

Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphacyclohexa-1,3-diene-2,3-dicarboxylate.  
A New Cyclic Bisylid.

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Sir:

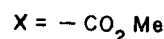
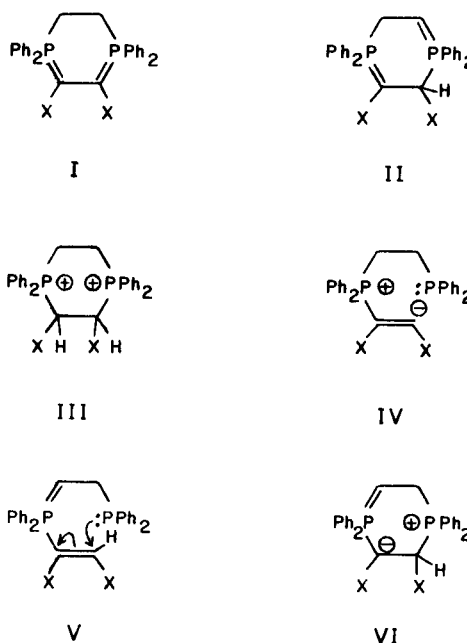
In continuing our studies of the reactions of tertiary phosphines with unsaturated systems (1) we have investigated the reaction of bis(diphenylphosphino)ethane ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) with dimethyl acetylenedicarboxylate and we wish to report the synthesis of the cyclic bisylid I.

The reaction is of interest for several reasons. In particular, few compounds containing two phosphorus atoms in simple, unsaturated six-membered rings have been synthesized (e.g., 2-4) and attempts (2,4) to prepare such compounds containing two phosphonium ylid links as in I have met with limited success (4). Furthermore, the mechanism of the reaction must involve several intramolecular steps, some of which are a little unexpected.

The reaction proceeds very smoothly in dry benzene at room temperature under nitrogen in high yield (> 80%) and the product precipitates almost immediately. Recrystallization from benzene gives yellow crystals of I containing one molecule of crystallization of benzene which cannot be removed even by pumping the crystals at  $50^\circ$  and  $8 \times 10^{-6}$  torr for several hours. The product decomposes above  $150^\circ$ .

The structure was proved in the following manner. The compound hydrolyzes slowly in boiling water to give the phosphine dioxide  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2(\text{O})\text{PPh}_2$  in high yield (confirmed by IR, UV, NMR, mass spectrum, m.p. and mixed m.p.). This indicates that the compound contains two phosphonium ylid linkages. The presence of these linkages is confirmed by the fact that on brief treatment with perchloric acid in methanol, the compound gives a bisperchlorate in good yield. Satisfactory elemental analyses were obtained.

Spectroscopic evidence further confirms the presence of two ylid linkages and shows that the structure is I rather than less likely isomers such as II. Thus, the infrared spectrum shows the carbonyl stretching frequency to occur at the unusually low value of  $1585 \text{ cm}^{-1}$  with shoulders at  $1594 \text{ cm}^{-1}$  and  $1618 \text{ cm}^{-1}$ . This is typical (5) of such carbonyl groups in phosphonium ylids. The NMR spectrum in deuteriochloroform shows a ratio of 20 aromatic



protons ( $\tau = 2 - 2.85$ ) to 6 benzene protons ( $\tau = 2.68$ ) to 10 methoxy and methylene protons ( $\tau = 6.1 - 8$ ). This last region is very poorly defined and no single, sharp methoxy signal appears although there are several small, sharp peaks in the region. This is possibly due to the presence of several conformational arrangements of the ester groups, a conclusion which is reinforced by the fact that at  $-40^\circ$  a broad methoxy signal begins to appear at  $\tau = 6.35$ . Addition of trifluoroacetic acid to the NMR sample causes the spectrum to be modified to show 22 aromatic and tertiary protons ( $\tau = 2.0 - 2.6$ ) to 6 benzene protons ( $\tau = 2.68$ ) to 10 methylene and methoxy protons ( $\tau = 6.1 - 6.9$ ) in which the methoxy protons occur as a sharp singlet at  $\tau = 6.57$  superimposed upon a broad multiplet of methylene protons. This spectrum is consistent with the doubly protonated structure III which would presumably be in a chair conformation with the two ester groups

in a *trans*-diequatorial arrangement. Furthermore, the two tertiary protons in III are each adjacent to two strongly electron-withdrawing groups which would shift them far downfield. Conclusive evidence that protonation of the adduct assigned structure I occurs at both carbon atoms bearing the ester groups comes from the NMR spectrum of this adduct in deuteriochloroform containing a little deuterated trifluoroacetic acid which shows a spectrum virtually identical to that of the compound in deuteriochloroform containing trifluoroacetic acid except that the signal in the aromatic region integrates for approximately two protons less. The adduct does not readily enter into Wittig reactions.

The mechanism of the reaction is thought to follow the sequence: phosphine + acetylenic ester  $\rightarrow$  IV  $\rightarrow$  V  $\rightarrow$  VI  $\rightarrow$  I. If this sequence is in fact the mechanism, the step V  $\rightarrow$  VI is a little unexpected in view of the readiness with which the related ylid  $\text{CH}_2=\text{PPh}_2(\text{CPh}=\text{CH}_2)$  cyclizes to give a four-membered ring containing a phosphonium ylid linkage (6).

Further investigations of the reactions of this and other compounds containing two tertiary phosphine groupings

with dimethyl acetylenedicarboxylate are in progress and the results of these experiments will be reported in a later publication.

#### Acknowledgment.

We wish to thank the National Research Council of Canada and the Ontario Department of University Affairs for generous financial support.

#### REFERENCES

- (1) A. N. Hughes and S. Uaboonkul, *Tetrahedron*, **24**, 3437 (1968); A. N. Hughes and M. Davies, *Chem. Ind. (London)*, 138 (1969).
- (2) A. M. Aguiar and H. Aguiar, *J. Am. Chem. Soc.*, **88**, 4090 (1966).
- (3) A. M. Aguiar, K. C. Hansen and G. S. Reddy, *ibid.*, **89**, 3067 (1967); A. M. Aguiar and K. C. Hansen, *ibid.*, **89**, 4235 (1967).
- (4) G. Märkl, *Z. Naturforsch. B*, **18**, 1136 (1963).
- (5) N. E. Waite, J. C. Tebby, R. S. Ward and D. H. Williams, *J. Chem. Soc., C*, 1100 (1969).
- (6) M. P. Savage and S. Trippett, *ibid.*, 591 (1968).

Received November 4, 1969

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