

## The Reaction of *o*-Phenylene Thionocarbonate with Trialkyl Phosphites

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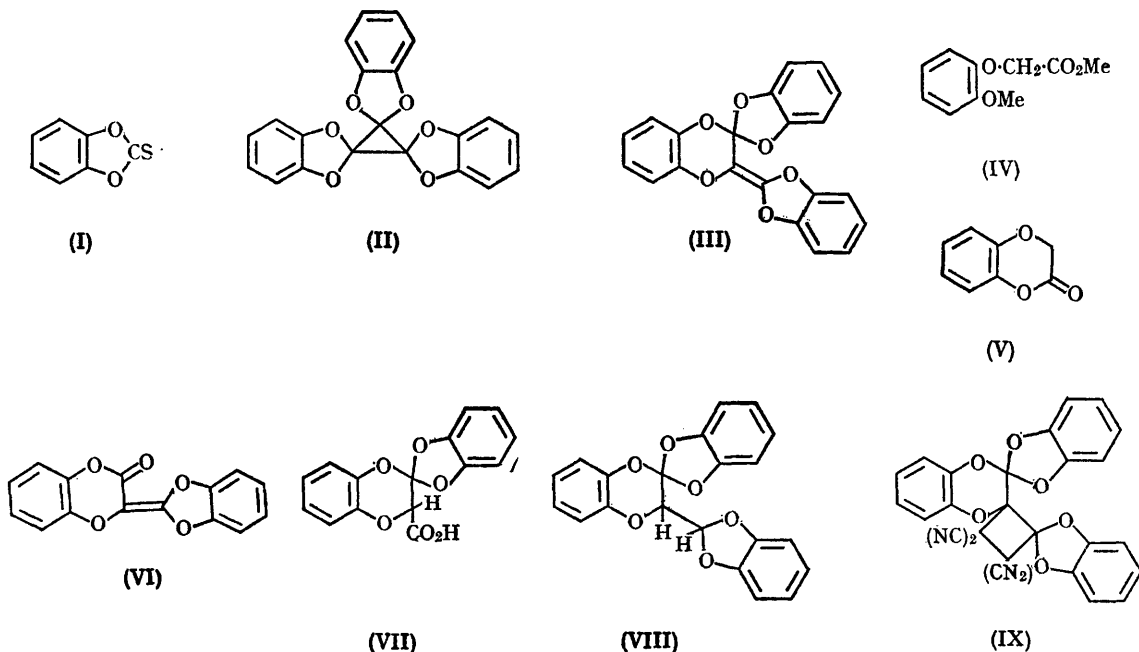
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COREY, CAREY, and WINTER have recently reported<sup>1</sup> the reaction of *o*-phenylene thionocarbonate (I) with trialkyl phosphites to yield (II), m.p. 177.5–178.5. Independently, we have found that (I) reacted with trimethyl or triethyl phosphite to give a product, C<sub>21</sub>H<sub>12</sub>O<sub>6</sub>, m.p. 178–179°, presumably the same compound, for which we suggest structure (III). Our evidence is as follows.

The infrared absorption shows a strong sharp band at 1756 cm.<sup>-1</sup> which we consider to be due to the trioxygenated olefinic group (tetramethoxyethylene shows a weak band at 1755 cm.<sup>-1</sup>).<sup>2</sup> Hydrogenation of (III) (5% palladium-charcoal) at laboratory temperature gave a product (VIII), in which the infrared absorption at 1756 cm.<sup>-1</sup> had disappeared and the n.m.r. spectrum (in carbon tetrachloride) showed two doublets ( $\tau$  3.57, 5.52;  $J = 3.6$  c./sec.) and aromatic protons as two

singlets at  $\tau$  3.07 and 3.13 and a multiplet centred at  $\tau$  3.33 with an area ratio of 1:1:4:4:4. Treatment of (III) with tetracyanoethylene yielded the tetracyanocyclobutane<sup>3</sup> product (IX) (needles, m.p. 156–157°) again with loss of the band at 1756 cm.<sup>-1</sup> in the infrared absorption spectrum. Hydrolysis of (III) by dilute sulphuric acid in acetone gave acidic material which after treatment with diazomethane yielded (IV), (V), catechol, and catechol monomethyl ether (g.l.c. identification). Neutral (needles, m.p. 183–184°) and acidic (needles, m.p. 151–152°) compounds also isolated

are considered to have structures (VI)  $\left[ \nu_{\max} \right]$  (Nujol) 1685 (CO), 1756 cm.<sup>-1</sup>  $\left( \begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} \right)$  and (VII).



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<sup>1</sup> E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, 87, 935.

<sup>2</sup> R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 1964, 197.

<sup>3</sup> A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, 1957, 79, 5316; J. K. Williams, *J. Amer. Chem. Soc.*, 1959, 81, 4013.