

SENSITIZED PHOTOOXIDATION OF THE DIMER OF SPIRO[2,4]HEPTA-4,6-DIENE:  
A NOVEL OXIDATIVE FRAGMENTATION OF THE CYCLOPROPYL GROUP

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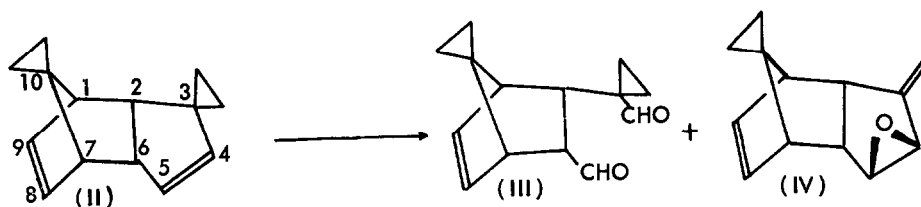
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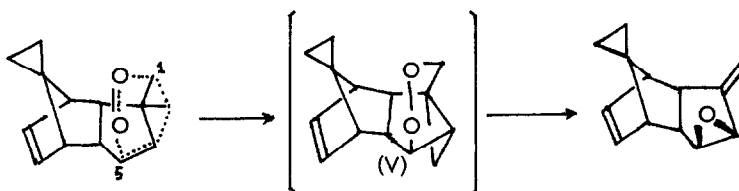
In our previous studies on the reaction of singlet oxygen with vinylcyclopropanes,<sup>1-5)</sup> we have observed, for the first time, the C=C bond cleavage of an alicyclic olefins bearing no heteroatom,<sup>1,2,4)</sup> and have shown that this should directly be related with the intermediate, dioxetane, by the reaction in deuterio-methanol<sup>3)</sup> and by an independent confirmation of subsequent photochemical transformation<sup>4)</sup> together with the observation of the ene-reaction taking place at a non-axial methine hydrogen of the cyclopropane ring, accompanied by a new skeletal rearrangement.<sup>4,5)</sup> Since these peculiar phenomena may need more elaborate studies to establish the structural cause of the process, which will be desirable to understand the singlet oxygen oxidation in general, we have now extended the study to unprecedented type of the chromophore, spirocyclic derivative. The results will be briefly reported in this communication.<sup>6)</sup>

The compound having this chromophore was easily prepared by Diels-Alder dimerization of spiro[2,4]-hepta-4,6-diene (I)<sup>7)</sup> and its structure was deduced to be II from the analysis of the NMR spectrum.<sup>8,9)</sup> When a chloroform solution of II (2 g) was irradiated by 500 W tungsten lamp with methylene blue under oxygen stream, a clean reaction had proceeded with a moderate rate. After irradiation for 40 hours, two products, III (a colorless liquid, 90 %), and IV (a colorless liquid, 5-7 %) were isolated by silica-gel column chromatography. Thin layer chromatographic detection of other product has been unsuccessful. The NMR spectrum of III showed two aldehydic proton signals at  $\delta$ : 9.50(d,  $J=2$  Hz) and 8.58(s), suffering an induced ring current effect of the adjacent cyclopropyl group. Thus, the cleavage has occurred on the double bond conjugated with the cyclopropyl group, and III constitutes a further example of the dioxetane related products in the reaction of vinylcyclopropanes. Other NMR spectral features of III [  $\delta$ : 2.05( $H_1$ , m), 3.68( $H_2$ , dd,  $J=9, 4$  Hz), 1.08(4H, m), 3.47( $H_6$ , ddd,  $J=9, 4,$

2 Hz), 2.50( $H_7$ , m), 6.40( $H_8$ , ddd,  $J=6, 4, 1.5$  Hz), 6.00( $H_9$ , ddd,  $J=6, 4, 1$  Hz) and 0.55(4H, apparently s)] are in full accord with the structure depicted. The other product (IV) has shown to be  $C_{13}H_{14}O$  ( $M^+/e$ : 186), revealing a loss of one carbon unit, and has only one cyclopropane ring retained [  $\delta$ : 0.45(4H, m) ]. The presence of an epoxy-group [  $\delta$ : 3.18(d,  $J=3$  Hz) and 3.33(d,  $J=3$  Hz),  $\nu$ : 1008, 845, 837, 813, 800 and 755  $cm^{-1}$  ] and a vinylidene group [  $\delta$ : 4.93(br. s) and 5.17(br. s),  $\nu$ : 890  $cm^{-1}$  ] was evident, and furthermore, there is a prominent peak due to retro-Diels-Alder process in the mass spectrum ( $m^+/e$ : 92), suggesting the intactness of  $C_1$ -,  $C_2$ -,  $C_6$ - and  $C_7$ -positions. These observations, combined with the rest of the NMR data [  $\delta$ : 2.23(2H, m), 2.95 (2H, m) and 5.96(2H, t,  $J=2$  Hz) ], lead to the formulation as shown. Apparently, IV belongs to none of the genuin product expected from the known processes of the reaction.



Thus, the overwhelming formation of the dioxetane with the absence of the ene-product is noteworthy, since the  $C_6$ -hydrogen of II is axial in the almost planar cyclopentene ring and fulfills the stereo-electronic requirement for the ordinary ene-process of the reaction.<sup>10)</sup> While, the formation of IV should be of interests in regard of the followings: Two modes of the cleavage processes previously observed in the reaction of gurjunene<sup>3)</sup> were: i) the cleavage of chemo-electronically excited cyclopropyl ketone, which was derived from the cyclo-reversion of the dioxetane, and ii) the rearrangement of the methylenecyclopropane formed by a decomposition of the allyl-hydroperoxide. Therefore, the oxygenation itself by singlet oxygen had not taken place on the cyclopropane ring. But IV should be contrastingly regarded as an offspring of the precursor which is derived by an oxygenation on the carbon atom of the cyclopropane ring, and should have an appropriate structure to cause a mild



fragmentation of one carbon unit. In these views, the structure V seems to be one of probable candidates for the precursor, since V, i) could be derived by a symmetry-allowed [ $\pi^2_s, \sigma^2_s, \pi^2_s$ ]-process for the excited state, and ii) formally corresponds to a "homo-Diels-Alder reaction" (1,5-addition) product.<sup>11)</sup> The conversion of V into IV would not be difficult, as visualized in the chart.<sup>12)</sup>

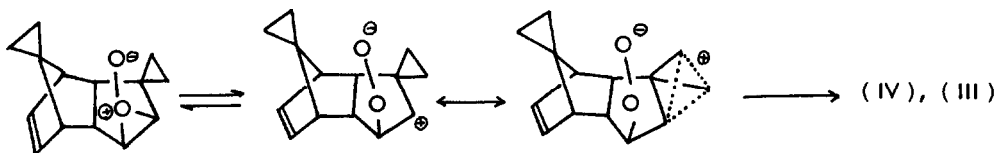
Relating studies on this chromophore are in progress and will be a subject of the forthcoming paper.

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#### REFERENCES & NOTES

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- 5) H. Takeshita, M. Hirama and S. Itô, *ibid.*, 1775(1972).
- 6) A dialdehyde was tentatively identified in the oxidation of homo-semibullvalene. cf., M. Sakai, D. L. Harris and S. Winstein, *J. Org. Chem.*, 37, 2631(1972).
- 7) C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, 83, 3866(1966).
- 8) All the NMR measurements were carried out in carbon tetrachloride solutions, and the chemical shifts were expressed in  $\delta$  value from tetramethylsilane as the internal standard.
- 9) The NMR evidence clearly suggested to be the endo-dimer ( $J_{1,2}=J_{6,7}=4$  Hz).
- 10) An explanation for this peculiarity could also be made in terms of non-concerted mechanism. The ene-process has been for a long time considered to be a typical concerted process (e.g., C. S. Foote, *Account Chem. Research*, 1, 104(1968).), but a basic question to this has aroused. Kearns and his co-leagues have already observed incorporations of some nucleophiles (azide and methoxide ions) into the products with a prevention of the formation of the normal products, and have interpreted the result as the trapping of the precursor (peroxirane) by the nucleophiles (W. Fenical, D. R. Kearns and P. Radlick, *J. Amer. Chem. Soc.*, 91, 7771(1969).). However, later on, Foote et al. (C. S. Foote, T. T. Fujimoto and Y. C. Chang, *Tetrahedron Lett.*, 45(1972).) and Kearns et al. (N. Hasty, P. B. Markel, P. Radlick and D. R. Kearns, *ibid.*, 49(1972).) have found complex behaviors of the azide ion, quenching of singlet oxygen and the incorporation into the

products by a free radical mechanism, thus it makes necessary to withdraw a part of the evidences relied on that. Nevertheless, the proposal should not be completely invalid, and our previous finding, an abstraction of non-axial hydrogen having C-H bond of increased  $s$ -character, can even be better explained by the involvement of such dipolar species like peroxirane. Present results too, by the same concept, could be explained as the scheme illustrated.



The charge-delocalized cyclopropylcarbinyll system would be more reactive (to give IV and/or III) than the neutral  $C_6$ -hydrogen (to give the ene-product) towards nucleophilic attack of the peroxide group.

- 11) S. Sarel and E. Breuer, *J. Amer. Chem. Soc.*, 81, 6522(1959).
- 12) It is also interesting to note that, the conversion of II to V may suggest a biogenetic sequence for illudane (T. C. McMorris and M. Anchel, *J. Amer. Chem. Soc.*, 85, 831(1963).) to marasmane (J. J. Dugan, P. de Mayo, M. Nisbet and M. Anchel, *ibid.*, 88, 2838(1966).), highly oxygenated fungal sesquiterpenic skeletons.