*Anal.* Calcd for $C_{14}H_{18}Cl_4O$: C, 48.84; H, 5.23; Cl, 41.28; O, 4.65. Found: C, 48.92; H, 5.32; Cl, 41.23; O, 4.56.

2,5,6-Trichloro-2,6-dimethyl-4-*tert*-butyl-3-cyclohexen-1-one (IX) had mp 117-118°; uv 220 nm ($\epsilon$ 6000); ir (KBr) 1740 cm$^{-1}$ (C=O); nmr $\delta$ 1.23 [s, 9, $CH_3$ of $C(CH_3)_3$], 1.92-1.94 (6, $CH_3$), 5.13 (d, $J$ = 0.15 Hz, 1, proton at C-5), 6.03 (d, $J$ = 0.15 Hz, 1, ring vinyl proton at C-3).

*Anal.* Calcd for $C_{12}H_{17}Cl_3O$: C, 50.79; H, 5.99; Cl, 37.56. Found: C, 50.61; H, 5.61; Cl, 37.86.

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# Macrocyclic Diphosphines. Synthesis and Stereoisomerism

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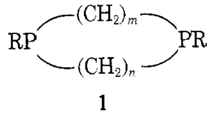
The synthesis of macrocyclic diphosphines is described. Diisopropyl polymethylenediphosphinates were obtained from Michaelis-Arbuzov reaction of diisopropyl phenylphosphonite and polymethylene dibromides. Subsequent reaction of diisopropyl polymethylenediphosphinate with polymethylene dibromide in the presence of sodium bis(2-methoxyethoxy)aluminum hydride under high dilution condition afforded two isomeric macrocyclic bis(phosphine oxides). The relative stereochemistry of the two isomers was established on the basis of their molecular dipole moments. Reduction of the macrocyclic bis(phosphine oxides) with trichlorosilane yielded the diphosphines with overall configuration retenton.

Recently, the syntheses of a number of macrocyclic compounds have been reported. To name a few, there are the macrocyclic polyethers,[1] the macrobicyclic diamines,[2] the macrobicyclic polyoxadiamines,[3] and the polyether sulfides.[4] These synthetic macrocycles typically contain rings or central cavities edged with electronegative binding atoms. They usually exhibit interesting ion-capture and conformational properties. In light of this, the chemistry of macrocyclic polyphosphines should be of potential interest because of the known versatility of phosphines as ligands for transition metals.[5] This paper reports the preparation of polymethylenediphosphines of general structures 1 with $m$, $n$ > 8, hoping that they might serve as interesting complexing agents on one hand, and as models for stereochemical study on the other hand.



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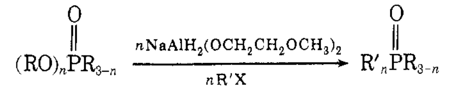
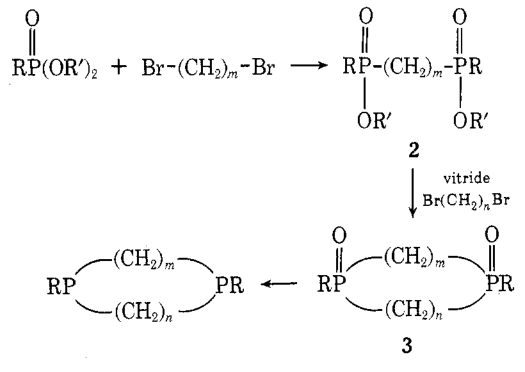
To date, of the cyclic tertiary diphosphines it appears that only 1,4-disubstituted diethylenediphosphines (1, $m = n = 2$) have been synthesized.[6,7] No investigation on the macrocyclic diphosphine has been reported. This may be due to the inherent difficulty associated with the synthesis of macrocyclic system. In general, the major problem encountered in macrocyclic synthesis is polymerization, arising from the predominance of intermolecular reaction over intramolecular cyclization. While this difficulty can usually be overcome by a high dilution condition, another problem arises as to the efficacy of a particular reaction at high dilution. The latter restriction can sometimes preclude the possibility of obtaining the macrocyclic system by this approach. With these in mind, we feel that, of the many methods of forming carbon-phosphorus bond,[8] the recently reported[9] reaction of phosphorus ester and alkyl halide in the presence of sodium bis(2-methoxyethoxy)aluminum hydride[10] (reaction 1) is the



$$(\mathrm{RO})_n\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{R}_{3-n} \xrightarrow[n\mathrm{R'X}]{n\mathrm{NaAlH_2(OCH_2CH_2OCH_3)_2}} \mathrm{R'}_n\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{R}_{3-n} \qquad (1)$$

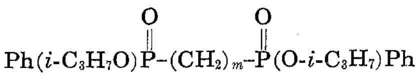
most appealing. The reaction has been reported to proceed under mild conditions. It is usually carried out under homogenous condition and is therefore amenable to high dilution.

**Scheme I**



We envisage therefore the synthesis of macrocyclic diphosphines according to Scheme I. The first step involves Michaelis-Arbuzov reaction of dialkyl phenylphosphonite and polymethylene dibromide and is patterned after our synthesis of linear polymethylene diphosphines.[11]

Table I
Yields and Melting Points of Diphosphinates



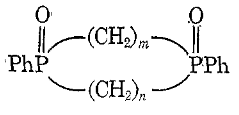
$$Ph(i\text{-}C_3H_7O)\overset{O}{\overset{\|}{P}}\text{-}(CH_2)_m\text{-}\overset{O}{\overset{\|}{P}}(O\text{-}i\text{-}C_3H_7)Ph$$

| Registry no. | $m$ | Yield, % | Mp, °C |
|---|---|---|---|
| 51021-90-0 | 8 | 94 | 64–65 |
| 51021-91-1 | 10 | 92 | 58–60 |
| 51021-92-2 | 12 | 92 | 37–38 |

**Preparation of Diisopropyl Polymethylenebis(phenylphosphinates) (2).** Diisopropyl polymethylenebis(phenylphosphinates) with $m$ = 8, 10, 12 were prepared by Michaelis–Arbuzov reaction of a mixture of 2:1 mole ratio of diisopropyl phenylphosphonite and 1,$m$-dibromoalkane at 150–190°. The reaction usually completed in 3.5 hr and the yields were excellent (Table I). Diisopropyl phenylphosphonite was synthesized by the procedure of Rabinowitz and Pellon[12] from 3:1 mole ratio of isopropyl alcohol and phenyldichlorophosphine in the presence of triethylamine.

**Preparation of 1,($m$ + 2)-Diphenyl-1,($m$ + 2)-diphosphacycloalkane 1,($m$ + 2)-Dioxide (3).** The series of the cyclic bis(phosphine oxide) with $m = n = 8$, $m = n = 10$, and $m = 10$, $n = 12$ were prepared by the Vitride-induced condensation of 2 with 1,$n$-dibromoalkanes in benzene under high dilution condition ($10^{-3}$ $M$). The reaction mixture, after 1 hr of reflux, turned turbid owing to formation of sodium bromide. Hydrolysis of the cooled and concentrated reaction mixture after 12 hr of reaction time afforded, through thin layer chromatographic separation, two isomeric cyclic bis(phosphine oxides) (A and B).

Table II
Yields, Melting Points, and $R_f$'s of Cyclic Bis(phosphine oxides)



| $m$ | $n$ | Isomer A Yield, % | Isomer A Mp, °C[a] | Isomer A $R_f$[b] | Isomer A $\mu$, D | Isomer A Registry no. | Isomer B Yield, % | Isomer B Mp, °C[a] | Isomer B $R_f$[b] | Isomer B $\mu$, D | Isomer B Registry no. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | 8 | 6.6 | 193–195 | 0.27 | 4.12 ± 0.01 | 51021-83-1 | 6.2 | 173–174 | 0.08 | 7.10 ± 0.12 | 51021-84-2 |
| 10 | 10 | 6.0 | 190–191 | 0.30 | 4.82 ± 0.04 | 51096-67-4 | 7.3 | 171–173 | 0.19 | 6.96 ± 0.09 | 51096-68-5 |
| 10 | 12 | 6.3 | 164–166 | 0.33 | 5.34 ± 0.04 | 51096-69-6 | 7.6 | 146–147 | 0.24 | 7.03 ± 0.03 | 51021-79-5 |

[a] Taken in sealed tube. [b] See Experimental Section for conditions.

These oxides were obtained as hygroscopic solids in moderate yields (Table II). Except for the difference in chromatographic $R_f$ values and melting points, the two isomers exhibit the same spectroscopic and mass spectrometric properties. Their structural identities are established on the following considerations. Their ir spectra show strong resemblance to those of the straight-chain bis(phosphine oxides)[11] and have two sharp phorphoryl absorptions at 1180 and 1125 cm$^{-1}$. In the pmr spectra, the methylene signals appear as a broad multiplet at $\delta$ 1.1–2.4 and the aromatic signals at $\delta$ 7.3–8.0 as an asymmetric multiplet in the correct ratio. The most conspicuous features of the mass spectra of the cyclic bis(phosphine oxides) are the very intense molecular ions. This is compatible with a cyclic structure and establishes the molecular weight of these compounds unambiguously.

**Assignment of Stereochemistry.** The existence of two isomers for the bis(phosphine oxides) is clearly due to the cis–trans isomerism of the two phosphoryl groups. Assignment of the relative stereochemistry to these compounds cannot, however, be deduced from spectroscopic data. We seek therefore to establish the stereochemistry on the basis of their molecular dipole moments.

It is well known that phosphoryl group P=O possesses a definite bond moment[13,14] primarily because of high polarization in the $\sigma$ bond which outweighs the $p_\pi \rightarrow d_\pi$ bond. The dipole moments of some tertiary phosphine oxides have recently been investigated.[14] It appears that the dipole moment of triphenylphosphine oxide is only slightly larger than those of the trialkylphosphine oxides (Table III). It seems reasonable to assume that the direction of the molecular dipole moment of dialkylphenylphosphine oxide follows that of its phosphoryl bond and has a magnitude somewhere between 4.35 and 4.44 D (a value of 4.4 D is assumed for calculation, *vide infra*).

The dipole moments of these bis(phosphine oxides) were thus determined from measurements of the dielectric constants and refractive indices of their very dilute solutions in benzene ($10^{-2}$ to $10^{-3}$ $M$) at 30.00 + 0.05°. It was found that all the B isomers had approximately equal molecular dipole moments (~7 D). The A isomers, however, exhibited smaller dipole moments with some variation (Table II).

We assign the more polar B isomers of the cyclic bis(phosphine oxides) to be the cis isomers. Their molecular dipole moments nearly approach twice the magnitude of that of dialkylphenylphosphine oxide. Simple calculation using eq 2 shows that the angle $\theta$ between the two phosphoryl dipoles of B isomer is approximately 75°. Considerations based on molecular models suggest that this situation is very unlikely for the trans isomer, for this would involve excessive bending of the ring. On the contrary, this angle separation of the phosphoryl groups is favorably well suited for the cis isomer. Models suggest two possible conformations for the cis isomer in benzene solution: one with two phosphoryl groups pointing toward the $C_2$ molecular axis (IIIa) and the other with the phosphoryl groups pointing away from the $C_2$ axis (IIIa′).

$$2\mu(R_2PhP{=}O)\cos\tfrac{1}{2}\theta = \mu[\text{bis(phosphine oxide)}] \qquad (2)$$

The less polar A isomers have therefore the trans stereochemistry. The fact that they are polar implies interesting conformational properties for these macrocycles. Had the trans isomers with $m = n$ assumed the centro-

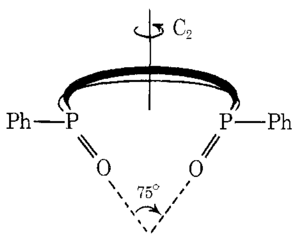
Table III
Molecular Dipole Moments of some Tertiary Phosphine Oxides

| Phosphine oxide | $\mu$, D |
|---|---|
| Triethyl | 4.37 |
| Tri-$n$-propyl | 4.36 |
| Tri-$n$-butyl | 4.35 |
| Tri-$n$-pentyl | 4.35 |
| Triphenyl | 4.44 |

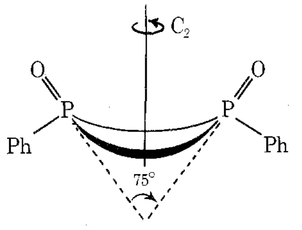
**Table IV**
**Yields and Melting Points of the Macrocyclic Diphosphines 1**

| | | Trans isomer | | | Cis isomer | | |
|---|---|---|---|---|---|---|---|
| *m* | *n* | Yield, % | Mp, °C | Registry no. | Yield, % | Mp, °C | Registry no. |
| 8 | 8 | 65 | 103–104 | 51021-80-8 | 60.5 | 55–56 | 51154-91-7 |
| 10 | 10 | 83 | 97–97.5 | 51021-81-9 | 80 | 90–91 | 51064-83-6 |
| 10 | 12 | 75 | 35–36 | 51021-82-0 | 92 | 42.5–43 | 51064-84-7 |

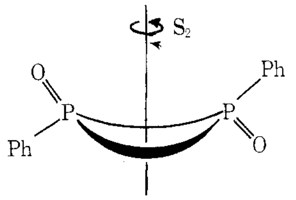
symmetric ($S_2$) conformation (IIIb), there would have been a net zero dipole moment for these molecules. It is possible that, with the flexibility of the large ring, some bending of the ring occurs, thus reducing the angle between the two phosphoryl groups from being antiparallel (IIIb′). This explanation is in agreement with the finding that the molecular dipole moment of the trans isomer increases on increasing ring size—a condition facilitating bending of the ring. Calculations show that the angles $\theta$ between the two phosphoryl groups in the trans isomers in benzene solution are about 124, 112, and 106°, respectively, for $m = n = 8$, $m = n = 10$, and $m = 10$, $n = 12$. The factors causing this ring bending are not known at the moment.



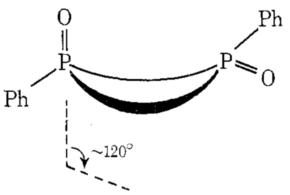
IIIa



IIIa′



IIIb

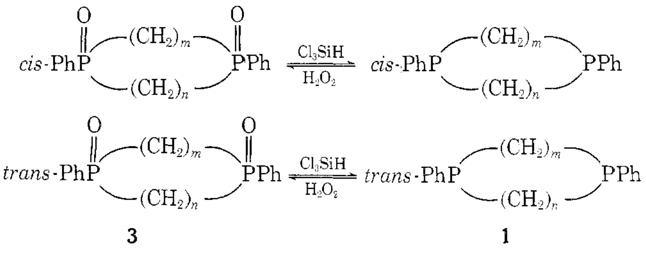


IIIb′

**Preparation of 1,(*m* + 2)-Diphenyl-1,(*m* + 2)-diphosphacycloalkanes (1).** The reduction of phosphine oxide to phosphine by silanes is generally stereospecific.[15-21] The stereochemical outcome of the reduction, however, depends on the nature of the silane, the basicity of the base catalyst, and the structural feature of the phosphine oxide. Reduction with trichlorosilane has been reported to proceed with high retention of configuration.[16]

The cyclic bis(phosphine oxides) were thus reduced by an excess of trichlorosilane in benzene at 60–70° to the diphosphines in good yields (Table IV). Reduction usually completed in 3 to 5 hr. The resulting diphosphines are air-stable white solids, having characteristic phosphine odor. Only one isomer was obtained in each case.

As long as the reduction proceeds stereospecifically at both phosphorus centers, the resulting diphosphine will have the same stereochemistry as the precursor oxide. That this is indeed the case is substantiated by reoxidation of the product diphosphine with hydrogen peroxide to yield the original isomeric bis(phosphine oxide). The oxidation is known to occur with retention of configuration.[22]



3 1

## Experimental Section

**General.** Benzene was dried by boiling with sodium wire under reflux for 5 hr and fractional distilled from fresh sodium wires through a 2-ft column before use. All reactions were carried out under nitrogen atmosphere. The melting points are all uncorrected. Infrared spectra were recorded on a Unicam SP 1000 spectrophotometer with polystyrene calibration; solid compounds were taken as KBr pellets, and liquid compounds as thin films (neat). Proton nuclear magnetic resonance spectra were recorded on a Varian T60 spectrometer; unless otherwise stated, the spectra were taken in deuterated chloroform, using tetramethylsilane as internal reference. Mass spectra were recorded on an AEI MS-902 spectrometer at a temperature of 180 to 195°. The operating conditions were a 70-eV electron energy, resolution of 1000 and 8 kV accelerating voltage. Microanalyses were performed by Scandanavian Microanalytical Laboratories, Denmark.

**Diisopropyl Phenylphosphonite.** Diisopropyl phenylphosphonite was prepared from 17.9 g (0.1 mol) of phenyldichlorophosphine and 18.0 g (0.3 mol) of isopropyl alcohol in the presence of 25.3 g (0.25 mol) of triethylamine by the procedure of Rabinowitz and Pellon.[12] A total yield of 15.2 g (67%) of highly air-sensitive diisopropyl phenylphosphonite was obtained [bp 68–70° (0.35 mm); lit.[23] bp 121–122° (10 mm)].

**Diisopropyl Polymethylenebis(phenylphosphinates).** The preparative procedure for all diisopropyl polymethylenebis(phenylphosphinates) was essentially similar by the Michaelis–Arbuzov reaction. A mixture of diisopropyl phenylphosphonite (20.0 mmol) and polymethylene dibromide (10.0 mmol) was heated under reflux at temperature of 155 to 190°. A stream of nitrogen was passed through the reaction system to carry off the liberated isopropyl bromide. The reaction was completed in 3.5 hr. Recrystallization of crude reaction product from *n*-hexane afforded pure diisopropyl polymethylenebis(phenylphosphinate) as white solid in excellent yield.

**(a) Diisopropyl octamethylenebis(phenylphosphinate):** mp 64–5°, 94% yield. *Anal.* Calcd for $C_{26}H_{40}P_2O_4$: C, 65.26; H, 8.43. Found: C, 64.90; H, 8.29.

**(b) Diisopropyl decamethylenebis(phenylphosphinate):** mp 58–60°; 92% yield. *Anal.* Calcd for $C_{28}H_{44}P_2O_4$: C, 66.29; H, 8.75. Found: C, 66.32; H, 8.63.

**(c) Diisopropyl dodecamethylenebis(phenylphosphinate):** mp 37–8°; 92% yield. *Anal.* Calcd for $C_{30}H_{48}P_2O_4$: C, 67.39; H, 9.05. Found: C, 66.53; H, 9.05.

**1,(*m* + 2)-Diphenyl-1,(*m* + 2)-diphosphacycloalkane 1,(*m* + 2)-Dioxides.** The recently discovered Vitride-induced phosphorus–carbon bond formation reaction of Kenyon and Wetzel[9] involving a phosphorus ester and an alkyl halide was employed to achieve cyclization at high dilution. The following is an illustrative procedure by which all the macrocyclic bis(phosphine oxides) were obtained.

To a well-stirred solution of 5.0 mmol of diisopropyl polymethylenebis(phenylphosphinate) in 60 ml of benzene in a 2-l. round-bottomed flask at 25° was added dropwise a solution of 14 mmol of vitride reagent in 50 ml of benzene over a period of 20 min. Vigorous effervescence due to the evolution of hydrogen gas occurred throughout the addition. When all the Vitride solution was added, the reaction mixture was kept well stirred for several minutes until bubbling stopped. It was then diluted with benzene to a total volume of 1 l., followed by addition of 5.0 mmol of polymethylene dibromide. Every precaution was taken to prevent oxygen from getting into the reaction system during addition and dilution. The diluted reaction mixture was heated under reflux at 80° for 12 hr. Turbidity due to the formation of sodium bromide occurred after 1 hr of heating. The reaction mixture, after cooling and concentrating to 500 ml, was hydrolyzed with minimum amount of water (2–3 ml) at 25° and filtered. The aluminum salts

Table V[a]

| $m$ | $n$ | Isomer | $w_2$ ($10^3$) | $\epsilon_{12} - \epsilon_1$ ($10^3$) | $\alpha\epsilon_1$ | $n_{12}^2 - n_1^2$ ($10^4$) | $\gamma n_1^2$ (10) | $P_0$, cm$^3$ | $\mu$, D |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 8 | A | 2.735 | 10.625 | 3.885 | 3.6 | 1.316 | 340.8 | 4.12 ± 0.01 |
| | | | 1.960 | 7.614 | 3.885 | 2.1 | 1.071 | | |
| | | B | 2.460 | 28.864 | 11.733 | 3.6 | 1.463 | 1012 | 7.10 ± 0.12 |
| | | | 1.323 | 14.609 | 11.043 | 2.1 | 1.588 | | |
| 10 | 10 | A | 2.473 | 11.952 | 4.833 | 3.6 | 1.456 | 467.8 | 4.82 ± 0.04 |
| | | | 1.602 | 7.526 | 4.698 | 2.1 | 1.311 | | |
| | | B | 2.282 | 22.578 | 9.894 | 2.1 | 0.920 | 973.9 | 6.96 ± 0.09 |
| | | | 1.606 | 15.495 | 9.648 | 2.1 | 1.308 | | |
| 10 | 12 | A | 2.528 | 14.166 | 5.604 | 3.6 | 1.424 | 573.0 | 5.34 ± 0.04 |
| | | | 2.178 | 11.776 | 5.407 | 2.1 | 0.964 | | |
| | | B | 2.337 | 22.312 | 9.547 | 3.6 | 1.541 | 992.8 | 7.03 ± 0.03 |
| | | | 1.880 | 17.709 | 9.420 | 2.1 | 1.117 | | |

[a] See ref 25 for method of calculation.

were washed with 100 ml of benzene. On evaporating to dryness, the combined filtrates yielded a white gummy solid, which, on separation by thin layer chromatography (silica gel) using acetone–ethanol (9:1) as eluting solvent, afforded two isomeric macrocyclic bis(phosphine oxides) A and B along with some other polymeric materials. The two isomeric bis(phosphine oxides) were readily recrystallized from chloroform–hexane as hygroscopic white solids in about 13% total yield.

(a) **1,10-Diphenyl-1,10-diphosphacyclooctadecane 1,10-Dioxide.** Isomer A: mp 193–195°; $R_f$ 0.27; 6.6% yield. *Anal.* Calcd for $C_{28}H_{42}P_2O_2$: C, 71.16; H, 8.96. Calcd for $C_{28}H_{42}P_2O_2 \cdot \frac{1}{2}H_2O$: C, 69.83; H, 9.00. Found: C, 69.47; H, 8.94. Isomer B: mp 173–174°; $R_f$ 0.08; 6.2% yield. *Anal.* Calcd for $C_{28}H_{42}P_2O_2 \cdot \frac{1}{4}H_2O$: C, 70.49; H, 8.98. Found: C, 70.43; H, 8.84.

(b) **1,12-Diphenyl-1,12-diphosphacyclodocosane 1,12-Dioxide.** Isomer A: mp 190–191°; $R_f$, 0.30; 6.0% yield. *Anal.* Calcd for $C_{32}H_{50}P_2O_2$: C, 72.70; H, 9.53. Found: C, 72.45; H, 9.38. Isomer B: mp 171–173°; $R_f$, 0.19; 7.3% yield. *Anal.* Found: C, 72.14; H, 9.92.

(c) **1,12-Diphenyl-1,12-diphosphacyclotetracosane 1,12-Dioxide.** Isomer A: mp 164–166°; $R_f$, 0.33; 6.3% yield. *Anal.* Calcd for $C_{34}H_{54}P_2O_2$: C, 73.35; H, 9.78. Found: C, 73.17; H, 9.73. Isomer B: mp 146–147°; $R_f$, 0.24; 7.6% yield. *Anal.* Found: C, 73.26; H, 9.78.

**Determination of the Molecular Dipole Moments of 1,($m$ + 2)-Diphenyl-1,($m$ + 2)-diphosphacycloalkane 1,($m$ + 2)-Dioxides. (i) Instruments.** The dipole moments of the macrocyclic bis(phosphine oxides) were determined from measurements of the dielectric constants and refractive indices of their dilute solutions in benzene at 30.00 ± 0.05°. The dielectric constants were determined by means of the Dipolemeter Type DM01, of Wissashaftlich-Technische Werkstätten, G.m.b.H. of Germany with measuring cell DFL2 which could achieve a sensitivity of $\Delta\epsilon/\epsilon \sim 10^{-5}$. The refractive indices were taken on a Carl Zeiss refractometer of Germany. Water at 30.00 ± 0.05° from a large thermostat was circulated through the measuring cell socket and refractometer, thus ensuring the measuring environment to be at the same constant temperature. In order to obtain the electrical and thermal stability of the instrument, the dipolemeter was turned on and the measuring cell maintained at the required temperature for 5 hr before use.

**(ii) Solvents.** The calibrating solvents for the dipolemeter were toluene, benzene, and cyclohexane whose dielectric constants at 30° were taken as 2.3668,[24] 2.2629,[25] and 2.0068,[25] respectively. The values of 0.8683 g/cm$^3$ and 1.49468[26] were used respectively for the density and the refractive index of benzene.

All the solvents were of spectroscopic grade. Toluene and benzene were further purified by boiling with sodium wire for 5 hr and fractional distilled from fresh sodium wire through a 2-ft column packed with glass beads. Cyclohexane was dried over well-heated silica gel for 12 hr with constant shaking and then fractional distilled. Only the middle fractions of the distillates were used throughout.

**(iii) Procedure.** Since these macrocyclic bis(phosphine oxides) are all hygroscopic, they were therefore pre-dried at 130° under low pressure (~0.1 mm) for 12 hr and used immediately. Two solutions ($10^{-2}$ to $10^{-3}$ *M*) of each compound in benzene, prepared in all-Pyrex glass volumetric flasks in dried atmosphere, were used.

In order to assure reproducibility of results, measurements were made only after the sample solution was let to stand in the measuring cell for at least 40 min to attain thermal equilibrium. For each solution, five readings taken to ±0.1 were recorded and their average represented the value to be used in the deduction of the dielectric constant.

**(iv) Calculations.** The molecular dipole moment of a compound can generally be determined by several methods, but the one most widely used is that involving experimental measurements of dielectric constants of a series of dilute solutions of the compound in nonpolar solvent. This method is based on the Debye theory[25] which assumes ideal behavior of the solution and is therefore only satisfactory for very dilute solutions. The calculated dipole moments and orientation polarizations of the macrocyclic bis(phosphine oxides), together with other experimental data are recorded in Table V.

**1,($m$ + 2)-Diphenyl-1,($m$ + 2)-diphosphacycloalkane.** The cyclic bis(phosphine oxides) were reduced by trichlorosilane in benzene. The following illustrates the procedure employed.

A solution of 0.2 mmol of bis(phosphine oxide) and 1.2 mmol of trichlorosilane in 5 ml of benzene was heated under reflux at 60° for 4–5 hr. It was then cooled and hydrolyzed with 30% aqueous sodium hydroxide solution at room temperature. The solid silicate was filtered off and washed at least three times with 10-ml portions of benzene. The combined filtrates, on drying with anhydrous $MgSO_4$ and evaporating under reduced pressure to dryness, afforded a white solid having a characteristic phosphine smell. The crude cyclic diphosphine was recrystallized from acetone or benzene–methanol. Yields of cyclic diphosphines obtained in this manner were satisfactory.

(a) **1,10-Diphenyl-1,10-diphosphacyclooctadecane.** Trans isomer: mp 103–134°; 65% yield. *Anal.* Calcd. For $C_{28}H_{42}P_2$: C, 76.33; H, 9.61. Found: C, 76.04; H, 9.53. Cis isomer: mp 55–56°; 60.5% yield. *Anal.* Found: C, 76.03; H, 9.79.

(b) **1,12-Diphenyl-1,12-diphosphacyclodocosane.** Trans isomer: mp 97–97.5°; 83% yield. *Anal.* Calcd. for $C_{32}H_{50}P_2$: C, 77.38; H, 10.15. Found: C, 76.97; H, 10.09. Cis isomer: mp 90–91°; 80% yield. *Anal.* Found: C, 76.81; H, 9.95%.

(c) **1,12-Diphenyl-1,12-diphosphacyclotetracosane.** Trans isomer: mp 35–36°; 75% yield. *Anal.* Calcd for $C_{34}H_{54}P_2$: C, 77.82; H, 10.37. Found: C, 77.27; H, 10.27. Cis isomer: mp 42.5–43°; 95% yield. *Anal.* Found: C, 77.23; H, 10.42.

**Oxidation of 1,($m$ + 2)-Diphenyl-1,($m$ + 2)-diphosphacy-**

**cloalkanes.** The cyclic diphosphines were readily oxidized by warming with an excess of hydrogen peroxide in water-acetone at 60° for 3 hr. In each case, removal of the solvent at reduced pressure afforded a white solid which was found to be completely isomerically pure from tlc and had a $R_f$ value similar to that of the isomeric cyclic bis(phosphine oxide) from which the diphosphine was obtained. The solid, when dried at 120° under low pressure (0.1 mm) for 12 hr, gave a melting point close to that of the original isomeric cyclic bis(phosphine oxide).

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# *Notes*

## Indications of Stereospecific Loss of Water from Bicyclic Ketones during Chemical Ionization Mass Spectrometry

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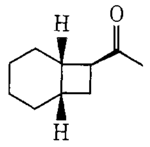
The application of mass spectrometry to studies of the stereochemistry of cyclic and acyclic molecules is of continuing interest.[1] In a recent example, the stereochemistry of two deuterated bicyclo[3.3.1]nonanols was unequivocally determined by electron ionization (EI) mass spectrometry.[2] The application of chemical ionization (CI) mass spectrometry to stereochemical problems has been studied only to a limited extent, but promising initial results have been obtained.[3] The loss of $H_2O$ from ketones[4] and aldehydes[5] has been examined by both methods of ionization. For ketones, a ten-member transition state was proposed. Aldehydes were reported to lose $H_2O$ *via* a five-membered transition state under both EI[5a,e] and CI[5e] conditions. One EI study suggested the presence of six-membered or even eight-membered transition states.[5b] In a CI study of labeled heptanals, scrambling of deuterium was noted.[5d] Migration of allylic hydrogens to carbonyl groups in the EI spectra of polycyclic cyclohexenediones has been related to the distance between the hydrogens and the carbonyl oxygens.[6]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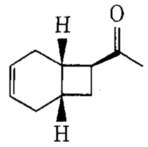
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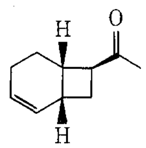
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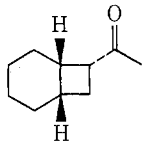
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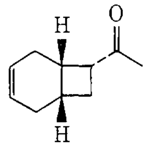
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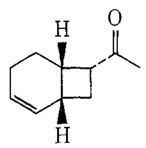
VI

During a mass spectrometric examination of six bicyclic ketones of established[7] structure I-VI we observed marked differences between the isobutane CI spectra of isomers. Salient portions of the EI and CI spectra obtained are given in Tables I and II.[8] These show the relative intensities (as fractions of the total sample ionization[9]) of the peaks at $(M + 1)^+$, $M\cdot^+$, $(M - 1)^+$, $(M + 1 - 18)^+$, and $(M - 18)\cdot^+$ in the EI and CI spectra.

The EI spectra show very weak $(M - 18)\cdot^+$ peaks, all of similar intensity. While there are intensity differences in the $M\cdot^+$ ions of the EI spectra, these differences are small and involve peaks of low intensity.

The CI spectra of the isomeric saturated ketones I and II are very similar. We have no explanation for the difference between the $(M - 1)^+$ intensities in these isomers. The CI spectra of the exo isomers of the unsaturated ketones, compounds III and V, are similar to the CI spectrum of the exo isomer I. We infer that the similar intensities of $(M + 1)^+$ and $(M + 1 - 18)^+$ in these three compounds arise from similar mechanisms for loss of $H_2O$. We have examined Dreiding models of these compounds, and find that in all three exo isomers the carbonyl group is isolated from hydrogens on the bicyclic system.

The two endo unsaturated ketones IV and VI have strong $(M + 1 - 18)^+$ ions [respectively 9 and 12 times stronger than $(M + 1 - 18)^+$ of their exo isomers III and V]. The models show that in all three endo isomers the carbonyl oxygen can closely approach hydrogens of the six-membered ring. In the endo isomer II transfer of aliphatic hydrogen to the carbonyl oxygen could occur *via* a