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X-Ray Crystallographic Study of a 1,3,2-Dioxaphosphorinane Dimer Containing Five-Coordinated Phosphorus in the 12-Membered Ring

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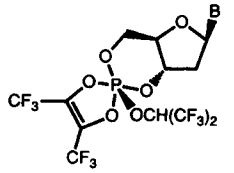
ABSTRACT

*Attempted preparation of phosphorane **9** with a 1,3,2-dioxaphosphorinane ring attached diequatorially to phosphorus led to a mixture of products from which was isolated 12-membered ring phosphorane **10**, formally the dimer of **9**, in low yield (22%). An X-ray crystal structure of **10** revealed a highly symmetrical molecule with trigonal bipyramidal geometry at both phosphorus atoms. The 12-membered ring is attached to phosphorus diequatorially. The ring is strongly puckered about phosphorus with an equatorial O-P-O angle of 110°. The chemical shift equivalence of the CH_2O resonances in the ^1H NMR spectrum of **10** shows the 12-membered ring to be highly mobile at ambient probe temperature. At −89°C, these resonances are fully decoalesced. The value of $\Delta G^{\ddagger}$ for the process that averages these peaks was found to be 10.1 kcal/mol at coalescence (−42.0°C).*

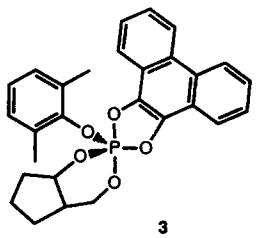
INTRODUCTION

1,3,2-Dioxaphosphorinanes containing five-coordinate phosphorus have been the subject of renewed study in the past several years [1]. When not in some way restricted in geometry, they have been seen to feature the attachment of the ring to phosphorus in apical-equatorial fashion. Indeed, an estimate from ab initio molecular orbital calculations of about 7 kcal/mol has been published for the increase in energy associated with a diequatorial chair [2]. The ring is generally in a *twist* or *boat* conformation rather than a chair form. The structural variety of such systems is illustrated by selected examples **1–5**. Only a few *chair-form* exceptions [3] to this generality have been seen, e.g., **6** [1m], but their existence suggests that the difference in energy between chair and twist or boat forms may be relatively small.

Several examples of five-coordinate phosphorus-containing 1,3,2-dioxaphosphorinanes with the ring constrained to be attached diequatorially to phosphorus have been reported, e.g., **7** [1n] and **8** [4]. All feature a *chair-form* six-membered ring. In order to have available for study



1 B = H
2 B = thymin-1-yl



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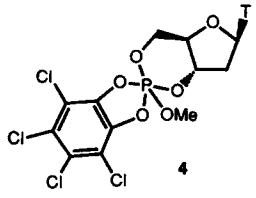

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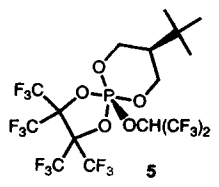

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Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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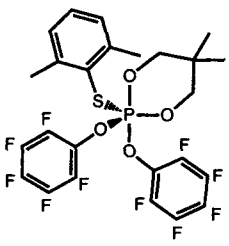

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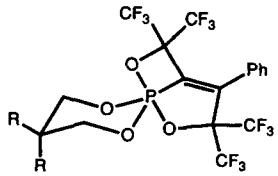
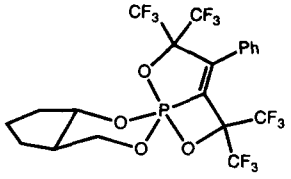


7 R = Me, H



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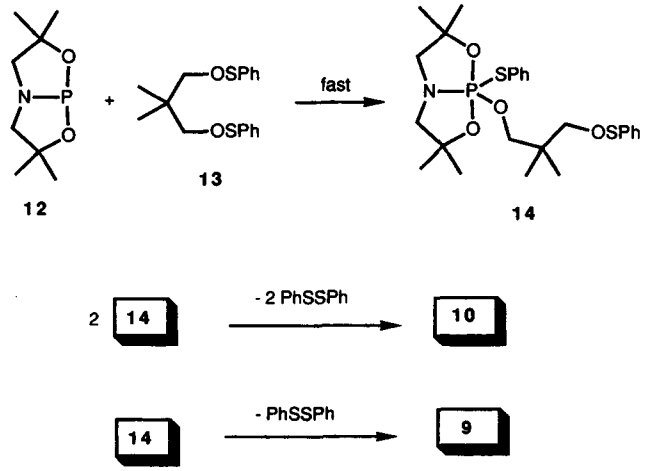
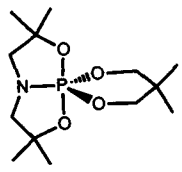


12 13 14

SCHEME 1

such a molecule that is symmetrically substituted about phosphorus, we sought to prepare phosphorane **9**. Since five-membered rings strongly prefer apical-equatorial attachment, there is little doubt that the six-membered ring of **9** would be oriented diequatorially. Interestingly, this approach gave what is formally the dimer of **9**, phosphorane **10**, as the isolable product. Phosphorane **10**, nonetheless, is of considerable structural interest.



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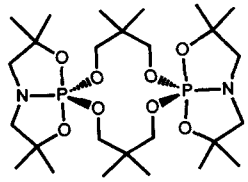

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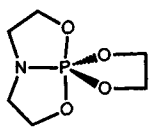
RESULTS AND DISCUSSION

Preparation of **10**

Typically, five-coordinate 1,3,2-dioxaphosphorinanes have been prepared by first constructing the six-membered ring. However, it seemed feasible to add the ring in the final step during which the coordination number of phosphorus would be expanded from three to five, especially since a five-membered ring had been similarly appended to prepare **11** [5]. This approach to **9** is shown in Scheme 1. The use of sulfenate esters to form pentacovalent



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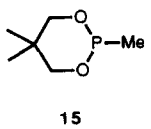
phosphorus-containing products has been successfully demonstrated most thoroughly by Denney and co-workers [6]. In the approach of Scheme 1, 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phospha-(III)bicyclo[3.3.0]octane, **12**, was readily prepared in good yield (67%) by a modification of the literature procedure [7], working at higher dilution and lower temperatures. Unfortunately, reaction of **12** with the bisbenzenesulfenate of 2,2-dimethylpropane-1,3-diol, **13**, via the literature method [5] gave dimer **10** as the only isolable product. Attempts to prepare isolable **9** rather than **10** by slow co-addition of the reactants were unsuccessful.

Evidence for the structure of **10** came from its chemical ionization mass spectrum that showed a weak molecular ion and a stronger peak corresponding to the mass of the monomer. The ^{31}P NMR spectrum of a solution of product **10** ($\delta^{31}P = -45.4$, CD_2Cl_2), however, showed only one peak and hence no evidence for the presence of both dimer and monomer of **9**. (Monomer **15** ($\delta^{31}P = 163$), e.g., displays a resonance 3–6 ppm *upfield* of that of the diastereomeric 12-membered ring dimer **16** ($\delta^{31}P = 165.5, 169.0$) [8]).

The ^1H NMR spectrum of the same solution of **10** showed only peaks assignable to the dimer. A single doublet in the CH_2O region of the ^1H NMR spectrum with a $^3J_{HP}$ value of 2.6 Hz was noted. By contrast 1,3,2-dioxaphosphorinanes containing five-coordinate phosphorus have enough structural rigidity that they can only populate chair or boat (twist) conformations and display sums of $^3J_{HP}$ for the two individual protons of the CH_2O group in the range 27–31 Hz [1b–d, f, g, n, o, 4]. For phosphorane **9**, two chair forms would be equally populated to give a single doublet with time-averaged J of the order 13–15 Hz. The sulfides of **16** also showed much reduced $^3J_{HP}$ values (4.5, 8.5 Hz for one diastereomer; 5.5, 6.6 Hz for the other) compared to the sulfides of the corresponding mono-

mer, **15** ($^3J_{HP}$ = 7.0, 21.0 Hz), though not to the extent noted for **10**. The sulfides retain strong axial or equatorial orientation preferences for the groups about



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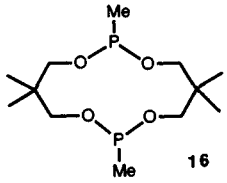

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phosphorus that are not present in **10**. The methylene protons within the bicyclic system appear at ambient temperature as a single doublet (J_{HP} = 12.5 Hz). The chemical shifts of the eight methyl groups on the bicyclic ring system are revealed as a single, uncoupled, resonance, while those on the 12-membered ring give rise to a single uncoupled 12-hydrogen resonance of their own.

When the formation of **10** was monitored by ^{31}P NMR spectroscopy, peaks at δ −28.2, −37.9, and −44.8 (relative intensities, 80:35:78) were seen immediately after the reaction mixture at −78° in CH_2Cl_2 was warmed to room temperature. A small amount of solid **10** (δ = −45.4) was formed near the surface of the reaction solution. Overnight, the resonance at −28.2 ppm had completely disappeared, while the ratio of the other two peaks was virtually unchanged. The amount of solid had markedly increased. The CH_2Cl_2 was removed and replaced by the less dense solvent CH_3CN to give product **10** as a precipitate. Heating of the supernatant solution at about 75°C failed to give more **10**. The other resonances at δ = −37.9 and −44.8 disappeared to give several new weak resonances along with a very intense peak at δ = −34.5. Thus, only one of the initial set of products, that corresponding to the resonance at −28.2, appears to yield dimer **10**. If indeed any of the other initially observed peaks corresponds to monomer **9**, the latter appears not to be converted to dimer **10**. The position of the resonance at δ = −28.2 suggests that it originates from intermediate **14** (or the bis adduct from reaction of **14** with another molecule of **12**) that reacts further to yield **10** and phenyl disulfide, also shown to be formed in the reaction (GC evidence). Indeed, reaction in CH_2Cl_2 of **12** with an equimolar amount of PhSOMe at −78°C gave predominantly a product with ^{31}P chemical shift at δ = −27.4.

Preparatively, dimer **10** was most readily obtained by allowing the CH_2Cl_2 solution of initially formed reaction products to warm slowly and then stand at room temperature. Crystalline **10** was formed near the surface of the solution. The yield of essentially pure **10** isolated in this way was only 22%. However, no attempt was made to maximize the yield. The observation of several ^{31}P NMR peaks in the initial product solution (vide infra) suggests that this method will not readily yield monomer **9**.

X-ray Crystallographic Study of **10**

A colorless, monoclinic crystal of **10** from CH_2Cl_2, subjected to X-ray crystallographic analysis, gave a well-refined structure with an R_w value of 4.9%. An ORTEP representation of the molecule is displayed in Figure 1. The crystal data are listed in Table 1. Pertinent bond distances appear in Table 2, while selected bond angles are recorded in Table 3.

The ORTEP view shows the molecule to be very symmetrical as also is revealed in the data of Tables 2 and 3. The geometries about P1 and P9 are essentially identical and very close to trigonal bipyramidal. This geometry can be seen in the bond angles about P1. The angle O2-P1-O8 is 175.2°, less the 5° below 180°. The sum of the bond angles about P1 in the equatorial plane (360.1°) attests to the coplanarity of N5, O21, O22, and P1. There is, however, some distortion from strict trigonal bipyramidal geometry revealed in the individual bond angles. Thus, the angle O21-P1-O22 is only 110.5°, and the others in the equatorial plane, O21-P1-N5 (127.6°) and O22-P1-N5 (122.0°), are expanded beyond 120°. The relatively small O21-P1-O22 angle, approximately 10° below the 120° value of an ideal trigonal bipyramid, is seen here in a ring system that is essentially unstrained. This allows the ring to be puckered considerably at P1 and P9. What is unknown is whether the O21-P1-O22 contraction occurs with little sacrifice of energy and in response to the conformational preference of the 12-membered ring. Alternatively, the 110° O-P-O equatorial bond angle could reflect some special aspects of this particular bicyclic system which undoubtedly includes a strong component of backbonding from the equatorial lone pair of N5 [10].

The fused five-membered rings are not quite planar, as shown, for example, by the torsion angle O2-C3-C4-N5 (19.1°). This renders each methyl group in the geminal pair slightly nonequivalent to its partner. However, the barriers toward pseudorotation within the five-membered rings, of course, are very low, and, as noted above, the eight methyl groups have the same chemical shift in the proton NMR spectrum at ambient temperatures.

Variable Temperature ^{1}H and ^{13}C NMR Studies

When a toluene-d_8 solution of **10** was cooled, the methylene ^{1}H NMR resonances of the 12-membered ring, observed at 500 MHz, broadened strongly and were fully decoalesced at −89°C into two equal intensity peaks at δ 3.6 and 4.7 (Figure 2). The higher field resonance showed a clearly discernable 6.9 Hz doublet splitting. The other peak was similarly broadened, but no couplings could

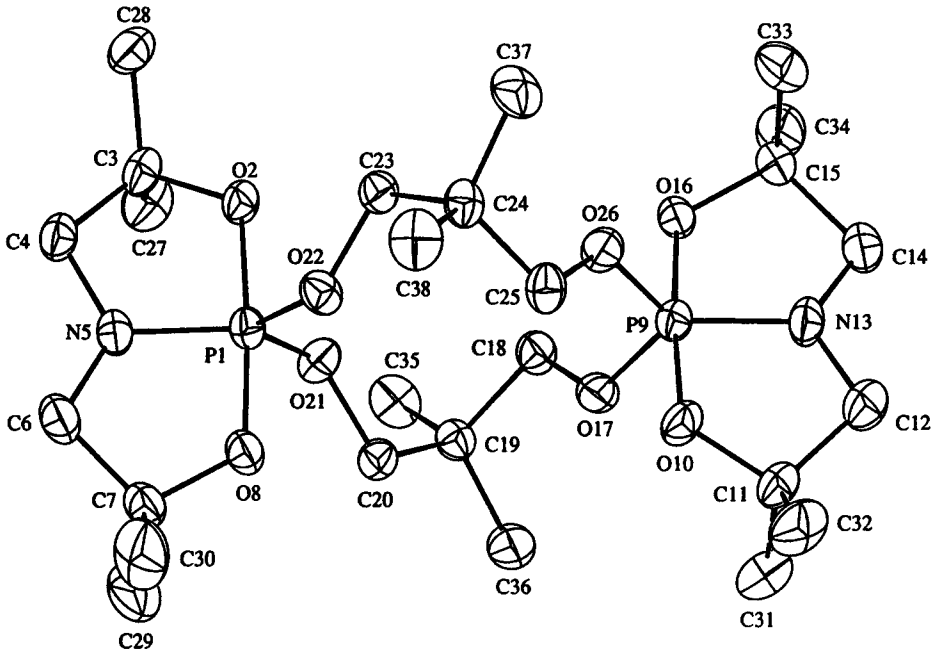


FIGURE 1 ORTEP drawing of the X-ray crystal structure of **10**.

TABLE 1 Crystal Data for 10 at −125°C

Mole formula	$P_2O_8N_2C_{26}H_{52}$
Mole weight	382.660
Space group	$P2_1/n$ (no. 14)
Crystal system	monoclinic
Cell dimensions	
a, Å	10.657 (1)
b, Å	19.325 (2)
c, Å	15.427 (1)
α, deg	
β, deg	92.16 (1)
γ, deg	
ν, Å^3	3174.75
Z	8.0
D_{calcd}, g/cm^3	1.219
Radiation, Å	λ (Cu) 1.54056
2θ range, deg	4.00–130.00
Scan technique	$\theta/2\theta$
Scan width, deg.	0.8000 + 0.1400 tan θ
Number of reflections used	5295
Absorption coefficient, cm^{-1}	16.188
Data to parameter ratio	9.166
Shift to error ratio	0.001
R	0.0474
R_w	0.0489

TABLE 2 Selected Bond Distances (Å) for **10**[a]

Atom 1	*Atom 2*	*Distance*	*Atom 1*	*Atom 2*	*Distance*
P1	O2	1.677 (3)	P9	O10	1.681 (3)
P1	O8	1.672 (3)	P9	O16	1.678 (3)
P1	O21	1.594 (3)	P9	O17	1.600 (3)
P1	O22	1.605 (3)	P9	O26	1.594 (3)
P1	N5	1.665 (3)	P9	N13	1.656 (3)
O2	C3	1.441 (4)	O10	C11	1.429 (5)
O8	C7	1.424 (5)	O16	C15	1.422 (5)
N5	C4	1.440 (5)	N13	C12	1.442 (5)
N5	C6	1.435 (5)	N13	C14	1.437 (6)
C3	C4	1.533 (6)	C11	C12	1.535 (6)
C6	C7	1.520 (6)	C14	C15	1.535 (6)

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

be identified. These observations are consistent with a decrease in the conformational mobility of **10** at lowered temperature. Careful measurements determined the coalescence temperature for this two-site, equal-population exchange to be −42°C. The rate constant at coalescence was calculated to be 1.3×10^3 s^{-1}. This corresponds to a $\Delta G^{\ddagger}$ at coalescence of 10.1 kcal/mol [11].

Since the CH_2O resonances of the 12-membered ring at −89°C do not show the expected 10–11 Hz [1b–d, f, g, n, o, 4] geminal couplings, the individual protons of each methylene group must be equivalent. Thus, two nonequivalent pairs of CH_2O are present, only one of which is coupled to phosphorus. The same pattern was noted for the methylene groups of the bicyclic ring system, $\Delta\delta$ = 0.20 ppm. The more upfield resonance showed the presence of coupling that was not fully resolved, while the downfield peak remained a singlet.

The resonances for the methyl substituents in

TABLE 3 Selected Bond Angles in Degrees for **10**[a]

Atom 1	*Atom 2*	*Atom 3*	*Angle*	*Atom 1*	*Atom 2*	*Atom 3*	*Angle*
O2	P1	O8	175.2 (2)	O10	P9	O16	175.6 (1)
O2	P1	O21	89.4 (1)	O10	P9	O17	89.7 (1)
O2	P1	O22	92.4 (1)	O10	P9	O26	92.6 (2)
O2	P1	N5	88.0 (2)	O10	P9	N13	87.8 (2)
O8	P1	O21	95.0 (2)	O16	P9	O17	93.3 (1)
O8	P1	O22	87.8 (1)	O16	P9	O26	89.4 (2)
O8	P1	N5	88.1 (2)	O16	P9	N13	87.8 (2)
O21	P1	O22	110.5 (2)	O17	P9	O26	110.4 (2)
O21	P1	N5	122.0 (2)	O17	P9	N13	123.6 (2)
O22	P1	N5	127.6 (2)	O26	P9	N13	126.0 (2)
P1	O2	C3	116.5 (2)	P9	O10	C11	116.0 (3)
P1	O8	C7	118.7 (3)	P9	O16	C15	117.4 (2)
P1	N5	C4	118.1 (3)	P9	N13	C12	119.6 (3)
P1	N5	C6	119.0 (3)	P9	N13	C14	120.1 (3)
C4	N5	C6	120.9 (3)	C12	N13	C14	120.1 (4)

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

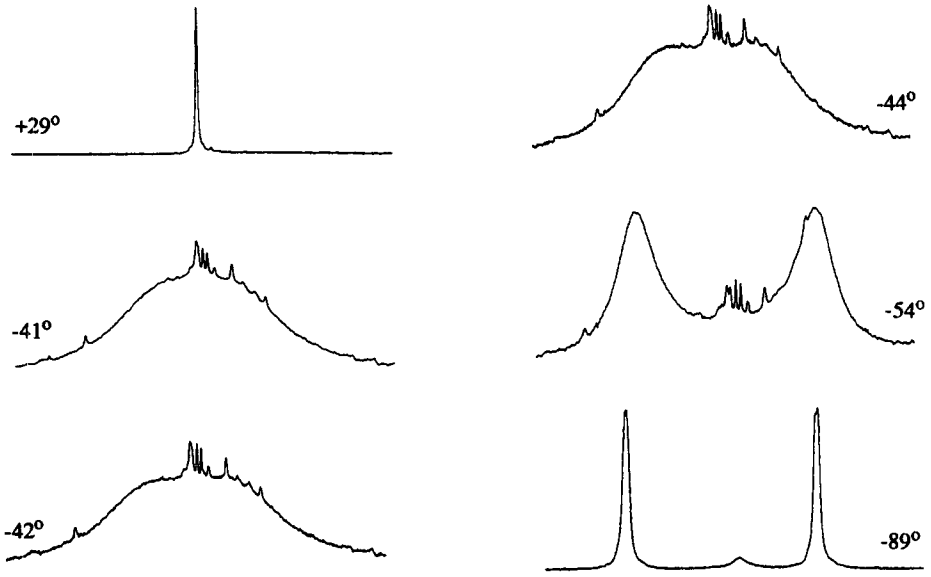


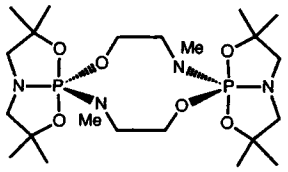
FIGURE 2 Variable temperature ^{1}H NMR spectra for the CH_2 groups of the 12-membered ring of **10** in toluene-d_8. Temperatures in degrees C.

the 12-membered ring remained sharp at −89°C. However, those for the methyl groups attached to the bicyclic ring system were resolved into two equal-intensity singlets separated by 0.16 ppm (80 Hz). The ^{13}C NMR spectrum of **10** at ambient temperatures in toluene-d_8 revealed a single doublet for the four methylene carbons in the twelve-membered ring (J_{CP} = 10.4 Hz) and a separate doublet for those of the bicyclic ring system (J_{CP} = 20.7 Hz). Similarly, no nonequivalence was seen within the two sets of four and eight methyl groups. Those attached to the bicyclic ring system were phosphorus coupled, $^3J_{CP}$ = 4.2 Hz. However, at −90°C, in parallel to the temperature effects noted in the ^{1}H NMR spectrum, the bicyclic ring methyls were resolved into two, equal-intensity doublets. The signals of the methylene carbons in the bicyclic ring broadened but did not decoalesce. A similar broadening of the methylene carbon resonances of the 12-membered ring was observed. The quaternary carbon resonances and those of the methyls on the twelve-membered ring remained sharp.

The temperature effects on the ^{1}H and ^{13}C spectra are totally consistent with one another. Evidently, a conformational exchange process persists at low temperatures, which averages the environments of the two protons of individual methylenes in both types of rings but leaves the CH_2 groups

nonequivalent in a pairwise fashion and also renders nonequivalent the methyl groups of the bicyclic rings. A more detailed interpretation of these results would be unwarranted. However, it is noteworthy that phosphorane **10** has not been effectively frozen out on the NMR time scale at −89°C temperature into the conformation present in the X-ray structure. That structure possesses three C_2 symmetry axes (D_2 point group) that render the methylene carbons within a given ring system equivalent and impart analogous equivalency to the methyl substituents.

A closely related phosphorane, **17**, which contains phosphorus atoms at opposite ends of a



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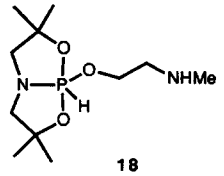

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10-membered ring was recently reported [9]. Its room-temperature ^1H NMR spectrum displays sizeable $^3J_{HP}$ values (J_{HCOP} = 14.1 Hz, J_{HCNP} = 9.3 Hz) for the CH_2 groups of the 10-membered ring. These couplings most likely are time-averaged values, as each resonance appears as a doublet of triplets. Phosphorane **17** evidently populates conformations with larger J_{HP} values than does the more flexible ring of **10**. Phosphorane **17** resulted when the attempted cyclization of **18** via the Atherton-Todd reaction failed to give the five-membered ring phosphorane.

SUMMARY

X-ray crystallography shows the twelve-membered ring phosphorane **10**, formally the dimer of **9**, to be a highly symmetrical molecule (D_2 symmetry) with close-to-trigonal-bipyramidal arrangements of the substituents about each of the phosphorus atoms. The ring is attached to both phosphorus atoms in diequatorial fashion. In solution, the ring system is highly mobile, as shown by ^{13}C and ^1H NMR spectroscopy at room temperature. At low temperatures, however, various of the ^1H and ^{13}C resonances become chemical shift nonequivalent. From coalescence temperature measurements for the 12-membered ring methylene protons, $\Delta G^{\ddagger}$ at coalescence was determined to be 10.1 kcal/mol. The formation of **10** by the present procedure is rather inefficient and accompanied by several unidentified side products.

EXPERIMENTAL

X-ray Crystallography

The structure of **10** was determined on a CAD4 diffractometer at −125°C. Cell constants were obtained from 25 reflections within $15<2\theta<30$. The space group was determined by subsequent least-squares refinement to be $P2_1/n$. Standard reflections showed decay (6%) during data collection. An anisotropic decay correction was applied. Lorentz and polarization corrections and an empirical absorption correction, based on a series of Ψ scans, were applied to the data. The structure was solved by direct methods using the SDP/VAX package. Nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located and included in the final structure factor calculations. Scattering factors [12] and Δ' and Δ'' factors [13] were taken from the literature. A more detailed description of the preceding procedures has been published [1f]. Crystal data, data collection, and refinement parameters are collected in Table 1 [14].

Spectral and Physical Data

The ^1H NMR spectra were recorded on Varian Unity-300, XL-300, and VXR-500 spectrometers. The ^{31}P spectra were determined at 121 and 32 MHz (Varian FT 80) with full proton decoupling. The ^{31}P NMR chemical shifts are expressed in parts per million (ppm) downfield from external 85% H_3PO_4. The ^{13}C NMR spectra were measured on a Varian VXR-500 instrument at 125 MHz. The ^{13}C chemical shifts are expressed in ppm downfield from internal TMS, referenced to the centerline of solvent. In the ^{13}C NMR data for **10**, the carbon atoms are numbered according to Figure 1. Mass spectra were obtained on a VG 7050-E instrument in the EI and CI modes. Samples of **10** were introduced through the solids probe inlet and mass spectra obtained at a probe temperature of 100°C. The GC data were obtained on a Varian 3300 instrument on an HP-5 capillary column (25 M × 0.32 mm) with flame ionization detection.

Preparation of 2,2-Dimethyloxirane

A round-bottomed flask, equipped with an addition funnel and a 20-cm Vigreux column with attached distillation head and condenser, was charged with 74 mL of distilled water and KOH (73.5 g, 87% noted purity). The resulting solution was heated at 75–90°C during the dropwise addition of 1-chloro-2-methyl-2-propanol [15] (62.3 g, 0.570 mol). Product 2,2-dimethyloxirane was formed immediately and collected in the receiver to give 39.0 g of colorless liquid (0.540 mol, 94% yield): bp 49–50°C (lit. 50–51°C [16]); ^1H NMR (300 MHz, $CDCl_3$) δ 1.34 (s, 6H, $C(CH_3)_2$), 2.61 (s, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, $\{^1H\}$) δ 22.97 (s, 2C, $C(CH_3)_2$), 54.36 (s, 1C, $C(CH_3)_2$), 54.78 (s, 1C, CH_2).

Preparation of 1,1,5,5-Tetramethyl-3-Azapentane-1,5-Diol

The procedure was a modified version of the literature method [7]. A mixture of 2,2-dimethylox-

irane (28.1 g, 0.390 mol) and NH_4OH (34.6 mL, approximately 30% NH_3, 0.290 mol of NH_3) in three, sealed glass pressure tubes was heated at about 100°C for 20 hours. The mixture was taken up with 30 mL of saturated aqueous NaCl and extracted with 4 × 80 mL of ethyl acetate. The combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was short-path distilled to give 18.8 g of a colorless liquid which became solid in the freezer (0.120 mol, 60% yield): bp 76–77°C at 0.05 mmHg (lit. 85–90°C at 0.01 mmHg [7]); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 12H, CH_3), 2.14 (broad s, 3H, NH and OH), 2.50 (s, 4H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 27.40 (s, 4C, *C*H_3), 61.05 (s, 2C, *C*H_2N), 69.91 (s, 2C, *C*OH).

Preparation of 3,3,7,7-Tetramethyl-2,8-Dioxa-5-Aza-1-Phospha(III)Bicyclo[3.3.0]Octane (**12**)

A toluene solution (800 mL) of hexamethylphosphorous triamide (11.4 g, 12.7 mL, 69.7 mmol) and 1,1,5,5-tetramethyl-3-azapentane-1,5-diol (11.2 g, 69.7 mmol) was refluxed vigorously for 4 hours. The solvent was removed by rotary evaporation, and the residue was short-path distilled to give 8.80 g of a colorless liquid which became solid when placed in a freezer (46.5 mmol, 67% yield): bp 55–56°C at 0.25 mmHg (lit. 29°C at 0.001 mmHg [7]); ^{1}H NMR (300 MHz, C_6D_6) δ 1.12 (s, 6H, CH_3), 1.18 (s, 6H, CH_3), 2.57 (dd, $^3J_{PH}$ = 8.0 Hz, $^2J_{HH}$ = −11.3 Hz, 2H, NCH_2), 2.93 (dd, $^3J_{PH}$ = 9.3 Hz, $^2J_{HH}$ = −11.3 Hz, 2H, NCH_2); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 28.35 (s, 4C, CH_3), 30.35 (d, $^2J_{PC}$ = 3.0 Hz, 2C, NCH_2), 63.79 (d, $^2J_{PC}$ = 3.7 Hz, 2C, $OC(CH_3)_2$); ^{31}P NMR (121 MHz, $CDCl_3$ {^{1}H}) δ 163.7 (s).

Preparation of 2,2-Dimethylpropane-1,3-bis(benzenesulfenate) (**13**)

To a solution of 2.2-dimethyl-1,3-propanediol (4.67 g, 44.9 mmol) and triethylamine (9.10 g, 12.5 mL, 89.7 mmol) in 250 mL of dry diethyl ether was added dropwise a solution of benzenesulfenyl chloride [6] (13.0 g, 89.7 mmol) in 150 mL of dry diethyl ether at 0°C with rapid stirring. The resulting mixture was slowly warmed to room temperature and continuously stirred overnight. The salt was removed by Schlenk techniques, and the solvent was removed under reduced pressure. The residue was recrystallized from *n*-pentane in a freezer (~−20°C) to give 12.9 g of a white solid (40.3 mmol, 90% yield): mp 54–55°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (s, 6H, $C(CH_3)_2$), 3.64 (s, 4H, CH_2O), 7.21, 7.30, 7.38 (3 m, 10H, C_6H_5); ^{13}C NMR (75 MHz, $CDCl_3$, {^{1}H}) δ 21.85 (s, 2C, $C(CH_3)_2$), 37.95 (s, 1C, $C(CH_3)_2$), 83.76 (s, 2C, CH_2O), 124.26 (s, 2C, *p*-Ph), 126.72 (s, 4C, *o*-Ph), 128.99 (s, 4C, *m*-Ph), 140.49 (s, 2C, *ipso*-Ph).

Preparation of **10**

The attempt to prepare monomer **9** from 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phospha(III)bicyclo-[3.3.0]octane (**12**) and 2,2-dimethylpropane 1,3-bis(benzenesulfenate) (**13**) by the method described for **11** [5] was not successful. A white solid, **10**, was obtained: mp 163–164°C; MS (EI) *m/z* 582; MS (Isobutene CI) *m/z* (M^+ + 1) 583. In a modified procedure, a solution of **13** (1.78 g, 5.55 mmol) in 2.5 mL of CH_2Cl_2 was added dropwise to a solution of **12** (1.05 g, 5.55 mmol) in 2 mL of CH_2Cl_2 at −78°C. A white precipitate was formed within 2 minutes. The mixture was stirred at −78°C for 30 minutes and then allowed to warm to room temperature, at which temperature the precipitate dissolved. On standing at room temperature for 2 days, the solution yielded well-formed, colorless crystals which appeared at the surface (0.36 g, 0.618 mmol, 22% isolated yield): mp 163–164°C; ^{31}P NMR (121 MHz, CD_2Cl_2, {^{1}H}) δ −45.0 (s); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 0.75 (s, 12H, 12-membered ring CH_3), 1.26 (s, 24H, five-membered ring CH_3), 2.74 (d, 8H, CH_2N, $^3J_{PH}$ = 12.5), 3.43 (d, 8H, CH_2O, $^3J_{PH}$ = 2.6 Hz); ^{13}C NMR (125 MHz, toluene-d_8, {^{1}H}) δ 14.23 (s, 4C, C35–C38), 29.00 (d, 8C, C27–C34, $^3J_{PC}$ = 4.2 Hz), 34.51 (s, 2C, C19, C24), 55.44 (d, 4C, C4, C6, C12, C14, J_{CP} = ($^2J_{PCN}$ + $^3J_{POCC}$) = 20.7 Hz), 69.09 (s, 4C, C3, C7, C11, C15), 71.89 (d, 4C, C18, C20, C23, C25, $^2J_{PC}$ = 10.4 Hz). Anal. calcd for $C_{26}H_{52}N_2O_8P_2$: C, 53.60; H, 9.00; N, 4.81. Found: C, 53.46; H, 8.94; N, 4.72.

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