

PHOTOCHEMICAL OXIDATION OF 6,6-DIARYLFULVENES¹

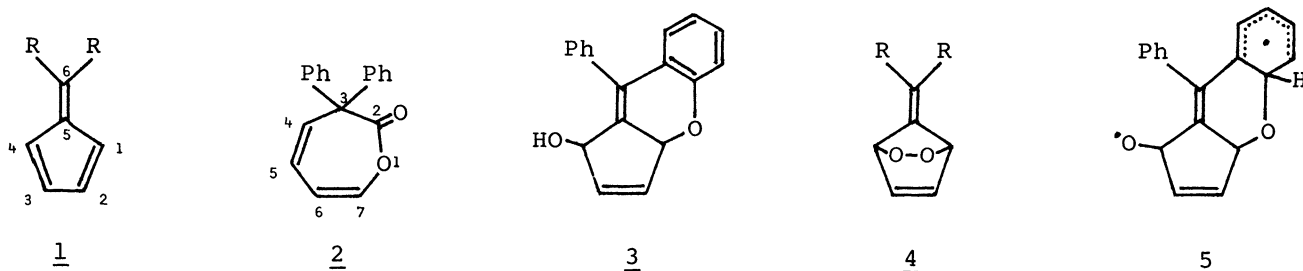
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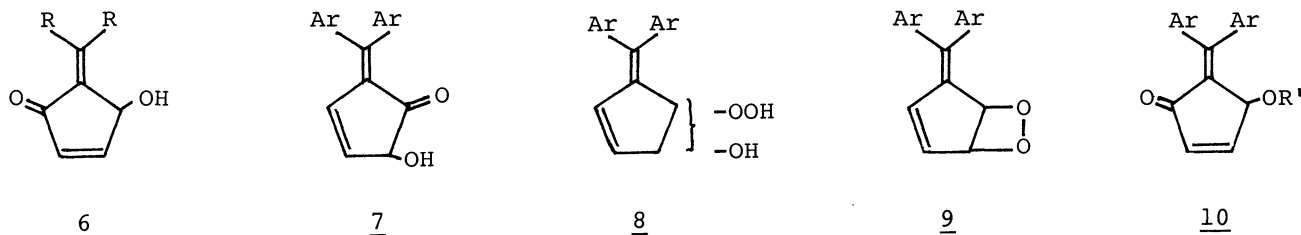
Sensitized photooxidation of 6,6-diphenylfulvene afforded 1,4-ketol, 2(3H)-oxepinone, and 4-phenyl-3-chromene derivatives, all of which arose from 1,4 addition of oxygen. While, 6,6-di-*p*-anisylfulvene gave, in addition to 1,4-ketol, 1,2 oxygen addition products as minor components. Reactions of 6,6-di-*p*-anisylfulvene 1,4-epidioxide have been also investigated.

In the previous papers, it has been reported that the sensitized photooxidation of fulvene derivatives, 6,6-dimethyl-,²⁻⁵ 6,6-dialkyl-,² 6,6-aralkyl-,² and 6-mono-substituted (isopropyl and phenyl)⁶ fulvenes, gave corresponding 2(3H)-oxepinone derivatives as major product depending on solvent used. This paper deals with the sensitized photooxidation of 6,6-diarylfulvene derivatives which affords different type of minor products from the previously reported ones.²⁻⁶

Sensitized photooxidation of 6,6-diphenylfulvene 1 (R=Ph) in methanol at -70° gave after chromatographic separation on silica gel⁷ gave 3,3-diphenyl-2(3H)-oxepinone 2, mp 137-138°,^{8,9} (4-6% yield) and a new type product 3, mp 121.5-122.0°, (6-8% yield).¹⁰ The structure of 3, a 4-phenyl-3-chromene derivative, was established on the basis of the following evidence: mass m/e 262 (M⁺); ir (KBr) 3600, 1648, and 1604 cm⁻¹; uv (EtOH) λ_{max} (logε) 233 (4.34, sh), 275 (3.84), and 308 nm (3.57);¹¹ nmr (100 MHz, CDCl₃, TMS) δ 1.55 (1H, s, OH, disappeared by addition of D₂O), 5.46 (1H, br.s,¹² H-1¹³), 5.58 (1H, br.s,¹² H-4, slightly sharpened by addition of D₂O), 6.32 (2H, m, H-2 and H-3),¹⁴ and 7.00-7.44 (9H, m, aromatic H). The formation of 3 would be accounted for by a reaction sequence, which postulates the homolytic cleavage of the oxygen-oxygen bond of the initially formed 1,4-epidioxide 4 (R=Ph), the attack of the resulting oxygen radical to a benzene ring to form the intermediate 5, and the apparent shift of a hydrogen atom.¹⁵

When the photooxidation of 1 (R=Ph) was conducted in methylene chloride at -70°,





the normal 1,4-ketol 6 (R=Ph)^{9,16} was obtained in 33% yield, in addition to 3 (5%). In this case, the isolation of the products was necessarily achieved by treatment of the reaction mixture with alumina at -70° before warming up to room temperature, followed by usual work-up and chromatography on silica gel.¹⁷ From the results, all of the characterized photooxidation products of 6,6-diphenylfulvene 1 (R=Ph) arose from the 1,4 addition of oxygen to the fulvene framework as reported previously.

On the other hand, it was found that the 1,2 addition products of oxygen rather than 2(3H)-oxepinone derivative, were isolated as minor products in the photooxidation of 6,6-di-*p*-anisylfulvene 1 (R=*p*-CH₃O-C₆H₄-). The photooxidation of 1 (R=*p*-CH₃O-C₆H₄-) in methylene chloride at -70°¹⁸ gave after work-up (treatment of the photolysate with silica gel at -70°)¹⁹ the 1,4-ketol 6 (R=*p*-CH₃O-C₆H₄-), mp 175-177°,^{9,16,20} 7, and 8 in 24, 7, and 1% yields, respectively. Assignment of the structure of 7 was based on the spectral evidence: ir (CHCl₃) 3400, 1710, 1600, and 1580 cm⁻¹; uv (EtOH) λ_{max} (logε) 233 (4.18), 251 (4.15, sh), 290 (4.07), and 355 nm (4.04); nmr (100 MHz, CDCl₃, TMS) δ 3.82 (6H, s, OCH₃), 4.65 (1H, dd, J₂₋₃=2.2 and J₂₋₄=1.8 Hz, H-2), 6.25 (1H, dd, J₃₋₄=7.0 Hz, H-3), 7.10 (1H, dd, H-4), and 6.80-7.40 (8H, two sets of AB type quartet, J_{AB}=9.0 Hz, aromatic H). Furthermore, the 1,2-ketol nature was confirmed by oxidation to the 1,2-diketone: ir (CHCl₃) 1720, 1600, and 1505 cm⁻¹; nmr (100 MHz, CDCl₃, TMS) δ 6.46 (1H, d, J₃₋₄=7.0 Hz, H-3), and 8.35 (1H, d, H-4), in addition to the signals due to methoxyl and aromatic protons, which was unequivocally characterized by formation of the quinoxaline derivative, mp 178°, and the carbonyl position at C-1 was established by conversion to 2-(di-*p*-anisyl)-methylcyclopentanone.²⁰ The third product 8 shows mass m/e 340 (M⁺=1 + O₂ + H₂O); ir (CHCl₃) 3530, 1645, 1600, and 1510 cm⁻¹; uv (EtOH) λ_{max} (logε) 224 (4.17) and 279 nm (4.06); nmr (100 MHz, CDCl₃, TMS) δ 3.72 (6H, s, OCH₃), 4.16 (1H, d, J₁₋₂=5.7 Hz, H-1), 4.56 (1H, dd, J₂₋₃=2.5 Hz, H-2), 6.24 (1H, dd, J₃₋₄=6.5 Hz, H-3), 6.40 (1H, d, H-4), and 6.60-7.70 (8H, two sets of AB type quartet, J_{AB}=8.8 Hz, aromatic H). From these data, though other additional chemical evidence could not be obtained, the 1,2-hydroxy-hydroperoxide structure 8 was tentatively proposed to this product.

Formation of the 1,2-ketol 7 might occur from a dioxetane intermediate 9 arising from 1,2-cycloaddition of oxygen to the 1,2-bond of fulvene 1.^{21,22}

Furthermore, we observed that the 1,4-alkoxyketones 10 were produced when the photolysate was treated with silica gel in the presence of alcohols. Thus, addition of methanol to the photolysate in methylene chloride at the stage of silica gel treatment at -70° afforded the 1,4-methoxyketone 10 (R'=CH₃): mass m/e 336 (M⁺); ir (neat) 1690, 1600, and 1510 cm⁻¹; uv (EtOH) λ_{max} (logε) 234 (4.23), 285 (3.90, sh), 312 (3.93, sh),

and 348 nm (3.99); nmr (100 MHz, CDCl_3 , TMS) δ 3.02 (3H, s, OCH_3), 3.84 (6H, s, anisyl OCH_3), 5.40 (1H, dd, $J_{1-2}=2.4$ and $J_{1-3}=1.1$ Hz, H-1), 6.52 (1H, dd, $J_{2-3}=6.1$ Hz, H-3), 7.50 (1H, dd, H-2), and 6.80–7.30 (8H, two sets of AB type quartet, aromatic H),²⁰ in 60% yield. Similarly, the ethoxy derivative 10 ($\text{R}'=\text{C}_2\text{H}_5$)²³ was obtained in 21% yield when ethanol was used. The fact that on treatment with silica gel - methanol - methylene chloride the 1,4-ketol 6 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4-$) completely remained unchanged, indicates that 10 would presumably arise from the silica gel catalyzed methanol addition and isomerization of the initially formed 1,4-epidioxide 4 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4-$).²⁴

When the photooxidation of 1 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4-$) was carried out in methanol at -70° , colorless crystals were separated from the solution at the end of the irradiation period. This material, thermally very unstable (immediately darkened at room temperature) was collected by filtration at low temperature and characterized to be the 1,4-epidioxide 4 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4-$) on the basis of the nmr spectrum (60 MHz, CDCl_3 , TMS, -54°): δ 3.79 (6H, s, OCH_3), 5.50 (2H, t, $J=2.0$ Hz, H-1 and H-4), 6.80 (2H, t, H-2 and H-3), and 6.82 and 7.03 (8H, AB type quartet, $J_{\text{AB}}=9.0$ Hz, aromatic H).²⁵

Finally, it is noted that in contrast to the previous findings on various thermal transformations of 6,6-dimethylfulvene 1,4-epidioxide 4 ($\text{R}=\text{CH}_3$)²⁶ the attempted thermal isomerization (-70° –room temperature) of 6,6-di-p-anisylfulvene 1,4-epidioxide 4 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4-$) in various solvents did not give any rearrangement product including 2(3H)-oxepinone derivative; only the 1,4-ketol 6 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4-$) was isolated in very low (6%) yield when pyridine was employed as a solvent.

Acknowledgment. We are grateful to the Ministry of Education of Japan and the Asahi Glass Foundation for support of this work.

References and Notes

- 1) Photochemical Oxidation of Fulvene Derivatives. VI. For Part V, see N. Harada, H. Uda, H. Ueno, and S. Utsumi, *Chem. Lett.*, 1173 (1973).
- 2) N. Harada, S. Suzuki, H. Uda, and H. Ueno, *J. Amer. Chem. Soc.*, 94, 1777 (1972).
- 3) N. Harada, H. Uda, and H. Ueno, *Chem. Lett.*, 663 (1972).
- 4) N. Harada, S. Suzuki, H. Uda, and H. Ueno, *Chem. Lett.*, 803 (1972).
- 5) For the independent work on the sensitized photooxidation of 6,6-dimethylfulvene, see W. Skorjanetz, K. H. Schulte-Elte, and G. Ohloff, *Helv. Chim. Acta*, 54, 1913 (1971).
- 6) A. Kawamoto, H. Kosugi, and H. Uda, *Chem. Lett.*, 807 (1972).
- 7) Tlc analysis of the cold photolysate showed that an almost single product was formed. However, the usual work-up was not enable to isolate this substance.
- 8) All new crystalline compounds in this communication gave satisfactory elemental analyses.
- 9) In comparison with the spectra of the previously reported analogs, satisfactory spectral data were obtained for this compound.
- 10) A number of products were detected by tlc analysis, but any other identifiable product could not be isolated in a pure form, and for the isolation of 3 alumina chromatography was more favorable.
- 11) For the uv maxima of 4-phenyl-3-chromene, see I. Iwai and J. Ide, *Chem. Pharm. Bull.*, 11, 1042 (1963).

- 12) A small coupling with an adjacent olefinic proton was observed.
- 13) Numbering of carbon atoms based on a fulvene nucleus is used in all compounds except 2 for convenience.
- 14) Addition of a shift reagent, $\text{Eu}(\text{dpm})_3$, resulted in shift of the signals due to two olefinic protons, H-2 and H-3, at δ 6.32 to δ 6.64 as a clean AB type quartet ($J=6.0$ Hz).
- 15) An alternative important role of the oxygen radical from fulvene 1,4-epidioxide has been postulated as one of the possible reaction paths in the formation of 5-isopropenyl-4-hydroxy -2-cyclopentenone from 6,6-dimethylfulvene.³
- 16) Structure of the 1,4-ketol 6 was further confirmed by conversion to the symmetric 1,4-diketone.
- 17) No identifiable product was obtained when the reaction mixture was worked up without treatment with alumina at -70° or even treated with silica gel at -70° (in contrast to the case of 6,6-di-*p*-anisylfulvene, see below).
- 18) We have also investigated the photooxidation at room temperature in various solvents. From the run in chloroform, however, only di-*p*-anisylketone (2%) was isolated as an identified product.
- 19) In this case simple work-up procedure was also unsatisfactory.
- 20) Catalytic hydrogenation of this compound yielded 2-(di-*p*-anisyl)-methylcyclopentanone, which was identified with the authentic sample.
- 21) 1,2-Dioxetane formation of fulvene derivative by photooxidation has been reported. J. P. Le Roux and J. -J. Basselier, *Compt. Rend. Acad. Sci., Paris, Ser. C*, 271(7), 461 (1970).
- 22) For such a decomposition of 1,2-dioxetane to 1,2-ketol, see D. A. Lightner and L. K. Low, *J. Chem. Soc. Chem. Commun.*, 625 (1972).
- 23) This compound showed the almost identical spectral properties with those of the methoxy analog.
- 24) For an analogous example of 1,4-methoxyketone formation, see Ref. 22.
- 25) The coupling pattern of the protons in the five-membered ring are very similar to those of the corresponding protons of 6,6-dimethylfulvene 1,4-epidioxide 4 ($\text{R}=\text{CH}_3$) and of the Diels-Alder adduct of 1 ($\text{R}=\text{p-CH}_3\text{O-C}_6\text{H}_4\text{-}$) and dimethyl acetylenedicarboxylate.
- 26) See Ref. 1.

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