at the top of the reaction vessel. To simulate conditions in control runs in which the visible source is absent a cartridge heater was inserted into the jacketed probe to compensate for the thermal gradient generated by the lamp across the solution or the matrix.

Initial double-irradiation experiments in fluid media were conducted with **1a** at 23° in neat alkenes. The photochemistry performed in fluid media contrasts markedly with that encountered in matrices (77 K) since competitive [3 + 2] cycloaddition and other bimolecular reactions are not arrested and recyclization is more facile. As a result a high steady-state concentration of ylide is unattainable; i.e., no colors analogous to those developed at 77 K are observed in solution at 23° upon irradiation.[7]

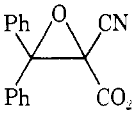
Despite the low steady-state concentration and reduced propensity of **1a** to undergo [3 → 2 + 1] cycloelimination a marked increase in dicyanocarbene formation may be achieved in solution at 23° using visible and ultraviolet sources simultaneously. Duplicate solutions of **1a** (0.1 g; 0.6 mmol) in 2,3-dimethyl-2-butene (10 ml) were prepared and irradiated for 12 h.[7] A tungsten-iodine visible lamp was utilized in conjunction with the 254-nm source[7] for irradiation of one sample. The results obtained support the contention that carbene formation from oxiranes, at least in part, may occur by photocleavage of carbonyl ylide intermediates such as **6.** The relative amounts of 2,2-dicyano-3,3,4,4-tetramethyl-5-phenyltetrahydrofuran (**5**) and 2,2,3,3-tetramethyl-4-phenyloxetane (**4a**) in the photolysate were determined from NMR spectra by integration of the benzylic proton signals at δ 5.08 and 5.39, respectively. The ratio of **5:4a** provides an index of the degree of preference for cycloaddition relative to cycloelimination and was found to be 1.9:1 in neat 2,3-dimethyl-2-butene (or ~1.3:1 if ether is added as solvent diluent) when the visible lamp was used. The visible source was then extinguished and replaced by the cartridge heater to compensate for the lamp. The average value for the ratio of **5:4a** was altered significantly (2.5:1) upon irradiation of the duplicate sample of **1a** solely with the ultraviolet source.[7] Clearly the effect of the visible radiation is to increase ylide fragmentation to carbene in the case of **6** albeit probably recyclization as well.

The photochemistry of the oxirane **1b** was also examined and the extent of [3 → 2 + 1] cycloelimination to dicyanocarbene (**7**) and benzophenone at ambient temperature is also modified when ultraviolet and visible sources are employed simultaneously. Minimal carbene formation (~5–10%) was observed in a control experiment upon irradiation (6 h) of **1b** in 2,3-dimethyl-2-butene solely with the ultraviolet source.[7] The yield of **4b** and **2** increases markedly (26 and 22%, respectively) when the system is illuminated (6 h) with the visible as well as ultraviolet sources. The extent of cyclopropane and oxetane formation was determined after separation by preparative TLC in which losses were certainly incurred; i.e., the data cited represent minimum values.

The effect of the double-irradiation technique for enhancement of fragmentation of **1a** is also apparent at subambient temperature in a solid matrix composed of 2,3-dimethyl-2-butene maintained at ~77 K using liquid nitrogen with the quartz Dewar.[10] The composition of the crude photolysate[7] obtained in a control run at 77 K using the cartridge heater rather than visible source was investigated. NMR and TLC analyses, conducted on the products after removal of excess alkene, indicate that little or no irreversible photochemistry occurs despite the fact that ylide formation is evident from the photochromic behavior observed during irradiation ($\lambda_{\max}$ 566 nm). In contrast double-irradiation of **1a** (0.1 g; 0.6 mmol) in solid 2,3-dimethyl-2-butene (10 ml) at ~77 K simultaneously through the quartz exterior with ultraviolet radiation[7] and Pyrex interior surfaces of the sample compartment (3 h) with visible light leads to formation of dicyanocarbene (**7**) as evidenced by the detection and isolation of the dicyanocyclopropane **2** (0.8 mg; ~1%).

The cyclopropane **2** was separated and collected by preparative GLC and characterized by comparison with an authentic sample.[9] Although other peaks are detected by analytical GLC the isolation and identification of these minor photoproducts with the exception of **4a** have not as yet been attempted; however, despite the clear indication that the visible light has a significant effect on the reaction course, not unexpectedly the conversion levels are low and the oxirane **1a** is recovered largely unchanged; i.e., the bimolecular reactions leading to cyclopropane **2** and oxetane **4a** are suppressed by the low-temperature, high-viscosity conditions of the matrix.

The double-irradiation technique was employed to produce the previously unknown cyanocarbomethoxy carbene from methyl 2-cyano-3,3-diphenylglycidate (**8**) which illustrates 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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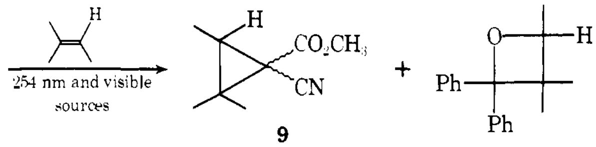

9 **10**

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).

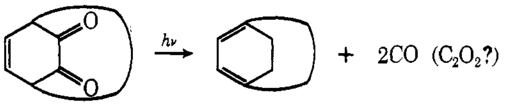
G. W. Griffin,* K. Ishikawa, I. J. Lev
Department of Chemistry, University of New Orleans
New Orleans, Louisiana 70122

Received March 19, 1976

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