converging to their limit for infinite μ. Thus, the matrix method (with the extrapolation to $\mu \rightarrow \infty$) provides information about the relative contributions of nearest neighbor, next nearest neighbor, etc. interactions.

We have also compared the potential function of eq 23 for water and 95% methanol, by varying the dielectric constant. Because of the higher dielectric constant of water, the potential has a shorter range than in methanol. This may be one reason why the truncation of the potential at $\mu = 3$ (for poly-L-glutamic acid in water) did not introduce an error into the procedure of Zimm and Rice. In treating electrostatic interactions in aqueous solutions of proteins, it will be necessary to obtain a reasonable estimate of the local dielectric constant in order to compute the electrostatic interaction energy; from the results obtained here, we have a basis for selecting an empirical potential for such computations.

It should be noted that there is not necessarily a contradiction between the assertion that the electrostatic potential is of shorter range in water than in methanol, and the observation that poly-L-lysine is α helical in methanol but randomly coiled in water; the helical conformation in methanol may arise from other factors (possibly strengthened hydrogen bonds) than the electrostatic repulsion between the charged ϵ-amino groups.

Acknowledgment. We would like to thank Mr. Hua Tjan for performing the nitrogen analyses to determine the concentrations of the poly-L-lysine solutions.

Communications to the Editor

Photochemistry of Cyclobutanone. Trapping of the Initial Ring-Opened Intermediate with Butadiene

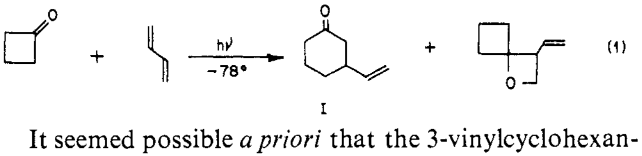
Sir:

Carbon–carbon cleavage at the carbonyl carbon (Norrish type I cleavage) is a photochemical reaction of considerable importance and current interest.[1] Particular attention has been focused on cyclic ketones and the question as to whether the various fragmentation and intramolecular disproportionation products are formed through an intermediate diradical[2] or *via* concerted pathways.[3] The need for understanding the fragmentation modes of cyclic ketones in mass spectrometry has further increased the significance of this area of photochemistry.

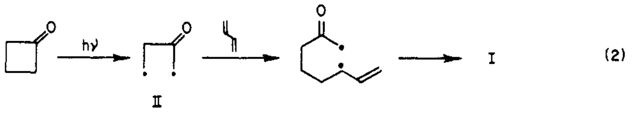
Support for the intermediacy of diradicals in the photochemical scission of cyclic ketones has been presented recently in the isomerization studies of appropriately substituted cyclohexanones,[4] cyclopentanones,[5] and 17-keto steroids.[6] However, that which is known of the chemical reactivity of the proposed diradicals is limited to clues provided by intramolecular reactions since such intermediates have never been trapped by external reagents. We have discovered a unique instance of an apparent trapping reaction and present here the experimental evidence and the unusual features of this reaction.

The photolysis of cyclobutanone has been studied in the gas phase[2,7] and in methanol solution.[8] From the former studies it has been concluded that the excited singlet state leads to fragmentation into ethylene and ketene. In accord with these findings we have observed that photolysis of cyclobutanone in liquid butadiene at 10° in a sealed tube yields acetic acid (2,2,4,4-cyclobutanone-d_4 yields dideuterio acetic acid) (19%), ketene dimer (32%), the adduct of ketene and butadiene[9a] (5%), as well as an oxetane (13%).[9b]

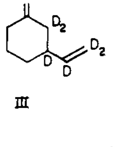
When the photolysis is run at −78°, a striking change occurs. None of the products derived from ketene are observed; instead one observes 3-vinylcycohexanone (I) as a major product of the reaction (32%).[10] Oxetane[9b] is also formed under these conditions (32%).



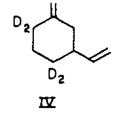
It seemed possible *a priori* that the 3-vinylcyclohexanone might be formed following a β cleavage (II) of the cyclobutanone ring as shown in eq 2. We have been



able to rule out this possiblity completely. Photolysis of cyclobutanone in butadiene-d_6 yielded 3-vinylcyclohexanone-d_6 (III) which exchanged two atoms of deu-



III



IV

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[1] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 244; R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, p 71; J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 379.

[2] S. W. Benson and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 64, 80 (1942); F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

[3] R. Srinivasan, *Advan. Photochem.*, **1**, 87 (1963).

[4] B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, *Chem. Ind.* (*London*), 1951 (1964); R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

[5] H. M. Frey, *Chem. Ind.* (*London*), 947 (1966).

[6] G. Quinkert, *Angew. Chem.*, 77, 229 (1965); H. Wehrli and K. Schaffner, *Helv. Chim. Acta*, **45**, 385 (1962).

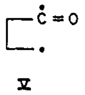
[7] H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **89**, 4795 (1967); N. E. Lee, H. O. Denschlag, and E. K. C. Lee, *J. Chem. Phys.*, **48**, 3334 (1968), and references cited therein.

[8] N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967), and references cited therein.

[9] (a) E. Vogel and K. Mullen, *Justus Liebigs Ann. Chem.*, **615**, 29 (1958); (b) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5725 (1970).

[10] The 3-vinylcyclohexanone was identified by direct comparison with an authentic sample prepared from cyclohexenone and vinylmagnesium bromide. This ketone has also been prepared in a different manner by J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

terium on equilibration with aqueous base. A second equilibration resulted in no further loss of deuterium.[11] This result was further confirmed by photolysis of 2,2,4,4-tetradeuteriocyclobutanone in butadiene. The 3-vinylcyclohexanone-d_4 (IV) produced exchanged two, and only two, deuterium atoms on treatment with aqueous base.[11] These findings strictly limit the mode of opening of the cyclobutanone ring to cleavage of the α carbon–carbon bond as shown in V. Thus the diradical V is tentatively proposed as the central reactive intermediate leading to the production of 3-vinylcyclohexanone (I). The possible intermediacy of a diradical such as V is further supported by the recent studies of Turro and McDaniel.[12a]



V

The orientation of addition[12b] of V[13] to butadiene is most interesting. It indicates that acyl radicals may be more reactive than alkyl radicals toward addition to butadiene. An estimate[14] of the enthalpy of addition of alkyl and acyl radicals to ethylene places them only 4 kcal apart with the latter being the less exothermic of the two. Although this number clearly favors the production of 2-vinylcyclohexanone, it is somewhat uncertain and only one of several factors which govern the relative reactivities of these free radicals, as Walling has pointed out.[14] Experimental determination of the relative reactivities of acyl and alkyl radicals has not been reported. Indeed, part of the importance of the present work stems from the fact that this may possibly be the first direct comparison of the relative reactivities of alkyl and acyl radicals toward conjugated olefins.

Acknowledgment. It is a pleasure to acknowledge discussions with Dr. Paul Engel. This work was generously supported by the National Science Foundation (Grant No. GP 6667) and the Research Corporation.

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(11) It was possible to assign the positions of the remaining deuterium atoms using nmr and especially mass spectrometry.

(12) (a) N. J. Turro and D. McDaniel, *J. Amer. Chem. Soc.*, **92**, 0000 (1970). (b) It is quite possible that mixture of 3-vinylcyclohexanone and 2-vinylcyclohexanone is formed in this reaction. An authentic sample of 2-vinylcyclohexanone has been prepared according to J. K. Crandall, J. P. Arrington, and J. Hen, *ibid.*, **89**, 6208 (1967). It would not have been detected under our photolysis reaction conditions (400-hr irradiation at −78° of a 10% solution of the substrate in butadiene as solvent with a 450-W Hanovia high-pressure mercury lamp using Pyrex as filter) since it is completely destroyed in a relatively short time. Except for the great difference in temperature, this might have been inferred from the work of Crandall, *et al.* On the other hand, we have established that the observed products, 3-vinylcyclohexanone and oxetane, are stable under our conditions.

(13) It has been assumed here that cyclobutanone reacts with butadiene in the open, diradical form. Clearly an addition reaction which occurs through a closed excited state of the ketone has not been eliminated. In the latter case one might expect initial bond formation to occur at oxygen rather than at carbon; see, however, J. A. Baltrop and H. A. Carless, *Tetrahedron Lett.*, 3901 (1968), for examples in which the opposite conclusion might possibly be reached.

(14) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 240–243.

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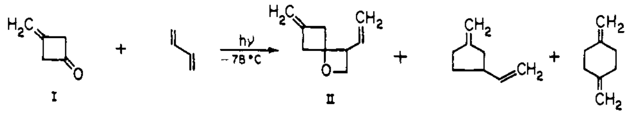
Oxetane Formation in the Photochemical Reaction of Cyclobutanones with Butadiene, Cyclopentadiene, and Piperylene

Sir:

The elucidation of the rules which govern intermolecular energy transfer in solution is one of the most pressing and fascinating problems in modern organic photochemistry. A rule of considerable importance is that which governs the outcome of the Paterno–Buchi reaction,[1] the formation of oxetanes from n,π^* triplet ketones and olefins. For oxetane formation to occur, the triplet energy of the olefin must be higher than that of the ketone in order that energy transfer not dominate the reaction.[2] Thus, conjugated dienes with cis and trans triplet energies of approximately 54 and 60 kcal, respectively, are expected to be poor substrates in oxetane formation with simple aliphatic ketones whose triplet energies are generally expected to be greater than 70 kcal.[2,3] We have discovered a most interesting seeming exception to this rule in the case of cyclobutanone. This is only an apparent exception since we have shown (*vide infra*) that cyclobutanone reacts with dienes through its excited singlet state. Since cyclohexanone and cyclopentanone behave in a completely normal fashion in the presence of dienes, this is the first case in which the effects of ground-state ring strain have appeared as controlling factors in oxetane formation—more generally stated—in the relative rates of intersystem crossing and photochemical reaction. In this sense, the present case complements those recently studied in which it is demonstrated[4] that singlet excited ketones may be efficiently trapped by electron-deficient olefins but where the structure of the ketone was not a controlling factor.

When 3-methylenecyclobutanone[5] (I) was photolyzed in liquid butadiene at −78° the oxetane II was formed in 17% yield.[6] The structural assignment is based on the mass spectrum: exact mass of molecular ion calcd for $C_9H_{12}O$, 136,0888; found, 136,0883; nmr (CCl_4) one-proton vinyl multiplet at τ 3.7–4.3, two-proton vinyl multiplet at 4.9, two-proton exocyclic methylene



I II

+ butadiene dimers

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(1) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, 76, 4327 (1954); D. R. Arnold, *Advan. Photochem.*, 6, 301 (1968).

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

(3) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, 66, 1144 (1962).

(4) J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, **30**, 1231 (1965); N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967); J. A. Baltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968). The importance of the excited singlet state to the understanding of the solution photochemistry of cyclobutanone is further demonstrated by the recent studies of N. J. Turro and D. McDaniel, *J. Amer. Chem. Soc.*, **92**, 5727 (1970).

(5) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

(6) A 10% solution of the ketone in butadiene as solvent was maintained at −78° while irradiation was carried out using a 450-W Hanovia high-pressure mercury lamp. A Pyrex filter was used. The products were isolated by vapor phase chromatography on TCEP. Other products formed in this reaction are discussed in the preceding communication: P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5726 (1970).