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SOLVENT DEPENDENCE IN THE PHOTOCHEMICAL OXIDATION OF 6,6-DIMETHYLFULVENE AND ISOLATION OF 5-ISOPROPENYL-4-HYDROXY-2-CYCLOPENTENONE

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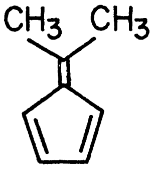
The photooxidation of 6,6-dimethylfulvene in benzene, carbon disulfide, chloroform, or acetone afforded preferentially 3,3-dimethyl-2(3H)-oxepinone (25 ~ 30 %), whereas in methanol 5-isopropylidene-4-hydroxy-2-cyclopentenone was predominantly isolated (50 %) after chromatography on alumina. Furthermore it has been found that 5-isopropenyl-4-hydroxy-2-cyclopentenone was also formed and easily isomerized to the above isopropylidene derivative during chromatography.

Very recently Skorianetz, Schulte-Elte, and Ohloff,[1] and we[2] found that the sensitized photooxidation of 6,6-dimethylfulvene (**1**) afforded 3,3-dimethyl-2(3H)-oxepinone (**2**),[1,2] 5-isopropylidene-4-hydroxy-2-cyclopentenone (**3**),[1,2] and 5,5-dimethyl-4-hydroxymethylene-2-cyclopentenone (**4**),[1] and, furthermore, we[2] also observed that the direct UV irradiation in benzene was more effective for producing the oxepinone **2** . We now wish to report the particular effect of methanol on product distribution and the isolation of 5-isopropenyl-4-hydroxy-2-cyclopentenone (**5**) as a new photooxidation product.



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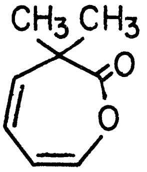

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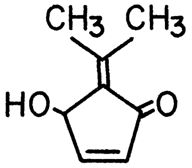

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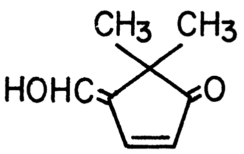

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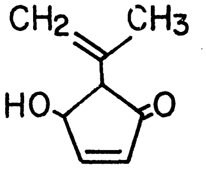

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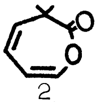
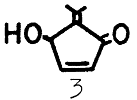
In order to obtain more information on the photooxidation of 6,6-dimethylfulvene (**1**) including the optimum condition for producing the oxepinone **2** , we have examined, at first, the direct photooxidation of **1** in various solvents. No considerable difference in the yield of the oxepinone **2** was observed from the photooxidation of **1** in carbon disulfide, chloroform, or acetone; the results were almost the same as in the case of benzene, as shown in the Table 1. On the other hand, a striking difference was observed in the case of methanol, and thus, the ketol **3** , now being the major product, was obtained in 50 % yield, and the

Table 1. Direct Photooxidation of 6,6-Dimethylfulvene in Various Solvents [a)]

Solvent	Irra. Time	Yield of  b) 2	Yield of  c,d) 3
Benzene	6 hr e)	27 % f)	4 %
Carbon Disulfide	2	25	4
Chloroform	4	30 f)	4
Acetone	2	29 f)	~ 0
Methanol	2	4.5	50

a) A solution of 200 mg of dimethylfulvene in 150 ml of each solvent in a Pyrex reaction tube was irradiated externally with a 500-W high-pressure mercury lamp at room temperature while a finely dispersed stream of oxygen was bubbled through the reaction mixture.

b) The oxepinone 2 was isolated from the total crude mixture of products by preparative tlc on silica gel with petroleum ether - ether (6 : 1).

c) For isolation of the ketol 3 , the substance, which was recovered from near the origin of the above silica gel tlc, was again subjected to preparative tlc on alumina with petroleum ether - ether (1 : 6).

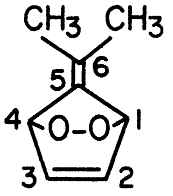
d) Alumina chromatography caused the isomerization of the isopropenyl derivative 5 to 3 , see the text.

e) At this stage the yellow color of the solution completely faded. Progress of the reaction could be monitored either by glc (SE-30) or tlc (SiO_2).

f) Other unidentified minor products (2 ~ 7 %) were obtained.

oxepinone 2 in 4.5 % yield, the result being almost identical with that of the sensitized photooxidation (Rose Bengal) of 1 in methanol, as reported previously.[1,2] Furthermore, it was found that the sensitized photooxidation of 1 in acetone again resulted in the predominant formation of the oxepinone 2 (30 %), in addition to the ketol 3 (17 %).[3,4,5]

Consequently, in both direct and sensitized photooxidations methanol[6] clearly facilitates the reaction pathway leading to the ketol 3 or its congener (see below) from the 1,4-epidioxide 6 , the most plausible intermediate in the photooxidation of 1 , rather than the competitive one to the aldehydic allene oxide 7 , the precursor of the oxepinone 2 ,[1,2] and among the solvents used acetone seems to be the most suitable solvent for the preparation of the oxepinone 2 .



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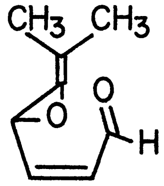

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During the course of the above experiments, we also found that a new product, 5-isopropenyl-4-hydroxy-2-cyclopentenone (5) was contained in the initial reaction mixture. Glc analysis (SE-30) of the total crude ketol fraction from the direct photooxidation in methanol before subjecting chromatography on alumina indicated that this fraction consisted of three components, 3 , 5 , and 4 ,[7] in the ratio of 4 : 4 : 1.7 (total *ca.* 80 %). Similarly, in the sensitized photooxidation the formation of the compound 5 was observed; almost equal amounts (total *ca.* 70 %) of 3 and 5 were contained in the ketol fraction from the run of a methanolic solution, while 5 was remarkably predominant (the ratio of 3 and 5 = 0∼2 : 10, total *ca.* 30 %) in the run in acetone solution. In the previous communication,[2] it was reported that the initial photolysate of the sensitized photooxidation in methanol showed apparently a single spot due to the ketol fraction on tlc (SiO_2 - ether, H_2SO_4 - heating) overlapped by a small spot as detected with a fluorescent lamp. Actually this larger spot was confirmed to be attributable to the compound 5 and the small spot to the compound 3 .

This compound 5 could be isolated either by preparative glc or careful column chromatography on silica gel[8] with petroleum ether - ether; and exhibits mass: M^+ 138, infrared bands at 3400 (OH), 1700 and 1590 (cyclopentenone), and 3075, 1640, and 900 cm^{-1} ($>C{=}CH_2$), and uv spectrum (EtOH): end absorption at 210 nm ($\varepsilon = 9200$); the nmr spectrum (60 MHz, CCl_4) includes signals at δ 1.82 (3H, br.s, $\gg CH_3$), 2.20 (1H, br, OH), 3.32 (1H, d, $J_{4-5} = 6.0$ Hz, C5-H), 4.83 (1H, br.s) and 5.19 (1H, br.s) ($>C{=}CH_2$), 5.05 (1H, m, C4-H), 6.35 (1H, q, $J_{2-3} = 6.0$ and $J_{2-4} = 1.5$ Hz, C2-H), and 7.67 ppm (1H, q, $J_{3-4} = 2.4$ Hz, C3-H), in agreement with 5-isopropenyl-4-hydroxy-2-cyclopentenone.

The compound 5 was fairly unstable to base, isomerizing to the isopropylidene derivative 3 . Thus, exposure of 5 to basic alumina with ether resulted in rapid conversion to the ketol 3 in 50 % yield, and, hence, 3 was only the ketol product isolated by chromatography on alumina. This behavior suggests that such an isomerization of 5 would be one of the reaction pathways to produce 3 during photooxidation, particularly promoted in methanol. However, the compound 5 in methanol underwent no isomerization when stored for 2 days in the dark or even when irradiated for 3 hr under the identical conditions with those of the photooxidation of 1 (Rose Bengal, O_2, 200-W Tungsten lamp, room temperature).[9] Furthermore, the presence of water was not effective for promoting isomerization of 5 to 3 as observed by the sensitized photooxidation of 1 in aqueous solvents; in 10 % aqueous acetone the ratio of 3 and 5 was *ca.* 1 : 5 and in 10 % aqueous methanol *ca.* 1 : 1, comparable with those under anhydrous conditions.[10] Consequently, the pathway to the formation of 3 via isomerization of 5 would not be essential during photooxidation.

On the other hand, as a mechanism for the formation of the isopropenyl ketol 5 , a possibility of the isomerization of the isopropylidene ketol 3 through photo-induced abstraction of the methyl hydrogen with the carbonyl oxygen atom was ruled out by the following experiment. On irradiation of a solution in acetone under the conditions of the photooxidation of 1 the isopropylidene ketol 3 completely remained unchanged after 2 hr,[11] and, therefore, the isopropenyl ketol 5 is also evidently the primary product from the 1,4-epidioxide 6 .

The above studies led us to conclude that the ketols 3 and 5 , being not interconvertible during photooxidation, were formed through alternative pathways from the 1,4-epidioxide 6 .[12] At present the important factor which affects the reaction course of the 1,4-epidioxide 6 leading either to 3 or 5 has not been clear.[15]

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References

1) W. Skorianetz, K. H. Schulte-Elte, and G. Ohloff, *Helv. Chim. Acta*, 54, 1913 (1971).
2) N. Harada, S. Suzuki, H. Uda, and H. Ueno, *J. Amer. Chem. Soc.*, 94, 1777 (1972).
3) Sensitized (Hematoporphyrin) photooxidation of 1 in methylene chloride also resulted in a predominant formation of the oxepinone 2 ; see Ref. 1.
4) In the same manner as described in the Table, preparative tlc on alumina was used for isolation of 3 .
5) The sensitized reaction proceeded more rapidly than the direct one and completed within 1 hr.
6) It seems that pyridine also exerts the same effect (predominant formation of 3) as methanol, see Ref. 1.
7) Compound 4 was isolated by silica gel chromatography in a large-scale experiment, and the physical properties are in accord with the reported ones.[1]
8) Gradual isomerization of 5 to 3 also occurred during chromatography on silica gel.
9) An alternative experiment also gave the identical result. After completion of the sensitized photooxidation of 1 in acetone, acetone was replaced with methanol and then the further irradiation of the resulting methanolic solution of the photolysate showed almost no change in the ratio of 5 and 3 .
10) In aqueous conditions the formation of the oxepinone 2 was greatly decreased.
11) Prolonged irradiation caused a little change of 3 , producing a few products, among which the compound 5 could not be detected, and even after irradiation for 7 hr 80 % of the starting ketol 3 was recovered.
12) Skorianetz, Schulte-Elte, and Ohloff[1] proposed that the ketol 3 would arise from a base-catalyzed fragmentation of the 1,4-epidioxide 6 , analogous to the base-catalyzed decomposition of dialkyl peroxides.[13,14]
13) M. Kornblum and H. E. de la Mare, *J. Amer. Chem. Soc.*, 73, 880 (1951).
14) For other examples of such a base-catalyzed ionic fragmentation from stable 1,4-epidioxides of dienes to ketols, see C. Dufraisse, G. Rio, and W. A. Burris, *Compt. rend.*, 244, 2674 (1957); H. C. Barrett and G. Büchi, *J. Amer. Chem. Soc.*, 89, 5665 (1967); M. Oda and Y. Kitahara, *Angew. Chem.*, 81, 702 (1969), *Tetrahedron Lett.*, 3295 (1969); J. A. Marshall, R. A. Ruden, L. K. Hirsh, and M. Phillippe, *ibid.*, 3795 (1971).
15) Homolysis of the oxygen-oxygen bond in 6 , followed by a hydrogen abstraction from the methyl group by the resulting oxygen radical and a hydrogen shift from C-1 (C-4) to C-5 would be one of the possible reaction courses to 5 .

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