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PHOTOCHEMICAL AND THERMAL REARRANGEMENTS OF 4,4,6,6-TETRAMETHYL-1-OXASPIRO[2.3]HEXAN-5-ONE

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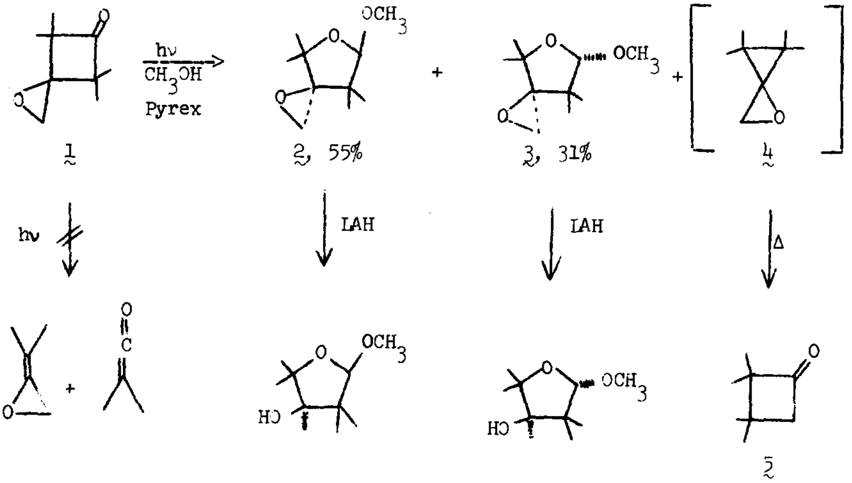
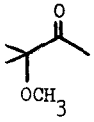
Recent interest in the preparation of allene oxides[1] and the unknown extent to which these novel heterocycles are involved in the reactions of cyclopropanones,[2] prompt us to report the results of our preliminary attempts to isolate these seemingly unstable compounds.

Irradiation (Pyrex filter) of a 0.1 M solution of epoxy ketone **1**[3] in dry methanol followed by glpc analysis revealed the presence of three products in addition to unreacted starting material. Isolation of these products[4] by preparative glpc yielded *cis*-acetal **2** (55%), *trans*-acetal **3** (31%), and 2,2,3,3-tetramethylcyclobutanone (12-14%). In a subsequent experiment, infrared analysis of the gases above the photolysate revealed the presence of carbon monoxide. The tetramethylcyclobutanone (**5**), therefore, probably arises from oxaspiropentane **4**[5], which in turn is formed by decarbonylation of **1**. The stereochemistries of acetals **2** and **3** were determined by the presence and absence respectively of an intramolecular



O-H stretch in the infrared spectra of their derived alcohols. These alcohols were obtained by reductive ring-opening with lithium aluminum hydride.[6]

Further evidence for the complete absence of cycloelimination products was obtained by our inability to detect methyl isobutyrate (dimethylketene-methanol adduct) or methoxy ketone 6 (dimethylallene oxide-methanol adduct[1c], by analytical glpc.



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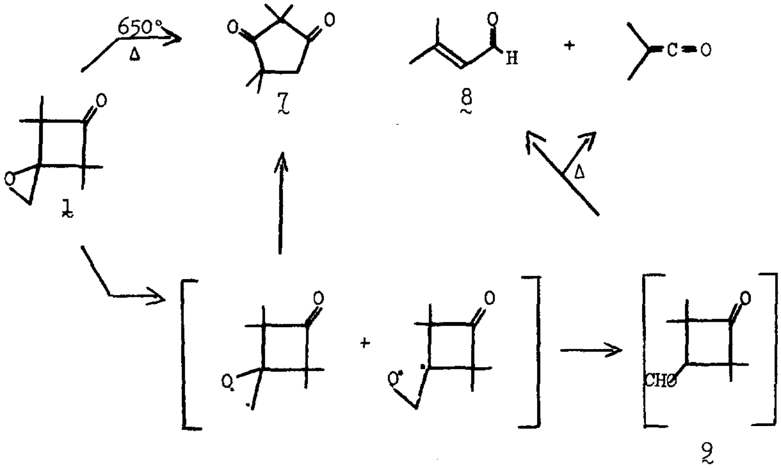
It is noteworthy that the thioepoxy analogue of 1 similarly gave the thio analogues of 2, 3, and 4 when photolyzed in methanol.[7]

Reduced pressure sublimation of 1 through a 30 cm quartz hot tube (quartz chip packed; 650°C) effected complete conversion, and analysis of the product mixture[4] (40% mass recovery) revealed the presence of dione 7 as the major product with lesser amounts of β,β-dimethylacrolein, 8, and tetramethylethylene. Examination of the crude pyrolysate by infrared spectroscopy immediately after pyrolysis also revealed the presence of dimethylketene (2119 cm^{-1}; bright yellow color). A mechanism proposed to account for the observed products involves initial C-O bond homolysis of the oxirane ring. Opening of the back C-O bond followed by a 1,2-alkyl migration leads to dione 7, while opening of the internal C-O bond followed by

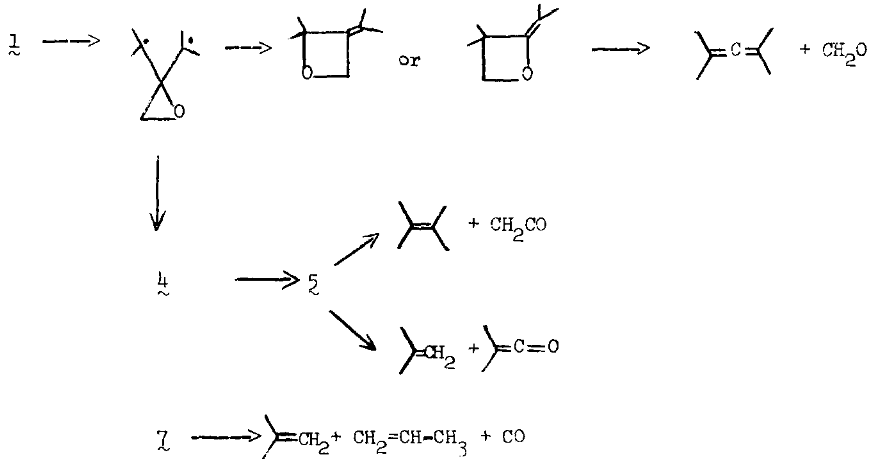


1,2-hydrogen migration leads to ketoaldehyde 9 which can then undergo subsequent thermolysis at 650°C to 8 and dimethylketene.

In order to assess whether different fragmentation modes may become important at temperatures higher than 650°C, we investigated the flash vacuum pyrolysis[8] (FVP) of 1. Mass spectral monitoring[9] of the pyrolysate under conditions where highly reactive species can normally be detected revealed that thermal fragmentation of 1 at temperatures above 750°C gave fragments having m/e 96, 84, 82, 80, 56, and 42. The appearance potential of m/e 84, which corresponds either to the parent m/e of tetramethylethylene or the desired allene oxide, was 9.9 eV; authentic tetramethylethylene had IP 8.6 eV which compares favorably with the literature value[10] (8.53 eV).

The FVP of 1 under conditions where products can be isolated allowed for the firm identification of the major thermal fragments at 950°C; these were tetramethylallene (m/e 96), tetramethylethylene (m/e 84), and isobutylene (m/e 56). A number of other minor products were observed which were all apparently hydrocarbons having parent m/e 82, 80, 72, 68, and 42 on the basis of glpc-mass spectrometry. No products containing oxygen could be unequivocally detected.

Although these results indicate that a different pyrolysis reaction does indeed occur at elevated temperatures, it most probably does not involve cycloelimination to allene oxide. We propose the following scheme to account for most of the observed products:



Neither photolysis nor pyrolysis of 1 led to cycloelimination products. Instead, both modes of decomposition resulted in the predominant formation of ring expanded products. The formation of acetals **2** and **3** from **1** is another example of the photochemical ring expansion reaction of cyclobutanones[11], while thermal rearrangement to **7** is analogous to the acid catalyzed Tiffeneau ring expansion reaction.[6]

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References

1. (a) J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7347 (1968);
   (b) R. L. Camp and F. D. Greene, *ibid.*, **90**, 7349 (1968);
   (c) H. M. R. Hoffmann and R. H. Smithers, *Angew. Chem.*, **82**, 43 (1970).

2. N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969), and references cited therein.

3. Ketone 1 was prepared in 62% yield from 2,2,4,4-tetramethyl-3-methylenecyclobutanone by treatment with *m*-chloroperbenzoic acid in methylene chloride.

4. Product structures are supported by nmr, ir, uv, mass spectral, and elemental analyses, and where possible, by comparison with authentic materials.

5. Studies have revealed the facility with which oxaspiropentanes isomerize to cyclobutanones: (a) W. L. Mock, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1964; (b) J. R. Wiseman and H. F. Chan, *J. Amer. Chem. Soc.*, **92**, 4749 (1970).

6. A. Rosowsky in A. Weissberger (ed.), *Heterocyclic Compounds*, **19**, Interscience, New York, 1964, pp 1-523.

7. J. G. Pacifici and C. Diebert, *J. Amer. Chem. Soc.*, **91**, 4595 (1969).

8. E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969).

9. P. Schissel, D. J. McAdoo, E. Hedaya, and D. W. McNeil, *J. Chem. Phys.*, **49**, 506 (1968).

10. J. Collins and F. P. Lossing, *J. Amer. Chem. Soc.*, **81**, 2064 (1959).

11. D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *ibid.*, **92**, 4349 (1970)