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ISOLATION AND PROPERTIES OF 6,6-DIMETHYLFULVENE 1,4-EPIDIOXIDE[1]

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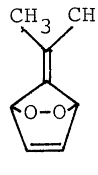
The 1,4-epidioxide (1) of 6,6-dimethylfulvene has been isolated and characterized when the sensitized photooxidation of dimethylfulvene was conducted in a concentrated methanolic solution at low temperature, and the thermal isomerizations of 1 to all of the photooxidation products of dimethylfulvene reported previously have been demonstrated.

The 1,4-epidioxide (1) of 6,6-dimethylfulvene has been postulated as the initial product of the photochemical oxidation of dimethylfulvene to account for the formation of all of the products, including not only 1,4-ketols, 2 and 3 , but also the novel rearrangement products, 4 , 5 , and 6 , *via* the aldehydic allene oxide 7 and cyclopropanone 8 .[2-5] However, the 1,4-epidioxide 1 could not be isolated or even any clear evidence for the existence and isomerization of 1 has not been obtained.[6,8] We now wish to report the isolation, properties and isomerization of 1 .

A concentrated methanolic solution of 6,6-dimethylfulvene (2 g in 40 ml) in the presence of Rose Bengal (20 mg) was irradiated with a 200-W tungsten lamp at -70° for *ca*. 10 hr while a stream of oxygen was bubbled through the reaction mixture. Under the condition, initially dimethylfulvene did not dissolve completely but gradually dissolved in the solution during irradiation, and at the end of the irradiation period[9] a considerable amount of colorless crystals was deposited from the solution.[10] This crystalline compound could be isolated by quick and careful filtration, washing with a small amount of cold methanol, and removing methanol *in vacuo* at -70°, and the structure, the desired 1,4-epidioxide 1 , was unequivocally established on the basis of the following nmr spectrum at -55°; δ (100 MHz, $CDCl_3$) 1.72 (s), 5.47 (t, *J* = 2.0 Hz), and 6.72 (t) with the area ratio of 3 : 1 : 1, as shown in Fig. 1.[11] The dried sample



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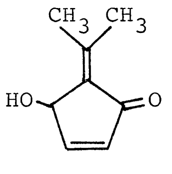

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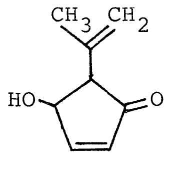

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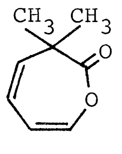

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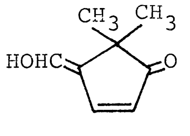

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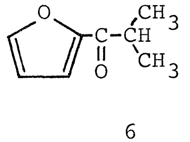

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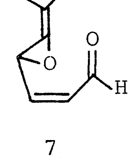

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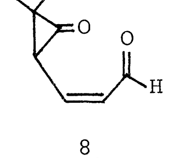

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of 1 was so unstable as to decompose explosively above -10°,[12] indicating a peroxide nature, but, in solution, 1 was converted into other compounds without explosion by slow warming up.

Thus, the thermal transformations of 1,4-epidioxide 1 were examined by treatment with a variety of solvents and reagents. In all experiments the reaction mixture was prepared at -70° and then slowly warmed up to room temperature in a period of *ca.* 12 - 14 hr.

1. Decomposition of 1 in methylene chloride, an aprotic solvent, gave the oxepinone 4 and the isopropenyl-1,4-ketol 3 in a ratio of *ca.* 10 : 1 (glc).[13] These compounds were separated by preparative tlc on silica gel and identified with the authentic samples. This thermal transformation of 1 to 4 and 3 was also followed by taking the nmr spectrum of 1 in a deuterochloroform solution. Figure 1 also indicates the nmr spectra of 1 at -10°, -5°, and 0°, respectively. From -20° a weak signal appeared as a sharp singlet at δ 1.36, which is attributable to the geminal dimethyl protons of 4 , and more raising temperature, especially between -10° ~ 0°, resulted in rapid increase in the intensity of this signal along with other signals, with disappearance of the signals due to 1 . The final spectrum clearly indicates that the product consisted mainly of the oxepinone 4 accompanied with a small amount of the isopropenyl-1,4-ketol 3 as shown in Fig. 1. The result, the preferential formation of 4 in methylene chloride or chloroform, was the same as that of the photooxidation of dimethylfulvene in such aprotic solvents[2,4] and apparently confirms the previous postulation for the formation of 4 from 1 through a facile thermal isomerization.[2,3] As mentioned above, the aldehydic allene oxide 7 and cyclopropanone 8 have been proposed as the plausible intermediates in the course of the isomerization of 1 to 4 . However, no clear evidence for the intervention of these compounds, 7 and 8 , could be observed even by the nmr analysis, because of the immediate appearance of the signals ascribable to 4 as indicated.[14]
2. On standing in methanol 1 gave a mixture of the isopropylidene- and isopropenyl-1,4-ketols, 2 and 3 , and the oxepinone 4 in a ratio of *ca.* 2 : 2.2 : 1. Predominant formation of 1,4-ketols, 2 and 3 , in methanol was identical with the result obtained in the photooxidation of dimethylfulvene in methanol.[2-4]
3. Treatment of 1 with methanolic potassium hydroxide afforded the furyl ketone 6 and two methanol addition products, 9 and 10 , of the isopropylidene-1,4-ketol 2 in a ratio of *ca.* 1 : 1.2 : 10.2, being again comparable to the result of the photooxidation of dimethylfulvene in an alkaline methanolic solution.[5]
4. Exposure of 1 to basic alumina or triethylamine with methylene chloride resulted in formation of the isopropylidene-1,4-ketol 2 , supporting that the presence of base favors the Kornblum - de la Mare - fragmentation[15] of the peroxide linkage even in methylene chloride. In the case of triethylamine 4 was also obtained as a minor product, the ratio of 2 to 4 was about 9 : 1.
5. Treatment of 1 with sodium borohydride in methanol gave a crystalline glycol 11 , mp 83.5 - 86°. The structure of 11 was elucidated on the basis of the following evidence: ν (KBr) 3300, 1685, 750 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.89 (6H, s, two olefinic methyls), 3.75 (2H, br., OH), 4.87 (2H, br.s, methine protons), 6.09 (2H, br.s, olefinic protons).[16]

From the above results (1 ~ 3) it has become apparent that all of the photooxidation products of dimethylfulvene reported previously[2-5] were produced thermally from the 1,4-

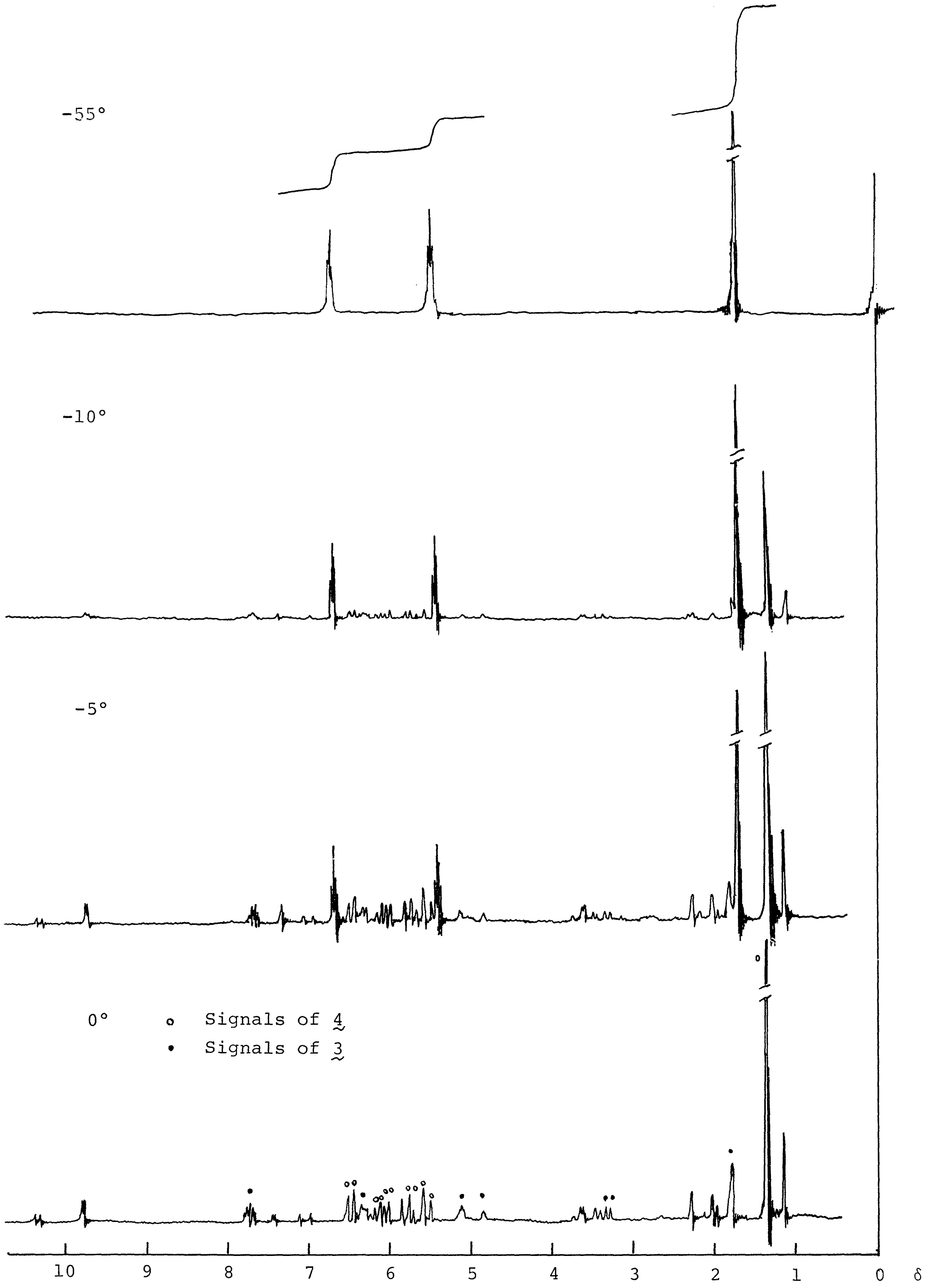
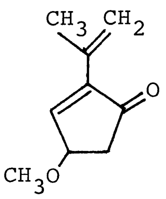


Figure 1. NMR Spectra of 6,6-Dimethylfulvene 1,4-Epidioxide (1) at Various Temperatures.



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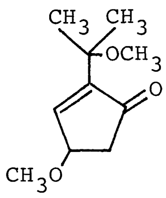

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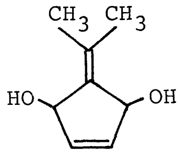

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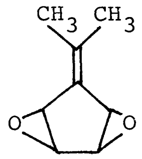

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epidioxide 1 . In the present studies the bisepoxide 12 could not be obtained by a thermal rearrangement of 1 in contrast to the fact that the thermal rearrangement of 1,4-epidioxides derived from cyclic dienes, including cyclopentadiene,[17] gave bisepoxides along with or without other products.[18,19]

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6) Hasselmann reported that 1,4-epidioxide 1 was formed by the sensitized photooxidation of dimethylfulvene in methanol at -80°,[7] but detailed experimental procedures and the properties of 1 have not been published[7].

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8) Existence of 1 in a photolysate at -30° was qualitatively shown by positive peroxide test with potassium iodide - acetic acid, see Ref.2.

9) Progress of the reaction (the consumption of dimethylfulvene) was monitored by tlc analysis on silica gel.

10) No crystalline substance was separated from the reaction mixture when a dilute solution of dimethylfulvene (1 g in 40 ml of methanol) was used.

11) Chemical shift values and coupling patterns of the bridge-head and olefinic protons are in good agreement with those observed for the corresponding protons of 6,6-di-*p*-anisylfulvene 1,4-epidioxide, N. Harada, S. Kudo, H. Uda, and S. Utsumi, to be published.

12) Actual yield and other physical properties could not be measured.

13) A trace of the hydroxymethylene ketone 5 was also produced as detected by tlc analysis.

14) Although weak methyl signals at δ 1.12 (weakened more at room temperature), 2.03, and 2.28, and a weak aldehyde signal at δ 9.77 (d, *J* = 2.5 Hz, changed to singlet at δ 9.73 at room temperature) were also observed, these signals could not be ascribed to either 7 or 8 .

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16) Satisfactory analytical data was obtained.

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