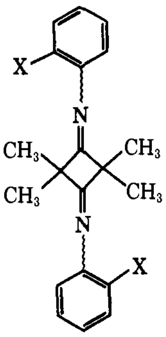
perature reported for the *o*-chlorobisimine **20**, compared with **21**.[19]



20, X = Cl; T_c<35°
21, X = H; T_c = 100°

Experimental Section

Instrumentation. All nmr spectra, except for the variable-temperature spectra, were recorded on a Varian Associates A-60 analytical nmr spectrometer with tetramethylsilane as the internal standard. The variable-temperature nmr spectra were recorded on a Varian Associates Model HA-100 nmr spectrometer. Mass spectra were run either on an AEI MS-9 or Varian Associates M-66 mass spectrometer, as indicated.

Chemicals. Acetone, Mallinckrodt, analytical reagent, was distilled and stored over Linde Molecular Sieve, Type 4A. *p*-Dichlorobenzene, Mallinckrodt, was purified by fractional sublimation at 25 mm.

Photocycloadditions. General Procedure. A solution of *ca.* 2 g of the ketenimine[2a,b] in *ca.* 200 ml of dry acetone was distributed among several Vycor tubes which were capped with red, sleeve-type serum caps. The tubes were degassed (several freeze–thaw cycles on vacuum line) by means of syringe needles through the serum caps and taped to a Quartz well, fitted with a Vycor sleeve, containing a 450-W Hanovia lamp. The tubes were irradiated at 18–20° and the remaining acetone was removed *in vacuo*. The product mixtures were analyzed by ir and nmr and subjected to chromatography on Florisil with the results described in the main text.

Photolysis of Acetone. Distilled and dried acetone (150 ml) was photolyzed in Vycor tubes for 30 hr under the conditions described in the General Procedure. The remaining acetone and volatile materials were removed *in vacuo* to give a colorless liquid. Analysis of this product by vapor phase chromatography on a 20% SE-32 on Chromosorb P column showed 11 peaks of which two can be classified as strong, one as moderate, and the rest as weak. One of the strong peaks was identified as 2,5-hexadiene.

Variable-Temperature Nmr Spectra. Samples of freshly chromatographed β adducts in purified *p*-dichlorobenzene (**6**, 0.83 *M*; **9**, 0.46 *M*), sealed in degassed tubes, were analyzed at various temperatures between 35° and above the coalescence temperatures on a Varian Associates HA-100 nmr spectrometer. The temperature control dial on the instrument was calibrated using ethylene glycol over the temperature range 60–120° leading to an estimated accuracy of the temperature control in the probe of ±2°. Using the protons in *p*-dichlorobenzene as an internal lock for the magnetic field, expanded field spectra of the methyl group protons in **6** and **9** were recorded at various temperatures after waiting 20 min for thermal equilibration in the probe. The series of spectra shown in Figures 1 and 2 could be obtained either by going from low to high or high to low temperature. These data were handled as described in the Results.

Acknowledgment. We thank the Petroleum Research Fund, administrated by the American Chemical Society, for Grant No. 2894-A4, in partial support of this work, and Professor Kenneth Servis for his invaluable assistance in carrying out the variable-temperature nmr study.

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(19) J. J. Worman and E. A. Schmidt, *J. Org. Chem.*, **35**, 2463 (1970).

Irradiation of α,β-Unsaturated Ketones. Search for Intermediate Oxabicyclobutanes[1]

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Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received May 26, 1971

Abstract: 3,4-Dimethyl-3-penten-2-one-*3-methyl*-d_3, 3-methyl-3-buten-2-one-*1,1,1*-d_3, and acrolein-*1*-d_1 were irradiated through a Vycor filter in hydrocarbon solvents. Spectral analyses of recovered starting materials showed no intramolecular scrambling of deuterium. These results indicate that the respective oxabicyclobutanes are not photochemical intermediates that could have led to an energy-wasting step that regenerates starting materials.

Oxabicyclobutanes have been considered as unstable intermediates in the n,π* photochemistry of several cyclic α,β-unsaturated ketones.[2] In these cases[2] no specific evidence was presented for the formation of oxabicyclobutanes. Their formation was primarily considered for the sake of novelty or as a means of introducing an energy wasting step that would shorten the lifetime of intermediate excited states. The latter consideration was based on the premise that intermediate oxabicyclobutanes would rapidly fragment back to starting enone with no net observable chemistry. The only reaction which superficially indicates an oxabicyclobutane intermediate is the Pyrex photolysis of purpurogallin[3] to yield the rearranged product, 6,7,8-trimethoxynaphthoic acid methyl ester. Even here, however, the necessity of an aqueous solvent suggests that features other than oxabicyclobutane formation may control the course of the reaction. Oxabi-

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(1) Taken from the doctoral dissertation of G. B. Schuster, University of Rochester, 1971.

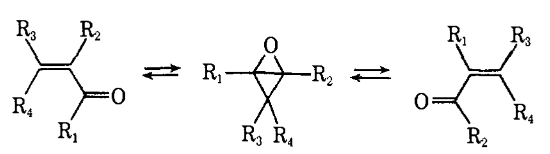
(2) (a) E. J. Corey, J. D. Bass, R. LaMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965); (c) H. E. Zimmerman, R. G. Lewis, J. J. McCollough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 1965 (1966); (d) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969); (e) N. Furatachi, Y. Nakadaira, and K. Nakanishi, *ibid.*, **91**, 1028 (1969).

(3) O. L. Chapman and T. J. Murphy, *ibid.*, **89**, 3476 (1967).

cyclobutane intermediates were also considered and eventually rejected in the photolysis of various acrylic acids through quartz to give β-lactones.[4] In these cases an oxetene intermediate was implicated by use of an appropriately substituted acrylic acid.

In all reports to date no specific attempt was made to prepare oxabicyclobutanes by photolysis of α,β-unsaturated carbonyl compounds. The goal of the work in this report was to irradiate α,β-unsaturated carbonyl compounds under conditions that would maximize the probability of oxabicyclobutane formation. Specially constructed systems were chosen so that oxabicyclobutane formation could be detected with high sensitivity.

Choice of Systems. The choice of systems and methods of analysis were based on the assumption that oxabicyclobutanes would not be stable but would fragment to α,β-unsaturated carbonyl compounds. Epoxidation studies of cyclopropenes support this assumption.[5] In the case of an intermediate oxabicyclobutane **3**, fragmentation could produce both isomers **1** and **2**. If irradiation of compound **1** formed isomer **2**, intermediate oxabicyclobutane formation would be probable. If, on the other hand, irradation did not produce isomer **2**, oxabicyclobutane formation could not be rigorously ruled out. The possibility would exist that the intermediate oxabicyclobutane may preferentially fragment to enone **1**; the critical test of photolyzing isomer **2** to the oxabicyclobutane which would then rearrange to compound **1** could fail if any other reaction pathway for compound **2** were substantially more efficient than oxabicyclobutane formation. Since negative results would only be meaningful when the same groups are used for R_1 and R_2, isotopic labeling was used to distinguish R_1 from R_2. Presumably secondary isotope effects would not lead to completely different chemistry for isomers **1** and **2**.



1 **3** **2**

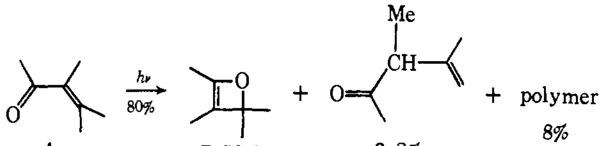
A further restriction on the chosen system was to have identical substituents for R_3 and R_4. This feature would eliminate the need to work with two isomeric series of compounds.

Last, it was desired to study α,β-unsaturated carbonyl systems which have relatively low quantum yields for reaction to irreversibly formed products. The smaller the quantum yield for irreversible destruction of enone, the greater the potential sensitivity for oxabicyclobutane formation. This kinetic consideration and the structural features mentioned above suggested the study of acyclic enones. Not only can they be readily synthesized with isotopically different substituents R_1 and R_2, but most acyclic enones possess low quantum yields for irreversible reaction.[6] Another goal of this work was to determine if reversible oxabicyclobutane formation were the reason for the observed low photochemical reactivities of many acyclic enones.

Three systems were investigated. By analogy with both bicyclobutane and cyclobutene formation from photolysis of butadiene,[7] labeled 3,4-dimethyl-3-penten-2-one (**4**) was investigated for oxabicyclobutane formation since this system does form an oxetene.[8] In case the cisoid conformation of enone **4**[9] is detrimental to oxabicyclobutane formation, the labeled transoid compound 3-methyl-3-buten-2-one (**5**) was also studied. Last, labeled acrolein (**6**) was irradiated since the alkyl substituents on the previous two enones might suppress oxabicyclobutane formation. Analogously, bicyclobutane formation is suppressed in acyclic alkyl substituted butadienes.[10]

Product Studies. Each undeuterated enone was irradiated under conditions likely to give oxabicyclobutanes. Triplet sensitization was not investigated since the analogous bicyclobutanes are formed only from singlet state reactions of butadienes.[10b,11] Furthermore, bicyclobutanes and cyclobutenes only can and do form from π,π* excited states of butadienes. Most irradiations of enones **4–6** were therefore conducted through a Vycor filter to excite the π,π* states. In the case of compound **4**, π,π* excitation does successfully lead to oxetene **7**.[8]

Enone **4** was irradiated in pentane solution using a medium-pressure mercury arc and a Vycor filter. When 20% of the enone remained as determined by uv analysis, the products were oxetene **7**,[8] β,γ-unsaturated ketone **8**, and unidentified polymer in the approximate yields shown. Longer irradiation produced a 5:95 equilibrium between enone **4** and oxetene **7** followed by polymer formation. No other products were detected by nmr, ir, uv, and vpc analysis. At equilibrium the concentration of enone was high enough to absorb all light in the π,π* region of absorption. It was therefore possible to irradiate the enone for a much longer time than suggested by its initial rate of disappearance.



4 **7**, 70% **8**, 2%

This feature contributed to a large sensitivity for detection of an oxabicyclobutane in this system.

The product study for methyl isopropenyl ketone (**5**) was done in pentane as well as dodecane solution in order to check for volatile products boiling near pentane. In all studies using a Vycor filter no volatile products were detected by vpc analysis in greater than 1% yield. The only apparent products were polymers which were not investigated.

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(4) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).

(5) (a) L. E. Friedrich and R. A. Cormier, *J. Org. Chem.*, **35**, 450 (1970); (b) J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.*, **91**, 6534 (1969); (c) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967).

(6) (a) N. C. Yang and M. J. Jorgenson, *Tetrahedron Lett.*, 1203 (1964); (b) R. A. Schneider and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 2023 (1967); (c) R. S. Tolberg and J. N. Pitts, Jr., *ibid.*, **80**, 1304 (1958); (d) J. W. Coomber and J. N. Pitts, Jr., *ibid.*, **91**, 547 (1969).

(7) R. Srinivasan, *ibid.*, **85**, 4045 (1963).

(8) L. E. Friedrich and G. B. Schuster, *ibid.*, **91**, 7204 (1969).

(9) (a) R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, 3425 (1960); (b) D. D. Faulk and A. Fry, *J. Org. Chem.*, **35**, 364 (1970).

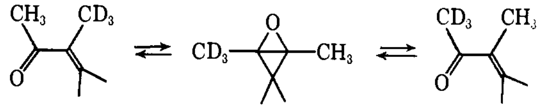
(10) (a) K. L. Crowley, *Tetrahedron*, **21**, 1001 (1965); (b) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966).

(11) W. G. Dauben and W. A. Spitzer, *J. Amer. Chem. Soc.*, **90**, 802 (1968).

In the gas phase the major photochemical reaction of acrolein (**6**) at 313 nm is decarbonylation with a quantum yield of *ca.* 0.01.[6d] No polymer was reported. In pentane solution, on the other hand, irradiation through Vycor gave only polymer. No carbon monoxide was detected when the reaction gases were exhausted into an evacuated ir cell and analyzed. No volatile products were detected by vpc.

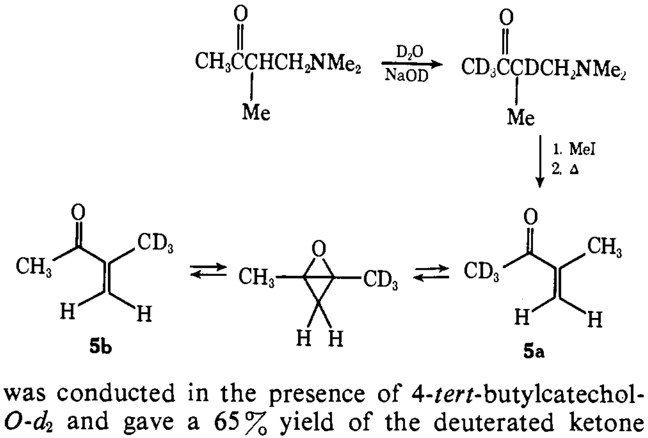
Synthesis. The desired position of isotopic labeling of enone **4** was dictated by its mass spectrum. Enone **4** showed a strong molecular ion at *m/e* 112 and a moderate fragmentation peak at *m/e* 97 corresponding to loss of a methyl radical. When enone **4** was treated with D_2O and base, the mass spectrum showed a molecular ion as expected at *m/e* 115 and the same fragmentation peak at *m/e* 97. The loss of methyl radical must therefore occur primarily if not solely at C-1.

Based on this information, enone **4a** was synthesized by alkylation of mesityl oxide with methyl-d_3 iodide.[12] Mass spectral analysis of isomer **4a** showed a molecular ion at *m/e* 115 and a loss of methyl radical at *m/e* 100. Oxabicyclobutane formation was therefore monitored by examination of the cation formed by loss of a methyl radical. If, on irradiation, the oxabicyclobutane was formed and fragmented to both isomers **4a** and **4b**, the cation formed by loss of the C-1 methyl would decrease in deuterium content. Starting with isomer **4a** enabled the analysis to detect interchange of the C-3 vinyl methyl and C-1 methyl. Starting with isomer **4b**, mass spectral analysis at best could have only shown interchange of the C-1 methyl with one or more of all the methyl groups retained in the fragmented cation. In addition isomer **4b** might have partially lost deuterium through enolization during reaction or isolation by preparative vpc. For these reasons isomer **4a** was prepared even though samples of compound **4b** were available.



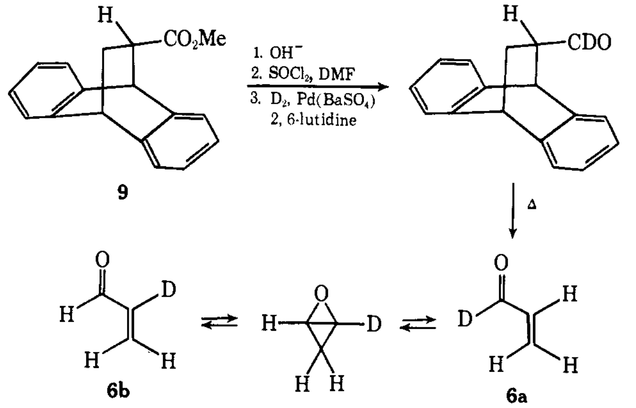
4a **4b**

Deuterated methyl isopropenyl ketone **5a** was synthesized by the route shown. The final pyrolysis was conducted in the presence of 4-*tert*-butylcatechol-*O*-d_2 and gave a 65% yield of the deuterated ketone after distillation. In this case nmr was used to detect the presence of isomer **5b** after irradiation of enone **5a**. Since there are only two methyl absorptions in the nmr spectrum of compound **5**, it was unnecessary to synthesize isomer **5b** in order to know which absorption corresponded to the C-3 vinyl methyl group.



5b **5a**

Acrolein-*1*-d_1 (**6a**) was synthesized by the following route starting with ester **9**.[13] The Rosenmund reduction was unusual since it was successfully done at room temperature and atmospheric pressure whereas normally elevated temperatures are required.[14]



9 **6b** **6a**

In order to isolate and purify small amounts of acrolein from the pentane solvent that was used in the irradiations, a method was devised to derivatize acrolein to its 2,4,6-trinitrophenylhydrazone. The method involved stirring the pentane solution with a second-phase solution of 2,4,6-trinitrophenylhydrazine[15] in acetonitrile. Following work-up and purifications, a minimum of 12 mg of acrolein in 10 ml of pentane could be isolated as its hydrazone and analyzed by nmr spectroscopy.

Results

A pentane solution of ketone **4a** was irradiated through Vycor. Two samples of the photolysis solution were withdrawn before the lamp was turned on. Also, four control samples of starting ketone **4a** in pentane were prepared as the photolysis progressed. When *ca.* 85% of ketone **4** had irreversibly reacted by vpc analysis, the photolysis was terminated. Initial samples, control samples, and a final sample of the reaction mixture were identically worked up and analyzed by mass spectral analysis (see Table I).

Table I. Deuterium Content[a] of Molecular Ion and Molecular Ion Minus Methyl for Enone **4a**, Irradiation in Pentane through Vycor

Sample	$M\cdot^+$	$M\cdot^+ - \text{Me}\cdot$	Order[b]
Control 1	2.993 ± 0.006	2.959 ± 0.007	3
Control 2	2.994 ± 0.005	2.963 ± 0.006	1
Control 3	2.985 ± 0.006	2.956 ± 0.006	5
Control 4	2.983 ± 0.009	2.951 ± 0.004	7
Start 1	2.985 ± 0.007	2.953 ± 0.006	2
Start 2	2.986 ± 0.006	2.954 ± 0.010	4
Final	3.077 ± 0.010	2.999 ± 0.010	6

[a] Errors are internal standard deviations with four degrees of freedom obtained by repetitively scanning the mass spectral ion cluster. [b] Order in which the samples were run on the mass spectrometer.

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(12) J. M. Conia, *Bull. Soc. Chim. Fr.*, **23**, 1392 (1956).

(13) P. D. Bartlett and F. A. Tate, *J. Amer. Chem. Soc.*, **75**, 91 (1953).

(14) E. Mosettig and R. Mozingo, *Org. React.*, **4**, 362 (1948).

(15) J. J. Blanksma and M. L. Wackers, *Recl. Trav. Chim. Pays-Bas*, **55**, 661 (1936).

Oxabicyclobutane formation would have been indicated by the decrease in deuterium content of the $M\cdot^+ - Me\cdot$ cation accompanied by the constant deuterium content of $M\cdot^+$. Actually, the deuterium content increased *ca.* 3% in both the $M\cdot^+ - Me\cdot$ and $Me\cdot^+$ ions. Even though these small increases appear to be real, we have no explanation for them and the results do not indicate oxabicyclobutane formation.

Using the four control and two starting values for total deuterium content of $M\cdot^+$ as a measure of random error, the standard one-tailed Student's *t* test at the 95% confidence level leads to the conclusion that if the external introduction of deuterium had not occurred, a minimum formation of *ca.* 0.6% oxabicyclobutane could have been detected. Since 1.22 mol of enone remained after 11.5 hr of irradiation, the maximum rate of oxabicyclobutane formation would be *ca.* 6.4×10^{-4} mmol/hr. This rate is smaller by a factor of *ca.* 4000 than the observed rate of oxetene formation.

Similar experiments were performed with added butadiene as a potential triplet quencher as well as experiments using a Pyrex filter (see Tables II and III).

Table II. Deuterium Content[a] of Molecular Ion and Molecular Ion Minus Methyl for Enone **4a**, Irradiation in Pentane through Vycor in the Presence of 1,3-Butadiene

Time, hr	$M\cdot^+$	$M\cdot^+ - Me\cdot$
0	2.977 ± 0.008	2.938 ± 0.012
12	2.977 ± 0.017	2.922 ± 0.009
26	2.980 ± 0.13	2.937 ± 0.009

[a] Errors are internal standard deviations with two degrees of freedom.

Table III. Deuterium Content[a] of Molecular Ion and Molecular Ion Minus Methyl for Enone **4a**, Irradiation in Pentane through Pyrex

Time, hr	$M\cdot^+$	$M\cdot^+ - Me\cdot$
0	2.994 ± 0.005	2.963 ± 0.014
47	3.005 ± 0.012	2.979 ± 0.009

[a] Errors are internal standard deviations with two degrees of freedom.

The purpose of adding a triplet quencher was to hopefully eliminate triplet pathways which might have possibly led to the external introduction of deuterium. Oxetene formation did not stop when butadiene was added and, as reported previously,[8] oxetane **7** did not form when a Pyrex filter was used. In these experiments no statistically significant increase or decrease was found in the deuterium content of the two ions.

Ketone **5a** was irradiated in pentane solution with both Vycor and Pyrex filters. The remaining enone was isolated by preparative vpc, and using the vinyl hydrogens of the enone as a standard for two hydrogens, the hydrogen contents in Tables IV and V were calculated. Here as with enone **4a** no oxabicyclobutane formation was observed since the number of hydrogens in the C-3 vinyl methyl group did not decrease. In order to obtain a measure of the random error in the nmr integral ratios, use was made of three independent nmr calculated hydrogen contents for the C-3 vinyl methyl group of starting enone **5a**. The standard deviation of the three values whose average was 3.011 was 0.035 with two degrees of freedom. Use of the one-tailed Student's *t* test at the 95% confidence level showed that a minimum of 7% oxabicyclobutane could have been detected.

Table IV. Hydrogen Contents[a] for Methyl Groups of Enone **5a**, Irradiation in Pentane through Vycor

Time, hr	C-1 methyl	DF[b]	C-3 vinyl methyl	DF[b]
0	0.372 ± 0.004	11	3.02 ± 0.02	11
4	0.382 ± 0.012	6	3.12 ± 0.02	6

[a] Errors are internal standard deviations of repetitive scans of the nmr integral. [b] Internal degrees of freedom.

Table V. Hydrogen Contents[a] for Methyl Groups of Enone **5a**, Irradiation in Pentane through Pyrex

Time, hr	C-1 methyl	C-3 vinyl methyl
0	0.376 ± 0.004	3.04 ± 0.02
22	0.354 ± 0.006	3.08 ± 0.02

[a] Errors are internal standard deviations with seven degrees of freedom from repetitive scans of the nmr integral.

The nmr spectrum of the hydrazone of deuterated acrolein **6a** in DMSO solution showed no absorption for the C-1 hydrogen of acrolein. Sequential addition of undeuterated hydrazone to the nmr tube showed that a conservative minimum of 2% hydrogen could have been detected at C-1. Acrolein **6a** was irradiated in pentane through Vycor until *ca.* 60% remained. Nmr spectral analysis of the 2,4,6-trinitrophenylhydrazone showed no hydrogen at C-1 in acrolein. The minimum detectable amount of oxabicyclobutane formation was 4%.

Conclusions

The lack of oxabicyclobutane formation is surprising in these systems. A strong defense cannot be made for a fast intersystem crossing or internal conversion which depopulates an oxabicyclobutane forming π,π^* singlet state. The π,π^* singlet state must live long enough to form at least oxetene **7** since the oxetene is only formed on π,π^* irradiation and is not quenched when butadiene is present. The lack of quenching, though, cannot rule out oxetene formation from a short-lived triplet state.

There appears to be a fundamental thermodynamic reason for lack of even small yields of oxabicyclobutanes since bicyclobutanes can be photochemically formed from butadienes. Because of the tremendous endothermicity associated with the hypothetical conversion of the first excited state of acrolein to the first excited state of oxabicyclobutane, the electronic reaction coordinate must enter the ground-state manifold of oxabicyclobutane before or during the final formation of the σ bonds. This same feature is also recognized to be true in the photochemical formation of bicyclobutanes[16,17] and cyclobutenes[18] from butadienes.

Assuming that the resonance energies are similar for butadiene and acrolein and that the ring strains are the same[19] for oxabicyclobutanes and bicyclobutanes, use

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(16) R. Srinivasan, *J. Amer. Chem. Soc.*, **90**, 4498 (1968).

(17) W. G. Dauben and J. S. Ritscher, *ibid.*, **92**, 2926 (1970).

(18) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969).

(19) The strains of three-, four-, five-, and six-membered rings either lacking or containing an oxygen atom are the same within 1 kcal/mol: A. S. Pell and G. Pilcher, *Trans. Faraday Soc.*, **61**, 71 (1965).

of Klages' method for heats of combustion or Franklin group equivalents for heats of formation show that the conversion of ground-state acrolein to oxabicyclobutane is *ca.* 20–30 kcal/mol *more* endothermic than the analogous conversion of butadiene to bicyclobutane. The higher relative energy of oxabicyclobutane to acrolein possibly prohibits the successful entrance of photochemical intermediates into the oxabicyclobutane ground-state manifold. Whether or not this is the correct reason for lack of oxabicyclobutane formation, this basic thermochemical feature must always be considered when comparing the chemistry of carbocyclic and heterocyclic compounds containing oxygen. Other explanations which are phenomenological in nature could also be examined, but they all suffer from the lack of experimental facts which must be gathered in further studies.

The lack of oxabicyclobutane formation with acyclic enones **4**–**6** eliminates the possibility that reversible oxabicyclobutane formation provides an energy wasting step in their overall reaction schemes. Such energy wasting processes have been considered in various cyclic enones.[2] To date, however, the only photochemical reaction which interchanges the C-3 vinyl and C-1 substituents of α,β-unsaturated carbonyl compounds is that of purpurogallin.[3] Either unsymmetrical oxabicyclobutanes do not fragment to both possible α,β-unsaturated carbonyl compounds or oxabicyclobutanes are not photochemically formed from enones as frequently as the literature suggests.[2] We are continuing other studies that will evaluate the probable, but unproven premise that oxabicyclobutanes do, at least, fragment to enones.

Experimental Section

General. Nmr spectra were taken on Varian A-60 or Jeolco C-60-HL spectrometers. Uv spectra were taken on a Cary 11 MS spectrometer. Ir spectra were taken on a Perkin-Elmer 137 spectrometer. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6E spectrometer. Vpc work was done on Perkin-Elmer 900, Hewlett-Packard 700, or Aerograph A-90P instruments. Melting points were determined on a calibrated Fisher-Johns melting point apparatus. Boiling points are uncorrected. The 450-W lamp used in irradiations was a Hanovia medium-pressure mercury arc. The following vpc columns were used: (A) di-*n*-decyl phthalate on Chromosorb A, 20 ft × $^1/_8$ in.; (B) SE-30 on Anakrom, 6 ft × $^1/_4$ in.; (C) QF-1 on Anakrom, 10 ft × $^1/_4$ in.; (D) SE-30 on Chromosorb W, 6 ft × $^1/_8$ in.; (E) FFAP on Chromosorb W, 10 ft × $^1/_8$ in.; (F) QF-1 on Firebrick, 10 ft × $^1/_4$ in.; (G) QF-1 on firebrick, 15 ft × $^1/_4$ in.

Irradiation of 3,4-Dimethyl-3-penten-2-one (4) through Vycor. Nitrogen was bubbled through a solution of 2.03 g (18.2 mmol) of 3,4-dimethyl-3-penten-2-one in 230 ml of Fisher Certified pentane for 2 hr. Uv analysis of the photolysis solution (dilution, 20 μl to 10.00 ml) at 237 nm showed an absorbance of 1.32. After irradiating the solution under nitrogen through a Vycor filter with a 450-W lamp for 1 hr, the uv absorption of the solution at 237 nm (dilution as above) decreased to 1.12. After a total of 9 hr of irradiation the uv absorption remained constant at 0.07. Heating a 20.0-ml portion of the solution at reflux for 46 hr gave an increase in the uv absorption to 0.91.

In a similar experiment, a solution of 0.112 g (1.00 mmol) of 3,4-dimethyl-3-penten-2-one (**4**) was prepared in 10 ml of Fisher Certified pentane. The solution was added to a 10-ml cylindrical (15-mm i.d.) quartz tube and degassed with three freeze–thaw cycles at 5 × 10^{-2} mm. Irradiation with Vycor filtered light *ca.* 4 cm from a 450-W lamp through an immerson well in a beaker of distilled water for 4 hr followed by vacuum transfer gave a clear colorless pentane solution. Analysis of the distillate by vpc (column A, 120°) showed an *ca.* 2% yield of 3,4-dimethyl-4-penten-2-one identified by coinjection with an authentic sample. Comparison with an equal volume injection of the starting solution of ketone in pentane indicated that *ca.* 90% of the original ketone was present. Uv analysis of the distillate at 237 nm indicated that *ca.* 20% of the original ketone was present. Heating a portion of the distillate at reflux for 62 hr resulted in the increase in the uv absorption at 237 nm to *ca.* 85% of its initial value.

Vpc analysis (column B, 50°) with the injector and detector temperatures at 90 and 100°, respectively, of the distillate showed a peak with short retention time. Collection (with detector filaments off) of the peak in a Dry Ice–acetone trap gave 2,3,4,4-tetramethyloxetene: uv (hexane) end absorption 215 nm (ϵ ~5000); ir (CCl_4) 1731, 1690, 1460, 1431, 1329, 1318, 1295, 1271, 1193, 1049, 730 cm^{-1}; nmr (CCl_4) δ 1.75 (3 H, q J = 1 Hz), 1.50 (3 H, q, J = 1 Hz), 1.39 (6 H, s).

Irradiation of 3,4-Dimethyl-3-penten-2-one (4) through Vycor in the Presence of Butadiene. Nitrogen was bubbled for 2 hr through a solution of 1.00 g (8.92 mmol) of 3,4-dimethyl-3-penten-2-one in 230 ml of Fisher Certified pentane containing *ca.* 0.5 g of butadiene. Analysis of the uv spectrum of the solution at 217 nm showed that the concentration of butadiene was *ca.* 0.03 *M*. Irradiation through Vycor with a Hanovia low-pressure mercury arc lamp for 4 hr caused the initial uv absorption at 237 nm to decrease from 1.21 to 0.40. Vpc analysis (column C, 130°) using tetralin as an internal standard showed 710 mg of starting enone.

Irradiation of 3,4-Dimethyl-3-penten-2-one (4) through Pyrex. Nitrogen was bubbled through 2.95 g (26.3 mmol) of 3,4-dimethyl-3-penten-2-one in 230 ml of Mallinckrodt Spectrar grade hexane for 8 hr. The solution was irradiated under nitrogen with a 450-W lamp through a Pyrex filter. After 35 hr, the uv absorption at 238 nm had not changed. Work-up gave *ca.* 2 g of an oil whose nmr and ir spectra were identical with the starting material.

Irradiation of Methyl Isopropenyl Ketone (5) through Vycor. A quartz tube containing 10 ml of a 0.136 *M* solution of freshly distilled methyl isopropenyl ketone[20] in Fisher Certified pentane was degassed by three freeze–thaw cycles at 5 × 10^{-2} mm. The tube was irradiated through a standard immersion well with Vycor-filtered light *ca.* 6 cm from a 450-W lamp in a beaker of distilled water for cooling purposes. After 8 hr the reaction solution was bulb-to-bulb distilled at 5 × 10^{-2} mm leaving 47 mg of residue: nmr ($CDCl_3$) δ 2.50–2.10 (3 units), 1.90–1.81 (5). Vpc analysis (column A, 110°) showed *ca.* 50% unreacted enone and four longer retention time peaks with total area less than 1% of unreacted enone.

A similar experiment was done in Eastman-Kodak Spectro grade dodecane. After 80% conversion nitrogen was bubbled through the solution. Volatile materials were condensed in a liquid nitrogen cold trap. Vpc analysis (column D, 45°) showed unreacted enone and a shorter retention time material in an area ratio of *ca.* 100:1. Nmr analysis of the condensed products showed starting material only.

Irradiation of Methyl Isopropenyl Ketone (5) through Pyrex. Nitrogen was bubbled for 2 hr through a solution of 1.40 g (16.7 mmol) of methyl isopropenyl ketone in 230 ml of Fisher Certified pentane. The solution was irradiated through a Pyrex filter with a 450-W lamp under nitrogen. After 20 hr the uv absorption of the solution at 217 nm was 90% of the original. Distillation of the pentane gave a residue whose nmr showed only starting enone and residual pentane.

Irradiation of Acrolein through Vycor. A quartz tube containing 10 ml of a 0.150 *M* solution of vacuum-distilled acrolein in Fisher Certified pentane was degassed by three freeze–thaw cycles at 5 × 10^{-2} mm. The tube was irradiated through a standard immersion well with Vycor-filtered light *ca.* 8 cm from a 450-W lamp in a beaker of distilled water for cooling purposes. After 30 min, bulb-to-bulb distillation at 5 × 10^{-2} mm and vpc analysis (column E, 70°) showed a 30% disappearance of acrolein and no other peaks.

In a similar experiment in heptane solution, the tube was irradiated for 1 hr and then cooled to −78° and attached to a evacuated 10-cm gas ir cell. Small peaks were seen consistent with heptane, but no CO absorptions were seen at 2119 and 2170 cm^{-1}.[21]

Treatment of 3,4-Dimethyl-3-penten-2-one with D_2O and Base. A two-phase mixture of 10.0 g (89.0 mmol) of 3,4-dimethyl-3-penten-2-one,[22] 100 ml of CCl_4, 6.00 g (56.5 mmol) of anhydrous

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[22] J. M. Conia, *Bull. Soc. Chim. Fr.*, **17**, 537 (1950).

sodium carbonate, and 53.6 g (2.69 mmol) of D_2O was magnetically stirred and heated at 80°. After 24 hr the D_2O layer was washed with two portions of CCl_4 and the combined CCl_4 layers were dried over anhydrous sodium sulfate. Distillation gave 8.10 g (81%) of deuterated enone **4b**: bp 67–70° (60 mm); nmr (CCl_4) δ 2.15 (0.98 H, m), 1.84 (6 H, s), 1.75 (3 H, s); nmr (PhH) δ 1.96 (0.98 H, m), 1.79 (3 H, q, J = 1 Hz), 1.58 (3 H, q, J = 1 Hz), 1.48 (3 H, s); mass spectrum (20 eV) *m/e* (rel intensity) 115 (100), 97 (76). The undeuterated enone showed in the mass spectrum (20 eV) *m/e* (rel intensity) 112 (89), 97 (59).

3,4-Dimethyl-3-penten-2-one-*3-methyl-d*$_3$ (4a). A solution of 29.4 g (0.300 mol) of mesityl oxide and 29.0 g (0.200 mol) of methyl-d_3 iodide in 100 ml of dry ether was added dropwise with stirring under nitrogen over a period of 4 hr to 13.4 g (0.320 mol) of NaH (55% mineral oil dispersion) in 100 ml of dry ether. After *ca.* 2 hr gas evolution ceased and water was added until frothing no longer occurred. The mixture was added to 100 ml of water, and the organic layer was washed with water and 10% aqueous HCl and dried over $MgSO_4$. Spinning band distillation gave 6.5 g (28%) of deuterated enone **4a**: bp 54–57° (20 mm); nmr (CCl_4) δ 2.15 (3 H, s), 1.85 (3 H, s), 1.76 (3 H, s); nmr (PhH) δ 1.98 (3 H, s) 1.79 (3 H, s), 1.46 (3 H, s); mass spectrum (20 eV) *m/e* (rel intensity) 115 (100), 100 (55).

4-*N*,*N*-Dimethylamino-3-methylbutan-2-one-*1,1,1,3-d*$_4$. A mixture of 0.50 g (22 g-atoms) of sodium metal which had been treated with 50 ml of D_2O was stirred under nitrogen for 1.5 hr with 24.0 g (186 mmol) of 4-*N*,*N*-dimethylamino-3-methylbutan-2-one.[20] The mixture was saturated with NaCl and extracted with six 25-ml portions of ether. The combined ether solutions were dried over $MgSO_4$ and evaporated. The residual amino ketone was treated with a second portion of NaOD in D_2O, and after work-up distillation gave 20.1 g (82%) of deuterated amino ketone: bp 52–54° (12 mm); nmr (CCl_4) δ 0.96 (3 H, s), 2.05 (1 H, d, J = 12 Hz), 2.13 (6 H, s), 2.48 (1 H, d, J = 12 Hz). The undeuterated amino ketone had nmr (CCl_4) δ 0.95 (3 H, d, J = 6 Hz), 2.02 (3 H, s), 2.12 (6 H, s), 2.22–2.79 (3 H, m).

Methiodide Salt of 4-*N*,*N*-Dimethylamino-3-methylbutan-2-one-*1,1,1,3-d*$_4$. A 28.4-g (0.200 mol) portion of methyl iodide was added dropwise to a solution of 20.0 g (0.15 mol) of 4-*N*,*N*-dimethylamino-3-methylbutan-2-one-*1,1,1,3-d*$_4$ in 10 ml of anhydrous EtOH at 0°. The mixture was stirred for 1 hr at 0°, 40 ml of dry ether was added, and the precipitate was suction filtered and washed with ether. The solid was dried at 0.1 mm to give 40.1 g (96%) of the methiodide salt of the deuterated amino ketone: mp >290°; nmr (D_2O, external TMS in $CDCl_3$) δ 0.96 (3 H, s), 2.62 (2 H, d, J = 11 Hz), 2.86 (9 H, s), 2.94 (2 H, d, J = 11 Hz).

4-*tert*-Butylcatechol-*O-d*$_2$. A 16.6-g (0.10 mol) portion of 4-*tert*-butylcatechol was added to a solution of 1 ml of PCl_3 in 40 g of D_2O. The mixture was stirred for 5 min and extracted with three 40-ml portions of ether. The combined ether solutions were dried over $MgSO_4$ and the solvent was evaporated on a rotary evaporator. The resulting material was dried at 0.1 mm to give 16.0 g (96%) of deuterated catechol: nmr (CCl_4) δ 1.11 (9 H, s), 6.22–6.72 (3 H, m).

Methyl-*1,1,1-d*$_3$ Isopropenyl Ketone (5a). A dry mixture of 20.0 g (73 mmol) of the methiodide salt of 4-*N*,*N*-dimethylamino-3-methylbutan-2-one-*1,1,1,3-d*$_4$ and 6.0 g (36 mmol) of 4-*tert*-butylcatechol-*O-d*$_2$ was heated at 230° under a steady stream of nitrogen for *ca.* 30 min until no more gas was evolved. The volatile products which were collected in a Dry Ice–acetone trap were distilled on a 18-in. spinning band to give 4.10 g (65%) of deuterated methyl isopropenyl ketone: bp 45–48° (130 mm); nmr (CCl_4) δ 1.81 (3 H, s), 2.15 (0.35 H, m), 5.69 (1 H, s), 5.84 (1 H, s).

9,10-Dihydro-9,10-ethanoanthracene-11-carboxylic Acid (9). A mixture of 30.0 g (0.134 mol) of 9,10-dihydro-9,10-ethanoanthracene-11-carboxlic acid methyl ester,[13] 30.0 g (0.536 mol) of 85% KOH pellets, 100 ml of water, and 400 ml of MeOH was stirred at reflux for 4 hr. The cooled solution was neutralized with 6 *M* aqueous HCl and the precipitate was filtered and washed with water. Recrystallization from hexane gave 27.5 g (82%) of the acid: mp 191–193° [lit.[23] mp 189°]; ir ($CHCl_3$) 1708 cm^{-1}; nmr ($CDCl_3$) δ 1.88–2.30 (2 H, m), 2.70–3.04 (1 H, m), 4.30 (1 H, t, J = 3 Hz), 4.63 (1 H, d, J = 1.6 Hz), 6.95–7.40 (8 H, m), 8.70 (1 H, broad singlet, exchangeable with D_2O).

9,10-Dihydro-9-10-ethanoanthracene-11-carbonyl Chloride. A 19.6-g (0.165 mol) portion of thionyl chloride was added to a solution of 27.5 g (0.110 mol) of 9,10-dihydro-9,10-ethanoanthracene-11-carboxylic acid and *ca.* 1 ml of DMF[24] in 350 ml of CH_2Cl_2. While protected with a $CaCl_2$ tube, the solution was stirred for 4 hr at which time the acid carbonyl absorption at 1708 cm^{-1} was completely replaced by the acid chloride carbonyl absorption at 1805 cm^{-1}. Volatile materials were removed on a rotary evaporator followed by the addition and rotary evaporation of three successive 60-ml portions of benzene. The resulting oil was crystallized from hexane to give 23 g (78%) of the acid chloride: mp 120–123° [lit.[25] mp 72–75°]; ir ($CHCl_3$) 1805 cm^{-1}; nmr ($CDCl_3$) δ 1.82–2.15 (2 H, m), 3.01–3.32 (1 H, m) 4.22 (1 H, t, J = 2.6 Hz), 4.75 (1 H, d, J = 2 Hz), 6.90–7.30 (8 H, m).

9,10-Dihydro-9,10-ethanoanthracene-11-carboxaldehyde-*13-d*$_1$. A mixture of 7.00 g (26.0 mmol) of 9,10-dihydro-9,10-ethanoanthracene-11-carbonyl chloride, 3.1 g (39 mmol) of 2,6-lutidine, and 0.35 g of 10% Pd on $BaSO_4$ in 50 ml of benzene was stirred under 1 atm of D_2 gas for 9 hr. As the reaction progressed, a white solid precipitated from the solution. A total of 560 ml (25 mmol) of gas was absorbed. The mixture was filtered and the benzene solution was washed with 1 *M* aqueous HCl and dried over Na_2SO_4. Rotary evaporation of the solvent and chromatography on 200 g of Merck silica gel gave 3.5 g of a white solid which eluted with 10% ether in benzene. Recrystallization from hexane gave 3.3 g (57%) of the deuterated aldehyde: mp 95–97° [lit.[26] mp (undeuterated) 95–96°]; ir (CCl_4) 2030, 1710 cm^{-1}; nmr ($CDCl_3$) δ 1.82–2.22 (2 H, m), 2.44–2.80 (1 H, m), 4.29 (1 H, t, J = 2.5 Hz), 4.55 (1 H, d, J = 2.1 Hz), 6.82–7.38 (8 H, m). The undeuterated aldehyde also showed an absorption at δ 9.25 (1 H, d, J = 1.5 Hz).

Acrolein-*1-d*$_1$ (6a). A mixture of 2.34 g (10.0 mmol) of 9,10-dihydro-9,10-ethanoanthracene-11-carboxaldehyde-*13-d*$_1$ and 0.50 g (4.6 mmol) of hydroquinone was heated at 310° with a Wood's metal bath. The volatile products were removed with a stream of nitrogen and condensed in a liquid nitrogen trap. Bulb-to-bulb distillation of the condensed product at 5×10^{-2} mm gave 0.20 g (35%) of acrolein-*1-d*$_1$. Vpc analysis (column E, 70°) showed that the material was 99% pure.

The 2,4,6-trinitrophenylhydrazone was prepared whose nmr in DMSO showed no absorption at 5.64 ppm downfield from DMSO. Addition of 2% undeuterated acrolein 2,4,6-trinitrophenylhydrazone clearly showed absorption at 5.64 ppm.

Acrolein 2,4,6-Trinitrophenylhydrazone. A solution of 40 μl of perchloric acid in CH_3CN (0.5 g of 70% aq $HClO_4$ in 5 ml of CH_3CN) and 0.110 g (0.455 mmol) of 2,4,6-trinitrophenylhydrazine in 5 ml of acetonitrile was added to 18 mg (0.75 mmol) of acrolein in 10 ml of pentane. The mixture was stoppered and stirred for 1 hr, the solvents were removed on a rotary evaporator, and the residue was dissolved in *ca.* 0.5 ml of warm acetonitrile and chromatographed on 10 g of Woelm neutral alumina (activity II). The column was eluted with *ca.* 30 ml of 10% ether in benzene, the solvent was evaporated, and the residue was recrystallized from 95% aqueous ethanol to give 63 mg (81%) of acrolein 2,4,6-trinitrophenylhydrazone: mp 157–159°; nmr (DMSO, ppm downfield from DMSO) δ 9.43 (1 H, broad singlet), 6.25 (2 H, s), 5.64 (1 H, d, J = 7.9 Hz), 3.69 (1 H, 5 peaks, spacing *ca.* 9 Hz), 3.19 (1 H, d, J = 18 Hz), 3.19 (1 H, d, J = 9 Hz).

Anal. Calcd for $C_9H_7N_5O_6$: C, 38.44; H, 2.51; N, 24.91. Found: C, 38.32; H, 2.43; N, 24.71.

Irradiation of 3,4-Dimethyl-3-penten-2-one-*3-methyl-d*$_3$ (4a) through Vycor. Nitrogen was bubbled for 2 hr through a solution of 1.00 g (8.70 mmol) of 3,4-dimethyl-3-penten-2-one-*3-methyl-d*$_3$ (**4a**) in 230 ml of Fisher Certified pentane. Two 5-ml portions of the solutions were withdrawn and saved. The solution was irradiated with a 450-W lamp through Vycor for 11.5 hr at which time vpc analysis (column F, 140°) with tetralin as an added internal standard showed 86% disappearance of starting enone. During the irradiation four 30-μl control samples of starting enone were prepared in 5 ml of pentane. The two starting samples, four control samples, and final reaction mixture were similarly worked up by solvent evaporation on a rotary evaporator and preparative vpc isolation of starting enone (column G, 150°). Each sample was analyzed for deuterium by mass spectral analysis (see Table I).

Irradiation of Enone 4a through Vycor in the Presence of Butadiene. Nitrogen was bubbled for 2 hr through a solution of 1.00 g (8.70 mmol) of enone **4a** in 230 ml of Fisher Certified pentane which contained *ca.* 0.5 g of butadiene. After deoxygenation,

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[25] Ciba Ltd., Belgian Patent 610863 (1962); *Chem. Abstr.*, **57**, 15034*b* (1962).

[26] F. Weiss and R. Rusch, *Bull. Soc. Chim. Fr.*, **31**, 550 (1964).

uv analysis at 217 nm showed the solution to be *ca.* 0.03 *M* in butadiene. The solution was irradiated with a low-pressure mercury arc lamp under nitrogen for 26 hr at which time vpc analysis (column C, 130°) with tetralin as in internal standard showed 80% disappearance of starting enone. Samples were withdrawn at 0, 12, and 26 hr and the solvent was evaporated and unreacted enone was isolated by preparative vpc (column G, 140°). The recovered enones were analyzed for deuterium by mass spectral analysis (see Table II).

Irradiation of Enone 4a through Pyrex. Nitrogen was bubbled for 2 hr through a solution of 750 mg (6.51 mmol) of enone **4a** dissolved in 230 ml of Fisher Certified pentane. A 7.5 ml sample was removed and saved. The remaining solution was irradiated with a 450-W lamp under a nitrogen atmosphere for 47 hr. Vpc analysis (column C, 130°) with tetralin as an internal standard showed 30% disappearance of starting enone. The solvent was evaporated from the starting sample and final solution, and enone was isolated by preparative vpc (column G, 140°). Analysis for deuterium content by mass spectroscopy gave the results in Table III.

Irradiation of Methyl-*1,1,1-d*$_3$ Isopropenyl Ketone (5a) through Vycor. Nitrogen was bubbled for 2 hr through a solution of 0.750 g (8.60 mmol) of enone **5a** in 230 ml of Fisher Certified pentane. The solution was irradiated through Vycor with a 450-W lamp for 4 hr (*ca.* 65% reaction). The solution was cooled to −78° and decanted from the resulting solid. The solvent was distilled through a 20 × 1.5 cm Vigreux column and the residue was subjected to preparative vpc (column G, 130°) to isolate unreacted enone. Starting and unreacted enone were analyzed by nmr and gave the results in Table IV.

Irradiation of Enone 5a through Pyrex. Enone **5a** was irradiated under the same conditions as through Vycor except a Pyrex filter was used. After 22 hr, unreacted enone was isolated by distillation of the solvent followed by preparative vpc collection (column G, 130°) and analyzed with starting enone by nmr spectroscopy for deuterium scrambling (see Table V).

Reproducibility of Nmr Integral Ratios. Three independent nmr spectra were taken of the same sample of deuterated enone **5a**. Using the vinyl hydrogen as a standard for two protons, the hydrogen contents of C-1 were calculated to be 3.038, 2.972, and 3.024 in the three samples. Ratios of integrals were calculated by a nonlinear least-squares solution of the equation, $R = y/x$, allowing for random error in both y and x.

Irradiation of Acrolein-*1-d*$_1$ (6a) through Vycor. A quartz tube containing 10 ml of a 0.175 *M* solution of acrolein-*d*$_1$ (**6a**) in Fisher Certified pentane was degassed by three freeze–thaw cycles at 5 × 10^{-2} mm. The tube was irradiated through Vycor with a 450-W lamp with the tube and quartz immersion well in a beaker of distilled water for cooling purposes. After 60 min, bulb-to-bulb distillation and vpc analysis (column E, 70°) showed 40% disappearance of acrolein. The 2,4,6-trinitrophenylhydrazone was prepared and analyzed by nmr in DMSO.

Mass Spectral Analyses for Deuterium Content. The mass spectrometer was operated with exit and detector slits wider than the width of the ion beam so that flat-topped peaks were produced. Each isotopic cluster was scanned repetitively to increase the internal degrees of freedom. The heights of the ion peaks in an isotopic cluster were processed by a least-squares computer program that minimized the weighted residuals of the peak intensities. Observed natural abundance ratios of undeuterated samples were used to correct for M:M + 1:M + 2 contributions. Peak heights obtained from different amplification channels of the Visicorder output were weighted accordingly.

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Wavelength-Dependent Photochemistry of 2-Aroyl-3-aryl-2*H*-azirines. Mechanistic Studies

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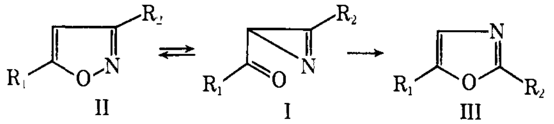
Abstract: Absorption of radiation by 2-(1′-naphthoyl)-3-phenyl-2*H*-azirine (Ie) in its long wavelength absorption band (λ_{max} 304 nm) results in phototransformation only to 5-(1′-naphthyl)-3-phenylisoxazole (IIe) while absorption in the short wavelength band (λ_{max} 238 nm) produced 5-(1′-naphthyl)-3-phenyloxazole (IIIe) and IIe in a 3:1 ratio. Intermediate ratios of IIe and IIIe were found in the 275- to 285-nm region of overlap of the two band systems. Emission spectroscopy, sensitization, and quenching studies, examination of other systems, and extended Hückel molecular orbital calculations support the earlier hypothesis that a higher energy state associated with the nitrogen n,π* transition leads to azirine C–C bond cleavage and subsequent rearrangement to oxazole while a lower energy excited state associated with the carbonyl n,π* transition causes electronic reorganization that promotes concerted rearrangement of azirine to isoxazole.

In two previous publications[1] it was reported that the photochemical behavior of 2-aroyl-3-aryl-2*H*-azirines Ia and Ib was affected in an exceptional manner by the wavelength of irradiation. It was shown, for instance, that solutions of Ia or Ib when irradiated with 313-nm or shorter wavelength radiation in the main body of their ultraviolet spectra are quantitatively converted to the corresponding oxazoles IIIa and IIIb, respectively. On the other hand, irradiation with 334-nm radiation near the long wavelength edge of the absorption spectra of the azirines produced the isoxazoles IIa and IIb almost exclusively. The long wavelength ultraviolet absorption end of Ib in ether solution showed



a, R$_1$ = R$_2$ = Ph
b, R$_1$ = Ph; R$_2$ = *p*-C$_6$H$_4$-OMe
c, R$_1$ = Ph; R$_2$ = Me
d, R$_1$ = Me; R$_2$ = Ph
e, R$_1$ = 1′-C$_{10}$H$_7$; R$_2$ = Ph

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[1] E. F. Ullman and B. Singh, *J. Amer. Chem. Soc.*, **88**, 1844 (1966); B. Singh and E. F. Ullman, *ibid.*, **89**, 6911 (1967).