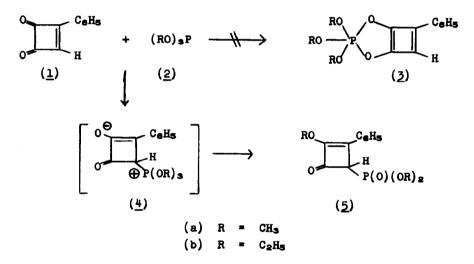
# NOVEL CONDENSATION OF PHOSPHITE ESTERS WITH PHENVLCYCLOBUTENEDIONE

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(Received in USA 29 August 1968; received in UK for publication 26 September 1968) The condensations of carbonyl compounds with phosphite esters have received extensive and thorough examination in the laboratories of F. Ramirez and have been reviewed recently(1). We wish to append to the previous studies the report that phenylcyclobutenedione (<u>1</u>) does not condense with phosphite esters (<u>2</u>) in a manner analogous to the reported  $\alpha$ -diketones and benzenoid quinones to yield <u>3</u> or products arising therefrom.



The product isolated in quantitative yield was shown to be 1-alkoxy-3dialkylphosphono-4-oxo-2-phenylcyclobutene (5) on the bases of spectral and other evidence. This change in reaction course apparently reflects the profound nature of the orbital symmetry barrier to formation of the cyclobutadiene molety of  $\underline{2}$ . The pathway suggested in the scheme is consistent with other nucleophilic additions to this system (2). Excess phosphite did not alter the reaction or produce further products.

Direct evidence for the intermediacy of  $\frac{4}{2}$  was sought by nmr examinations of reaction mixtures immediately after mixing. However, the reaction was so fast that only  $\frac{5}{2}$  was detected within two minutes of mixing  $\frac{1}{2}$  and  $\frac{2}{2}$  at room temperature with either CDCl<sub>3</sub> or benzene-d<sub>8</sub> as the solvent. This result is also in contrast to the experience of Ramirez, who was able to study solutions of the primary adduct of  $\frac{2a}{2}$  and  $\frac{\text{trans}}{\text{dibenzoylethylene(1)}}$ . Under similar conditions and with heating, the related diphenylcyclobutenedione and 3-methoxy-4-phenylcyclobutenedione did not react at all with  $\frac{2}{2}$ .

The <sup>1</sup>H nmr spectra (CDCl<sub>s</sub> solutions at 60 MHz) of <u>5a</u> and <u>5b</u> both had conjugated phenyl absorptions centered at 7.40 & (3H) and 7.85 & (2H) and the C-4 proton at 3.80 & (J<sub>PH</sub> = 5.3 Hz). The COCH<sub>s</sub> of <u>5a</u> appeared at 4.10 & (3H singlet) and the P(0)(OCH<sub>s</sub>)<sub>2</sub> appeared as a pair of doublets at 3.67 and 3.74 & (J<sub>PH</sub> = 11.0 Hz). The appearance of this absorption as four lines instead of two was indicative of an asymmetric center(1,3) which in this case was present at C-4. The ethoxy groups of <u>5b</u> showed analogous absorptions.

Mass spectral data and elemental analyses were consistent with the assigned structures. Infrared absorptions of both <u>5a</u> and <u>5b</u> appeared at 1100 (s, broad) POC, 1260 (s) PO, 1640 (8) C=C, and 1760 cm<sup>-1</sup> (s) C=O. The 1640 and 1760 cm<sup>-1</sup> absorptions have been observed for C=C and C=O, respectively, in analogous four-membered rings(2b,4). Furthermore, the ultraviolet spectra of acetonitrile solutions of <u>5a</u> and <u>5b</u> had absorptions at 318 nm (12,740  $\in$ ) and 320 nm (14,550  $\in$ ), respectively. These spectra also correlate well with those of analogous compounds(4,5).

An alternate structure for the product, 2-alkoxy-l-dialkylphosphono-3-oxo-4-phenylcyclobutene, arising <u>via</u> a proton shift during formation(6) was also considered. However, the available spectral evidence, <u>1.e.</u> conjugated phenyl in the nmr, large asymmetry effect on the phosphono molety in the nmr, and large phenylacetylene fragment at m/e 102 in the ms, weighed in favor of the assigned structure 5.

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