new methods, were established by high-resolution mass spectrometry; agreement with theory was within 3 ppm.

Further investigations are under way to test the hypotheses here advanced.

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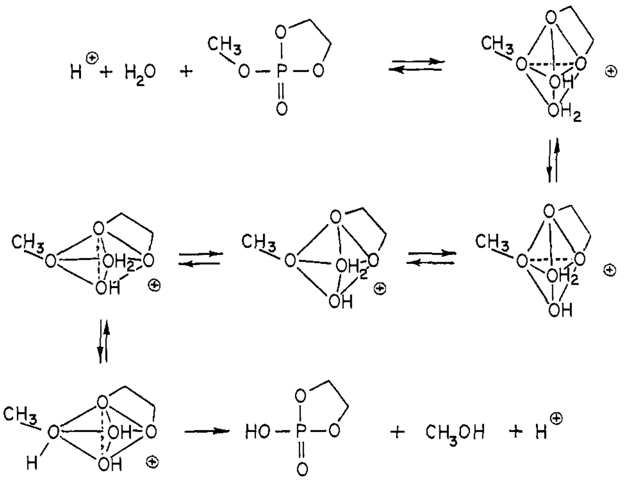
## The Geometry of the Transition State in the Hydrolysis of Phosphate Esters[1]

*Sir:*

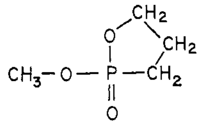
Five-membered cyclic esters of phosphoric and phosphonic acids undergo acid and alkaline hydrolysis at rates $10^5$–$10^8$ times as fast as their acyclic analogs;[2,3] some of these reactions, in both acid and base, occur at these enhanced rates without ring cleavage.[4–8] An analysis of these facts led to the hypothesis[4] (a) that these hydrolyses proceed by way of a trigonal bipyramidal intermediate where the ring is constrained to span one apical and one equatorial position. Now, in the accompanying communication,[7] consideration of the rates of hydrolysis of cyclic phosphinates has led us to the further hypothesis (b) that, with phosphorus compounds, a strong preference obtains for placing oxygen atoms in the apical positions and alkyl groups in the equatorial positions of trigonal bipyramids; the restrictions parallel those discovered by Schmutzler and his collaborators[9] for the structures of the alkylfluorophosphoranes, $R_nPF_{5-n}$.

We now wish to report that the methyl ester of propylphostonic acid, A, undergoes hydrolysis at an enhanced rate but almost exclusively with ring cleavage; using nmr and vpc techniques, less than one part in 500 of methanol could be detected in the reaction product, and preliminary rate measurements indicate that part of this methanol arises from the subsequent hydrolysis of the major product, methyl hydroxypropylphosphonate. This result contrasts sharply with that for the acid-catalyzed hydrolysis of methyl ethylene phosphate, where 30% of the product arises from hydrolysis of the methyl ester group without ring opening. The rates of these reactions—both ring openings and hydrolysis without ring opening (where it occurs)—are nearly a million times those of their acyclic analogs.

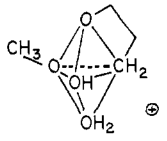
These data may tentatively be explained by assuming (c) that the hydrolysis of phosphates may, and in some instances must, involve a "pseudo-rotation" of trigonal bipyramidal intermediates, analogous to the "pseudo-rotation" that has been postulated[10] to explain the rapid interchange of fluorine atoms in $PF_5$ and[9] in $RPF_4$. The mechanism[11] is illustrated for the acid-catalyzed hydrolysis of methyl ethylene phosphate to produce methanol and ethylene hydrogen phosphate. The scheme can be formulated as a symmetrical one. Water adds to occupy an apical position in a trigonal bipyramid; the shift of a proton produces an equatorial water molecule that can serve as "pivot" for pseudo-rotation. The pseudo-rotation places a methoxy group in the apical position of a new trigonal bipyramid; after a proton shift, a methanol molecule can leave from this apical position. In both trigonal bipyramids, the five-membered ring spans one apical and one equatorial position, with reduced ring strain. The corresponding hydrolysis with ring opening can occur from the original trigonal bipyramid with a proton shift but without pseudo-rotation.



On the other hand, such a pseudo-rotation must be energetically unfavorable for the trigonal bipyramid formed from methyl propylphostonate by addition of water and a proton. Pseudo-rotation of the trigonal bipyramid, B, about the methylene group as pivot would force the five-membered ring into a diequatorial configuration with the C–P–C ring angle expanded toward 120°; this would introduce considerable strain into the intermediate. Pseudo-rotation about the equatorial hydroxyl group of **B** as pivot would force the methylene group into an apical position; the unfavorable energy of alkyl groups in the apical positions was postulated as (b) above and was the subject of the previous communication.[7] In neither case, then, can pseudo-rotation occur readily in the trigonal bipyramid derived from methyl propylphostonate. Since the methoxy group cannot assume an apical position, it is retained in the product; hydrolysis occurs with ring opening.



A



B

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[1] This work was supported by the National Science Foundation under Grant No. GP-2098. One of us (E. A. D.) holds an NIH Predoctoral Fellowship, 5-F1-GM-20,008.

[2] J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956); H. G. Khorana, G. M. Tener, R. S. Wright, and J. G. Moffatt, *ibid.*, **79**, 430 (1957).

[3] A. Eberhard and F. H. Westheimer, *ibid.*, **87**, 253 (1965).

[4] P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

[5] F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

[6] M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88**, 1503 (1966).

[7] E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431 (1966).

[8] F. Kerst, unpublished.

[9] R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, **4**, 496 (1965), and references therein.

[10] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

[11] The mechanism has certain features in common with that postulated for displacement reactions of some octahedral platinum complexes; see R. G. Pearson and F. Basolo, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 189.

This hypothesis (c) requires much further testing before it can be accepted, but it is consistent with the information so far available concerning the rates of hydrolyses of phosphate, phosphonate, and phosphinate esters. It may further account for the accelerated hydrolyses of strained silicon compounds.[12]

Methyl propylphostonate was synthesized by the method previously[3] used for ethyl propylphostonate; its composition was established by high-resolution mass spectrometry and its structure by nmr spectroscopy. Rates of hydrolysis were measured by following the appearance of the nmr singlet for the methyl group of methanol; the chemical shift for this peak differs appreciably from that for the doublet from the methyl group of methyl propylphostonate.

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(12) L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weyenberg, *J. Am. Chem. Soc.*, **79**, 3295 (1957); L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

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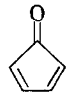
## 2,4-Di-*t*-butyl- and 3-*t*-Butylcyclopentadienones

*Sir:*

Cyclopentadienone (**1**) is recognized as being unusually reactive toward normal Diels–Alder dimerization and numerous efforts to isolate it have been unsuccessful.[1] The evidence that **1** may indeed exist as a metastable species derives from successful trapping experiments in which **1** was found to react largely, if not exclusively, as a dienophile.[1b,c] Testimony to the pronounced reactivity of **1** is that, except for indenone and one further example (see below), only tri- and tetrasubstituted derivatives of **1** have been isolated as monomers.[1] Krüerke and Hübel reported[2] the isolation of a crystalline (yellow) di-*t*-butyl-**1**; however, their characterization of this material was incomplete and no chemical or spectral properties of it were determined.



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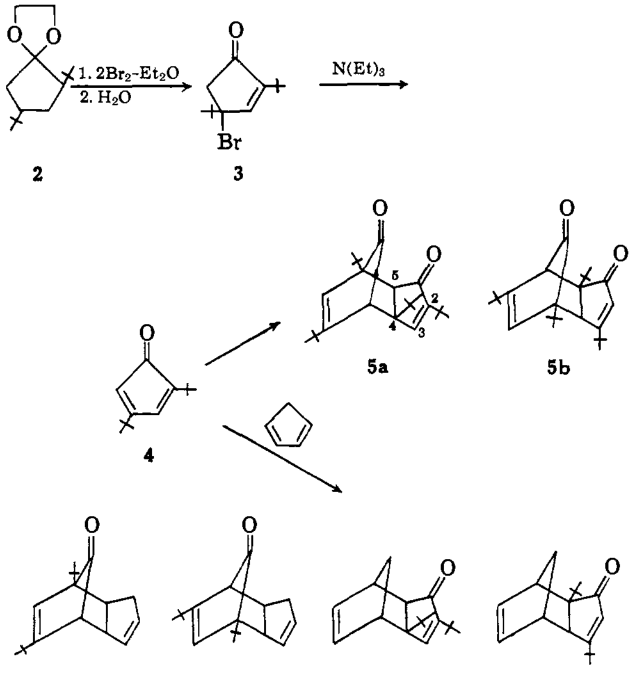
We have sought to probe the origin of the reactivity of **1** by attempting to acquire fundamental information from its simple derivatives whose dimerization reactions are sterically dissuaded yet whose $\pi$-electronic systems are relatively unperturbed. In this preliminary note we will describe the synthesis and spectral properties of 2,4-di-*t*-butyl- and 3-*t*-butylcyclopentadienones (**4** and **10**, respectively).

Nitric acid oxidation of a mixture of stereoisomeric 2,4-di-*t*-butylcyclohexanols led to 10–54% of 2,4-di-*t*-butyladipic acid, which was converted to 2,4-di-*t*-butylcyclopentanone (40%) upon pyrolysis with barium hydroxide at 290°. Ketalization of this ketone gave **2** (75%). Bromination (2 equiv) of **2** in ether followed by treatment with aqueous bicarbonate led to 18% (73% unisolated) of purified **3**, mp 80–83°; $\nu(CCl_4)$ 1700 (C=O) and 1603 cm$^{-1}$ (C=C); $\tau(CCl_4)$ 8.85 and 8.80 (*t*-Bu), 7.07 ($CH_2$), and 2.77 (vinyl); all nmr absorptions are sharp singlets.[3] The details of this bromination reaction are yet obscure. Treatment of **3** with neat triethylamine led quantitatively to **4**, mp 30–31° (yellow). Dimerization of **4** proceeds slowly (see Table I) at 25° to give a single product which probably is either **5a** or **5b**, although two additional sterically more crowded *endo* adducts are possible. On the basis of the *single* vinyl and bridgehead proton resonances at $\tau$ 3.35 and 7.12, respectively, we feel that **5a** is most likely the product. Cyclopentadiene and **4** react at 25° more rapidly than the self-dimerization of **4** to give approximately an equal mixture (from nmr and infrared) of **6a** or **6b** and **7a** and/or **7b** (**4** reacts, in this instance, equally well as a diene and dienophile). The *single* vinyl proton resonance at $\tau$ 3.30 (spectrum taken of the mixture) is most compatible for **6a**, in which event this material comprises 50 mole % of the product. The spectral properties of **4**–**7** are summarized in Table I.



**2** **3** **4** **5a** **5b** **7a** **7b** **6a** **6b**

6,6-Dimethyl-2,5-heptanedione was converted to **8** (30%) by high dilution reaction with sodium amide in refluxing benzene. Bromination (NBS) of **8** led to 53% of **9**, mp 39–40°, $\nu(CCl_4)$ 1718 (C=O) and 1590

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(1) (a) M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**, 261 (1965); (b) K. Hafner and K. Goliasch, *Chem. Ber.*, **94**, 2909 (1961); (c) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964).

(2) U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961).

(3) **3** (mp 90–91°) may be obtained by repeated recrystallization from pentane. Bromination of the ketone of **2** gave predominantly 5-bromo-2,4-di-*t*-butylcyclopent-2-enone which did not dehydrobrominate readily with triethylamine. This bromide was obtained in minor quantities from the bromination of **2** and was difficultly removed from **3**.[4] A second isomer of **3** (mp 100–101°) was isolated from bromination of **2**. Spectral and analytical data indicate that it is 5-bromo-3,5-di-*t*-butylcyclopent-2-enone.

(4) The microanalytical C and H percentages on all of the stable compounds reported were in agreement with expectation within ±0.3. Samples of dienone **4** gave percentages that were slightly below this limit due to trace contamination by 5-bromo-2,4-di-*t*-butylcyclopent-2-enone (by nmr)[3] which cosublimed with **4** upon purification.