of cyclopropyl may be related to the change in sign of q_i. Either torsional or conjugative effects could account for this. If it is correct to assume internuclear, as opposed to bent, cyclopropyl bonds, torsional effects should clearly favor **2**. Thus, where conjugative effects are small, as they might be in an anionic species, the resultant could favor **2**. The interesting possibility that anionic cyclopropyl conjugation has a different conformational preference than cationic conjugation also deserves serious consideration. It should be recalled that the Walsh model of cyclopropane has a quasi-cyclopropenyl system internal to the ring which could be more effective at accepting an electron pair than the external (to the ring) p system, which is so adept at electron-pair donation. Delocalization into the former would require the symmetrical conformation **2** observed for the anion radicals. Steric effects seem to be ruled out by the fact that C(R) is approximately the same in both anion radicals cited, whereas steric repulsions should be more pronounced in the 9 position of anthracene than in the 1 position of naphthalene.

In contrast to the anion radical, and as expected, 9-cyclopropylanthracene's cation radical has $C(\text{R}) = 0.6$, *i.e.*, favoring the bisected form.

We have calculated the energy difference, ΔE_{SB}, between the symmetrical and bisected conformations by using eq 2, which embodies eq 1 and the integrated

$$\text{C(R)} = \frac{a_\beta(\text{R})}{a_\beta(\text{CH}_3)} = \frac{\int_0^{\pi/2} e^{-\Delta E \cos^2 \theta/RT} \cos^2 \theta \, d\theta}{{}^1/_2 \int_0^{\pi/2} e^{-\Delta E \cos^2 \theta/RT} \, d\theta} \qquad (2)$$

Boltzmann equation. The conjugational (or torsional) energy was assumed to be of the form $E = \Delta E_{\text{SB}} \cos^2 \theta$. Integrating (2) for various values of ΔE_{SB} at the temperatures of interest gives C(R), which can be compared with the experimental value. For both anion radicals $\Delta E_{\text{SB}} = -0.9$ kcal. This value is essentially unaffected if a potential of the form $E = \Delta E_{\text{SB}} \cos \theta$ is assumed. The 9-cyclopropylanthracene cation radical yields $\Delta E_{\text{SB}} = +1.0$ kcal. Thus the anion and cation radicals of 9-cyclopropylanthracene have ΔE_{SB} values which are nearly equal in magnitude but of opposite sign.[11]

Table I

Substrate[a]	Charge type	α_β	a_γ	C(R)
9-Methylanthracene (1)	Anion radical	4.27		1.00
9-Ethylanthracene (2)	Anion radical	2.5		0.59
9-Isopropylanthracene (3)	Anion radical	0.62		0.14
9-Cyclopropylanthracene (4)	Anion radical	6.64	0.17	*1.55*
1,4-Dimethylnaphthalene (5)	Anion radical	3.26		1.00
1,4-Dicyclopropylnaphthalene (6)	Anion radical	4.77	0.17	*1.46*
9-Methylanthracene (7)	Cation radical	7.79		1.00
9-Ethylanthracene (8)	Cation radical	3.6	0.3	0.46
9-Isopropylanthracene (9)	Cation radical	1.6	0.16	0.20
9-Cyclopropylanthracene (10)	Cation radical	4.8	0.26	*0.62*

[a] The anion radicals were generated using sodium or potassium in THF and the spectra recorded at −50 to −70°. The cation radicals were generated using concentrated sulfuric acid and the spectra recorded at ambient temperatures.

Work is in progress to distinguish between torsional and conjugative effects as the cause of symmetrical cyclopropyl conformations in anionic species.

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[11] The q_i at the 9 position of anthracene is calculated (HMO) to be ∼±0.19 in the cation and anion radicals ($\rho_i = 0.19$).

Mechanism of Photochemical Alcohol Addition to α,β-Unsaturated Ketones

Sir:

Many examples of photochemical solvent addition to α,β-unsaturated carbonyls have been reported,[1,2] but few have been concerned with the stereochemistry[3] and none with the mechanism of the reaction. We report here the more germane aspects of the mechanism of alcohol addition to 1-acetylcyclohexene (I). The reaction occurs readily with methanol, ethanol, and *t*-butyl alcohol in the condensed phase to give mixtures of *cis* and *trans* adducts (II–IV) in yields and with compositions shown.[4] Reactions were carried only to 35–55% conversion to minimize secondary photochemical reactions (fragmentation) of the photoadducts which occur more efficiently than the photoaddition itself.[5] The predominance of *cis* product in each mixture clearly indicates that the stereochemistry of products is kinetically rather than thermodynamically dictated. A parallel is noted in the stereochemistry of enol ketonization which appears to be governed by the direction of approach of the proton donor.[6,7] Evidence for the intermediacy of enols in the I → IV addition was obtained both by oxygenation studies and by direct observation.

The irradiation of an oxygen-saturated solution of I in *t*-butyl alcohol followed by hydrogenation of hydroperoxide intermediates afforded V (15%),[8] VI (40%), and VII (14%).[4] Very interesting results were obtained from experiments involving irradiation followed by oxygenation in the dark. No V was formed, and the *trans*:*cis* ratio of alcohols (VI and VII) dropped to 40:60 as the ketonization reaction became competitive. It is thus clear that two enols are produced and

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[1] A. Schönberg, "Präparative Organische Photochemie," Springer Verlag, Berlin, 1958, pp 73–77; G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, pp 120–152; A. M. Moore, *Can. J. Chem.*, **41**, 1937 (1963); A. Wacker, H. Dellweg, L. Träger, A. Kornhauser, E. Lodemann, G. Türck, R. Selzer, P. Chandra, and M. Ishimoto, *Photochem. Photobiol.*, **3**, 369 (1964); S. Y. Wang, *Federation Proc. Suppl.*, **15**, S-71 (1965).

[2] I. A. Williams and P. Bladon, *Tetrahedron Letters*, 257 (1964), have observed a radical-type addition to a 16-en-20-one steroid.

[3] T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **88**, 2602 (1966).

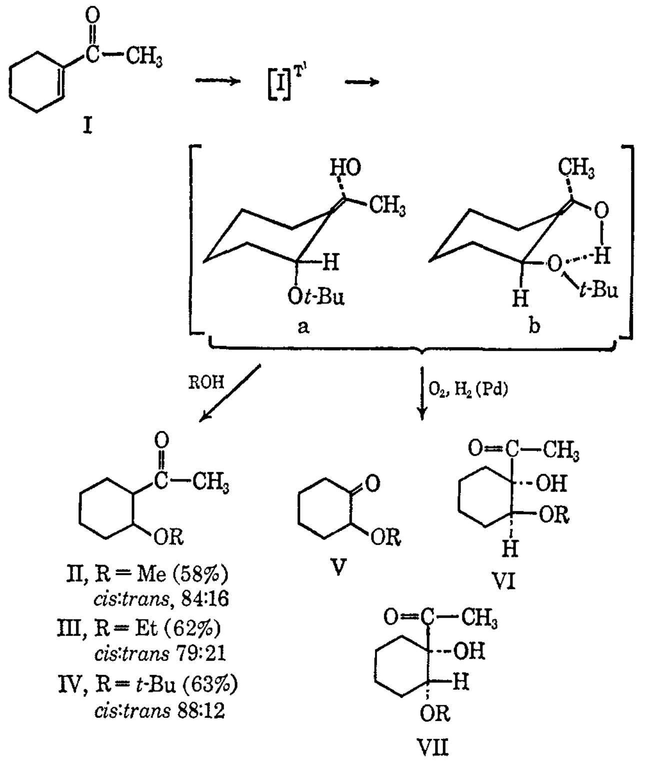
[4] All new compounds have expected spectral properties and gave correct analytical data. Stereochemical assignments are based on unambiguous independent syntheses and/or *cis–trans* equilibration studies.

[5] This was demonstrated in experiments using pure IV. The light-absorption properties of I are such as to "protect" IV during the early stages of photoaddition. The use of a filter would be expected to permit higher conversions of I to IV.

[6] H. E. Zimmerman, *J. Am. Chem. Soc.*, **79**, 6554 (1957), and references cited therein.

[7] S. K. Malhotra and F. Johnson, *ibid.*, **87**, 5493 (1965).

[8] 2-*t*-Butoxycyclohexanone is formed photochemically from the two isomeric hydroperoxides. Its origin will be discussed in the full paper.



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).