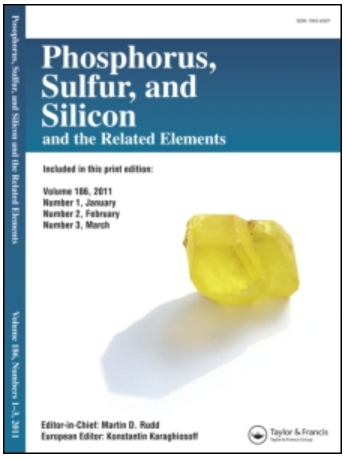

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Ozonolysis of 3,4-Dimethylsulfolene Revised Once More - the End of an Old Puzzle

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OZONOLYSIS OF 3,4-DIMETHYLSULFOLENE REVISED ONCE MORE - THE END OF AN OLD PUZZLE

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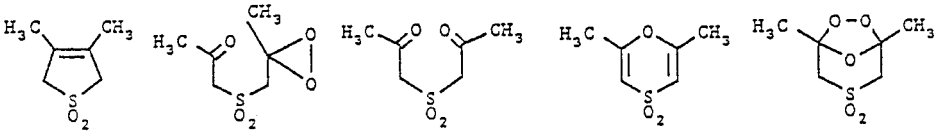
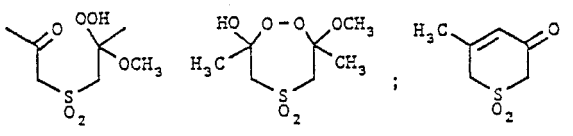
Abstract Reinvestigation of ozonolyses of 3,4-dimethylsulfolene (1) removes ealier errors and uncertainties. A novel mechanistic proposal on the ozonolyses of cyclopentenes is presented.

Introduction

Contradictious results are reported on ozonolyses of 3,4-dimethylsulfolene (1) in different solvents. In spite of the simplicity of the reacting compounds a reasonable explanation on the base of the commonly accepted olefin ozonolysis mechanism appears rather difficult. Therefore, the object of the present work was a careful reinvestigation of this reaction including elucidation of all questionable structures. Our interest was focussed on subsequent formulas:



1 2 3 4 5



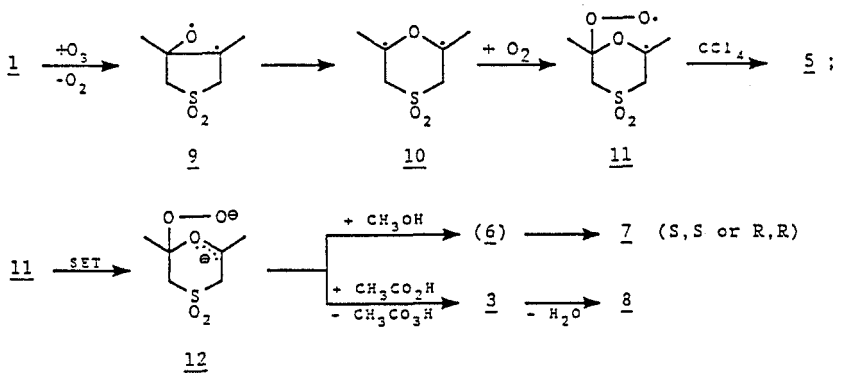
6 7 8

A paper of 1934[1] described ozonolytic cleavage of 1 to 2 in chloroform, reduction of 2 gave rise to diketone 3. A subsequent paper[2] described the formation of 4 in acetic acid. Criegee and Lohaus[3] corrected the structure of 2 to be ozonide 5, in methanol as solvent they reported the generation of a hydroperoxy ether of structure 6 or 7. Treating this compound with benzoyl chloride/pyridine the divinylsulfone 4 should be formed. However a compound with the real structure of 4 has been synthesized lateron via an

unambiguous way[4].

During our reinvestigations we could establish structures 3, 5 and 7, the latter proved to be the S,S (or R,R)-isomer (X-Ray)[5]. "Compound 4 from ozonolyses" proved to be 8 (already known from literature[6]). Our mechanistic proposal is as follows:

1. Mono-oxygen transfer from ozone[7] to the C,C double bond generating 1,3-C,O-diradical 9 (a C,O-homolyzed oxirane)[8].
2. Rearrangement of 9 forming 1,3-diradical 10 (a C,C-homolyzed oxirane)[8], corresponding to an oxidative ring enlargement.
3. Dioxygenation of 10 forming ozonide 5 via 1,5-C,O-diradical 11, or zwitterion 12 after preceding SET within a protic solvent.
4. Zwitterion 12 represents a mesomerism stabilized carboxonium peroxide which follows the known substitution rules of ambident carboxonium cations[9] ending up in the formation of 7 via 6 or 8 via 3:



REFERENCES

1. E. de Roy van Zuydewijn, J. Böeseken, Recl. Trav. Chim. Pays-Bas 53, 673 (1934).
2. H.J. Backer, J. Strating, ibid. 54, 170 (1935).
3. R. Criegee, G. Lohaus, Liebigs Ann. Chem. 583, 12 (1953).
4. C.F. Campana, C.M. Lukehart, M.D. Owen, Sulfur Lett. 13, 133 (1991).
5. G. Maas, Dept. of Organic Chemistry, University of D-6750 Kaiserslautern 1991
6. L. Skattebøl, B. Boulette, S. Solomon, J. Org. Chem. 33, 548 (1968).
7. A.F. Hollemann, E. Wiberg in Lehrbuch der Anorganischen Chemie, 91-100. Aufl., S. 461, de Gruyter 1985.
8. C. Wesdemiotis, B. Leyh, A. Fura, F.W. McLafferty, J. Am. Chem. Soc. 112, 8655 (1990).
9. S. Hünig, Angew. Chem. 76, 400 (1964); I.E. 3, 548.

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