

SENSITIZED PHOTOOXIDATION OF SPIRO[2,4]HEPTA-4,6-DIENE

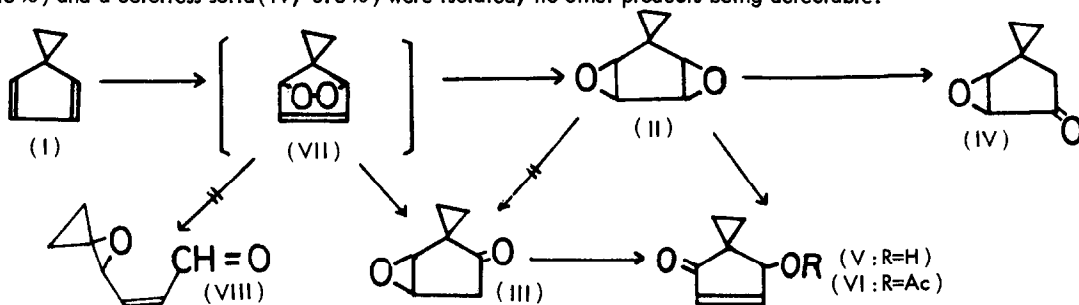
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The sensitized photooxidation of cyclopentadienes is of current interest, especially the C-C bond cleavage after rearrangement of the initially formed 1,4-endoperoxide.<sup>1)</sup> In continuation of our interest in this field,<sup>2)</sup> we have carried out sensitized photooxidation of the spirocyclic derivative of this simple chromophore to determine the substituent effect of the cyclopropyl group. The absence of skeletal transformation in the present reaction is in contrast to the results of previous studies in this field.

A chloroform solution of spiro[2,4]hepta-4,6-diene (I, 2 g) was irradiated by a 500 W tungsten lamp under oxygen atmosphere at 0-5° (with methylene blue), the reaction was completed within 2 hours. By silica-gel column chromatography of the reaction mixture, colorless crystals (II, mp 94-95°, 48%), a colorless liquid (III, 48%) and a colorless solid (IV, 0.6%) were isolated, no other products being detectable.



The structure of II ( $M^+/e: 124$ )<sup>3)</sup> was deduced to be the cis-4,5-6,7-bisepoxyspiro[2,4]heptane on the basis of the NMR spectrum<sup>4)</sup> [ $\delta$ : 0.88(4H, m), 3.19(2H, dd,  $J=3$ , 1 Hz) and 3.62(2H, dd,  $J=3$ , 1 Hz)]. Second product (III) was shown to be an epoxyketone ( $\nu$ : 1740, 1240, 935, 930 and 838  $\text{cm}^{-1}$ ), and the presence of the  $\alpha$ -cyclopropylketo-group being evidenced by the down field shift of the cyclopropane methylene groups [ $\delta$ : 1.21(4H, m)], while the other NMR signals indicated the position of the epoxy group as  $\beta$ ,  $\gamma$ - to the carbonyl group, i.e., the higher signal [3.41(d,  $J=4$  Hz)] is attributable to a proton vicinal to the spiro-carbon atom, while the lower signal [3.90(m)] exhibited further splitting by adjacent methylene signals [2.61(overlapping m)]. The minor product (IV) was shown on the basis of the NMR spectrum [ $\delta$ : 0.5-0.9(4H, m), 1.70(d,  $J=18$  Hz), 2.62(d,  $J=18$  Hz), 3.30(d,  $J=3$  Hz), 3.47(d,  $J=3$  Hz)] to be the isomer of III.

When the reaction was carried out at room temperature,<sup>5)</sup> the only isolable product was V (colorless liquid, 24%) whose structure was shown to be 7-hydroxy-spiro[2,4]hept-5-en-4-one on the basis of the NMR spectral analysis [ $\delta$ : 1.20(4H, m), 2.94(OH, br. s), 4.62(dd,  $J=3$ , 1 Hz), 6.34(dd,  $J=6$ , 1 Hz), and 7.64(dd,  $J=6$ , 3

Hz)]. V gave the corresponding acetate (VI), a colorless liquid [ $\delta$ : 1.0–1.4(4H, m), 2.06(3H, s), 5.65(dd,  $J=3$ , 1.2 Hz), 6.42(dd,  $J=6$ , 1.2 Hz), and 7.52(dd,  $J=6$ , 3 Hz)]. VI was formed when III was left in a solution of chloroform and acetic anhydride for 72 hours at room temperature. On the other hand, similar treatment of II caused no change. Under more drastic conditions, both II and III gave mixtures of polymeric material. However, when a chloroform solution of II was kept in a silica gel column (Wako Gel C 200) for 48 hours, and then eluted with chloroform, IV (37%) and V (22%) were formed by acid-induced isomerization (recovery of II = 28%). The absence of III was clear from the NMR spectral analysis, suggesting that IV and V are formed during the work up. We also examined the effect of irradiation of II for a further 2 hours under the condition of its formation; a substantial amount of II was recovered unchanged, and the NMR spectrum of the reaction mixture failed to reveal signals of III or IV. Therefore, II and III must be formed independently from a common precursor, the endoperoxide (VII), being analogous to the previous observation.<sup>6)</sup>

In general, the isomerization of initially formed endoperoxides is regarded as a thermal process. However, it has been established that 2,3-dioxabicyclo[2,2,2]oct-5-ene derivatives can be also isomerized by sensitization with triplet species of arylketones like benzophenone,<sup>6)</sup> and in certain cases the endoperoxides of cyclopentadienes rearrange on irradiations to the bisepoxides.<sup>1b)</sup> Although VII has not been isolated, and it is not possible to show the nature of the rearrangement experimentally,<sup>3)</sup> this facile reaction of VII, like that of other endoperoxides derived from cyclopentadienes, is interesting in view of its isoelectronic relation with norbornadiene which is known to exhibit an intramolecular  $\pi$ -interaction.<sup>7)</sup>

In addition to this, the following unique features were observed in this reaction; i) unlike reactions previously studied, I gives products possessing the original carbon skeleton (II and III), and no subsequent rearrangement of other C–C bond cleavage of II, such as formation of VIII, was observed, and ii) endoperoxides are ordinarily known to give  $\alpha,\beta$ -epoxyketones, but the rearrangement of VII exclusively yielded the  $\beta,\gamma$ -isomer (III), whose mode of the formation has not been previously recognized.

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#### References and Notes

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- 3) Mass spectra of all the epoxides in this series showed characteristic fragmentation,  $(M-30)^+/e$ , whose significance, in connection with oxidative fragmentation of the cyclopropyl group,<sup>2)</sup> will be reported elsewhere.
- 4) All the NMR spectra cited in this paper were taken in  $CDCl_3$  solutions.
- 5) A decrease of the total yield was mainly due to the dimerization of I.<sup>2)</sup>
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