Tetrahedron Letters No.17, pp. 1181-1182, 1971. Pergamon Press. Printed in Great Britain.

DIOXETANE INTERMEDIATE IN THE SENSITIZED PHOTOOXIDATION OF THUJOPSENE

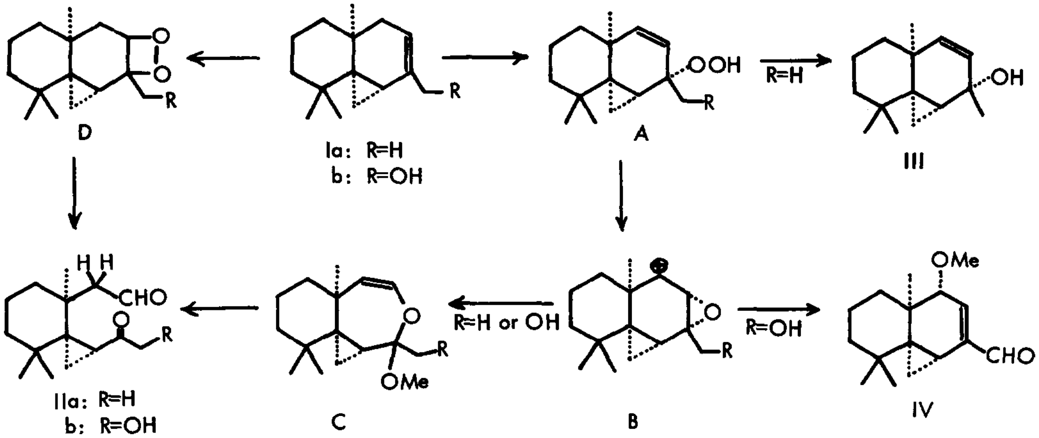
Shô Itô, Hitoshi Takeshita and Masahiro Hirama

Department of Chemistry, Tohoku University

Sendai, Japan

(Received in Japan 11 January 1971; received in UK for publication 19 March 1971)

In our previous studies (1,2) on the sensitized photooxidation of thujopsene (Ia) and thujopsenol (Ib), we have demonstrated the formation of considerable amounts of C=C bond cleavage products, the keto-aldehydes (IIa and IIb) and those formed therefrom, in addition to allylic alcohols (e.g. III) and their offsprings. As C=C bond cleavage of this type was unprecedented for α-cyclopropylolefines, we have rationalized the reaction path I ⟶ A ⟶ B ⟶ C ⟶ II depicted below, taking the known examples into account. However, the formation of II might not proceed through the intermediates A, B and C, but involve the alternative intermediate, a dioxetane D, although A and B are apparently the precursors of III and the methoxy-aldehyde IV, respectively. In the light of the accumulating data on dioxetanes (3), the experimental discrimination of these two path ways was attempted.



Ia was irradiated in methanol-d_1 (isotopic purity 98%) under the same condition as was previously described (1) and the ketoaldehyde IIa' was isolated by preparative thin layer chromatography. Mass spectrum of IIa' was identical with that of the non-deuterated ketoaldehyde IIa (isotopic abundance ratio M^+ 237/236 Found: 0.205, Calcd for $C_{15}H_{24}O_2$: 0.1667). Furthermore, the NMR spectra of IIa and IIa' were also completely identical with each other, exhibiting the methylene signals at 2.96 ppm (ddq, J=13.9, 3.7, 0.9 Hz) and 2.14 ppm (ddd, J=13.9, 2.9, 1.3 Hz) and the aldehydic proton signal at 9.69 ppm (dd, J=3.7, 2.9 Hz), all in the same intensity. Thus the present result clearly demonstrates the absence of any hydrogen abstraction process in the formation of IIa from Ia and excludes the path B $\longrightarrow$ C $\longrightarrow$ IIa, leaving the dioxetane D as only possible intermediate for the reaction.

The previous study (1,2) shows that this C=C bond cleavage amounts to 28 to 33% (based on the yield of the products). This is surprizingly large ratio if one considers the presence of allylic methyl and/or methylene groups from which a hydrogen can be abstracted. Dioxetane intermediate in sensitized photooxidation might therefore have some generality for C=C bond cleavages.

References and Footnotes

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