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CONCERNING THE CYCLOELIMINATION ROUTE TO OXIRENES

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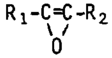
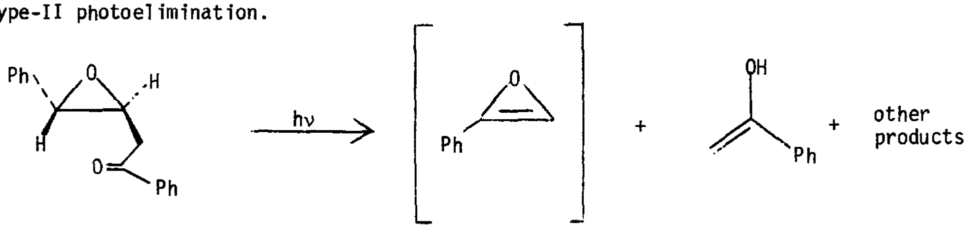
Oxirenes (1) are as yet unknown as isolable compounds, although they have been considered



$$R_1\text{-C=C-}R_2 \text{ (O)}$$

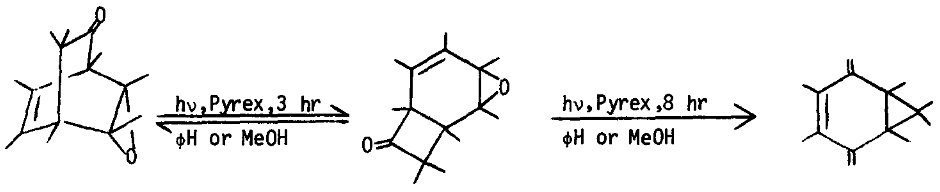
1

as possible intermediates in the peroxidation of acetylenes,[1] and in other acetylene oxidations,[2] in the reaction of methylene with carbon monoxide,[3] and in the Wolff rearrangement of α-diazoketones.[4,5] These methods all involve formation of the heterocyclic ring from acyclic precursors.[6] Alternatively, oxirenes might be prepared from oxiranes via an elimination reaction. For example, it was suggested[7] that phenyloxirene may be an intermediate in the photolysis of *trans*-1,4-diphenyl-3,4-epoxybutan-1-one, the C=C bond being formed as a consequence of a Norrish Type-II photoelimination.



Cycloeliminations are often used to introduce a double bond in a strained ring.[8] A recent paper[9] in which the authors state their intent to use this approach to oxirenes[10] prompts us to report preliminary results of our own efforts along these lines.

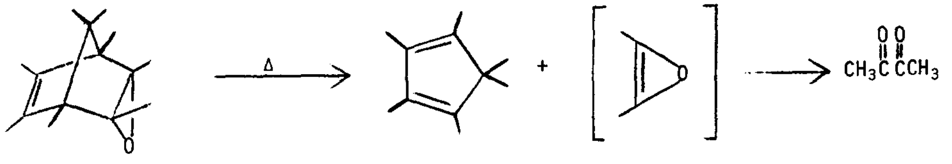
As an extension of our interest in the photochemistry of β,γ-epoxyketones[11] we prepared[12] and irradiated[13] compound 2 [14,15] [uv(CH_3OH) 293 nm (ε200) 230(2000)]. Initially, irradiation of 2 in benzene or methanol through Pyrex gave a mixture of 2 and its 1,3-acyl shift isomer 3 ($\nu_{C=O}$ 1760 cm^{-1}). Prolonged (8 hr) irradiation of this mixture through Pyrex gave triene 4,[16] isolated yield 30%, as a consequence of decarbonylation and dehydration. Triene 4 polymerized



2 3 4

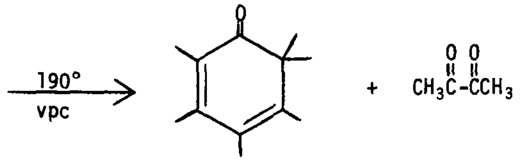
on standing or on further irradiation.[17]

Irradiation of 2 through Vycor was more interesting. Cyclobutanone 3 formed rapidly, then was consumed. After 30 min, 4 was isolated in 20% yield and a new product, hexamethylcyclopentadiene 5,[18] was detected by vpc in 3% yield. After 2 hr, 4 was entirely gone due to photopolymerization and the yield of 5 reached a maximum (∿27%). We also isolated biacetyl 6[19] by vpc of the crude photoproduct, and the vpc trace also showed the presence of some hexamethyl-2,4-cyclohexadienone 8.[20] Nmr examination of the crude photolysis product before vpc showed that neither 5 nor 6 was present. The most logical explanation of these results is that a photoproduct is formed which, on pyrolysis (vpc), gave 5 and 6. A reasonable candidate is 7, formed by the decarbonylation of 2 and/or 3; a possible precursor to the biacetyl is dimethyloxirene 9.[21]



7 5 9 6

We were quite certain that the starting epoxide 2 was pure and did not contain any of its dienone precursor.[12] In light of the above formation of 5, it seemed possible that the traces of 8 isolated by vpc from the crude photoproduct came from the pyrolysis of small amounts of unphotolyzed 2. We therefore subjected a CCl_4 solution of 2 directly to vpc (190°, 5' x 0.25 in column, 20% FFAP on 60/80 Chromosorb W, 60 ml/min He). Dienone 8 was isolated in 15-20% yield, and biacetyl came off with the solvent peak in approximately 8-10% yield. It is

2 

$CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}CH_3$

8 **6**

possible that **8** formed from **2** via a cycloelimination, and that the other fragment is dimethyloxirene or the corresponding ketocarbene. Thus far we have not detected dimethylketene (or products derived therefrom) in the product mixture.

These studies are being continued.

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5. For a review and other results, see H. Meier and K-P. Zeller, *Angew. Chem., Intern. Ed. Engl.*, **14**, 32 (1975).

6. There are several early claims of oxirene syntheses which have later been corrected; for an example, see W. Madelung and M.E. Oberwegner, *Ann.*, **490**, 201 (1931) corrected by W.G. Dauben, C.F. Hiskey and M.A. Muhs, *J. Am. Chem. Soc.*, **74**, 2082 (1952).

7. A. Padwa, D. Crumrine, R. Hartman and R. Layton, *J. Am. Chem. Soc.*, **89**, 4435 (1967).

8. For a review, see H. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).

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10. The authors proposed to use a retro [2+2] photoreaction to generate an oxirene and an aromatic system, but were unable to synthesize the particular desired precursor.

11. R.K. Murray, Jr., T.K. Morgan, Jr., H. Hart and V.J. Hull, J. Org. Chem., 38, 3805 (1973).

12. By the action of m-chloroperbenzoic acid on the known [H. Hart and G.M. Love, J. Am. Chem. Soc., 93, 6264 (1971)] corresponding dienone.

13. All irradiations were carried out with a Hanovia 450 W lamp.

14. The compound gave a satisfactory elemental analysis and had spectra (ir, uv, nmr, mass) consistent with the assigned structure.

15. For a mechanistic discussion of β,γ-epoxyketone photochemistry, see R.K. Murray, Jr., T.K. Morgan, Jr., J.A.S. Polley, C.A. Andruskiewicz, Jr., and D.L. Goff, J. Am. Chem. Soc., 97, 938 (1975).

16. Uv(CH_3OH) 275 nm (ε 35,000); nmr (CCl_4) δ0.53(s,3H), 1.03(s,3H), 1.17(s,6H), 1.87(s,6H), 4.97(br s,2H), 5.23(br s,2H).

17. Compound 4 gave hexamethylbenzene and acetone in quantitative yield on treatment with hydrochloric acid for 5 min at room temperature.

18. Identified by comparison of its nmr (δ0.83,6H and δ1.67,12H) and mass spectra with those reported; L. deVries, J. Org. Chem., 25, 1838 (1960); A.G. Harrison, P. Haynes, S. McLean and F. Meyer, J. Am. Chem. Soc., 87, 5099 (1965); S. McLean and P. Haynes, Tetrahedron, 21, 2343 (1965).

19. Identified by odor, retention time, ir and nmr spectra, and by the formation of 2,3-dimethylquinoxaline on reaction with o-phenylenediamine.

20. Identical (nmr, ret. time) with an authentic sample; H. Hart, P.M. Collins and A.J. Waring, J. Am. Chem. Soc., 88, 1005 (1966).

21. α-Diketones isolated as a consequence of acetylene oxidations have been rationalized via oxirene intermediates.[1] In the present case, 6 could be formed by air oxidation of 9 or by dimerization and fragmentation. The mechanism by which biacetyl is produced remains to be determined.