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 species[13] are involved from these two sources does not compete with radiationless decay. In view of the likelihood that intermediate diradicals or exciplexes[13] 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 reactions[14] may preclude observation of similar behavior in the analogous intermolecular systems.[15]

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(7) L. Chapman and G. Wamppfler, *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. Kemppainen, *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. Loeschen, *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 $(\phi_{\text{total}} - \phi_{\text{T}})/(1 - \phi_{\text{ISC}}) = 0.08$.

(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. Barltrop, and H. A. J. Carless, *ibid.*, **93**, 3079 (1971).

(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-acetonaphthone–norbornene system is <0.002; A. D. R., unpublished results.

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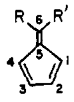
Photochemical Oxidation of 6,6-Disubstituted Fulvenes

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-dimethylfulvene[2] 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.



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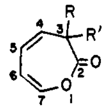

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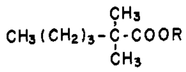

$$\mathrm{CH_3(CH_2)_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}COOR}$$

a, R = R′ = CH_3
b, R = CH_3; R′ = C_2H_5
c, R = CH_3; R′ = Ph
d, R,R′ = $-(CH_2)_5-$

3, R = H
4, R = CH_3

A solution of dimethylfulvene (**1a**, 1.5 g) in dry benzene (900 ml) was irradiated[5] at room temperature for 8 hr[6] with moderately rapid introduction of oxygen.[7] Concentration of the solvent and chromatography on

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(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.

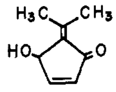
(6) Progress of the reaction was monitored by glc analysis on an SE-30 column, and at this stage the yellow color of the solution completely faded.

(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**.

silica gel gave the oxygen-incorporated product, 3,3-dimethyl-2(3*H*)-oxepinone (**2a**), in 19% yield.[8–10] Spectral data were in accord with the assigned structure: mass M$^+$ 138.0653; calcd for $C_8H_{10}O_2$, mol wt 138.0681; ir (neat) 1745 (C=O), 1640 and 1600 cm^{-1} (conjugated diene); uv (EtOH) λ_{max} 242.5 nm (ϵ 6110) (cyclic conjugated diene of type –CH=CHCH=CH–); nmr (100 MHz, CCl_4, TMS) δ 1.34 (s, 6 H, *gem*-dimethyl), 5.54 (d, 1 H, H-4), 5.64 (q, 1 H, H-6), 6.08 (q, 1 H, H-5), and 6.46 ppm (d, 1 H, H-7) (J_{4-5} = 10.2, J_{5-6} = 6.0, and J_{6-7} = 7.3 Hz). On catalytic reduction (PtO_2–MeOH) the product **2a** underwent complete hydrogenolysis of the enol–lactone linkage giving rise to a saturated carboxylic acid in 86% yield, which was found to be 2,2-dimethylhexanoic acid (**3**) from the spectral properties of the free acid and the methyl ester (**4**), and definitely identified with the authentic samples, prepared from isobutyronitrile by condensation with *n*-butyl bromide ($NaNH_2$–benzene)[11] followed by hydrolysis (KOH–ethylene glycol). These results manifest the correctness of the assigned structure **2a** for the photooxidation product of dimethylfulvene (**1a**), and thus this photooxidation reaction should apparently involve a novel photoinduced rearrangement of the carbon framework of fulvene.

In similar fashion, irradiation of 6-ethyl-6-methyl- (**1b**), 6-methyl-6-phenyl- (**1c**), and 6,6-pentamethylenefulvenes (**1d**) under the identical condition[8] afforded the corresponding 3,3-disubstituted 2(3*H*)-oxepinones **2b**, **2c** (mp 77–78°), and **2d** in 20–26% yield, respectively,[9,10] whose absorption maxima in ir and uv and splitting pattern of olefinic protons in nmr closely resemble those of **2a**. Thus, although the actual isolation yields of the compounds **2** were low, this photooxidation reaction would serve as a useful method for synthesis of 3,3-disubstituted 2(3*H*)-oxepinone derivatives,[12] because of ready availability of the starting 6,6-disubstituted fulvenes and simple operation of the reaction.

Sensitized photooxidation of a methanolic solution of dimethylfulvene (**1a**) with a 200-W tungsten lamp at room temperature employing Rose Bengal again resulted in formation of the oxepinone **2a**, accompanied by several other volatile products in comparative amounts. When irradiation was conducted at low temperature, −70°,[13] no oxepinone **2a** was detected in the initial cold photolysate (by tlc on SiO_2–benzene), but it was observed that the primary product (or products) of this low-temperature photooxidation was thermally considerably labile, and that **2a** was again obtained in 5–6% yield even by careful work-up without application of heat.[14] Tlc analysis (SiO_2–ether) indicated that apparently the initial photolysate showed a single spot (H_2SO_4, heating), but in which a small spot was overlapped as detected with a fluorescent lamp, and that this fluorescent spot gradually grew up on standing at room temperature. This product, **5**, now being thermally stable, was isolated by careful work-up and chromatography on alumina in 50% yield, and exhibits ir bands at 3350 (br, OH) and 1688 and 1635 cm^{-1} (doubly conjugated five-membered ring ketone), and nmr peaks at δ 2.05 and 2.21 (s, 3 H each, two nonequivalent olefinic methyls), 3.00 (br, 1 H, OH, disappeared by addition of D_2O), 5.05 (br d, 1 H, methine proton), 6.10 (d, 1 H, α-olefinic proton), and 7.23 ppm (q, 1 H, β-olefinic proton), in agreement with 5-isopropylidene-4-hydroxy-2-cyclopentenone[10,15] corresponding to the monoketo form of dihydroxydimethylfulvene.



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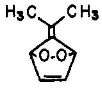

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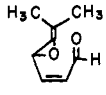

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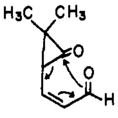

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Although, at present, 1,4-epidioxide (**6**), the most plausible intermediate, could not be isolated or even detected spectroscopically,[13] both the oxepinone **2** and the hydroxycyclopentenone derivative **5** would presumably arise from a thermal isomerization of **6**. Thus, formation of the oxepinones **2** would be accounted for by a reaction sequence, which postulates the rearrangement of 1,4-epidioxide (**6**) to the aldehydic allene oxide **7**, analogous to the formation of 4,5-epoxy-*cis*-2-pentenal from cyclopentadiene,[15] the isomerization of **7** to form the formal valence tautomer, the cyclopropanone (**8**),[16] and finally the rearrangement of **8** accompanied by opening of the cyclopropane ring.[17,18] Experiments on the scope, the minor products, and the mechanism are in progress.

Acknowledgments. We are grateful to Professor Y. Yamada, Tokyo College of Pharmacy, for measurement of the high-resolution mass spectrum. This work was supported in part by a research grant from the Ministry of Education of Japan.

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(8) This reaction condition is not the optimum one for producing compounds **2**.

(9) Glc and nmr analyses of the crude photolysate indicated that compound **2** was a sole volatile product in each reaction.

(10) All new compounds gave satisfactory elemental analyses.

(11) M. Murayama, *Chem. Pharm. Bull.*, **6**, 186 (1958).

(12) There have been only a few reports on the preparation of 2(3*H*)-oxepinone derivatives; see M. Foà, L. Cassar, and M. Tacchi Venturi, *Tetrahedron Lett.*, 1357 (1968); L. Cassar, G. P. Chiusoli, and M. Foà, *Chim. Ind.* (*Milan*), **50** (5), 515 (1968).

(13) Under these conditions, −80°, formation of 1,4-epidioxide (**6**) has been reported. See ref 2. However, detailed experimental procedures and the properties of **6** have not been published.

(14) For isolation of **2a**, silica gel column chromatography was used.

(15) Very recently formation of 4-hydroxy-2-cyclopentenone (in alkaline alcoholic solution, room temperature) or 4,5-epoxy-*cis*-2-pentenal (in neutral media, 0°–room temperature) from cyclopentadiene by sensitized photooxidation was reported: K. H. Schutte-Elte, B. Willhalm, and G. Ohloff, *Angew. Chem.*, **81**, 1045 (1969); W. R. Adams and D. J. Trecker, *Tetrahedron*, 27, 2631 (1971).

(16) Facile isomerization of an allene oxide to a cyclopropanone has recently been observed: J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7347 (1968); R. L. Camp and F. D. Greene, *ibid.*, **90**, 7349 (1968); J. Grimaldi and M. Bertrand, *Tetrahedron Lett.*, 3269 (1969).

(17) For an analogous example of transformation of a cis-ene dione to an enol lactone, see H. H. Wasserman and D. L. Pavia, *Chem. Commun.*, 1459 (1970).

(18) We thank a referee for suggesting this reaction pathway leading to **2** rather than the intervention of a tricyclic dioxetane (**9**).

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