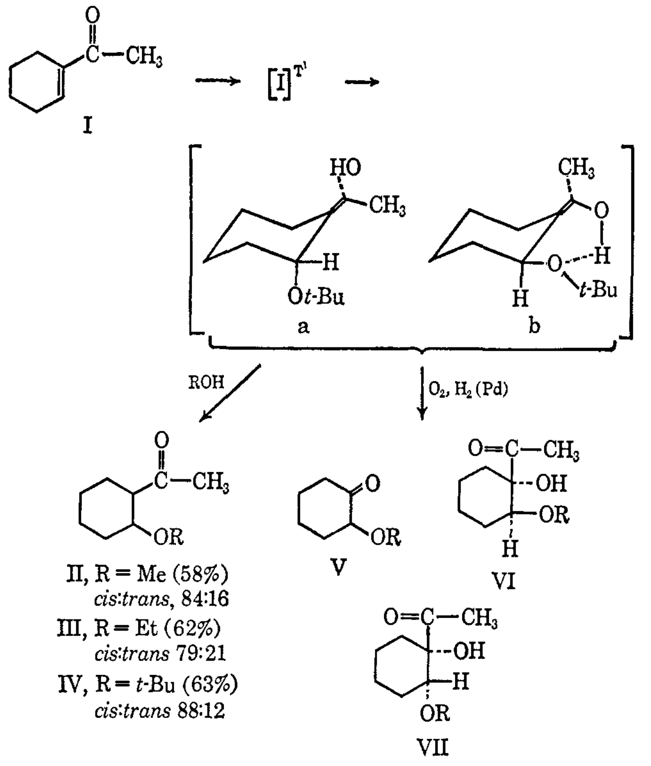

that one is much longer lived than the other. It is reasonable to assume that the longer-lived enol (b) has the hydrogen-bonded structure shown, while the short-lived isomer (a) exists predominantly in the conformation having an axial *t*-butoxy group.[7] Attack on b by oxygen would be expected to be relatively nonselective while that on a should be primarily axial in direction. The difference in the VI:VII ratio between the direct and indirect oxygenation experiments is in accord with these conclusions: a gives mainly VI and b gives roughly equivalent amounts of VI and VII.

The nmr spectrum of a freshly irradiated solution of I in *t*-butyl alcohol exhibits a rather intense singlet at τ 1.05. After the solution had been warmed to 80–85° for 2 hr its spectrum no longer possessed that signal. Moreover, oxygenation followed by hydrogenation of the solution no longer afforded VI or VII. The τ 1.05 signal would thus appear to be due to the hydroxyl proton of b. It is tentatively assumed that ketonization of a occurs sufficiently rapidly that it was virtually complete by the time the nmr spectrum could be obtained.

The use of acetophenone as a photosensitizer at concentrations such that it absorbed over 90% of incident light did not appreciably alter the rate of disappearance of I. Attempts to quench the reaction with piperylene or oxygen were unsuccessful, and it must therefore be concluded that a rather short-lived triplet of I is responsible for the reaction. The same products and ratios were obtained using either a broad-spectrum light source with Pyrex filters or a 2537-A resonance lamp with quartz. This suggests that initial $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ excitation leads to a common excited state. This product-forming state is almost certainly the $\pi \rightarrow \pi^*$ triplet since the directionality of the dipole in that triplet appears to be in better accord with the observed directionality of alcohol addition. Moreover, $n \rightarrow \pi^*$ triplets have been observed to be active in hydrogen-abstraction processes,[9] and no products attributable to this were observed in experiments with either I or 1-butyrylcyclohexene. The latter substrate gave solvent addition products analogous to IV but was not observed to undergo a competing type II cleavage.

The possibility that a triplet-derived intermediate, *trans*-1-acetylcyclohexene,[10] might be involved cannot be ruled out on the basis of these data. Alternatively, an oxabicyclobutane intermediate could be involved. The latter possibility seems remote, however, as its alcoholysis would be expected to give other products as well as those observed. Experiments designed to detect ground-state *trans*-1-acetylcyclohexene are in progress.

Acknowledgment. The authors are indebted to the National Institutes of Health (Grant GM 07861) for the financial support of this study. B. J. R. is grateful to Dr. G. J. Fonken for many helpful discussions.

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(9) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **88**, 2652 (1966); J. N. Pitts, Jr., L. D. Hess, E. J. Baum, E. A. Schuck, J. K. S. Wan, P. A. Leermakers, and G. Vesley, *Photochem. Photobiol.*, **4**, 305 (1965).

(10) Solvent addition to *trans*-cycloalkenes has been described by P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966). Other pertinent data are in press (private communication).

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Molecular Photochemistry. V. Photocycloaddition of Alkyl Ketones to Electron-Deficient Double Bonds[1,2]

Sir:

The bimolecular photocycloaddition of carbonyl compounds to olefins[3–5] (oxetane formation) is usually considered to involve electrophilic attack by the oxygen atom of the n,π^* triplet state[6] to form a biradical intermediate.[7–9] The evidence which implicates an electrophilic n,π^* triplet is: (a) the stereochemistry of the major adduct in oxetane formation is predicted from Markovnikov addition or consideration of the most stable biradical intermediate;[3–6] (b) the addition is retarded by triplet quenchers;[4,5] (c) the ketones which undergo smooth photochemical reduction through the n,π^* triplet generally add smoothly to olefins;[10,11] (d)

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(1) Part IV of this series: N. J. Turro and R. M. Southam, *Tetrahedron Letters*, 545 (1967).

(2) The authors thank the Air Force Office of Scientific Research (Grant AFOSR-1000-66) and the National Science Foundation (Grant NSF-GP-4280) for their generous support of this work.

(3) G. Büchi, C. F. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **78**, 876 (1956); **76**, 4327 (1954).

(4) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

(5) (a) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964); (b) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

(6) Compare the electrophilic character of hydrogen abstraction by the oxygen atom of the carbonyl n,π^* triplet: C. Walling and M. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965); A. Padwa, *Tetrahedron Letters*, 3465 (1964).

(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Co., New York, N. Y., 1965, p 209.

(8) J. F. Harris, Jr., and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 1553 (1962).

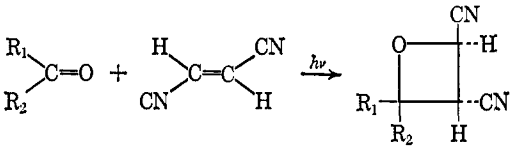
(9) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, p 132.

(10) Exceptions occur when the olefin has a lower triplet energy than the ketone, since energy transfer to the olefin becomes important.[4,11]

(11) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963).

irradiation of benzophenone in 2-butene yields the same mixture of isomeric oxetanes starting with either *cis* or *trans* olefin.[12] These results are consonant with simple models for the carbonyl n,π^* state[13,14] which predict an electrophilic attack on the π system of a C=C bond by oxygen which should occur preferentially in the plane of the carbonyl group and thereby produce a biradical (irrespective of the multiplicity of the n,π^* state) since the orbitals which must form the C–C bond in the oxetane are orthogonal to each other immediately after the C–O bond is formed. The simple MO model for the n,π^* state predicts an electron-rich π system above and below the plane of the carbonyl function. We wish to report results on oxetane formations which appear to involve *nucleophilic attack by the n,π^* singlet state and which do not require a long-lived biradical intermediate.*

Irradiation[15] of acetone, 2-pentanone, 2-hexanone, cyclopentanone, and cyclohexanone in the presence of *trans*-1,2-dicyanoethylene (**2**) results in the stereospecific formation of oxetanes in good yield.[16] Sensitized isomerization of **2** to *cis*-1,2-dicyanoethylene also occurs, but at a rate slower, in general, than the cycloaddition reaction.

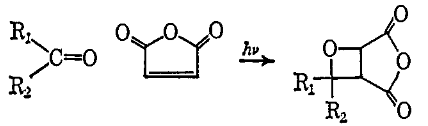


(1)

1a–c **2** **3a–c** (53–89%)

a, $R_1 = R_2 = CH_3$; **b**, $R_1R_2 = -(CH_2)_4-$; **c**, $R_1R_2 = -(CH_2)_5-$

Oxetanes are also formed in fair to good yield when solutions of maleic anhydride in alkyl ketones are irradiated.



(2)

1a–c **4** **5a–c** (34–67%)

In contrast to these reactions, irradiation of acetone in the presence of isobutylene yields a complex mixture of products, with both oxetanes being formed in low yield (<5%) The failure of acetone to add to isobutylene probably reflects competing energy transfer and not a low reactivity toward oxetane formation. Furthermore, acetone acts as a sensitizer for the norbornene dimerization with no detectable oxetane formation.[11]

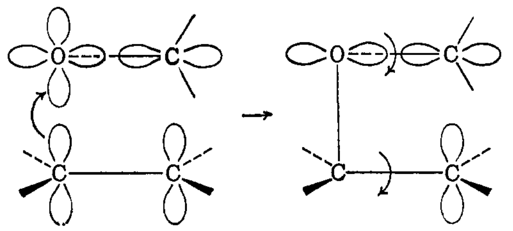


Figure 1. General mechanism for electrophilic addition of the oxygen of the n,π^* state to C=C bonds.

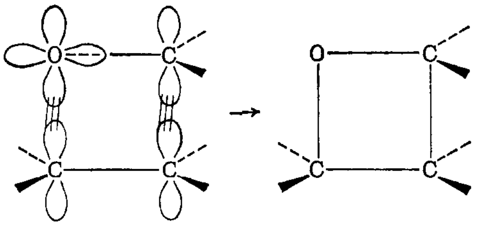


Figure 2. General mechanism for nucleophilic addition of π^* system to electron-deficient double bonds.

Quenchers such as 1,3-pentadiene, 2,5-dimethyl-2,4-hexadiene, and naphthalene, which are known to deactivate alkyl ketone triplets on each solution encounter, do not inhibit the rate of the cycloaddition reaction, in marked contrast to the observed quenching of the cycloaddition of benzophenone to alkyl olefins.[5] That the triplet state of the dicyanoethylene is not the reactive state in reaction 1 was established by 3660-A irradiation of an acetone solution of xanthone (E_T = 74 kcal/mole)[17] and **2** (xanthone absorbs nearly all the incident light in this region). Rapid isomerization of **2** to the *cis* isomer occurred, but no oxetane could be detected.

The above results demand that reaction 1 either (a) results from the n,π^* singlet state on **2** or (b) results from the n,π^* triplet at a rate close to that for diffusion-controlled reaction. Since **2** was found to strongly quench the fluorescence of cyclopentanone, we must conclude that at least part of the reaction occurs by attack of the n,π^* singlet of alkyl ketones on **2**. This result contrasts with recent work by Wagner,[18] who failed to intercept acetone singlets even with tributyltin hydride, a potent hydrogen donor.

At a concentration of 0.1 *M* **2**, we observe nearly equal rates for type II cleavage and cycloaddition with 2-hexanone. The cleavage reaction[19] occurs with a rate constant of $\sim 10^9$ sec^{-1} in T_1 and $\sim 10^7$ sec^{-1} in S_1 of 2-hexanone [19,20] This result implies rate constants of $\sim 10^{10}$ and $\sim 10^8$ l. mole^{-1} sec^{-1} for reaction from T_1 and S_1, respectively. Furthermore, the type II cleavage from S_1 is strongly quenched by added **2**.

Our results clearly are incompatible with electrophilic attack by the n,π^* triplet state. We therefore

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(12) D. Arnold and A. Glick, unpublished results. Negligible isomerization of the unreacted olefin occurred during the irradiation period. This result argues strongly for a biradical intermediate of sufficient lifetime to cause loss of stereochemistry.

(13) M. Kasha in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins University, Baltimore, Md., 1961, p 31.

(14) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963).

(15) Typical reaction conditions are irradiation of a 4:1 molar ratio of ketone to olefin in a Pyrex test tube to cut off wavelengths lower than 2900 A. Samples could be run neat or dissolved in cyclohexane without affecting the results with the dicyanoethylene. The results with maleic anhydride are solvent dependent, and either a large excess of ketone is used or the samples are dissolved in acetonitrile.

(16) The addition of acetone to 1,2-dicyanoethylene was first reported by J. J. Beerboom and M. von Witteman, *J. Org. Chem.*, **30**, 1231 (1965). Yields were determined by nmr and are based on 100% conversion. Structures of adducts were determined from analysis of their mass, nmr, and infrared spectra. The reaction is also stereospecific starting with *cis*-1,2-dicyanoethylene.

(17) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(18) P. J. Wagner, *ibid.*, **89**, 2503 (1967).

(19) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(20) Calculated from data in ref 19 and R. F. Borkman and D. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

propose that these reactions[21] involve attack on electron-deficient double bonds by the nucleophilic π^* orbital either to form the oxetane concertedly or by rapid closure of any intermediate species.

It should be noted[22-24] that our description may be formulated as an *electron transfer* from the π^* orbital of the n,π^* state to the electron-poor olefin.

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[21] Careful examination of solutions of **2** in several alkyl ketones did not reveal the presence of detectable concentrations of ground-state complexes of ketones and **2**.

[22] For a related example in radical chemistry see S. Okamura, K. Takakura, and K. Hayashi, *Pure Appl. Chem.*, **12**, 387 (1966).

[23] For a related interpretation of electrophilic hydrogen abstraction by the n,π^* state see S. G. Cohen and J. I. Cohen, *J. Am. Chem. Soc.*, **89**, 164 (1967).

[24] Benzophenone does not undergo photoaddition to **2**, but merely causes rapid *cis–trans* isomerization to *cis*-1,2-dicyanoethylene. This result probably derives either from the extremely rapid rate of intersystem crossing (10^{10} sec^{-1}) of aromatic ketones or a π^* orbital which is less reactive toward addition.

[25] Alfred P. Sloan Fellow, 1966–1968.

[26] National Institutes of Health Graduate Trainee, 1966–1967.

[27] National Science Foundation Graduate Trainee, 1965–1967; National Institutes of Health Predoctoral Fellow, 1967–present.

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Book Reviews

Einführung in die Laser-Mikro-Emissionsspektralanalyse. By Dr. Rer. Nat. Habil. HORST MOENKE, Jena, and Dr. Rer. Nat. LIESELOTTE MOENKE-BLANKENBURG, Jena. Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig, C 1, Germany. 1966. 182 pp. 15 × 22 cm. MDN 26.

The authors make the point in their introduction that solid-state lasers, ruby- and neodymium-doped glass in particular, have undergone such rapid technological development that they can now be functionally incorporated in a unified piece of equipment for laser microprobe emission spectral analysis. In carrying out an analysis the laser beam is focused with microscope optics to a spot of only a few microns diameter on the sample. The radiation from the plume ejected by a laser shot is projected on the slit of a spectrograph which is integral with the microprobe components. The material in the plume can be further excited as it passes through an auxiliary spark gap permanently mounted in the equipment.

The book first proceeds with a discussion of the working characteristics of lasers, flash tubes, and Q-switches, followed by somewhat detailed descriptions of the complete microprobe installations which the authors have developed and tested. Although the emphasis here is on the equipment made by VEB Carl Zeiss, Jena, there is also some mention of the products of other manufacturers. Much practical information on commercial spectrographs and on the optics both for concentrating the laser beam and for imaging the plume on the spectrograph slit is included. There follows a chapter on techniques for conducting laser microprobe analyses while almost the last third of the book is devoted to specific applications. This part should be especially helpful to anyone considering adding the laser probe method to his arsenal of spectral-analytical emission methods, since it is not particularly centered on any one manufacturer's equipment. Described are analyses of mineral inclusions, metallographic samples, silicates and ceramics, archaelogical artifacts, and criminalistic evidence, to name a few examples. A fold-out table arranged in a periodic system array shows the many elements to which the laser microprobe has been applied successfully.

In the final pages of the book there is a discussion of the comparative merits of electron and laser microprobe methods, and a list of 137 references.

It is evident that a severe linguistic problem arises when a newborn technology burgeoning with its Fachsimpel vernacular must be described in another tongue. The authors solve this in a practical way by the liberal use of English interspersed in the German text—"laser" must obviously remain "laser", but "Q-switch" appears either translated or simply remains "Q-switch" while "spike" stays "spike", and even "output" and "input" often go untranslated. Perhaps inadvertently, the authors have performed a service to their English-speaking readers when they do produce translations of some of these expressions, by providing, so to say, dictionary entries long before they will appear in formal dictionaries.

This interesting little book really contains a wealth of practical information on applying, as a new tool, the laser microprobe method of emission spectral analysis.

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