

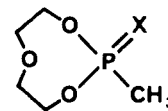
- (15) Compared with that of the corresponding hydrocarbon, the strain of **7** ( $n = 3$ ) might be appreciably released owing to the longer C-S and S-S bonds. See ref 14 for *trans,trans*-1,5-cyclooctadiene.
- (16) (a) J. Morgenstern and R. Mayer, *J. Prakt. Chem.*, **34**, 116 (1966); (b) H. Boelens and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **91**, 141 (1972); (c) F. C. V. Larsson, L. Brandsma, and S.-O. Lawesson, *ibid.*, **93**, 258 (1974).
- (17) As an exception, **9** ( $R^1 = \text{CH}_3$ ;  $R^2 = \text{SCH}_3$ )<sup>16c</sup> has been reported to rearrange at  $\sim 10^\circ\text{C}$ .

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 Received October 3, 1977

### Conformational Study of Eight-Membered-Ring Organophosphorus Heterocycles

Sir:

In contrast to the numerous studies available concerning the conformation of five-<sup>1</sup> and six-membered<sup>2</sup>-ring phosphonite molecules, relatively little attention has been devoted to the corresponding seven-<sup>3,4</sup> and eight-membered rings. This paper describes some stereochemical and chemical features concerning the eight-membered rings **1** and **2**, a class of compounds which has received virtually no attention.<sup>5</sup> Particularly important questions to be answered in this area include the geometry and conformation of the ring system, the preferred orientation of the groups attached to the phosphorus, examination of a possible transannular phosphorus-oxygen interaction through the ring, and the possibility of a dimerization reaction as already observed for five-, six-, and seven-membered-ring phosphonites;<sup>6</sup> this dimerization would lead here



**1**, X = lone pair; **2**, X = S

to the formation of a sixteen-membered-ring crown ether.

Compound **1** is prepared by reacting  $\text{CH}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$  and diethylene glycol in benzene under inert gas atmosphere. Compound **2** is readily obtained by direct addition of sulfur to a benzene solution of **1**.<sup>7</sup> Molecules **1** and **2** are identified by elemental analysis, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy.

The <sup>1</sup>H NMR spectra of molecules **1** and **2** have been recorded at 250 MHz and at 100 MHz with phosphorus decoupling. The spectra have been analyzed as ABCDX systems (X phosphorus) using the iterative program LAOCOON III. There is no evidence for the existence of long-range coupling constants between the ring protons. The results are shown in Table I. The <sup>13</sup>C and <sup>31</sup>P data are shown in Table II.

The dihedral angle  $\phi$  between protons i and j on adjacent carbons can be calculated from vicinal coupling according to relation  $J_{ij} = A \cos^2 \phi + B \cos \phi$ .<sup>8</sup> For each compound (**1** and **2**), spectral analysis leads to a set of four equations in three unknowns. Assuming a tetrahedral HCH angle, the best fit yields the following results: **1**,  $A = 9.4$ ,  $B = -0.9$ ,  $\phi = 60.8^\circ$ ; **2**,  $A = 9.2$ ,  $B = -1.1$ ,  $\phi = 60.4^\circ$ . Such angle values are indicative of a fixed staggered conformation around the C<sub>4</sub>-C<sub>5</sub> and C<sub>7</sub>-C<sub>8</sub> bonds.

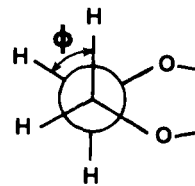


Table I. <sup>1</sup>H NMR Spectral Parameters of Molecules **1** and **2**

	Chemical shift <sup>a</sup>				Coupling constants, Hz					
	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	<sup>2</sup> J(H <sub>1</sub> H <sub>2</sub> )	<sup>3</sup> J(H <sub>1</sub> H <sub>3</sub> )	<sup>3</sup> J(H <sub>1</sub> H <sub>4</sub> )	<sup>3</sup> J(H <sub>2</sub> H <sub>3</sub> )	<sup>3</sup> J(H <sub>2</sub> H <sub>4</sub> )	<sup>2</sup> J(H <sub>3</sub> H <sub>4</sub> )
<b>1</b>	4.00	3.69	3.73	3.25	-12.5	1.8	10.3	2.0	1.6	-12.9
<b>2</b>	4.66	3.24	3.54	2.98	-12.4	1.8	10.3	1.8	1.7	-13.5

<sup>a</sup> <sup>1</sup>H chemical shifts are in parts per million downfield from Me<sub>4</sub>Si.

Table II. <sup>13</sup>C and <sup>31</sup>P NMR Spectral Parameters of Molecules **1** and **2**

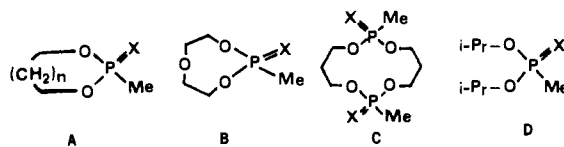
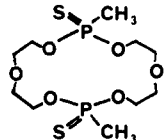
	Chemical shifts <sup>a</sup>				Coupling constants (Hz)						
	<sup>31</sup> P	<sup>13</sup> C <sub>4,8</sub>	<sup>13</sup> C <sub>5,7</sub>	<sup>13</sup> CH <sub>3</sub>	<sup>3</sup> J(PH <sub>1</sub> )	<sup>3</sup> J(PH <sub>2</sub> )	<sup>4</sup> J(PH <sub>3</sub> )	<sup>4</sup> J(PH <sub>4</sub> )	<sup>2</sup> J(PC <sub>4</sub> )	<sup>3</sup> J(PC <sub>5</sub> )	<sup>1</sup> J(P <sup>13</sup> CH <sub>3</sub> )
<b>1</b>	188.9	70.4	75.9	22.6	5.6	23.8	0.0	0.9	12.0	1.3	12.5
<b>2</b>	92.7	66.8	74.3	21.4	10.2	27.2	<0.3	<0.3	7.8	1.0	125.1

<sup>a</sup> <sup>31</sup>P chemical shifts are in parts per million with positive values downfield from external 85% H<sub>3</sub>PO<sub>4</sub>; <sup>13</sup>C chemical shifts are in parts per million downfield from Me<sub>4</sub>Si.

Table III.  $^1J(\text{PC})$  Coupling Constants (Hertz)

	A <sup>b</sup>				B <sup>b</sup>	C <sup>b</sup>	D <sup>b</sup>
	n = 2	n = 3	n = 4	n = 5 <sup>a</sup>			
X = lone pair	43.7	41.3	32.3	27.4	12.5	25.0	18.7
X = S	96.2	109.4	109.4	112.2	125.1		117.0

<sup>a</sup> For this compound, C<sub>6</sub> bears a dimethyl group and not a CH<sub>2</sub> group. <sup>b</sup> See structures below.

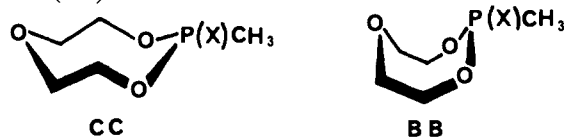
Table IV.  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR Data on the Sixteen-Membered-Ring Dimeric Forms of Molecule 1


	$\delta(^{31}\text{P})^a$	$\delta(\text{O}^{13}\text{CH}_2)^a$	$\delta(\text{O}^{13}\text{CH}_2)^a$	$J(\text{P}^{13}\text{CH}_2)^b$	$J(\text{P}^{13}\text{CH}_2)^b$	$J(\text{P}^{13}\text{CH}_3)^b$
Isomer a	96.1	70.42	65.86	7.8	6.8	117.2
Isomer b	96.3	70.20	65.45	7.3	6.7	116.3

<sup>a</sup>  $^{31}\text{P}$  chemical shifts are in parts per million with positive values downfield from external 85%  $\text{H}_3\text{PO}_4$ ;  $^{13}\text{C}$  chemical shifts are in parts per million from  $\text{Me}_4\text{Si}$ . <sup>b</sup>  $J$  (in hertz).

The magnitude of the two  $^3J(\text{POCH})$  NMR coupling constants and their large difference in compounds **1** and **2** (18.2 and 17. Hz, respectively) are only compatible with (POC, OCH) dihedral angles close to 180 and 60°. <sup>2,9</sup>

For discussing the eight-membered-ring stereochemistry, we shall use the nomenclature defined for cyclooctane, <sup>10</sup> although, strictly speaking, it does not apply here. Among the many possible conformations for the ring, the  $^3J(\text{hh})$  and  $^3J(\text{POCH})$  coupling constants, which imply  $\phi \sim 60^\circ$  and (POC, OCH)  $\sim 180$  and  $60^\circ$ , are only compatible with a fixed chair-chair conformation (CC) or a fixed boat-boat conformation (BB).



From Dreiding models examination, the BB conformation will give rise to severe nonbonded interactions between hydrogen atoms of carbons 4 and 8. Thus, we conclude that molecules **1** and **2** exist in chair-chair conformation in solution. Such a conformation corresponds to a (POC, OCC) dihedral angle close to 90° which is in agreement with the small  $^3J(\text{POCC})$  NMR coupling constant observed in **1** and **2** (1.3 and 1.0 Hz, respectively<sup>11</sup>). The boat-boat conformation would correspond to a 60° dihedral angle.

In three coordinate phosphorus compounds, the  $^3J(\text{POCH})$  values are subject to a POC, OCH dihedral angle dependence and effect of phosphorus lone pair orientation. In 2R-1,3,2-dioxaphosphorinanes, for axial orientation of the R group, the  $^3J(\text{POCH}_{\text{eq}})$  coupling constant is close to 10 Hz;<sup>2</sup> for equatorial orientation of the R group,  $^3J(\text{POCH}_{\text{eq}})$  is close to 25 Hz.<sup>2</sup> Thus, in molecule **1**, the  $^3J(\text{POCH}_2)$  (23.8 Hz) is in agreement with an equatorial orientation of the methyl group on the phosphorus atom. This result contrasts with the preferred axial orientation of the  $\text{CH}_3$  group in the corresponding 1,3,2-dioxaphosphorinane<sup>2</sup> and could help to shed some more light on the problem of the preferred orientation of the R group in 2R-1,3,2-dioxaphosphorinanes.<sup>2,12</sup> For tetracoordinate phosphorus compounds an equatorial orientation of the methyl

group is known in the solid state for six-<sup>9</sup> and eight-membered rings.<sup>13</sup> However, as the  $^3J(\text{POCH})$  NMR couplings are almost insensitive to the bond orientation around phosphorous in tetracoordinate phosphorus compounds, it is difficult to give here a definite answer concerning the P=S bond orientation in molecule **2**.

The  $^1J(\text{PC})$  NMR coupling of compound **1** (Table III) shows an interesting feature. Plotting the  $^1J(\text{PC})$  values of various 1,3-dioxaphosphorus molecules, including the eight-membered ring analogous to **1** in which the O<sub>6</sub> has been replaced by a C(CH<sub>3</sub>)<sub>2</sub> group,<sup>14</sup> one obtains a smooth variation if one excludes the point corresponding to compound **1**. Such a fact and the equatorial orientation of the methyl group strongly suggests, in **1**, the existence of a transannular phosphorus-oxygen O<sub>6</sub> interaction as observed in similar heterocyclic eight-membered rings.<sup>13,15</sup> When molecule **1** is left in benzene solution (10%), in a sealed tube, additional peaks appear in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. After sulfurization of the corresponding species and column chromatography, one obtains in a poor yield ( $\sim 1\%$ ) the sixteen-membered ring which corresponds to the dimeric forms of molecule **2** which can be separated. These two dimeric forms have been characterized by mass spectrometry, molecular weight measurements (tonometry), and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectroscopy (Table IV).

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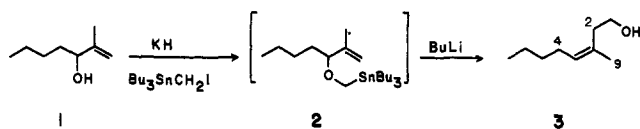
Received August 15, 1977

### A Highly Stereoselective Synthesis of Z-Trisubstituted Olefins via [2,3]-Sigmatropic Rearrangement. Preference for a Pseudoaxially Substituted Transition State

Sir:

Sigmatropic rearrangements of the [2,3] and [3,3] type are some of the most widely used reactions for the stereoselective preparation of di- and trisubstituted olefins.<sup>1</sup> Previous examples<sup>2</sup> of these reactions have led mainly to *E* olefins via cyclic transition states having the greatest possible number of pseudo-equatorial substituents. We have found, however, that this preference for transition states having pseudo-equatorial substitution may not be as general as previously assumed. We report here a convenient and efficient [2,3]-sigmatropic Wittig rearrangement which produces *Z*-trisubstituted homoallylic alcohols in high yields and with  $\geq 95\%$  stereoselectivity. To the best of our knowledge this reaction is the first example of a [2,3]-sigmatropic rearrangement having a transition state which prefers pseudoaxial substitution.<sup>3</sup>

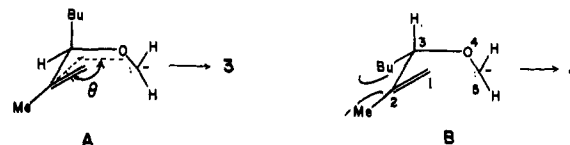
As outlined below, when the allylic alcohol **1** was deprotonated (KH, THF) and alkylated with iodomethyltributyltin<sup>4</sup>



(30 min, 25 °C), the allyl stannylmethyl ether **2** (NMR (CCl<sub>4</sub>)  $\delta$  4.80 (=CH<sub>2</sub>, m), 3.45 (-OCH<sub>2</sub>Sn, ABq,  $\Delta\nu_{AB}$  = 27 Hz,  $J$  = 10 Hz), 3.30 (>CHO-, m)) was formed quantitatively.<sup>5</sup> Although this material could be isolated, direct treatment of the chilled reaction mixture with excess *n*-butyllithium resulted in tin/lithium exchange and smooth [2,3]-sigmatropic rearrangement (30 min, -78 °C) to the homoallylic alcohol **3** (>95% yield; NMR (CCl<sub>4</sub>)  $\delta$  5.22 (=CH-, br t,  $J$  = 8 Hz), 3.56 (-CH<sub>2</sub>OH, t,  $J$  = 8 Hz), 2.24 (=C(Me)CH<sub>2</sub>-, t,  $J$  = 8 Hz), 1.69 (=CMe-, br s)). VPC (Carbowax) analysis showed **3** to be 96-97% one isomer and an examination by  $^{13}\text{C}$  NMR strongly suggested this isomer to be the *Z* one shown. This tentative assignment followed from the upfield<sup>6</sup> value ( $\delta$  34.4) of carbon 2 and a normal value ( $\delta$  21.6) for the relatively unhindered carbon 9.<sup>7</sup> Conformation was obtained by comparison with authentic *E* isomer **4** prepared by the method of Johnson.<sup>8</sup> Coinjection VPC and  $^1\text{H}$  NMR showed that the minor isomer in **4** was identical with the major isomer in **3** and vice versa. Furthermore the  $^{13}\text{C}$  NMR of **4** showed a shielding pattern for

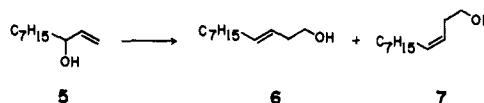
C-2 ( $\delta$  43.0) and C-9 ( $\delta$  16.0) which was opposite to that observed in the [2,3]-sigmatropic rearrangement product **3**. Thus the olefinic stereochemistry of our product may be unambiguously assigned as *Z*.

Aside from the obvious synthetic potential of this reaction, the transition-state geometry is of special interest. It is clear from the stereochemistry of **3** that transition state A having a pseudoaxial butyl substituent is strongly preferred over transition state B.<sup>9</sup> Since the stereoelectronics of the two

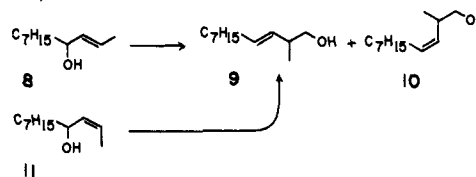


transition states are virtually identical, the observed preference for A implies that the steric interaction of the butyl substituent with the C-1 methylene is much less severe than the alternative butyl/vinyl methyl interaction in B. This state of affairs is understandable given the two reasonable assumptions that the transition state is very early<sup>10</sup> (C-1 is sp<sup>2</sup> and C-3 is sp<sup>3</sup>) and that the planes defined by C-1-C-2-C-3 and C-1-C-3-O-4-C-5 are not quite perpendicular ( $\theta > 90^\circ$ ). A careful examination of the geometry of A reveals that, while the pseudo-equatorial substituent (hydrogen in A) almost eclipses the methyl attached to C-2, the pseudoaxial substituent (butyl in A) is in fact rather far removed from the C-1 methylene.

Further support for our postulated transition-state geometry came from a study of the [2,3]-sigmatropic rearrangement of allylic ethers having different substitution patterns. If for example the vinyl methyl in **2** was replaced by hydrogen then the model above would predict a marked decrease in the selectivity for transition state A and thus for the *Z* product. When the allylic alcohol **5** was rearranged as above, a 40:60 mixture of homoallylic alcohols **6** and **7** (>95% yield) was obtained.<sup>11,12</sup>



A similar result was found with the *trans* allylic alcohol **8**: a roughly 35:65 mixture of compounds **9** and **10** (96% yield) was produced. The *cis* allylic alcohol **11** on the other hand would be expected to strongly destabilize transition state A relative to B, and in fact rearrangement of **11** led exclusively to **9**: 91% yield; IR (neat) 965 cm<sup>-1</sup>; NMR (CCl<sub>4</sub>)  $\delta$  5.35 (-CH=CH-,  $J$  = 15 Hz).



Synthetically the reaction has a number of interesting features. The rearrangement proceeds smoothly in cyclic systems so long as the  $\beta$  carbon is relatively unhindered. 2-Cyclohexenol for example was converted to the hydroxymethylcyclohexene **12** in 93% yield. The more hindered octalols **13** and **14** reacted



only sluggishly to yield mixtures of [1,2] and [2,3] rearranged products in low yield. It is also possible to trap the intermediate alkoxymethyl lithium intermediates with reactive electrophiles prior to rearrangement. For that reaction the stannylmethyl ether (e.g., **2**) is first isolated and then transmetalated in a second step in the absence of strong chelating agents. Thus