with the c axis is 26.2° in **2** while in **1** it is 27.7°. The S···S contact distance within the stacks of **2** is somewhat larger than the sum of the van der Waals radii, in contrast to the significantly shorter analogous Se···Se contact distance of 3.863 Å found in **1**. Because of the modified tilting toward the c axis the analogous graphite packing (rhombohedral modification)[16] in the stacks of **1** is somewhat more distorted than in **2**.

The most significant change relative to **2** occurs within the ribbons (Figure 3), in which the molecules are connected by way of the Se–N parallelograms. Although Se possesses a larger van der Waals radius than S, the Se···N contact distance of 2.898 Å (sum of van der Waals radii: S···N = 3.35; Se···N = 3.5 Å)[15] is even shorter than the S···N contact distance in **2**, 3.104 Å. This decrease is also manifested in the value of the smaller lattice constant in the b direction of **1** (Table I). Within the Se–N parallelograms the Se···Se contact distance is 3.857 Å and the N···N contact distances are 2.910 Å, which are both less than the sums of the van der Waals radii (4.0 and 3.0 Å, respectively). The Se···Se contact distances along the ribbons are similar to those within the stacks. As a result of the difference in orientation with respect to the c axis, the coplanarity of the molecules in the ribbon-like arrays is more easily achieved in **1** than in **2**. In **1** the molecular planes within the ribbons exhibit a deviation of only 0.02 Å from each other as compared to the value of 0.16 Å obtained for **2**.

The strong secondary valence or extravalent bonds within the ribbons are also demonstrated by the solution properties of **1** and **2**. For example, **1** is substantially less soluble than the already difficultly soluble **2**.[23] The fact that relative to **2** shorter intermolecular contact distances appear in **1** simultaneously with a reduction of the π-bond orders of the chalcogen–nitrogen bonds suggests a correlation between the chalcogen–nitrogen bond lengths and the contact distances in compounds containing SN_2– and SeN_2– units. At the time of publication of the structure determination of **2** we had proposed the existence of a correlation between S–N bond orders and contact distances in compounds containing the SN_2– grouping.[2a] In Figure 4 the chalcogen–nitrogen contact distances (≤ sum of the van der Waals radii + 0.2 Å) from crystal structures of compounds with SN_2– or SeN_2– units are plotted against the chalcogen–nitrogen bond distances. In both cases a linear relationship between contact and bond distances is found. From the slope of the straight lines it can be deduced that in compounds with SN_2– fragments the dependence of contact distance on bond distance is stronger than it is in structures having SeN_2– units.

Acknowledgments. A. Gieren and V. Lamm thank the Deutsche Forschungsgemeinschaft for support of this work. We thank H. D. Roth for helpful discussions.

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Structures of Some Bicyclic and Tricyclic Phosphoranes in Solution

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Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903. *Received November 5, 1979*

Abstract: A series of phosphoranes has been prepared from 5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octane (**4**) and 6-aza-2,10-dioxa-1-phosphabicyclo[4.4.0]decane (**9**). Two bicyclic derivatives, one from **4**, one from **9** (**11** and **13**), which have two methoxy groups bonded to phosphorus have favored structures in which the rings span from equatorial to apical positions. Compounds derived from **4** in which a five-membered ring containing two oxygens (**15** and **18**) or two sulfurs (**19**) bonded to phosphorus undergo intramolecular ligand reorganization at room temperature via a C_{2v} structure in which the five-membered ring spans two equatorial positions. At reduced temperatures the ligand reorganization is slowed on the NMR time scale. Condensation of biacetyl with **9** affords a phosphorane, **14**, which undergoes rapid ligand reorganization at room temperature. This process does not involve a five-membered ring which spans two equatorial positions.

A number of caged polycyclic phosphoranes have been synthesized and their structures have been studied by X-ray crystallography and NMR measurements.[1] The few compounds of this class that have been investigated by X-ray crystallography exist as trigonal bipyramids (TBP) or very nearly so in the solid state. An understanding of the structures of these molecules in solution has not been realized. A few observations have provided some limitations on the structural possibilities. For example, compounds containing a five-membered ring bonded to phoshorus which is at the bridgehead of a bicyclic ring system containing six-membered rings (a typical example is **1**) have NMR spectra that are only consistent with rapid intramolecular permutational isomerizations, "pseudorotations". These isomerizations have been found to be rapid over the entire range of temperatures investigated. Various mechanisms for the isomerizations have been discussed and low-energy structures have been suggested.[2,3] A number of similar compounds containing one or more five-membered rings in the bicyclic moiety have also been prepared, for

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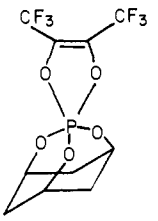
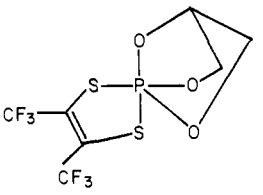


1



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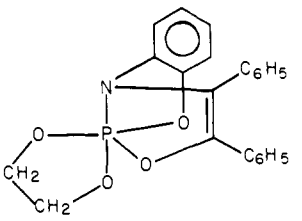
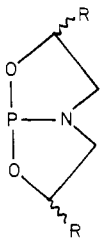


3

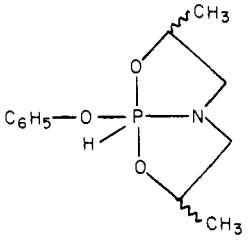
example, **2**.[4] These substances show significant barriers toward intramolecular ligand reorganization. It has not been possible to define the structure of the low-energy state nor has it been possible to define the nature of the energy barrier associated with the ligand reorganization process. It does seem reasonable to associate the energy barrier with an increase in strain in one or more of the five-membered rings during the reorganization process.

The compound **3** has been recently prepared and its structure in the crystalline state has been shown to be essentially TBP, with the ligands arranged as shown.[5] At room temperature the ^1H NMR spectrum reveals that the protons of the methylene groups are equivalent. No definitive statement can be made as to how this equivalence arises.[6]

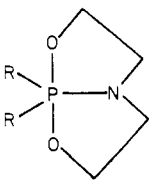
Recently the interesting phosphorus compounds **4** and the diastereoisomers **5** have been prepared.[7] Various phosphoranes



4, R = H
5, R = CH_3



6

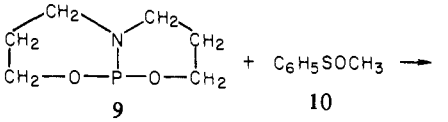


7, R = C_6H_5
8, R = C_2H_5O

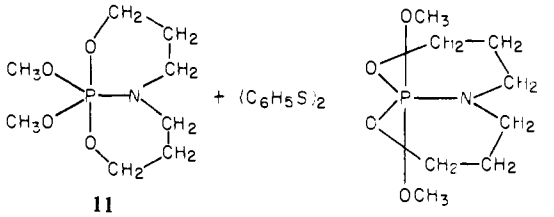
derived from **5**, mixed isomers, were prepared with **6** being an example. In earlier work in this laboratory, **7** and **8** were synthesized by exchange of the appropriate oxyphosphorane and diethanolamine.[8] Although it was reported that **4** was prone to oligomerization, it has been used in this study because of the simplicity of the NMR spectra of its derivatives as compared to similar materials prepared from the mixture of isomers, **5**. The purpose of this study has been to prepare phosphoranes from **4** and to compare their properties with those of other phosphoranes as well as with those derived from **9**, the six-membered-ring analogue of **4**. Compound **9**, a new substance, has been prepared in much the same manner as **4**. Unlike **4**, which must be stored at reduced temperature to inhibit polymerization, compound **9** is indefinitely stable at room temperature.

Results and Discussion

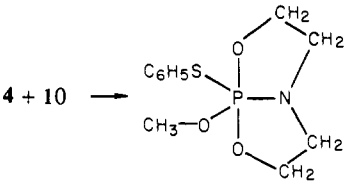
Reaction of **4** and **9** with 2 mol of methyl benzenesulfenate (**10**) gave in each case phosphoranes **13** and **11**. When **4** and **10** were



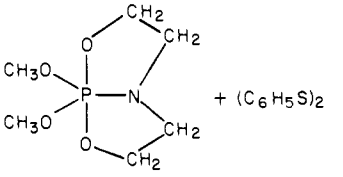
9 **10**



11 **11a**

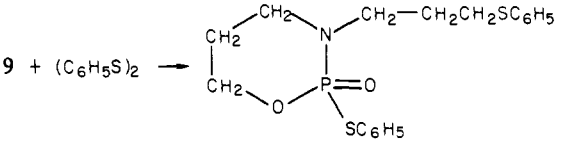


12



13

allowed to react in equimolar amounts, the mixed oxythiophosphorane **12** was the major product. This material absorbs at δ −28 in its ^{31}P NMR spectrum; addition of another mol of **10** leads to the disappearance of the absorption and formation of a new absorption at δ −42. The reaction of **4** and **10** (2 mol) is remarkably clean in that **13** is essentially the only phosphorus-containing product. The same is not true for the reaction of **9** and **10** in that varying amounts of thiophosphate are always formed. This compound was prepared independently by allowing **9** to react with diphenyl disulfide. The formation of the thio-



phosphate during the reaction of **9** and **10** can be accounted for by the reaction of **9** with diphenyl disulfide, which is a product of phosphorane formation.

The assigned structures of **11** and **13** rest in the main on their method of preparation[9] and their NMR spectra. Both show upfield ^{31}P NMR chemical shifts, relative to 85% phosphoric acid; that of **13** at δ −42 is characteristic of five-membered ring containing phosphoranes while that of **11** at δ −66 is characteristic of acyclic or six-membered ring containing phosphoranes. The proton decoupled ^{13}C NMR spectrum of **11** shows that there are four different kinds of carbons with appropriate couplings to phosphorus. The presence of coupling immediately rules out fast ionizations as a means of rendering the pairs of carbons equivalent. Similarly that of **13** shows three different kinds of carbons with appropriate couplings. The ^1H NMR spectrum of **11** has a doublet

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(5) A. Schmidpeter, D. Shomburg, W. S. Sheldrick, and J. H. Weinmaier, *Angew. Chem., Int. Ed. Engl.*, **15**, 781 (1976).
(6) The authors, ref 5, suggest that a structure with the five-membered dioxygen-containing rings spanning two equatorial positions leads to the equivalence of the hydrogens. It has been noted on many occasions by Ramirez and Ugi, ref 2 and references cited therein, that intramolecular ligand reorganization via a "turnstile rotation" mechanism can account for the observed equivalence without requiring that the ring adopt a diequatorial disposition.
(7) D. Houalla, F. H. Osman, M. Sanchez, and R. Wolf, *Tetrahedron Lett.*, 3041 (1977).
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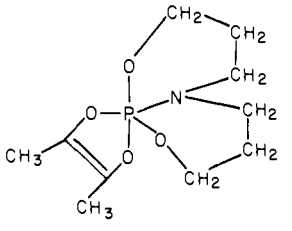
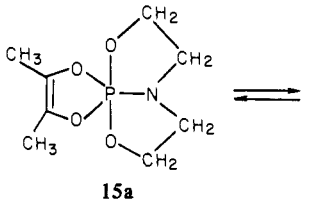
for the hydrogens of the methyl groups. The hydrogens of the methylene groups adjacent to nitrogen are found as two overlapping triplets as are those of the methylene hydrogens on the carbon bonded to oxygen. The hydrogens of the remaining methylene groups are found as at least a six-line pattern. The ^{1}H NMR data are satisfied if **11** adopts a TBP structure in which the two methoxy groups are in equatorial positions and the rings span equatorial apical positions with the nitrogen in an equatorial position. In this structure the nitrogen would have to be sp^2 hybridized or be undergoing rapid inversion to satisfy the ^{1}H NMR data. Alternatively, **11** could adopt a TBP, **11a**, in which both rings span e–e positions and the methoxy groups are placed in apical positions. In order for this structure to satisfy the ^{1}H NMR data the nitrogen would also have to be sp^2 hybridized or undergoing rapid inversion about nitrogen. Although this latter structure cannot be totally ruled out by the data, the fact that the coupling between the phosphorus and the hydrogens of the methyl groups is 13 Hz is supportive of the structure with two equatorial methoxy groups. Gorenstein and Westheimer[10] have reported that an apical methoxy group has J_{POCH_3} = 10.5 Hz and equatorial 13.5 Hz. The structure of **13** must be that illustrated, as will be discussed, and it has J_{POCH_3} = 13.2 Hz, which is essentially the same as that of **11**. Furthermore, Tripett[11] and his co-workers have shown that there is a highly preferred orientation of the lone pair on nitrogen when the nitrogen occupies an equatorial position in a TBP. The lone pair lies in the plane of the equatorial belt, which is of course the situation with **11**. In **11a** just the opposite is found. The spectral data do not establish that **11** is rigid and quite clearly it can be undergoing intramolecular ligand reorganization.

Compound **13** also has an extremely simple ^{1}H NMR spectrum with hydrogens of the methoxy groups absorbing as a doublet, which is due to POCH coupling, and those of the methylene group adjacent to oxygen as a doublet of triplets, which is due to POCH and HCCH coupling as are those of the methylene groups adjacent to nitrogen. In this case PNCH and HCCH coupling are responsible for the pattern. Only one structure leads to equivalent pairs of hydrogens of the methylene groups and that is the structure entirely analogous to that assigned to **11**. Once again it is not possible to determine whether **13** is rigid or pseudorotating. The structure analogous to **11a** has two five-membered rings spanning diequatorial positions and thus it must be higher in energy than **11**, there being no compensating factors which would lower its energy.

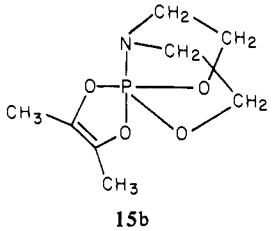
Condensation of **9** and **4** with biacetyl yielded phosphoranes **14** and **15**. The phosphorane **14** absorbs at δ –42 in its ^{31}P NMR



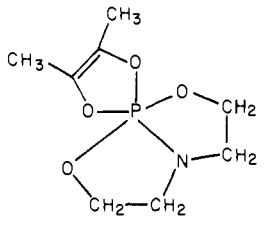
14



15a



15b



15c

spectrum, which is strong evidence for a five-membered ring containing phosphorane. The ^{1}H NMR spectrum of **14** consists of a singlet at δ 1.82 for absorptions of equivalent methyl group hydrogens. There is also a region of absorption which extends from δ 1.43 to 4.60, and which is due to hydrogens of the methylene groups. The ^{1}H NMR spectrum is very different from that of **11**. One does not find pairs of equivalent methylene group hydrogens, which indicates that **14** does not adopt a structure in which the five-membered ring spans two equatorial positions. Such a structure would be expected to be of high energy relative to the structure **14** shown.[12] The ^{13}C NMR spectrum of **14** at room temperature with total proton decoupling shows equivalent methyl group carbons with coupling to phosphorus as well as equivalent coupled olefinic carbons. The pairs of methylene group carbons are found as three doublets, which is due to coupling to phosphorus. The observation of coupling demonstrates that ionization processes which would lead to loss of coupling are not occurring rapidly on the NMR time scale. The ^{1}H and ^{13}C NMR spectra are in agreement with a phosphorane, **14**, which is undergoing intramolecular ligand reorganization with exchange of the a–e ligands of the five-membered ring and exchange of the two oxygen a–e ligands of the bicyclic moiety. The nitrogen remains in an equatorial position which is in accord with its usually lower apicophilicity than that of oxygen.[13] The variable temperature ^{13}C NMR spectra show that below –63 °C the olefinic carbons are nonequivalent. The $\Delta G^{\ddagger}$ for the process that renders them nonequivalent is 9.7 kcal/mol. It must be noted that the interconversions discussed above are not the only way in which the dynamic NMR data can be interpreted. The low-temperature ^{13}C NMR spectrum also shows that the original pairs of equivalent methylene group carbons are no longer equivalent. This would of course be the case if **14** is now the rigid TBP indicated. There is an alternate SP structure which also accommodates the data. It is only very slightly displaced from the TBP depicted.

The phosphorane **15a,b**, ^{31}P NMR δ –3, from biacetyl and **4** has a very simple ^{1}H NMR spectrum at room temperature. There is found a resonance at δ 1.7 which is due to hydrogens of equivalent methyl groups, a doublet of triplets at δ 2.95 which is assigned to four equivalent hydrogens on carbons adjacent to nitrogen, and a doublet of triplets at δ 3.85 which arises from four equivalent hydrogens on carbon adjacent to oxygen. This pattern arises because of POCH, PNCH, and HCCH couplings. The ^{13}C NMR spectrum is equally simple with only four doublets each one of which can be assigned to two equivalent pairs of carbons with the appropriate coupling to phosphorus of all carbons. Ionization processes cannot account for these simple spectra because they would lead to loss of coupling. The only way the ^{1}H NMR spectrum can arise is if **15a** is present or is passed through during intramolecular reorganization. In this particular instance then the ^{1}H NMR spectrum uniquely defines the intermediate or transition state through which the reorganization occurs. That **15a** is not the lowest energy structure is demonstrated by the low-temperature ^{13}C NMR spectrum, which has two doublets for carbons of nonequivalent methyl groups, two doublets for unsaturated carbons, and broad resonances for the two different carbons of the methylene groups. Such a spectrum could arise from **15b**. There is one SP structure, **15c**, which also satisfies the low-temperature ^{13}C NMR data. It would seem to be an extremely strained structure, whereas **15b** should be essentially strain free. It is thus concluded that the intramolecular ligand reorganization involves **15b** converting into **15b** through an intermediate or transition state **15a**. The free energy of activation for this process is 11 kcal/mol. This lower energy as compared to other systems is probably due to the desire for nitrogen to enter an equatorial position and for an extra oxygen to enter an apical position.

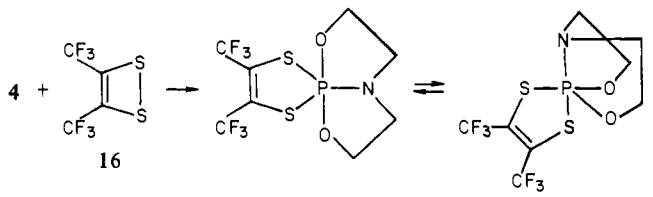
Condensation of **4** with the dithiete **16** and the bissulfenate **17** led to phosphoranes **18** and **19**. The ^{1}H NMR spectra of both

(10) D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

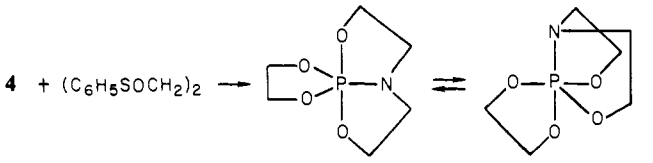
(11) S. A. Bone, S. Tripett, and P. J. Whittle, *J. Chem. Soc., Perkin Trans. 1*, 80 (1977).

(12) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Theime Verlag, Stuttgart, 1973, pp 49–95.

(13) J. Emsley and C. D. Hall, "The Chemistry of Phosphorus", Wiley, New York, 1976, p 67.



16 18



19

18 and **19** at room temperature show that both must be passing through the same type of C_{2v} structure as **15a**. The variable temperature ^{19}F NMR spectra of **18** indicate that below −32 °C, the coalescence temperature, there are two nonequivalent trifluoromethyl groups and the activation energy required to render them equivalent is 11 kcal/mol. The variable temperature ^{13}C NMR spectra of **19** show that below −45 °C, the coalescence temperature, the two carbons of the dioxy-containing five-membered ring are nonequivalent. The activation energy required to render them equivalent is 11 kcal/mol.

Clearly these data are in full agreement with structures entirely analogous to **15a** and **15b**. The uniqueness of the ^1H NMR spectra establish that in all three cases a C_{2v} structure lies on the path for intramolecular ligand reorganization. This appears to be the first unequivocal demonstration of definite structures of caged bicyclic phosphoranes in solution.

Experimental Section

^1H NMR spectra were run on Varian Model T-60 and FT-80 spectrometers. All chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{13}C, ^{31}P, and ^{19}F NMR spectra were run on a Varian Model FT-80 spectrometer equipped with a 10-mm, variable-temperature, broad-band probe. All ^{31}P chemical shifts are reported in parts per million relative to 85% phosphoric acid (external) δ (negative upfield); ^{19}F chemical shifts are in parts per million relative to trichlorofluoromethane (internal). ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane (internal). In all cases the ^{13}C spectra were obtained using full proton decoupling, a 30° flip angle, and a 2-s repetition rate with no pulse delay.

Preparation of 3,3′-Iminodipropanoic Acid Dimethyl Ester. In a 1-L flask equipped with a dry ice condenser, an addition funnel, and a stirrer, there was prepared a solution of ca. 34 g (2 mol) of ammonia in 400 mL of dry methanol. To this was added, over a period of 30 min, 344.5 g (4 mol) of freshly distilled methyl acrylate. After stirring for an additional 30 min at room temperature the mixture was then heated under reflux for 15 h. After the solvent was removed, at reduced pressure, the residual oil was distilled to yield 107 g (28%) of a colorless liquid: bp 95–100 °C (1.5 mm); IR (thin film) 3300 (N—H), 1730 cm^{-1} (C=O); ^{13}C NMR (D_2O) δ 30.1 ($-CH_2CO_2CH_3$), 42.2 ($-CH_2N$), 52.7 (CH_3), 172.6 (−C=O); ^1H NMR ($CDCl_3$) δ 1.60 (s, 1 H), 2.54 (m, 4 H), 2.94 (m, 4 H), 3.75 (s, 6 H); mass spectrum m/e 189 (calcd, 189).

Preparation of Dipropanolamine. To a solution of 35 g (0.92 mol) of lithium aluminum hydride in 500 mL of dry ether, cooled in an ice bath, was added over a period of 2 h 88 g (0.46 mol) of 3,3′-iminodipropanoic acid dimethyl ester. After having been stirred at room temperature for 1 h the mixture was heated under reflux for 24 h. The reaction mixture was hydrolyzed by the addition of 35 mL of water, 35 mL of 15% potassium hydroxide solution, and finally 105 mL of water. The resulting solid was subjected to continuous ether extraction for 48 h. After the ether was removed at reduced pressure, the residual oil was distilled. Redistillation of the crude material afforded 14.3 g (37%) of dipropanolamine: bp 122–124 °C (0.07 mm); ^{13}C NMR (acetone-d_6) δ 31.4 ($-CH_2OH$), 46.0 (CH_2N), 60.1 ($-CH_2CH_2OH$); ^1H NMR ($CDCl_3$) δ 1.75 (quintet, 4 H), 2.85 (t, 4 H), 3.60 (s, 2 H), 3.80 (t, 4 H).

Preparation of 2,10-Dioxa-6-aza-1-phosphabicyclo[4.4.0]decane (9). To a solution of 14.1 g (106 mmol) of dipropanolamine in 40 mL of dry toluene at 90 °C, under nitrogen, was added 17.3 g (106 mmol) of hexamethylphosphorous triamide. This mixture was refluxed for 48 h. After the solvent was removed at reduced pressure, the residual oil was distilled to yield 2.8 g (16%) of a colorless liquid: bp 56–60 °C (0.08 mm); ^{31}P NMR ($CDCl_3$) δ 129.8; ^{13}C NMR ($CDCl_3$) δ 24.1 (d, J_{CCOP} = 6.5 Hz), 46.3 (d, J_{CNP} = 5.5 Hz), 62.3 (d, J_{COP} = 1.8 Hz); ^1H NMR ($CDCl_3$) δ 0.89–1.86 (m, 4 H), 2.40–3.38 (m, 4 H), 3.52–4.35 (m, 4 H). Anal. Calcd for $C_6H_{12}NO_2$: C, 44.72; H, 7.45. Found: C, 44.94; H, 7.82.

Preparation of 2,8-Dioxa-5-aza-1-phosphabicyclo[3.3.0]octane (4). To a stirred solution of 7.52 g (71.5 mmol) of diethanolamine in 120 mL of dry toluene, heated to 85 °C, was added, under nitrogen, a solution of 11.68 g (71.5 mmol) of hexamethylphosphorous triamide in 15 mL of dry toluene. This solution was allowed to reflux, under nitrogen, for 4 days. After removal of the solvent, at reduced pressure, the residual oil was distilled (bp 39–40 °C, 0.01 mm) to yield 5.12 g (54%) of a colorless liquid which solidified upon standing: mp 35–37 °C; ^{31}P NMR ($CDCl_3$) δ 139 (lit.[7] 139.6); ^{13}C NMR (benzene-d_6) δ 53.7 (d, J_{CNP} = 6 Hz), 67.5 (d, J_{COP} = 10 Hz); ^1H NMR (benzene-d_6) δ 2.43–3.84 (m).

Reaction of 9 with Methyl Benzenesulfenate (10). To a solution of 0.29 g (1.8 mmol) of **9** in 1.5 mL of $CDCl_3$ at −20 °C under an atmosphere of argon was added 0.51 g (3.6 mmol) of methyl benzensulfenate (**10**). The reaction mixture was allowed to warm to room temperature slowly. After removal of the solvent, at reduced pressure, the residue was molecularly distilled (bp 35 °C, 0.03 mm): ^{31}P NMR ($CDCl_3$) δ-65.9; ^{13}C NMR ($CDCl_3$) δ 27.15 (d, J_{CCOP} = 2.5 Hz), 51.5 (d, J_{CNP} = 2.5 Hz), 55.7 (d, CH_3, J_{COP} = 11.5 Hz), 60.7 (d, J_{COP} = 9.5 Hz); ^1H NMR ($CDCl_3$) δ 1.80 (m, 4 H), 3.16 (d of t, J_{HCNP} = 13, J_{HCCH} = 6.5 Hz, 4 H), 3.68 (d, J_{HCOP} = 13 Hz, 6 H), 4.08 (d of t, J_{HCOP} = 16, J_{HCCH} = 7 Hz, 4 H).

Reaction of 4 with Methyl Benzenesulfenate (10). In a preliminary experiment 0.47 g (3.5 mmol) of **4** was mixed with 0.98 g (7.0 mmol) of methyl benzenesulfenate (**10**) in toluene-d_8 at −20 °C. The progress of the reaction was monitored by observing the ^{31}P NMR spectrum of this mixture: (15 min, −20 °C) δ +138 (starting material, <1%) −28 (>90%), −42 (<5%); (20 min, 25 °C) δ −28 (67%), −42 (33%); (2 days, 25 °C) δ −42 (100%).

To 2.96 g (22.3 mmol) of **4** dissolved in 4 mL of methylene chloride, cooled to −20 °C, was added, under nitrogen, 6.25 g (44.6 mmol) of methyl benzenesulfenate. After stirring for 2 h the reaction mixture was allowed to return to room temperature and it was stored in a desiccator for 9 days. After the solvent was removed at reduced pressure the residual oil was molecularly distilled (bp 37 °C, 0.01 mm). This material contained 30% diphenyl disulfide (^1H NMR); however, a second such distillation afforded 2.30 g (53%) of a material containing <2% diphenyl disulfide. The spectral data were as follows: ^{31}P NMR (CD_2Cl_2) δ −41.1; ^{13}C NMR ($CDCl_3$, 25 and −50 °C) δ 42.8 (d, J_{CNP} = 22 Hz), 54.8 (d, CH_3OP, J_{COP} = 9.2 Hz), 58.5 (s, $-CH_2OP$); ^1H NMR (CD_2Cl_2) δ 3.00 (d of t, J_{HCNP} = 11.6, J_{HCCH} = 6.5 Hz, 4 H), 3.51 (d, J_{HCOP} = 13.2 Hz, 6 H), 3.79 (d of t, J_{HCOP} = 11.7, J_{HCCH} = 6.5 Hz, 4 H).

Reaction of 4 with 2,3-Butanedione. To a solution of 2.25 g (16.9 mmol) of **4** in 3 mL of methylene chloride, cooled to −30 °C, was added, under nitrogen, 1.56 g (18.1 mmol) of 2,3-butanedione dissolved in 2 mL of methylene chloride. The reaction mixture was allowed to warm slowly and to stand overnight at room temperature. After the solvent and excess butanedione were removed at reduced pressure, colorless crystals remained. These were sublimed (68–70 °C, 0.01 mm) to yield 0.51 g (13.8%) of the product (**15**): ^{31}P NMR (CH_2Cl_2, external lock) δ −3; ^{13}C NMR ($CDCl_3$, 25 °C) δ 10.9 (d, J_{CCOP} = 12.2 Hz), 45.4 (d, J_{CNP} = 11.2 Hz), 61.6 (d, J_{COP} = 5.6 Hz), 129.4 (d, J_{COP} = 2.0 Hz); (CH_2Cl_2, acetone-d_6, −30 °C) δ 11.1 (d, J_{CCOP} = 12.5 Hz), 45.1 (d, J_{CNP} = 11.2 Hz), 62.0 (d, J_{COP} = 5.6 Hz), 125–135 (very broad mound); (−65 °C) δ 11.0 (d, J_{CCOP} = 12.4 Hz), 11.2 (d, J_{CCOP} = 12.7 Hz), 45.1 (broad), 62.0 (broad), 125.9 (d, J_{COP} = 1.4 Hz), 132.6 (d, J_{COP} = 4.3 Hz); ^1H NMR (benzene-d_6) δ 1.7 (s, 6 H), 2.95 (d of t, J_{HCNP} = 15, J_{HCCH} = 6 Hz, 4 H), 3.85 (d of t, J_{HCOP} = 14, J_{HCCH} = 6 Hz, 4 H). The product was thermally unstable and could not be stored even at 0 °C.

Reaction of 9 with 2,3-Butanedione. To a solution of 0.31 g (1.9 mmol) of **9** in 1.5 mL of benzene-d_6, under argon and cooled to 15 °C, was added 2,3-butanedione. The latter was added slowly and dropwise until a slight yellow color persisted. Spectral data were as follows: ^{31}P NMR (benzene-d_6) δ −41.6; ^{13}C NMR (CD_2Cl_2, 25 °C) δ 10.8 (d, CH_3COP, J_{CCOP} = 12.4 Hz), 25.9 (d, CH_2CH_2OP, J_{CCOP} = 2.7 Hz), 48.5 (d, CH_2NP, J_{CNP} = 5.1 Hz), 65.9 (d, CH_2OP, J_{COP} = 10.1 Hz), 128.8 (s); (−63 °C) δ 10.8 (d, CH_3COP, J_{CCOP} = 12.4 Hz), 25.9 (d, CH_2CH_2OP, J_{CCOP} = 2.7 Hz), 48.5 (d, CH_2NP, J_{CNP} = 5.1 Hz), 65.9 (d, CH_2OP, J_{COP} = 10.1 Hz), resonance due to olefinic carbons not visible; (−85 °C) δ 9.93–10.56 (CH_3COP), 23.35–24.49 ($-CH_2CH_2CH_2$), 46.97–47.06 ($PNCH_2$), 64.88–65.37 ($POCH_2$), 130.9 (d, COP, J_{COP} = 3.8 Hz), 124.1 (d, COP, J_{COP} = 2.5 Hz); ^1H NMR ($CDCl_3$) δ 1.43–4.60 (m, 12 H), 1.82 (s, 6 H).

Reaction of 9 with Diphenyl Disulfide. To a solution of 0.32 g (2.0 mmol) of **9** in $CDCl_3$, cooled to −30 °C and under argon, was added 0.44 g (2.0 mmol) of diphenyl disulfide. The reaction mixture was allowed

to warm to room temperature slowly. The spectral data were as follows: IR (thin film) 1250 cm^{-1} (P=O); ^{31}P NMR ($CDCl_3$) δ +22.3; ^{13}C NMR ($CDCl_3$) δ 26.4 (d, ring CH_2CH_2OP, J_{CCOP} = 4.9 Hz), 27.9 (d, side chain CH_2CH_2NP, J_{CCNP} = 1.9 Hz), 30.8 (s, $CH_2SC_6H_5$), 47.2 (s, side chain CH_2NP), 47.6 (d, ring CH_2NP, J_{CNP} = 1.9 Hz), 69.7 (s, CH_2OP), plus resonances in the range δ 125–135 (aromatic carbons); ^1H NMR ($CDCl_3$) δ 1.36–2.51 (m, 4 H), 2.70–3.79 (m, 6 H), 3.96–4.60 (m, 2 H), 7.26–8.06 (m, 10 H). Attempts to purify this material by molecular distillation failed.

Reaction of 4 with Dithiete (16). To a solution of 0.99 g (7.5 mmol) of **4** in 2 mL of methylene chloride, cooled to −78 °C and under a nitrogen atmosphere, was added 1.71 g (8.0 mmol) of freshly distilled dithiete (**16**) dissolved in 2 mL of methylene chloride. After stirring at this temperature for 1 h the reaction mixture was allowed to warm to room temperature. After the volatiles were removed at reduced pressure, there remained a red-brown oil which could not be purified and had to be stored in solution to prevent its decomposition: ^{31}P NMR (CD_2Cl_2) δ +20.9; ^{13}C NMR ($CDCl_3$) δ 48.7 (d, J_{CNP} = 7.5 Hz), 65.8 (s), 121.3 (d of q, J_{CF} = 275.4, J_{CCSP} = 16.1 Hz), 125 (m); ^1H NMR (CH_2Cl_2) δ 3.33 (d of t, J_{HCNP} = 17.0, J_{HCCH} = 6.4 Hz), 4.22 (d of t, J_{HCOP} = 16.0, J_{HCCH} = 6.4 Hz); ^{19}F NMR ($CDCl_3$, 25 °C) δ −60.5 (d, J_{FCCSP} = 2.1 Hz); (−32 °C) δ −58 to −61 (very broad mound); (−65 °C) δ −58.8 (d, J_{FCCSP} = 10.6 Hz), −61.0 (d, J_{FCCSP} = 10.0 Hz).

Reaction of 4 with Ethane 1,2-Bis(benzenesulfenate). To a solution of 0.39 g (2.97 mmol) of **4** in 1 mL of methylene chloride, cooled to −78 °C and under argon, was added 0.83 g (3 mmol) of ethane 1,2-bis(benzenesulfenate) dissolved in 1 mL of methylene chloride. After stirring for 1 h at this temperature the reaction mixture was allowed to warm to room temperature, slowly. After removal of the solvent, at reduced pressure, the residual oil was triturated with pentane. Further purification was not possible because of the thermal instability of the product: ^{31}P NMR (CD_2Cl_2) δ −6.0; ^{13}C NMR (CD_2Cl_2, 25 °C) δ 45.1 (d, J_{CNP} = 11.3 Hz), 61.4 (d, NCH_2CH_2OP, J_{COP} = 5.1 Hz), 61.4 (d, OCH_2CH_2OP, J_{COP} = 3.5 Hz); (−45 °C) δ 44.8 (d, J_{CNP} = 11.0 Hz), 61.4 (d, NCH_2CH_2OP, J_{COP} = 4 Hz); (−70 °C) δ 44.7 (d, J_{CNP} = 11.0 Hz), 59.5 (d, OCH_2CH_2OP, J_{COP} = 3 Hz), 61.4 (d, NCH_2CH_2OP, J_{COP} = 4 Hz), 63.3 (s, OCH_2CH_2OP); ^1H NMR (CD_2Cl_2) δ 2.93 (d of t, J_{HCNP} = 15, J_{HCCH} = 6.1 Hz, 4 H), 3.80 (d, OCH_2CH_2OP, J_{HCOP} = 13.8 Hz, 4 H), 3.84 (d of t, NCH_2CH_2OP, J_{HCOP} = 13.5, J_{HCCH} = 6.1 Hz, 4 H).

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Stereoelectronic Effects in the Reactions of Epimeric 2-Aryloxy-2-oxy-1,3,2-dioxaphosphorinanes and Oxazaphosphorinanes

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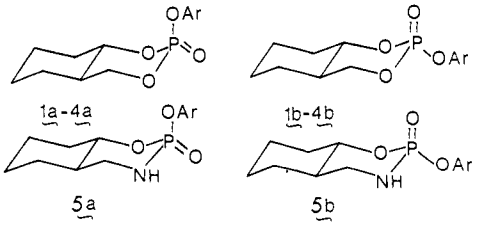
Abstract: Configurational and conformational analysis of isomeric 2-aryloxy-2-oxo-*trans*-5,6-tetramethylene-1,3,2-dioxaphosphorinane (**1–4**) (ArO = *p*-methoxyphenoxy, *p*-nitrophenoxy, phenoxy, and 2,4-dinitrophenoxy) and isomeric 2-*p*-nitrophenoxy-2-oxo-*trans*-5,6-tetramethylene-1,3,2-oxazaphosphorinane (**5**) is presented. Based upon ^1H NMR coupling data and ^{31}P and ^{13}C NMR and IR spectra the axial aryloxy isomers of **1–5** of these *trans*-decalin-type six-membered-ring phosphorinanes are in chair conformations. However, NMR and IR data support the assignment of a twist-boat conformation for "equatorial" isomers of the 2,4-dinitrophenoxy ester **4b** and the *p*-nitrophenoxy ester of **5b**. Mixed chair and twist-boat conformations are found for the other aryloxy esters **1b–3b**. The axial isomers **1a–5a** are 1.5–2 kcal/mol lower in energy and hydrolyze in base 4–17 times slower than their epimers. Only the twist-boat isomers of 2,4-dinitrophenoxy ester **4b** and the *p*-nitrophenoxy ester **5b** react with 100% inversion of configuration with methoxide. All other compounds react with 4–83% inversion of configuration. Speculations on the stereoelectronic effects in these reactions are considered.

Introduction

Deslongchamps[2] and more recently Kirby[3] have established that the orientation of lone pairs controls the decomposition of tetrahedral carbon species. In this stereoelectronic theory cleavage of specific bonds is facilitated by antiperiplanar (app) lone pairs on directly bonded oxygen or nitrogen atoms. Lehn and Wipff[4] and Gorenstein et al.[5–9] have proposed that similar stereoelectronic effects control the hydrolysis of phosphate esters. These predictions were based upon molecular-orbital calculations and obviously require experimental confirmation. In this paper we report on the reactions of the epimeric pairs of 2-aryloxy-2-oxy-1,3,2-dioxaphosphorinanes **1a,b–4a,b** and 1,3,2-oxazaphosphorinanes **5a,b**, designed to test this theory.



The present combination of conformational analysis and kinetic, stereochemical, and equilibration studies of the epimeric pairs of dioxaphosphorinanes and oxazaphosphorinanes has provided the most detailed definition to date of the associative mechanism of reaction at phosphorus. Unfortunately for the test of the stereoelectronic theory it is now recognized that low-energy twist-boat

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