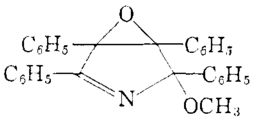
FORMATION OF EPOXIDES IN THE PYRROLE AND FURAN SERIES BY PHOTOÖXIDATION

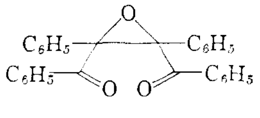
Sir:

Although the oxidation of indoles by air and light has been studied extensively,[1,2,3] little is known about the course of pyrrole photoöxidation.[4,5,6,7] 2,3,4,5-Tetraphenylpyrrole (I), for example, has been reported[7] to yield only tars when irradiated with oxygen. We now have found that under *very mild conditions*, *i.e.*, exposure to air in methanolic solution during irradiation with a 150-watt reflector flood light, in the presence of methylene blue, 2,3,4,5-tetraphenylpyrrole undergoes ready oxidation, yielding products in 85% yield.

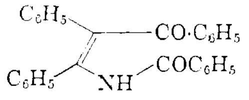
The main product (55%) is the epoxide, 5-methoxy-3,4-epoxy-2,3,4,5-tetraphenyl-Δ^1-pyrroline (II), m.p. 164–165° [*Anal.* Calcd. for $C_{29}H_{23}NO_2$: C, 83.43; H, 5.55; N, 3.36; OCH_3, 7.43. Found: C, 83.45; H, 5.43; N, 3.15; OCH_3, 7.42]. II shows no OH, NH or carbonyl absorption in the infrared, is reduced to I with zinc in acetic acid, and is converted by 1 *N* HCl to *cis*-dibenzoylstilbene oxide (III), m.p. 172–173° [*Anal.* Calcd. for $C_{28}H_{20}O_3$: C, 83.15; H, 4.98. Found: C, 83.25; H, 5.09]. Proof of structure of III, hitherto unreported, rests on its infrared and ultraviolet absorption spectra[8] ($\lambda^{CHCl_3}_{max}$ 5.93 μ; $\lambda^{Et_2O}_{max}$ 249 mμ, ϵ 30,000) conversion to tetraphenylfuran with hydrogen iodide in glacial acetic acid, and reduction to dibenzoyldiphenylethane in ethanolic sodium hydrosulfite.[9]



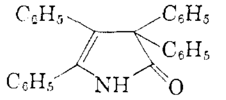
II



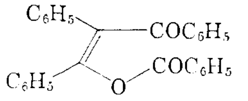
III



IV



V



VI

$[C_6H_5CO]_3C-C_6H_5$

VII

The second oxidation product from I (30%) was identified as α-N-benzoylamino-α'-benzoylstilbene (IV), m.p. 191° [*Anal.* Calcd. for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47. Found: C, 83.18; H, 5.43; N, 3.47]. IV shows infrared bands at 5.95 μ and 6.04 μ, can be hydrolyzed to dibenzoylphenylmethane, and was synthesized independently by benzoylation of α-amino-α'-benzoylstilbene.[10]

Photoöxidation in the presence of potassium hydroxide led to a rearrangement of the benzilic acid type[11] with formation of the lactam, V (35%), m.p. 213–215° ($\lambda^{CHCl_3}_{max}$ 2.95 μ, 3.19 μ and 5.85 μ) identical with the product[12] independently prepared from 2,2,3,4-tetraphenylcrotonolactone and ammonia.

Epoxide formation also was observed in the photoöxidation of tetraphenylfuran. Whereas the oxidation in methanol led chiefly to *cis*-dibenzoylstilbene and 2,5-dimethoxy-2,3,4,5-tetraphenyl-2,5-dihydrofuran, both III (45%) and VI (20%), m.p. 151–152°, were formed during photoöxidation in acetone. Compound VI ($\lambda^{CHCl_3}_{max}$ 5.75 μ, 5.99 μ) is identical with the enol benzoate recently shown[13] to result from the benzoylation of dibenzoylphenylmethane.[14]

The details of this work and discussion of the mechanisms involved will be reported separately.

CONTRIBUTION NO. 1602 FROM
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RECEIVED MARCH 7, 1960

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(1) P. M. Ray, *Ann. Rev. Plant Physiol.*, **9**, 81 (1958).

(2) B. Witkop, *et al.*, *Experientia*, **8**, 36 (1952), and references cited therein.

(3) Z. Yoshida and M. Kato, THIS JOURNAL, **76**, 311 (1954), and references cited therein.

(4) W. Metzger and H. Fischer, *Ann.*, **527**, 1 (1937).

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(6) R. H. Linnel and S. Umar, *Arch. Biochem. and Biophys.*, **57**, 264 (1955).

(7) J. Martel, *Compt. rend.*, **244**, 626 (1957).

(8) H. House and D. J. Reif report λ_{max} 252 mμ, ϵ 15,100 for α-phenyl-*cis*-benzalacetophenone oxide, THIS JOURNAL, **77**, 6525 (1955).

(9) R. E. Lutz and F. W. Wilder, *ibid.*, **56**, 2065 (1934).

(10) E. P. Kohler and N. K. Richtmyer, *ibid.*, **50**, 3104 (1928).

(11) See C. Dufraisse and J. Martel, *Compt. rend.*, **245**, 457 (1957), for a related rearrangement of one of the photoöxidation products of 2,4,5-triphenylimidazole.

(12) F. Klingemann and W. F. Laycock, *J. Chem. Soc.*, **59**, 142 (1891).

(13) We thank Prof. F. M. Beringer and Dr. P. S. Forgione for an authentic sample of VI, F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).

(14) G. O. Schenck, *Angew. Chem.*, **60**, 244 (1948), has reported that tribenzoylphenylmethane (VII) is formed in the photoöxidation of tetraphenylfuran. In view of earlier confusion of VII with VI [J. Meisenheimer and K. Weibezan, *Ber.*, **54**, 3195 (1921)], it is more probable that Schenck's product, like ours, is the enol benzoate, VI.