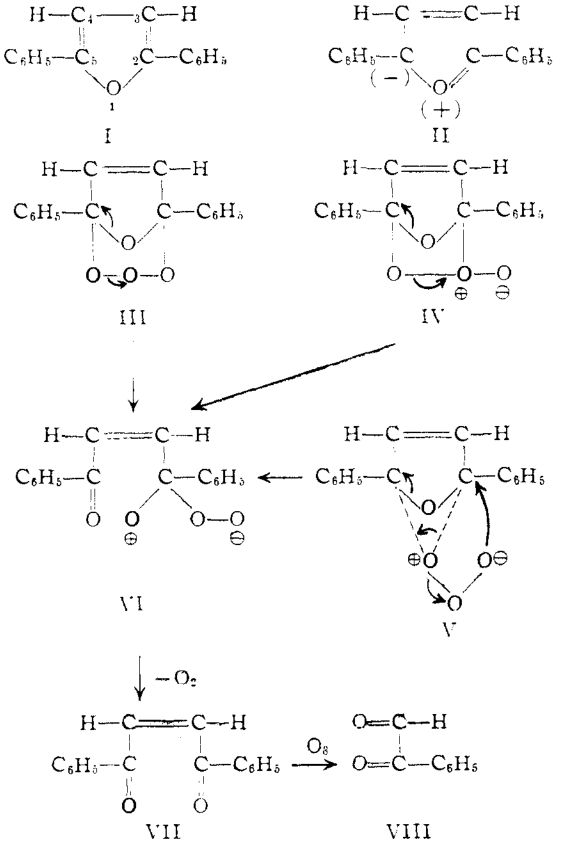
COMMUNICATIONS TO THE EDITOR

1,4-ADDITION OF OZONE TO FURANS AND PYRROLES

Sir:

Wibaut and co-workers[1,2] have obtained products from the ozonolyses of methylated pyrroles and furans which cannot be accounted for by cleavage of the double bonds in the normal structures of these substances. Similarly, we have obtained a 14% yield of phenylglyoxal (VIII) from ozonolysis of 2,5-diphenylfuran (I). The solvent was a methanol–acetone mixture, the temperature was −40°, two mole equivalents of ozone were absorbed, the peroxidic ozonolysis products were reduced with hydrogen over palladium catalyst and the other major product was benzoic acid (81% yield).

Wibaut and co-workers[1,2] have explained "abnormal" results such as these as being reactions of ionic structures such as II. It hardly seems likely, however, that ozone would polarize the molecule to, and attack, such an unstable structure as II, especially since the reactive positions of the furan and pyrrole ring systems are 2 and 5.[3] We have felt that the "abnormal" reactions are the result of the 1,4-addition of ozone. We wish now to report confirmatory evidence for this.



When the ozonolysis just described was stopped after the absorption of one mole equivalent of ozone and the reaction mixture was partially evaporated, a 12% yield of *cis*-1,2-dibenzoylethylene (VII) precipitated (m.p. 130–135°, identification by a mixture melting point with an authentic sample[4]) Similar results were obtained using a mixture of ozone and nitrogen instead of ozone and oxygen, showing definitely that the reaction is one of ozone and not of oxygen.

This material cannot arise from ozonolysis of II. The furan ring has been cleaved but the 3,4 bond is still intact. The *cis* configuration, which is that of the labile isomer,[5] proves that the double bond at the 3 and 4 positions was formed before the ring was cleaved. This can occur only by a 1,4-addition of ozone to the conjugated system of the furan. Any one of structures III, IV or V could have been the intermediate.

We believe a similar mechanism holds true for the reactions of Wibaut and co-workers.[1,2] Further, we believe ozone will attack the ends of other conjugated systems, if the ends are spatially close together. We have found previously that this holds true with anthracene.[6]

We wish to thank the University of Texas Research Institute and the Research Corporation for grants which made this work possible.

---

(1) J. P. Wibaut and A. R. Gulje, *Koninkl. Ned. Akad. Wetenschap.*, Proc. Ser. B, **54**, 330 (1951).

(2) J. P. Wibaut, paper presented at International Ozone Conference, Chicago, Illinois, November 28–30, 1956.

(3) R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, Chapters 4 and 6.

(4) (a) J. B. Conant and R. E. Lutz, This Journal, **45**, 1303 (1923); (b) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 978 (1934).

(5) L. R. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950).

(6) P. S. Bailey and J. B. Ashton, *J. Org. Chem.*, **22**, 98 (1957).

Department of Chemistry
The University of Texas
Austin, Texas
Philip S. Bailey
Henry O. Colomb, Jr.

Received June 25, 1957

ISOLATION AND BEHAVIOR OF *spiro*[2,5]OCTA-1,4-DIENE-3-ONE

Sir:

Recently[1] spectroscopic evidence was reported for the formation of *spiro*[2,5]octa-1,4-diene-3-one (III) as a transient intermediate in solvolytic reactions of 2-*p*-hydroxyphenyl-1-ethyl bromide (I). We now report the successful isolation of this interesting reactive molecular species.

Passage of an ethereal solution of 2-*p*-hydroxyphenyl-1-ethyl bromide (I) through a column of a basic alumina[2] gives a *ca.* 10^{-3} *M* solution of *spiro*[2,5]-octa-1,4-diene-3-one (III) free from phenolic species.

If carefully treated glassware is employed, so as to ensure a dry neutral glass surface, ether solutions of this species can be evaporated at reduced pressure to give a crystalline solid, soluble in most

---

(1) S. Winstein and R. Baird, This Journal, **79**, 756 (1957).

(2) J. Castells and G. A. Fletcher, *J. Chem. Soc.*, 3245 (1956).