

other evidence. This change in reaction course apparently reflects the profound nature of the orbital symmetry barrier to formation of the cyclobutadiene moiety of 3. 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 4 was sought by nmr examinations of reaction mixtures immediately after mixing. However, the reaction was so fast that only 5 was detected within two minutes of mixing 1 and 2 at room temperature with either CDCl_3 or benzene- d_6 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 2a and trans-dibenzoyl ethylene(1). Under similar conditions and with heating, the related diphenylcyclobutenedione and 3-methoxy-4-phenylcyclobutenedione did not react at all with 2.

The ^1H nmr spectra (CDCl_3 solutions at 60 MHz) of 5a and 5b both had conjugated phenyl absorptions centered at 7.40 δ (3H) and 7.85 δ (2H) and the C-4 proton at 3.80 δ ($J_{\text{PH}} = 5.3$ Hz). The COCH_3 of 5a appeared at 4.10 δ (3H singlet) and the $\text{P}(\text{O})(\text{OCH}_3)_2$ appeared as a pair of doublets at 3.67 and 3.74 δ ($J_{\text{PH}} = 11.0$ 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 5b showed analogous absorptions.

Mass spectral data and elemental analyses were consistent with the assigned structures. Infrared absorptions of both 5a and 5b appeared at 1100 (s, broad) POC, 1260 (s) PO, 1640 (s) C=C, and 1760 cm^{-1} (s) C=O. The 1640 and 1760 cm^{-1} 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 5a and 5b had absorptions at 318 nm (12,740 ϵ) and 320 nm (14,550 ϵ), respectively. These spectra also correlate well with those of analogous compounds(4,5).

An alternate structure for the product, 2-alkoxy-1-dialkylphosphono-3-oxo-4-phenylcyclobutene, arising via a proton shift during formation(6)

was also considered. However, the available spectral evidence, i.e. conjugated phenyl in the nmr, large asymmetry effect on the phosphono moiety in the nmr, and large phenylacetylene fragment at m/e 102 in the ms, weighed in favor of the assigned structure 5.

ACKNOWLEDGMENT

The author wishes to thank Dr. T. H. Regan, Mr. D. P. Maier, and Miss T. J. Davis for obtaining and discussing the nmr, ms, and uv data, respectively.

REFERENCES

1. F. Ramirez, Accts. Chem. Res., 1, 161 (1968) and Pure Appl. Chem., 9, 337 (1964).
2. (a) L. Skattebøl and J. D. Roberts, J. Am. Chem. Soc., 80, 4085 (1958);
(b) E. J. Smutny, M. C. Caserio, and J. D. Roberts, ibid., 82, 1793 (1960).
3. R. C. De Selms and T.-W. Lin, Tetrahedron, 23, 1479 (1967) (footnote on page 1486).
4. M. C. Caserio, H. E. Simmons, Jr., A. E. Johnson, and J. D. Roberts, J. Am. Chem. Soc., 82, 3102 (1960).
5. F. B. Mallory and J. D. Roberts, ibid., 83, 383 (1961).
6. Cf., F. Ramirez, J. F. Pilot, and C. P. Smith, Tetrahedron, 24, 3735 (1968).