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RECONFIRMATION OF THE DIOXETANE INTERMEDIATE FOR THE DICARBONYL FRAGMENTATION PROCESS DURING THE SINGLET OXYGEN-OXIDATION OF A VINYLCYCLOPROPANE BY A NEW EXPERIMENTAL PROBE

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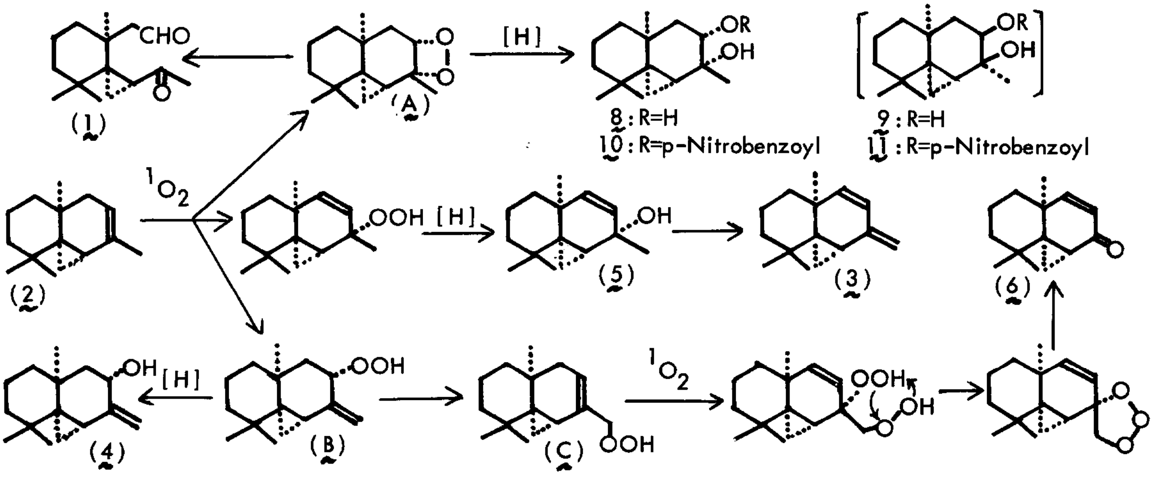
Recently, Frimer *et al.*[1)] have raised a question to the occurrence of dioxetanes in the singlet-oxygen oxidation of vinylcyclopropanes[2,3)] on the basis of reported ^{19}F-NMR spectroscopic and solvolytic studies for the electron densities of cyclopropanes,[4,5)] and have given an alternative explanation, Hock rearrangement,[6)] with their own experiments. In this communication, we like to present a new evidence that the dioxetanes are in fact the precursor of the dicarbonyl derivatives characterized in the former experiments.[2)] Originally, our proposal was made on the basis of the findings, a) the undetectability of a deuterio-ketoaldehyde, 1-$\underline{d}$, from the reaction of thujopsene (2) in methanol-$\underline{d}_1$,[2)] and b) the occurrence of a cleavage process of the cyclopropane ring in the oxygenation of gurjunene, suggesting a generation of an electronically excited cyclopropyl carbonyl group during the visible-light irradiations.[3)]

Using our new method of preparation of *cis*-1,2-glycols form olefins *via* dioxetanes by Rose Bengal (RB)-sensitized photooxidation,[7)] 2 and relatively large amounts of RB were irradiated in methanol by means of a tungsten lamp under an oxygen atmosphere. The reaction mixture was fractionated, after a reduction with dimethyl sulfide, by silica gel chromatography to give previously characterized products, thujopsadiene (3, 2 %), an allyl alcohol (4, 1 %), another allyl alcohol (5, 32 %) and 1 and its secondary products (28 %), together with mayurone (6, 3 %) which was previously obtained from the reaction with thujopsenol (7).[2)]

Furthermore, a new compound, 8 (16 %), colorless needles, mp 65-66°C [$\delta^{8)}$: 0.37 (1H, t, J=5 Hz), 0.53, 1.00, 1.09, and 1.42 (each 3H, s), and 4.44 (1H, dd, J=13, 4 Hz)], was isolated. 8 was identical with one of the *cis*-glycols (8 and 9) obtained in 1 : 1 from 2 and osmium tetraoxide. Although 8 and 9 [δ: 0.03 (1H, t, J=6 Hz), 0.77, 0.82, 1.04, and 1.36 (each 3H, s), and 4.27 (1H, dd, J-11, 4 Hz)] were unseparable even by means of high-pressure liquid chromatography, their mono-*p*-nitrbenzoates, 10, colorless crystals, mp 156-157°C [δ: 0.71 (1H, t, J=5 Hz), 0.58, 1.04, 1.16, and 1.44 (each 3H, s), and 5.05 (1H, dd, J=13, 4 Hz)], and 11, colorless crystals, mp 143-144°C [δ: 0.23 (1H, t, J=6 Hz), 0.81, 0.86, 1.16, and 1.37 (each 3H, s), and 4.90 (1H, dd, J=12, 4 Hz)], were isolated by column chromatography. The stereochemistry of the oxygen part of 8 and 10 was deduced to be same to that of 4[2)] by the NMR evidences. Namely, an equatorial conformation for all secondary hydroxyl groups of 8, 9, 10, 11, and 4 (dd, J=9.5, 7.5 Hz)[2)] was obvious, but only 8 and 10 were shown to fall in the same category of 4 in respects of resonance patterns of methyl singlets. On the other hand, 9 and 11 should belong to the inversed conformers.

Thus, an established *cis*-glycol structure of 8 together with no occurrence of a methoxylation product, which should be a product of any solvolytic process, clarified the precursor to be the dioxetane (A), and an apparent discrepancy with the Frimer's results seems to be due to a difference of types of substrates; Frimer *et al.* have used acyclic olefins, but we have used conformationally rigid cycloolefins. In this respect, Itô has already pointed out a strict relationship with the geometry of two functional groups, the cyclopropane ring and the reacting double bond.[9]

Finally, we would like to mention that a sharp decrease of the yield of 4 might be linked to the formation of 6 in this RB-sensitized photooxygenation, where a rearrangement of the allylhydroperoxide (B), a precursor of 4, into an isomer, C, should be facilitated,[7] and a further oxygenation product of C should enable to form 6. An explanation was tentatively shown in the chart.



References and Notes

1) A. Frimer, D. Rot, and M. Sprecher, Tetrahedron Lett., 1927 (1977).
2) a) S. Itô, H. Takeshita, T. Muroi, M. Ito, and K. Abe, Tetrahedron Lett., 3091 (1969). b) H. Takeshita, T. Sato, T. Muroi, and S. Itô, *ibid.*, 3095 (1969). c) S. Itô, H. Takeshita, and M. Hirama, *ibid.*, 1181 (1971).
3) a) S. Itô, H. Takeshita, M. Hirama, and Y. Fukazawa, Tetrahedron Lett., 9 (1972). b) H. Takeshita, M. Hirama, and S. Itô, *ibid.*, 1775 (1972).
4) R. G. Pews, J. Am. Chem. Soc., 89, 5605 (1969).
5) B. R. Ree and J. C. Martin, J. Am. Chem. Soc., 92, 1660 (1970).
6) G. O. Schenck and K. H. Schulte-Elte, Ann. Chem., 618, 185 (1958).
7) H. Takeshita and T. Hatsui, unpublished results. Will be presented in 38th Annual Meetings of Chemical Society of Japan (April, 1978, Tokyo).
8) The NMR spectra were recorded on a JEOL FX 100 Model Spectrometer, and the chemical shifts were expressed in δ scale from TMS, internal standard, in CDCl$_3$ solutions. The spectrum of 9 was measured as a mixture with 8.
9) *Eg.*, T. Kobayashi and S. Itô, Abstract Papers of Annual Symposium on Photochemistry in Japan, p 101 (Oct., 1975, Tokyo).