

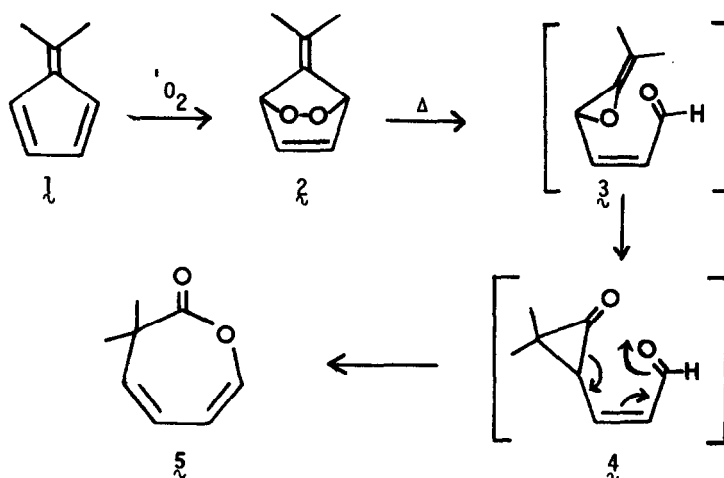
A NEW EPOXYKETONE PHOTOREARRANGEMENT INVOLVING A  
CYCLOPROPANONE INTERMEDIATE

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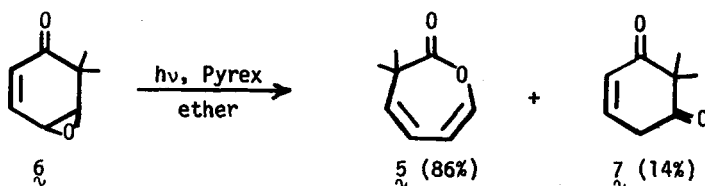
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Studies on the photochemical oxidation of 6,6-dimethylfulvene (**1**)<sup>1,2</sup> showed that the initially formed endo-peroxide **2**<sup>2d,3</sup> rearranges thermally to the enol-lactone **5** and other products.<sup>4</sup> The allene-oxide **3** and unsaturated cyclopropanone-aldehyde **4** were proposed as intermediates. We

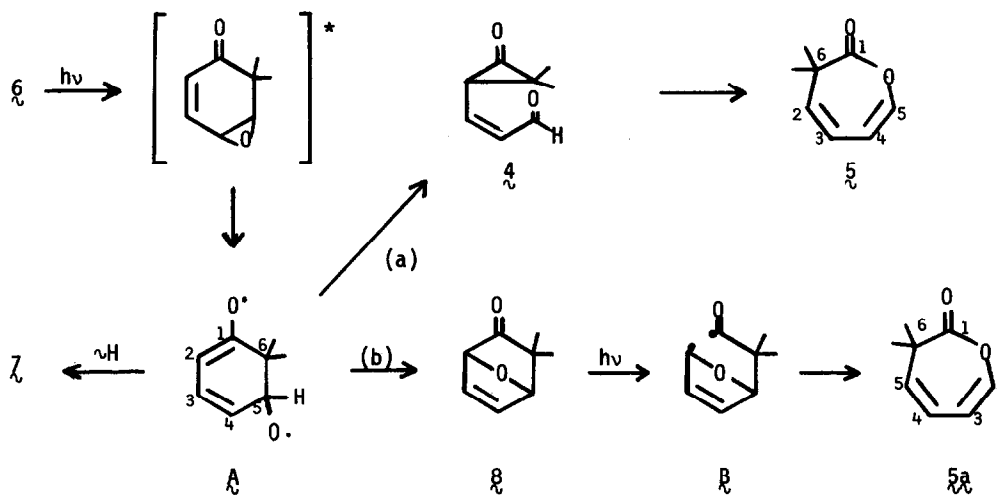


wish to describe a novel and unexpected photoisomerization of 2,4-cyclohexadienone-4,5-epoxides<sup>5</sup> which proceeds via the same intermediate **4** (and substituted analogs).

Irradiation of the epoxyenone **6**<sup>6,7</sup> gave a quantitative yield of **5**<sup>8,9</sup> and **7**<sup>9,10</sup>. The photoisomerization could be sensitized (acetophenone, benzophenone) and quenched (trans-1,3,5-hexatriene, but not piperylene).



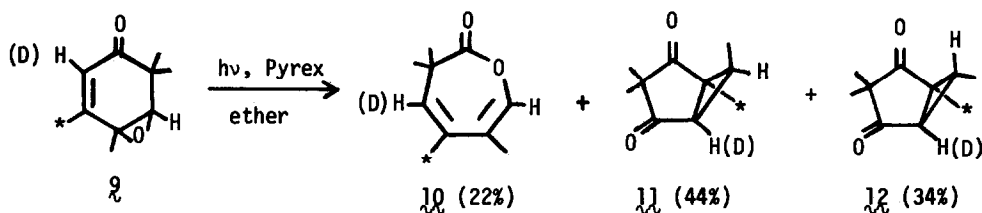
The mechanisms shown in the scheme were considered.



Excitation to the triplet and epoxide cleavage should give diradical  $A^5$  which can rearrange to 7 by a 1,2-hydrogen migration.<sup>11</sup> There are at least two plausible paths from  $A^5$  to 5. Cleavage of the C5-C6 bond and rebonding (C6-C2 and C5-O) would give the cyclopropanone 4,<sup>12</sup> which can rearrange to 5 by an electrocyclic process. Alternatively, ring closure to 8 followed by Type I cleavage would give 8 which also might rearrange to 5.

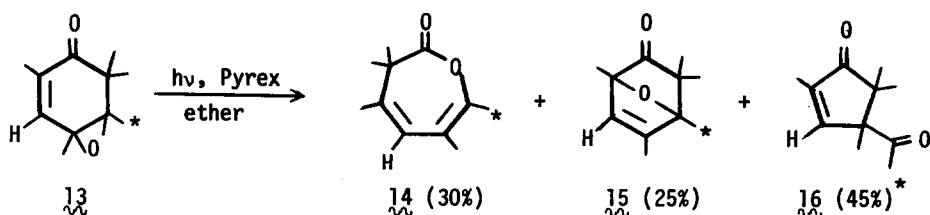
There are different labeling consequences of paths (a) and (b) as shown by the numbers on structures 5 and 5a in the scheme. If path (b) prevails, the carbon sequence in the enol-lactone (5a) and starting epoxyketone (6) will be identical, the epoxide oxygen being inserted between C1 and C2. But if path (a) obtains, the carbon sequence is altered, C6 being inserted between C1 and C2 (5).

Although it was not feasible to perform the necessary labeling experiment with 6, several substituted analogs which were readily labeled underwent a similar rearrangement. Irradiation of 9<sup>13</sup> gave 10-12.<sup>9,10,14</sup> Irradiation of 9-d<sub>4</sub><sup>15</sup> (labeled with deuterium at the C2 proton and



the C3-methyl group) gave 10-d<sub>4</sub> labeled as shown,<sup>16</sup> consistent only with path (a).

In a parallel experiment, irradiation of 13<sup>6,17</sup> gave 14-16.<sup>9,10</sup> The formation of 15 shows that the first step of path (b) is sometimes followed. However, separate irradiation of 15 under the same conditions did not give any 14, eliminating 15 as a reaction intermediate.<sup>18</sup> Irradiation of labeled 13 (\* = CD<sub>3</sub>) confirmed the predictions of path (a).



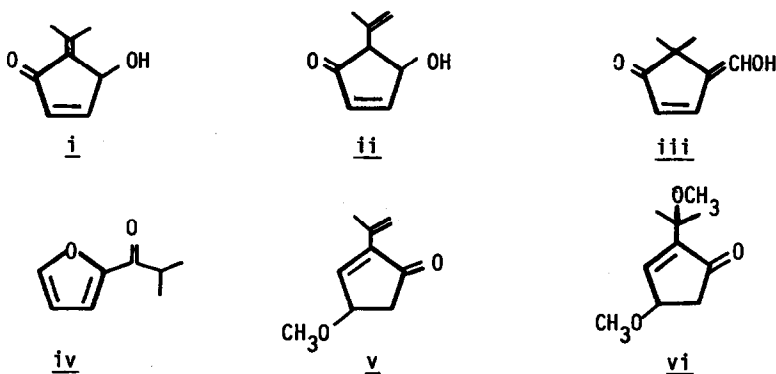
In an attempt to trap the cyclopropanone  $\underline{4}$ , we irradiated  $\underline{6}$  in methanol at room temperature and at  $-78^\circ$ ; only  $\underline{5}$  and  $\underline{7}$  were formed, in about the same ratio as in ether.<sup>19</sup> However, irradiation of  $\underline{6}$  in tetrahydrofuran at  $-105^\circ$  allowed us to observe a weak band at  $1815 \text{ cm}^{-1}$  which disappeared on warming, and which may be attributed to the cyclopropanone carbonyl of  $\underline{4}$ .<sup>20</sup>

Further studies are in progress.

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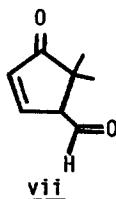
#### References and Notes

1. W. Skorianetz, K.H. Schulte-Elte and G. Ohloff, Helv. chim. Acta, **54**, 1913 (1971).
2. (a) N. Harada, S. Suzuki, H. Uda and H. Ueno, J. Am. Chem. Soc., **94**, 1777 (1972); (b) N. Harada, H. Uda and H. Ueno, Chem. Lett., 663 (1972); (c) N. Harada, S. Suzuki, H. Uda and H. Ueno, Chem. Lett., 803 (1972); (d) N. Harada, H. Uda, H. Ueno and S. Utsumi, Chem. Lett., 1173 (1973).
3. The endoperoxide has been isolated at  $-70^\circ$ .<sup>2d</sup>
4. The product composition depends on the solvent. Whereas  $\underline{5}$  predominates in nonpolar solvents (benzene, methylene chloride, chloroform), cyclopentenones i-iii are formed in methanol,<sup>1,2a,b</sup> and in methanolic KOH the major products were iv-vi.<sup>2c,d</sup>

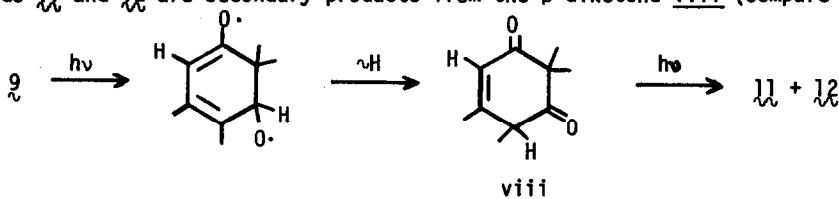


5. For the first study in this series, and for leading references to other  $\gamma, \delta$ -epoxy- $\alpha, \beta$ -unsaturated ketone photoisomerizations, see H. Hart and E-m. Shih, J. Org. Chem., **41**, 3377 (1976).

6. Synthesized by the *m*-chloroperbenzoic acid oxidation of the corresponding dienone.
7. K. Alder, F.H. Flock and H. Lessenich, Chem. Ber., **90**, 1709 (1957).
8. Ir, nmr, uv and mass spectra agreed with those reported previously.<sup>1,2a</sup> The yield of **5** was considerably better from **6** than from **1**.
9. A correct elemental analysis was obtained.
10. Ir, nmr, uv and mass spectra were consistent with the assigned structure; details will be presented in a full account.
11. The alternative 1,2-alkyl shift would give **vii**, which was not observed, although this is the main path taken by the fully methyl-substituted analog of **6**.<sup>5</sup>



12. Unlike the rearrangement of **2**, the allene-oxide **3** is not a necessary intermediate in this path.
13. H. Hart and P. Lavrik, J. Org. Chem., **39**, 1793 (1974).
14. Compounds **11** and **12** are secondary products from the  $\beta$ -diketone **viii** (compare with **7**).



15. Prepared by treatment of **9** with dimethyl sulfoxide- $d_6$  and potassium *t*-butoxide, room temperature, 3 hr.
16. The vinyl protons in **10** appear at  $\delta$ 5.13 and 6.13 (adjacent to O); both allylic methyls appear at  $\delta$ 1.80. In **10**- $d_4$ , the vinyl proton at  $\delta$ 5.13 was absent. Irradiation of **10** (Corex) give **ix**, with ring juncture protons at  $\delta$ 2.82 and 4.67 (adjacent to O). Irradiation of **10**- $d_4$  gave **ix**- $d_4$  lacking the peak at  $\delta$ 2.82. For unusual photoisomerizations of enol lactones similar to **5**, **10**, and **14**, but with phenyl substituents, see K. Sato, H. Hagiwara, H. Uda, M. Sato and N. Harada, J. Am. Chem. Soc., **98**, 8281 (1976).
17. P.M. Collins and H. Hart, J. Chem. Soc. C, 895 (1967).
18. Compound **15** was recovered unchanged. Separate irradiation of **16** showed that it too was not an intermediate in the formation of **14**.
19. This result shows that in the photochemical oxidation of **1**, products **i-vi**<sup>4</sup> cannot be derived from **4**; they may come from reaction of the solvent or base with **2** or **3**.
20. N.J. Turro, Acc. Chem. Res., **2**, 25 (1969).

