for 1 h at which time phosphorane decomposed yielding cis epoxide 8 in 91% yield based on internal standard. No appreciable increase of the trans epoxide, present as impurity in the starting dioxetane solution, was observed. Epoxide 8 was isolated from the reaction mixture by preparative VPC, 10 × 0.25 in. 20% Carbowax 20M on Chromosorb P: column 170 °C, injector 240 °C, flow rate 120 mL/min, retention time of cis epoxide 3 min. NMR (CCl_4) δ 7.20 (s, 10 H), 4.31 (s, 2 H); IR (CCl_4) 3100 (m), 3060 (m), 3000 (m), 1630 (w), 1510 (m), 1460 (s), 1420 (m), 1370 (m), 1320 (w), 1290 (w), 1260 (w), 1180 (s), 1120 (w), 1070 (w), 1070 (m), 900 (s), 720 (m), 690 cm^{-1} (s). Identical properties were shown by an authentic sample prepared by the reaction of *cis*-stilbene with *m*-chloroperbenzoic acid.[6]

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the National Institutes of Health for support.

Registry No.—**5**, 61570-41-0; **6**, 61570-42-1; **7**, 61570-43-2; **8**, 1689-71-0; *trans*-stilbene, 103-30-0; *dl*-diphenylethanediol, 655-48-1.

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Communications

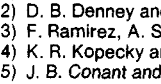
Twelve-Membered-Ring Molecules Containing P and S. Preparation and Identification

Summary: The twelve-membered-ring dimers of 2-*tert*-butyl-1,3,2-dithiaphosphorinane which are in equilibrium with the six-membered-ring monomer and the corresponding 2-thiono derivatives have been prepared, isolated, and identified.

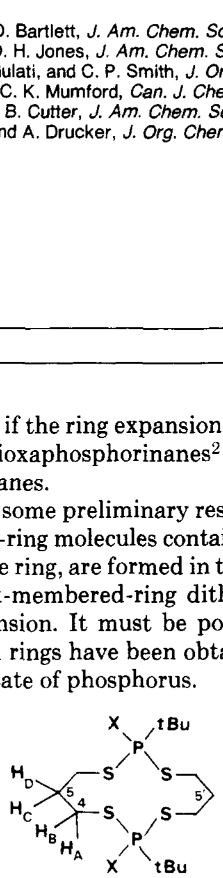
Sir: Macrocyclic molecules containing phosphorus are of potential interest because of the known versatility of phosphorus as a ligand,[1] and as models for stereochemical study. In previous studies, it was shown that twelve- and ten-membered-ring phosphonite molecules can easily be obtained from 1,3,2-dioxaphosphorinanes[2] and 1,3,2-dioxaphospholanes[3] as they dimerize on standing. These large-membered-ring three-coordinated phosphorus molecules which are at room temperature in equilibrium with their monomeric six- and five-membered-ring parent molecules were not isolated. The corresponding thiono derivatives (P=S) were isolated and well characterized as crystalline compounds.

Differences exist in the chemical behavior of the analogous heterocycles where the ring oxygen is replaced by a sulfur. For example, 2-methyl-1,3,2-dithiaphospholane does not show any tendency to ring expansion reaction, whereas the corresponding 1,3,2-dioxaphospholane cannot be isolated as a monomeric species at room temperature.[3] Thus, it was interesting to check if the ring expansion reaction which takes place with 1,3,2-dioxaphosphorinanes[2] can be observed with dithiaphosphorinanes.

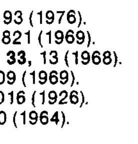
We report here some preliminary results which show that twelve-membered-ring molecules containing phosphorus and sulfur atoms in the ring, are formed in the preparation of the corresponding six-membered-ring dithiaphosphorinane by simple ring expansion. It must be pointed out that these twelve-membered rings have been obtained in the trivalent and tetravalent state of phosphorus.



1, X = lone pair
1S, X = S



2, 2′, X = lone pair
2S, 2′S, X = S



3

1,3-Propanedithiol was added dropwise to a benzene solution of *tert*-butyldichlorophosphine and pyridine.[4–6] The reaction was conducted under nitrogen at 30 °C, and followed by ^{31}P NMR spectroscopy. After addition of half an equivalent of 1,3-propanedithiol, the ^{31}P (^{1}H) NMR spectrum shows two lines at 182.6 and 182.3 ppm, corresponding to compound 3 which is a mixture of two diastereomeric molecules owing to

Table I. ^{13}C **and** ^{31}P **NMR Spectral Data of Dimeric Species 2, 2′, 2S, 2′S**

Compd	Solvent	$\delta(^{31}P)^a$	$\delta(C_4)^b$	$\delta(C_5)$	$J(PH_A)^c$	$J(PH_B)$	$J(PH_C)$	$J(PH_D)$	$J(PC_4)$	$J(PC_5)$
2, cis	C_6D_6	104.0	31.6	34.0					19.4	
2′, trans	C_6D_6	121.0	33.3	34.1	8.0	15.0	1.0	1.0	24.7	4.8
2S cis	$CDCl_3$	116.1	33.0	31.7	13.5	13.0	1.0	1.0	3.8	3.2
2′S trans	$CDCl_3$	120.2	32.1	32.7	17.5	16.0	1.0	1.0	3.8	1.5

[a] The ^{31}P chemical shifts are in parts per million downfield from H_3PO_4 (85%). [b] The ^{13}C chemical shifts are in parts per million downfield from TMS. [c] The coupling constants are in hertz.

Table II. ^{1}H **NMR Spectral Data of Dimeric Species 2, 2′, 2S, 2′S**

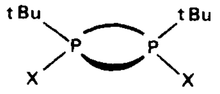
Compd	Solvent	$\delta(H_A)^a$	$\delta(H_B)$	$\delta(H_C)$	$\delta(H_D)$	$\delta(t\text{-Bu})$	$J(H_AH_B{}^b)$	$J(H_AH_C)$	$J(H_AH_D)$	$J(H_BH_C)$	$J(H_BH_D)$
2, cis	C_6D_6			~1.90	~1.90	1.14					
2′, trans	C_6D_6	2.83	2.44	1.90	1.90	1.14	−13.0	6.5	6.5	6.5	6.5
2S, cis	$CDCl_3$	3.24	3.03	2.24	2.22	1.34	−14.0	7.0	7.0	7.0	7.0
2′S, trans	$CDCl_3$	3.31	2.86	2.25	2.25	1.32	−13.8	7.0	7.0	7.0	7.0

[a] The proton chemical shifts are in parts per million downfield from TMS. [b] The coupling constants are in hertz.

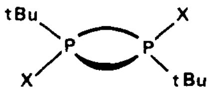
the chiral phosphorus center. Molecule **3** itself was not isolated but its thiono methoxy derivative was characterized by the usual techniques (elemental analysis; ^{1}H, ^{13}C, ^{31}P NMR spectra; mass spectrometry). After completion of the dithiol addition, the reaction mixture exhibits in the ^{31}P (^{1}H) NMR spectrum the following peaks, where the chemical shifts are given in parts per million downfield from H_3PO_4 as the external reference: M (97.3), D_2 (104.0), P (115.5), D_1 (121.0 ppm).

A silica column chromatography performed under nitrogen of the final reaction mixture using hexane–benzene (3:1) as eluent allows separation of a first and third pure fraction, each showing one peak in the ^{31}P (^{1}H) NMR spectrum, D_1 (121.0) and M (97.3 ppm), respectively. A second fraction shows two peaks at D_2 (104.0) and M (97.3 ppm).

By NMR spectral analysis (^{1}H, ^{13}C, ^{31}P) (Tables I and II), elemental analysis, and mass spectrometry, the species corresponding to peaks M, D_1, and D_2 are unambiguously assigned to 2-*tert*-butyl-1,3,2-dithiaphosphorinane (**1**) and the corresponding twelve-membered-ring dimers **2** and **2′** (mp 119–121 °C), respectively. These dimers differ by the relative orientation of the *tert*-butyl group with respect to the mean plane of the molecule. Up to now, we have been unsuccessful in obtaining a pure sample of **2**, which is always contaminated by **1**. Peak P (115.5 ppm) corresponds to higher polymeric species which are now under investigation.



2, X = lone pair
2S, X = S

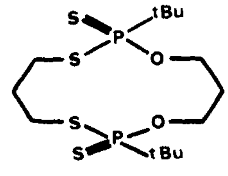


2′, X = lone pair
2′S, X = S

Addition of elemental sulfur[7] to a mixture containing **1**, **2**, and **2′** gives rise to the expected thiono derivatives **1S** (mp 77–78 °C), **2S** (mp 162–164 °C), and **2′S** (mp 250–252 °C). These compounds, separated by silica column chromatography with benzene as eluent, have been characterized by elemental analysis, mass spectroscopy, molecular weight measurement (osmometry), and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Tables I and II). In the ^{1}H NMR spectrum, the protons attached to carbons 5 and 5′ are equivalent in **2′S** and nonequivalent in **2S**. Thus, **2′** and **2′S** correspond to the stereoisomers in which the *tert*-butyl groups are in a trans relationship with respect to the mean plane of the twelve-membered ring (presence of an inversion center i).

When a solution of pure dimer **2′** is left in a sealed NMR tube, it shows additional ^{31}P NMR peaks which appear with time. After a few hours at 80 °C, a mixture of both isomers **2** and **2′** is observed. If the tube is heated at 160 °C, a mixture of the two dimers **2** and **2′** (3:1) with the monomeric species **1** is obtained. The equilibrium ratio of the three species **2′**, **2**, and **1** at 160 °C is 3:1:6. A mixture of the species **2** and **1** leads to a similar equilibrium. Thus, the trans isomer **2′** is thermodynamically more stable than **2**. Different kinetics rates are obtained in nonsealed tubes, probably owing to the presence of catalytic reagents which accelerate the reaction.

Besides the synthesis of a new category of heterocyclic phosphorus molecules, one of the interesting point of the reaction described in this paper is the existence of **3** as a stable intermediate. Thus **3** can react with various difunctional compounds (diols, diamines, dithiols, etc.) leading to various large-membered-ring molecules. As an example, the twelve-membered-ring **4** has been prepared.



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The synthesis of various rings which differ by the size (11, 12, 13) and the nature of their heteroatoms is being actively continued.

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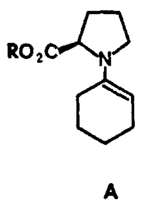
Asymmetric Induction. 2.[1]
Enantioselective Alkylation of Cyclohexanone via a Chiral Enamine[†]

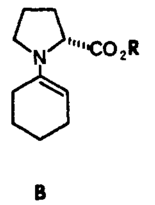
Summary: Asymmetric induction was observed in the alkylation of the cyclohexanone enamine prepared from (+)-*trans*-2,5-dimethylpyrrolidine. Alkylation with methyl iodide, *n*-propyl bromide, and allyl bromide afforded the corresponding 2-*n*-alkylcyclohexanones with optical purities of 83, 93, and 82%, respectively. Very low levels of dialkylation product formation were observed.

Sir: In 1968 Horeau published[2] the first enantioselective alkylation of a ketone, using the imine anion derived from isobornylamine and cyclohexanone. Recent modifications to this scheme have raised the enantiomeric ratio to greater than 9:1.[1,3] We wish to report here a complementary technique that affords similarly high degrees of enantioselectivity in the alkylation of enamines.

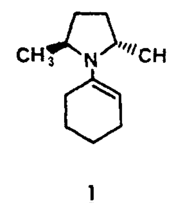
In 1969 Yamada reported[4] the first in a series of investigations[5] of the alkylation of the chiral enamines formed using various proline esters, and though the best optical yield obtained was 55%, the more typical values fell in the range from 10 to 30%. These results, taken together, are consistent with the participation of two sets of transition states differing by geometrical isomerization (represented by A and B). Of the four transition states resulting from the distinct pathways of approach of the alkylating agent (back and front on both A



A



B



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[†] We wish to dedicate this paper to Professor Robert Burns Woodward on the occasion of his sixtieth birthday.