

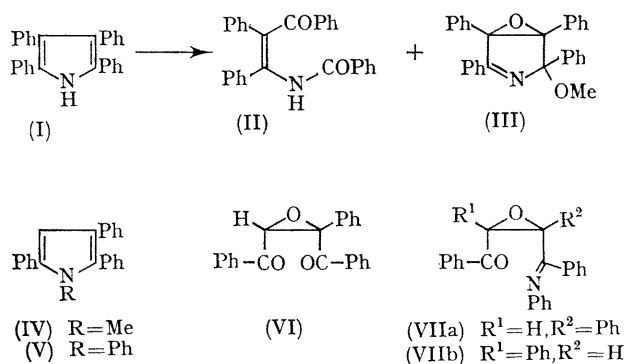
## Photosensitized Oxygenation of *N*-Substituted Pyrroles

By HARRY H. WASSERMAN\* and ALFRED H. MILLER†

(Department of Chemistry, Yale University, New Haven, Connecticut 06520)

We have shown<sup>1</sup> that 2,3,4,5-tetraphenylpyrrole (I) is converted by dye-sensitized photo-oxidation in methanol to the products (II) and (III).<sup>2</sup> We now report results of photo-oxidation studies on *N*-substituted pyrroles which are of interest in connection with the mechanism of epoxide formation in these systems.

1-Methyl-2,3,5-triphenylpyrrole (IV), and 1,2,3,5-tetraphenylpyrrole (V) were irradiated (*ca.* 15 hr., 150 w flood-lamp) at high dilution (1–2 g. l.<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) with Methylene Blue as the sensitizer. The reaction mixture from oxidation of (IV) yielded benzoic acid (12%) and *cis*-dibenzoylstyrene oxide (VI) [65%, m.p. 91–92° (lit.<sup>3</sup> 92–94°), n.m.r.  $\tau$  1.97 (m,4H) and 2.50 (m,11H), 5.54 (s,1H); u.v.  $\lambda_{\max}$  (EtOH) 256 ( $\epsilon$  26,000);<sup>4</sup>  $m/e$  328 ( $M^+$ ), 223 (C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>), 105 (C<sub>7</sub>H<sub>5</sub>O) and 77 (C<sub>6</sub>H<sub>5</sub>); i.r. (KBr), C=O absorption at 1672 cm.<sup>-1</sup>]. Reduction of (VI) (NaHSO<sub>3</sub>, EtOH, reflux) gave 1,2,3-triphenylbutane-1,4-dione. With HI in glacial acetic acid, (VI) was converted to 2,3,5-triphenylfuran.

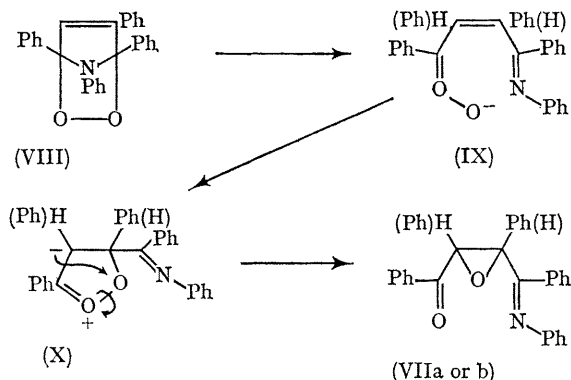


The corresponding *N*-phenylpyrrole (V) yielded an inseparable mixture of the Schiff bases (VIIa) and (VIIb)† [70%, m.p. 133–134.5°,  $m/e$  403 ( $M^+$ ); i.r. strong C=O

† National Institutes of Health Postdoctoral Fellow, 1968.

‡ Satisfactory elemental analyses have been obtained for all new compounds reported.

absorption at  $1670\text{ cm}^{-1}$ ; n.m.r.  $\tau$  5.9 and 6.2 (2s, 2:1



ratio, total, 1H)]. Acid-catalyzed hydrolysis of (VII a,b) yielded the oxide (VI).

We suggest that the oxygenation proceeds through the transannular peroxide (VIII) which, as an analogue of an ozonide,<sup>5</sup> may cleave to form the carbonyl oxide zwitterion (IX). Intramolecular addition to form the cyclic dipolar species (X) would then lead to epoxide formation [(VIIa) and (VIIb)]. Isolation of (VI) with the *N*-methyl compound appears to be a consequence of the ready hydrolysis of the C=NMe group, during the work-up. Formation of an equimolar mixture of (VIIa) and (VIIb) indicates a lack of selectivity in the mode of initial decomposition of (VIII) to (IX).

We thank the National Institutes of Health for financial support.

(Received, December 16th, 1968; Com. 1717.)

<sup>1</sup> H. H. Wasserman and A. Liberles, *J. Amer. Chem. Soc.*, 1960, **82**, 2086.

<sup>2</sup> The isolation of an intermediate hydroperoxide analogous to the primary product in the sensitized photo-oxidation of lophine has been reported: C. Dufraisse, G. Rio, A. Ranjon, and O. Poughot, *Compt. rend.*, 1965, **261**, 3133; G. Rio, A. Ranjon, and O. Poughot, *ibid.*, 1966, **263**, 634; C. Dufraisse, A. Etienne, and G. Martel, *ibid.*, 1957, **244**, 970; G. Sonnenberg and D. White, *J. Amer. Chem. Soc.*, 1964, **86**, 5685; E. H. White and M. G. Harding, *ibid.*, p. 5687.

<sup>3</sup> R. Lutz, W. Welstead, jun., R. Bass, and J. Dale, *J. Org. Chem.*, 1962, **27**, 1111.

<sup>4</sup> A. Liberles, Ph.D. Dissertation, Yale University, 1960; H. H. Wasserman and N. E. Aubrey, *J. Amer. Chem. Soc.*, 1955, **77**, 592.

<sup>5</sup> R. Criegee, *Rec. Chem. Progr.*, 1957, **18**, 111.