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PHOTOCHEMICAL OXIDATION OF 6,6-DIMETHYLFULVENE IN ALKALINE METHANOLIC SOLUTION

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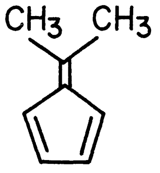
Both direct and sensitized photooxidations of 6,6-dimethylfulvene in alkaline methanolic solutions gave, in addition to two methanol addition products of 5-isopropylidene-4-hydroxy-2-cyclopentenone: 2-isopropenyl- (5 ∼ 12 %) and 2-(2'-methoxyisopropyl)- (21 ∼ 28 %) 4-methoxy-2-cyclopentenones, α-furyl isopropyl ketone (3 %) which would be presumably formed via rearrangements of the intermediates postulated previously for the formation of the oxepinone and 4-hydroxymethylenecyclopentenone derivatives.

Skorianetz, Schulte-Elte, and Ohloff[1] and we[2,3] recently found that 6,6-dimethylfulvene (**1**) underwent both direct and sensitized photooxidations and subsequent rearrangements to give 3,3-dimethyl-2(3*H*)-oxepinone (**2**),[1-3] 5-isopropylidene-4-hydroxy-2-cyclopentenone (**3**),[1,2] 5,5-dimethyl-4-hydroxymethylene-2-cyclopentenone (**4**),[1] and 5-isopropenyl-4-hydroxy-2-cyclopentenone (**5**),[3] and that the yields of these compounds were dependent on solvent employed (especially in the case of methanol) and/or on isolation procedure.[3] We now wish to report the photochemical oxidation of **1** in an alkaline methanolic solution,[4] giving α-furyl isopropyl ketone and two methanol addition products of the isopropylidene ketol **3**



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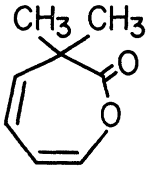

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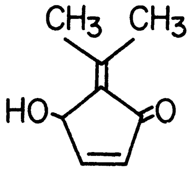

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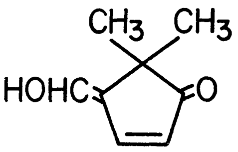

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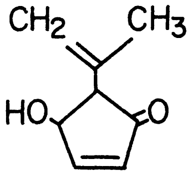

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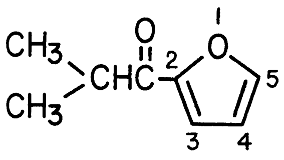
A solution of dimethylfulvene (**1**, 300 mg) in methanol (150 ml) containing potassium hydroxide (80 mg) in a Pyrex reaction tube was irradiated externally with a 500-W high-pressure mercury lamp at room temperature for 20 hr while a finely dispersed stream of oxygen was bubbled through the reaction mixture. Concentration of the solvent and preparative tlc on silica gel with ether and petroleum ether (1 : 1) gave, at the expense of the oxepinone **2** and the hydroxymethylene compound **4**,[6] three neutral products, **6**, **7**, and **8** in 3, 5, and 21 % yields, respectively. Product **6** exhibits mass M$^+$ 138, ir bands at 1670 (a conjugated ketone). and 3125, 1570, 1465, 1260, 1160, 1094, and 885 cm^{-1}, indicative of a furan ring, uv maxima at 226 (ε, 2500) and 269.5 nm (ε, 14400), identical with those of α-furyl methyl ketone, and nmr peaks (100 MHz, CCl_4) at δ 1.16 (d, J = 6.7 Hz, 6H) and 3.30 (m, 1H) [$-CH(CH_3)_2$], 6.46 (q, J_{3-4} = 3.5 and J_{4-5} = 1.7 Hz, 1H, C4-H), 7.08 (q, J_{3-5} = 1.0 Hz, 1H, C3-H), and 7.50 ppm (q, 1H, C5-H), in agreement with α-furyl isopropyl ketone, and was definitely identical with the authentic sample, prepared from furfural by condensation with isopropyl magnesium bromide followed by Collins[7] oxidation.



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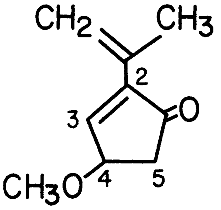

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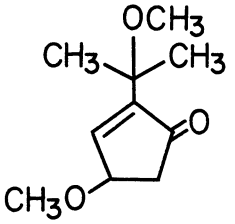

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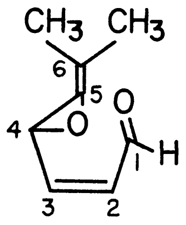
Structure of two other products 7 and 8 were assigned as 2-isopropenyl-4-methoxy-2-cyclopentenone and 2-(2'-methoxyisopropyl)-4-methoxy-2-cyclopentenone, respectively, on the basis of the following spectral data, 7 : ir 3070, 1716, 1640, 1593, 920, and 885 cm^{-1} ; uv (EtOH) λ_{max} = 256 nm (ε, 6530); nmr (100 MHz, CCl_4) δ 1.94 (s, 3H, $>\!\!-CH_3$), 2.30 (q, 1H) and 2.68 (q, 1H) (J_{gem} = 17.7, J_{4-5} = 2.4 and 6.0 Hz, C5-methylene protons), 3.37 (s, 3H, OCH_3), 4.40 (m, 1H, C4-H), 5.20 (br.s, 1H) and 6.17 (br.s, 1H) ($>\!=CH_2$), and 7.20 ppm (d, J_{3-4} = 2.5 Hz, C3-H), 8 : ir 1709 and 1640 cm^{-1}; uv (EtOH) λ_{max} = 212 nm (ε, 8870); nmr (100 MHz, CCl_4) δ 1.32 (s, 3H) and 1.36 (s, 3H) (gem. dimethyl), 2.27 (q, 1H) and 2.61 (q, 1H) (J_{gem} = 18, J_{4-5} = 2.0 and 5.5 Hz, C5-methylene protons), 3.21 (s, 3H) and 3.37 (s, 3H) (two OCH_3), 4.35 (m, 1H, C4-H), and 7.29 ppm (d, J_{3-4} = 2.3 Hz, 1H, C3-H).[8] These two compounds 7 and 8 appeared to be formed by base-catalyzed addition of methanol to the isopropylidene ketol 3 .[9] Actually, on treatment of 3 with methanolic potassium hydroxide at room temperature for 2 hr the compounds 7 and 8 were obtained in 14 and 41 % yields, respectively. Nature of the carbon skeleton, a cyclopentenone, of the compound 8 was confirmed by catalytic hydrogenation giving rise to two cyclopentanone derivatives, 2-isopropyl- (44 %, ir: 1737 cm^{-1}) and 2-(2'-methoxyisopropyl)- (13 %, ir: 1737 cm^{-1}) 4-methoxycyclopentanones.

Considerably rapid reaction was observed under sensitized conditions. Thus, the sensitized photooxidation of 1 (1 g) in methanol (150 ml) containing potassium hydroxide (160 mg) and Rose Bengal (80 mg), employing a 200-W Tungsten lamp, was completed within 2 hr, and gave the comparable result with the above direct photooxidation, yielding 6 (3 %), 7 (12 %), and 8 (28 %).

The aldehydic allene oxide 9 and the valence tautomer, the cyclopropanone 10 have been postulated as plausible unisolated reactive intermediates in the formation of the oxepinone 2 [1,2] and the hydroxymethylene ketone 4 .[1] The furan compound 6 would be also derived from either 9 or 10 (or an equivalent reactive species: a ring-opened zwitterionic counterpart[10]) by attack of the aldehydic carbonyl oxygen atom to C-4 followed by elimination of a proton from C-4, as shown in 11 .



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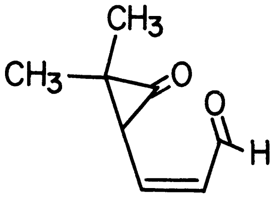

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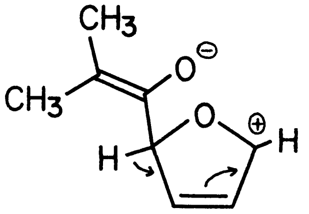

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Furthermore, on the preparative-scale sensitized photooxidation of 1 in neutral media (methanol) as reported previously (-70°, careful working-up, alumina chromatography),[2] it was found that the furan derivative 6 was also isolated as a minor product (1 ~ 2 %). It should be noted that in this case 6 could not be detected in the crude photolysate before subjecting to chromatography on alumina either by glc or tlc (SiO_2). In the same manner, 6,6-pentamethylenefulvene also afforded cyclohexyl α-furyl ketone (12) (ca. 3 %. mp 42 ~ 43°) and 5-cyclohexylidene-4-hydroxy-2-cyclopentenone (ca. 10 %),[11] whose absorption maxima in ir and uv, and splitting pattern of olefinic protons in nmr closely resemble those of the corresponding dimethyl analogues 6 and 3 , respectively.

From these results, the formation of the furan derivatives 6 and 12 apparently seems to be subsidiary due to action of a base, alcoholic potassium hydroxide or alumina. At present, however, clear evidence has not been obtained.

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References

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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, Chemistry Lett., in press.
4) It has been reported[5] that the sensitized photooxidation of cyclopentadiene in dilute alkaline alcoholic solutions gave 4-hydroxy-2-cyclopentenone (20 %), different from the products, 4,5-epoxy-cis-2-pentenal (58 ~ 70 %) and cis-1,2:3,4-diepoxycyclopentane (7 ~ 10 %), in neutral media.
5) K. H. Schulte-Elte, B. Willhalm, and G. Ohloff, Angew. Chem., 81, 1045 (1969); W. R. Adams and D. J. Trecker, Tetrahedron, 27, 2631 (1971).
6) An acidic fraction has not been investigated further.
7) J. C. Collins, W. W. Hess, and F. J. Frank, Tetrahedron Lett., 3363 (1968).
8) These compounds gave satisfactory elemental analyses.

9) For the formation of **7** and **8** there would also be a possibility of methanol addition to the isopropenyl ketol **5** . Alternatively, however, the isomerization of **5** to **3** would occur under the condition used, because of the instability of **5** to base.[3]

10) For the reactions of allene oxides, see J. K. Crandall, W. H. Machleder, and M. J. Thomas, *J. Amer. Chem. Soc.*, **90**, 7346 (1968), and of cyclopropanones, see N. J. Turro, *Accounts Chem. Res.*, **2** , 25 (1969), and references therein.

11) The direct photooxidation of 6,6-pentamethylenefulvene in benzene gave 3,3-pentamethylene-2(3*H*)-oxepinone.[2]

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