

Table I. First-Order Rate Constants at 50° for the Gas-Phase Isomerizations of Methylbicyclopentenes and Methylcyclopentadienes

Starting isomer	Product	k , sec ⁻¹
1	3	1.94×10^{-4}
1	4	1.2×10^{-4}
2	3	3.6×10^{-5}
2	4	4.64×10^{-5}
3	4	8.2×10^{-6}
4	3	5.8×10^{-6}

the spread. No thermal interconversion of **1** and **2** was detected; kinetic schemes postulating $k_{1,1} = k_{2,3} = 0$, but $k_{1,2}, k_{2,1} \neq 0$, cannot be made to accommodate the results.

The [$\sigma_2s + \sigma_2s$] intramolecular cycloaddition formulation advanced previously⁷ satisfies the gas-phase results, both with respect to partitioning to two methylcyclopentadienes (since each of the two may react using bonds 12,54 or 43,51) and the relatively tight spread of rate constants; mechanisms based on diradical intermediates can do neither.

While the quantitative discrepancies between the solution-phase isomerization results obtained in our earlier work⁷ and by McLean and Findlay⁸ must still be resolved, the direct isomerization of **2** to **3** is fully authenticated and the s_a symmetry-allowed isomerization rationale remains the only suggested mechanism consistent with uncontested experimental findings.

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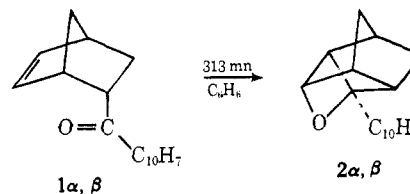
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Intramolecular Photocycloadditions of Naphthyl Ketones¹

Sir:

Despite the intense effort being devoted to the study of cycloaddition reactions between carbonyl derivatives and olefins, very little information is available on the photoreactivity of naphthyl systems. In an important study, Yang and coworkers² have shown that oxetanes may be formed from certain naphthyl ketones and 2-methyl-2-butene, but that the quantum yields are relatively low (<0.005). These workers concluded that factors other than the nature of the low-lying triplet states may contribute to the photochemical behavior of these compounds. Wagner and Hammond³ have made the intriguing suggestion that the reactive state in these cycloadditions may be the singlet state, the π, π^* triplets being unreactive. In view of the widespread interest in the mechanism of photocyclo-

addition,⁴ we initiated kinetic studies on the photocyclizations of naphthoynorbornenes **1 α** and **1 β** .⁵



Quantum yields were routinely determined by monitoring the rate of disappearance of the carbonyl chromophore by ultraviolet absorption spectroscopy. It was shown independently for **1 α** that this rate corresponded with the rate of appearance of oxetane **2 α** , and that no other products were formed. In addition, high yields of oxetanes were produced in both cases. Quantum yield and quenching data are shown in Table I from which it can be seen that both reactions

Table I. Quantum Yield and Quenching Data

Ketone	E_T^a	$\phi(\text{total})$	$\phi_{1,1}^b$	$k_q\tau^c$, M ⁻¹	ϕ_{ISC}^f
1α	57.5 ^d	0.135	0.065	5000	0.16
1β	59 ^e	0.175	0.065	4300	0.13

^a Triplet excitation energy in kcal/mol. ^b Quantum yield of ketone disappearance which can be quenched by 1 M 1,3-cyclohexadiene. ^c Initial slopes. ^d Measured by A. A. Lamola; $\tau_T = 0.52$ sec. ^e Assigned by analogy to 2-acetonaphthone; see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298. ^f Determined by the method of A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

proceed *via* two excited states one of which is quenchable and the other not. These conclusions were reached by studying the dependency of Φ_{-K} on the concentration of 1,3-cyclohexadiene concentration. Plots of Φ_{0-K}/Φ_{-K} vs. [Q] gave lines which rose steeply between quencher concentrations of 2.10^{-5} – 10^{-4} M and then became level from *ca.* 10^{-3} to 1 M quencher concentrations. The $k_q\tau$ values given in Table I were calculated from the lower ranges of quencher concentrations and it is believed that loss of quencher due to dimerization is minimal since the concentrations were low and Φ_{ISC} is small. It is likely that those portions of these reactions which are quenchable involve the π, π^* states owing to the estimated lifetimes: **1 α** , 2.5×10^{-6} ; **1 β** , 4.8×10^{-6} sec.⁶ Furthermore, it was possible to effect cyclization of **1 α** by the use of Michler's ketone ($E_T = 61$ kcal/mol) as a photosensitizer. A limiting value of 0.39 was found for ketone disappearance by extrapolation of the quantum yield data to zero concentration of sensitizer.⁷ This value

(4) (a) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970); (b) N. C. Yang and W. Eisenhardt, *ibid.*, **93**, 1277 (1971); (c) K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **44**, 215 (1971); (d) R. A. Caldwell and S. P. James, *J. Amer. Chem. Soc.*, **91**, 5184 (1969); (e) H. Morrison and S. R. Kurowsky, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 142.

(5) See R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969), for a discussion of the chemical aspects of these studies. Pure endo isomers were used in the present studies and the oxetanes formed were isolated in good yields. The long-wavelength ultraviolet absorption maxima are given for benzene solutions: **1 α** , 296 nm (ϵ 6380); **1 β** , 284 (ϵ 8700), 327 (ϵ 1550), and 342 nm (ϵ 1500).

(6) These values were obtained by assuming a quenching rate of 5×10^9 l./mol sec. For comparison, the lifetime (k_d^{-1}) of 2-acetonaphthone has been shown to be 3×10^{-6} sec by G. S. Hammond and P. A. Leermakers [*J. Amer. Chem. Soc.*, **84**, 207 (1962)].

(1) Presented at the XXIIIrd IUPAC Meeting, Boston, Mass., July 1971, Abstracts, p 96.

(2) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964).

(3) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 99 (1968).

represents the triplet efficiency for the cyclization and is in good agreement with the value (0.40) calculated from the ratio of the quantum yield of quenchable reaction to the quantum yield of triplets for this system.

Information on the reactivity of the other excited state involved in these cyclizations was obtained from quenching studies with triethylamine (TEA). It was observed that additional quenching of ketone disappearance and oxetane appearance was effected by addition of from 0.85 to 4.26 *M* TEA to solutions which already contained sufficient diene (1 *M*) to quench all of the triplet state reaction. From the slopes of Stern-Volmer plots obtained under these conditions, the following lifetimes may be calculated assuming diffusion-controlled quenching:⁸ 4×10^{-12} (1α) and 4×10^{-12} (1β) sec.

The foregoing results seem best interpreted in terms of photocyclizations *via* two excited states: the lowest triplet state (π, π^*) and an upper state of unknown configuration and multiplicity.^{9,10} In this context, we would like to point out an additional feature of interest; namely, the differing efficiencies with which the two reactive states undergo cyclization. For example, the lowest triplet state cyclizes with an efficiency of *ca.* 0.4, whereas the upper state cyclizes about fivefold less efficiently.¹¹ Thus, the upper reactive state returns to ground-state ketone more efficiently than does the lower state.¹² Clearly, thermal equilibration between whatever intermediate species¹³ are involved from these two sources does not compete with radiationless decay. In view of the likelihood that intermediate diradicals or exciplexes¹³ derived from upper and lower triplets would survive long enough to come to thermal equilibrium, we favor the lowest singlet state as the most likely alternative reactive state.

In summary, this work has demonstrated that naphthyl ketones can undergo cycloaddition *via* two excited states at least in intramolecular reactions. The great advantage that intramolecularity confers on

these reactions¹⁴ may preclude observation of similar behavior in the analogous intermolecular systems.¹⁵

Acknowledgments. We are indebted to the National Science Foundation and to the Rutgers University Biomedical Science Support Grant (USPHS-FR-7058), administered by the Rutgers Research Council, for financial support. A. D. R. thanks the Johnson and Johnson Co. for a fellowship.

(14) For an interesting discussion of this point, see M. I. Page and W. P. Jencks, *Proc. Nat. Acad. Sci., U. S.*, **68**, 1678 (1971).

(15) For example, the efficiency of ketone disappearance in the α -acetoneaphthone-norbornene system is <0.002 ; A. D. R., unpublished results.

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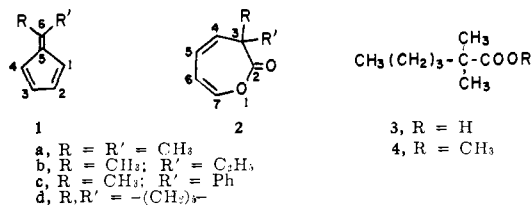
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Photochemical Oxidation of 6,6-Disubstituted Fulvenes

Sir:

Photosensitized oxidations, especially the formation of 1,4-epidioxides from dienes and allylic hydroperoxides from olefins, are now very common and synthetically useful reactions for the introduction of oxygen functional groups.¹ Fulvene derivatives, 6,6-dimethylfulvene² and 1,2,3,4-tetraphenylfulvene,³ have been reported to undergo photosensitized oxidation to afford the normal diene adduct, 1,4-epidioxide, and in the case of the latter it has also been found that the resulting 1,4-epidioxide was further rearranged photochemically to the 1,2-3,4 diepoxy derivative.^{3,4} We now wish to report the photochemical oxidation of 6,6-disubstituted fulvenes, which, through a different rearrangement pathway, leads to 3,3-disubstituted 2(3*H*)-oxepinones.



A solution of dimethylfulvene (**1a**, 1.5 g) in dry benzene (900 ml) was irradiated⁵ at room temperature for 8 hr⁶ with moderately rapid introduction of oxygen.⁷ Concentration of the solvent and chromatography on

(1) (a) For the reviews, see A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, Chapter 39, and C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (b) for the third mode of reaction of singlet oxygen, formation of 1,2-dioxetanes, see P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970), and references therein.

(2) J. Hasselmann, Dissertation, Göttingen, 1952; *cf.* E. Koch, *Tetrahedron*, **24**, 6295 (1968).

(3) Ch. Dufraisse, A. Etienne, and J.-J. Basselier, *C. R. Acad. Sci., Paris*, **244**, 2209 (1957); J.-J. Basselier, *ibid.*, **258**, 2851 (1964).

(4) Very recently photosensitized oxidation of 1,2,3,4,6-pentaphenylfulvene was reported. In this case, in addition to 1,4-epidioxide, the 1,2-dioxetane derivative was also formed: J. P. Le Roux and J.-J. Basselier, *ibid.*, *Ser. C*, **271** (7), 461 (1970).

(5) An immersion-type 500-W high-pressure mercury lamp and a Pyrex water jacket as a filter were used.

(6) Progress of the reaction was monitored by glc analysis on an SE-30 column, and at this stage the yellow color of the solution completely faded.

(7) It has been found that slow formation of **2a** was observed in ordinary benzene by reaction with dissolved oxygen, and that introduction of oxygen into the solution caused dramatically rapid formation of **2a**.

(7) L. Chapman and G. Wampffler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969), and A. G. Schultz, D. C. DeBoer, W. G. Herkstroeter, and R. H. Schlessinger, *ibid.*, **92**, 6086 (1970).

(8) These values represent minimum lifetimes since k_q may be slower than diffusion controlled. For example, TEA has been shown to quench valerophenone triplets at nearly the diffusion-controlled rate by P. J. Wagner and A. E. Kempainen, *ibid.*, **91**, 3085 (1969). Fluorenone and benzophenone triplets, however, are quenched at reduced rates by TEA: see, S. G. Cohen, N. Stein, and H. M. Chao, *ibid.*, **90**, 521 (1968); S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968); R. A. Caldwell, *ibid.*, 2121 (1969); G. A. Davis, P. A. Carapellucci, K. Szoc, and J. Gresser, *J. Amer. Chem. Soc.*, **91**, 2264 (1969); and R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1969). Biacetyl fluorescence has been shown to be quenched by TEA at the diffusion-controlled rate by N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **91**, 7113 (1969).

(9) It has been shown that 9-anthraldehyde behaves similarly in an intermolecular oxetane reaction: see N. C. Yang and R. L. Loesch, *Tetrahedron Lett.*, 2571 (1968).

(10) The possibility that the two reactive states are in rapid equilibrium seems remote in view of the expected magnitude of the energy gap. For example, the $n, \pi^* - \pi, \pi^*$ triplet separation for 2-naphthaldehyde has been shown to be *ca.* 15 kcal/mol: see D. R. Kearns and W. A. Case, *J. Amer. Chem. Soc.*, **88**, 5087 (1966).

(11) The efficiency of upper state cyclization is taken to be $(\phi_{\text{total}} - \phi_{\text{T}})/(1 - \phi_{\text{T}}) = 0.08$.

(12) Similar results have been noted for the reaction of ethoxybutenes with the S_1 and T_1 states of acetone: see N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).

(13) N. C. Yang, J. T. Cohen, and A. Shani, *ibid.*, **90**, 3264 (1968); N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971); R. A. Caldwell, *ibid.*, **92**, 1439 (1970); N. J. Turro, C. Lee, N. Schore, J. Bartrop, and H. A. J. Carless, *ibid.*, **93**, 3079 (1971).