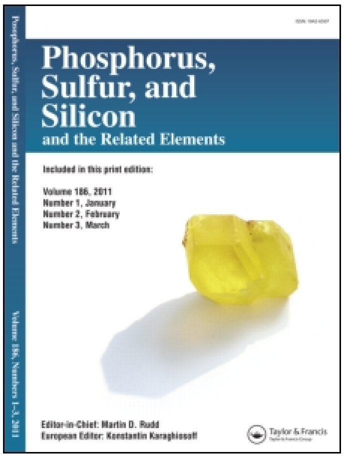

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REACTIONS OF 4-ALKYL-1-TRITYL-1-PHOSPHA-2,6,7-TRIOXABICYCLO[2.2.2]OCTANE CATIONS WITH BASES

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REACTIONS OF 4-ALKYL-1-TRITYL-1-PHOSPHA-2,6,7-TRIOXABICYCLO[2.2.2]OCTANE CATIONS WITH BASES

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The syntheses of 4-alkyl-1-trityl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane tetrafluoroborates (alkyl group = Me, **4**; Et, **5**; *t*-Bu, **6**) are described. Compounds **4**, **5** and **6** in the presence of base (pyridine, DBU) or base (pyridine, DBU) plus H_2O undergo Arbuzov ring opening reactions to give pyridinium salts or a mixture of hydrolyzed products and pyridinium salts, respectively. The configurations of the products are addressed by means of NMR spectroscopic and X-ray crystallographic studies. The acyclic trityl salts $[(RO)_3CPh_3]^+BF_4^-$(R = Et, **7**; neopentyl, **8**) were also prepared and their reactions with base or base plus H_2O were carried out for comparison with the reactions of the polycyclic trityl salts.

Keywords: bicyclic; phosphite; cations; bases; hydrolysis; structure

INTRODUCTION

As an extension of our studies of polycyclic phosphorus systems such as phosphites **1–3**[1–12] we synthesized the corresponding trityl salts **4–6** in order to examine their vulnerability to nucleophilic attack. Thus, we investigated reactions of these salts with pyridine, DBU, H_2O, pyridine/H_2O and DBU/H_2O to determine how the reactivity of these salts varied with size of R and with the nature of the nucleophile. The acyclic unconstrained analogues of these bicyclic salts, namely, $[(RO)_3PCPh_3]+BF_4^-$ (R = Et, **7**;

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neopentyl, **8**) were synthesized for comparison in these reactions. The structures of the products were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies, and were confirmed in two cases by single crystal X-ray diffraction studies.

(1)

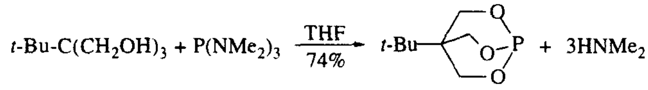
1: R = Me
2: R = Et
3: R = *t*-Bu

4: R = Me
5: R = Et
6: R = *t*-Bu

RESULTS AND DISCUSSION

Syntheses

Preparations for compounds **1**[3] and **3**[3] were reported earlier and **2** can be purchased (see Experimental). We report here a modification of the preparation for **3**, however, that improves the yield from 53%[2] to 74%. The modification is the substitution of $P(NMe_2)_3$ in reaction 2 in place of $P(OMe)_3$.[3]

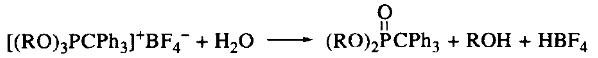


3

(2)

It should be noted that **1**, **2**, and **3** are highly toxic to mammals.[4] For example, the mouse ip LD_{50} for **2** is 1.1 mg/kg and is 0.040 mg/kg for **3**. Thus, safety precautions are required in handling these compounds.

The polycyclic trityl salts **4**, **5** and **6**, whose syntheses are shown in reaction 1, are stable to water. Thus D_2O solutions of these compounds exhibit only one ^{31}P signal in the 50–55 ppm region, corresponding to the resonance for the polycyclic trityl salt. Hence, they are generally prepared in relatively high yield and can be handled easily. In contrast, the acyclic trityl salts **7** and **8** are moisture-sensitive. When exposed to water, hydrolyzed products are formed according to equation 3. The rate of hydrolysis for **7** is much faster than that of **8**, presumably due to the lower steric hindrance of the ethyl group in **7**. Hence, **7** and **8** can be prepared in pure form only under anhydrous conditions.



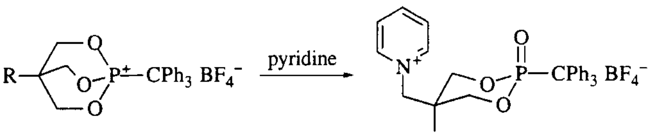
$$[(RO)_3PCPh_3]^+BF_4^- + H_2O \longrightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}CPh_3 + ROH + HBF_4 \qquad (3)$$

7: R = Et **9**

8: R = neopentyl **10**

Reactions of salts with dry pyridine

When **4** was reacted with excess dry pyridine (reaction 4), only one ^{31}P (CD_3CN) signal at 20.14 ppm was observed in the reaction mixture, corresponding to compound **11** which was isolated and characterized by ^1H NMR and ^{13}C NMR spectroscopies. The low solubility of **11** (even in CH_3CN) thwarted attempts to crystallize it from a variety of solvents for X-ray diffraction studies. Thus we synthesized **12** from salt **5**, assuming that the larger alkyl group would increase solubility. Indeed, crystals of compound **12** were obtained from acetonitrile by diffusing diethyl ether into an acetonitrile solution of **12**. Compound **12** (Figure 1) features an equatorial CH_2Py^+moiety relative to the equatorial CPh_3 group as expected for nucleophilic attack at a CH_2 carbon and on steric grounds. An outstanding feature of the pyridinium salts **11** and **12** is their stability to water. Once isolated, **11** and **12** showed no evidence for hydrolysis as evidenced by melting point and ^1H, ^{13}C and ^{31}P NMR spectroscopies of residues obtained from water solutions.

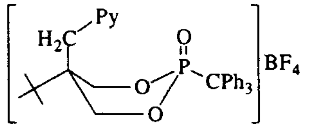


(4)

4: R = Me
5: R = Et
6: R = *t*-Bu

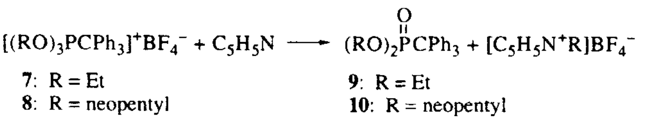
11: R = Me
12: R = Et
13: R = *t*-Bu

In contrast to reaction 4 realized with **4** and **5**, the reaction of **6** with excess dry pyridine gave rise to a curious result. In the reaction solution (CD_3CN) only one ^{31}P signal at 19.30 ppm was observed, suggesting from its proximity to the ^{31}P signals of **11** and **12**, that the analogous reaction product **13** had formed. Attempts to isolate **13** always ended with recovery of the starting material **6**, indicating that **13** is stable only in solution. It is likely that polar solvents such as pyridine or CD_3CN stabilize **13** through dipole-dipole solvation effects with the P=O group and ion-dipole interactions with the pyridinium moiety. In the absence of solvation effects, the bulky *tert*-butyl substituent of **13** prefers the equatorial position (as does the bulky CPh_3 group) and so **13** reverts to the polycyclic starting material by expelling pyridine as a consequence of nucleophilic attack of the axial P=O oxygen on the axial CH_2 group attached to the pyridinium moiety when the molecule is in the boat conformation shown below.



13

When the acyclic compounds **7** and **8** were treated with excess pyridine in CD_3CN, only one ^{31}P NMR signal was observed in each case (26.76 ppm and 25.95 ppm, respectively) corresponding to **9** and **10**, respectively, as shown in reaction 5. Both **9** and **10** were isolated from the reaction mixture and were identified spectroscopically. When **4** or **6** was treated with only one equivalent of pyridine, no reaction product was detected by ^{31}P NMR spectroscopy. On the other hand acyclic **7**or **8** in the presence of one equivalent of pyridine quickly produced **9** or **10**, respectively, as shown by ^{31}P NMR spectroscopy. The increased reactivity of acyclic **7** and **8** with pyridine compared to polycyclic **4** or **6** may be a result of the greater positive entropy associated with the reactions involving **7** or **8** in which an additional bond breakage occurs.



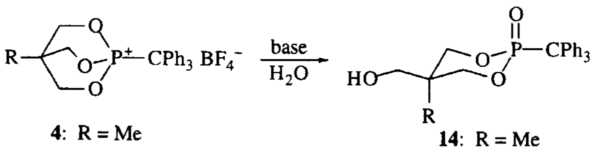
$$[(RO)_3PCPh_3]^+BF_4^- + C_5H_5N \longrightarrow (RO)_2\overset{\overset{O}{\|}}{P}CPh_3 + [C_5H_5N^+R]BF_4^- \quad (5)$$

7: R = Et
8: R = neopentyl

9: R = Et
10: R = neopentyl

Reactions with pyridine/water

When trityl salt **4** was treated with a mixture of pyridine and water, the single product **14** in reaction 6 was obtained. From X-ray diffraction studies, this compound was found to possess an equatorial CH_2OH group (Figure 2). Under the same reaction conditions, compound **15** was obtained from **6**. The configuration and dominant conformation of **15** are likely to be the same as those of **14**.



4: R = Me
6: R = *t*-Bu

14: R = Me
15: R = *t*-Bu

(6)

When **4** was treated with excess pyridine followed by the addition of water about one minute later, two ^{31}P signals with chemical shifts at 21.69 ppm and 19.92 ppm in CD_3CN appeared, which correspond to compounds **14** and **11**, respectively.

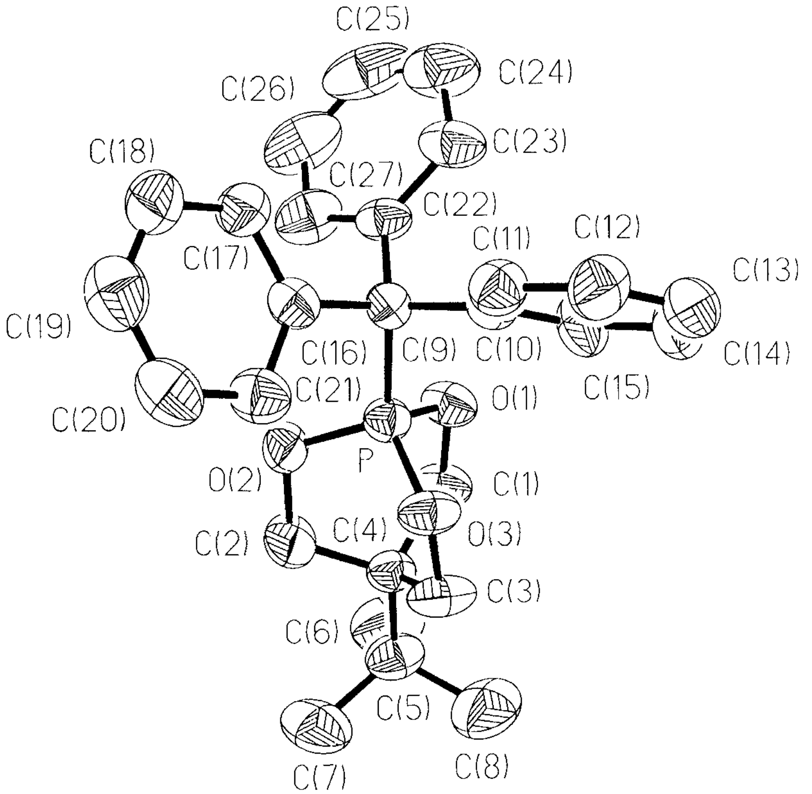
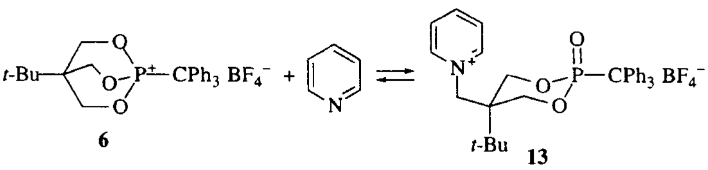


FIGURE 1 Computer drawing of **4** with ellipsoids drawn at the 50% probability level

The integration ratio of the two peaks depended on when water was added to the reaction. The sooner water was added, the larger the proportion of **14** that was formed. These results indicate that the rate of formation of the hydroxy product **14** is faster than that of the pyridinium product **11**. This accords with the fact that OH^- is a better nucleophile than pyridine. In contrast, when trityl salt **6** was treated with dry pyridine followed by the addition of water, a single ^{31}P signal at 20.10 ppm (CD_3CN) was observed, corresponding to compound **15** formed in reaction 6. In order to establish that **15** forms by OH^- attack on **6** in the reaction mixture (even though the concentration of **6** under these conditions is undetectably small by ^{31}P NMR spectroscopy) we carried out a series of ^{31}P NMR-scale reactions. When **6** was treated with one equiv of pyridine, a peak for **13** was not observed by ^{31}P NMR spectroscopy. With increasing amounts of pyridine, the concentration of **13** rises at the expense of **6**. For example, in the presence of ten equivalents of pyridine the integration ratio of **6** to **13** is 6:1. With a large excess of pyridine (107 equivalent of pyridine), only **13** was observed by ^{31}P NMR spectroscopy. This experiment and the previously-obtained result that **13** reverts to **6** during the isolation allows the conclusion that equilibrium 7 was established.



(7)

When water is added to this basic reaction mixture, the OH^- generated attacks **6** forming **15**. Equilibrium 7 thus shifts to the left and **13** is consumed.

The reactions of the acyclic analogues **7** and **8** with pyridine and water proceed analogously giving **9** and **14**, respectively, which were detected by ^{31}P NMR spectroscopy. In these cases, no matter which nucleophile (pyridine or OH^-) attacks the substrate salt, the same product (**9** or **10**, respectively) is formed. Thus these two nucleophilic reactions are neither distinguishable by ^{31}P NMR spectroscopy nor by the structure of the phosphorus-containing product.

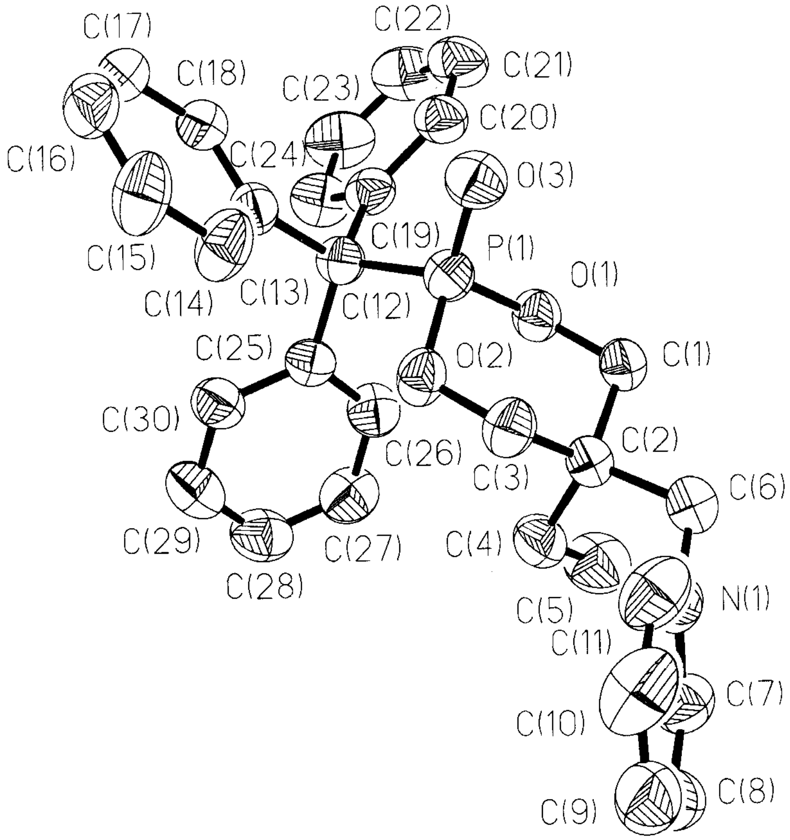


FIGURE 2 Computer drawing of **12** with ellipsoids drawn at the 50% probability level

Reactions of salts with DBU

When compound **5** reacted with one equivalent of DBU in CD_3CN, three ^{31}P NMR signals appeared (53.07, 22.56 and 20.11 ppm). The peak at 53.07 ppm corresponds to the starting material **5** and was the major peak. When excess DBU was injected, a new peak at 94.95 ppm appeared corresponding to phosphite **2** while the peak at 20.11 ppm increased. We were unable to identify the origins of the two peaks at 22.56 ppm and 20.11 ppm and attempts to isolate the corresponding species failed.

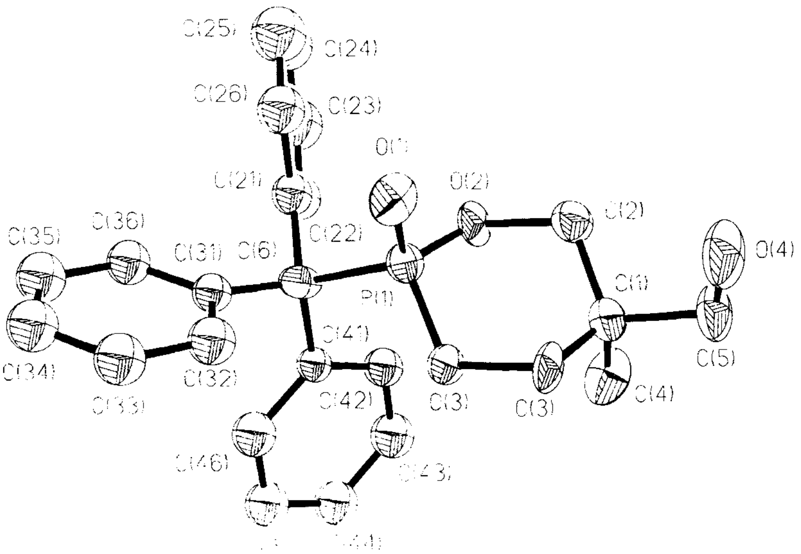
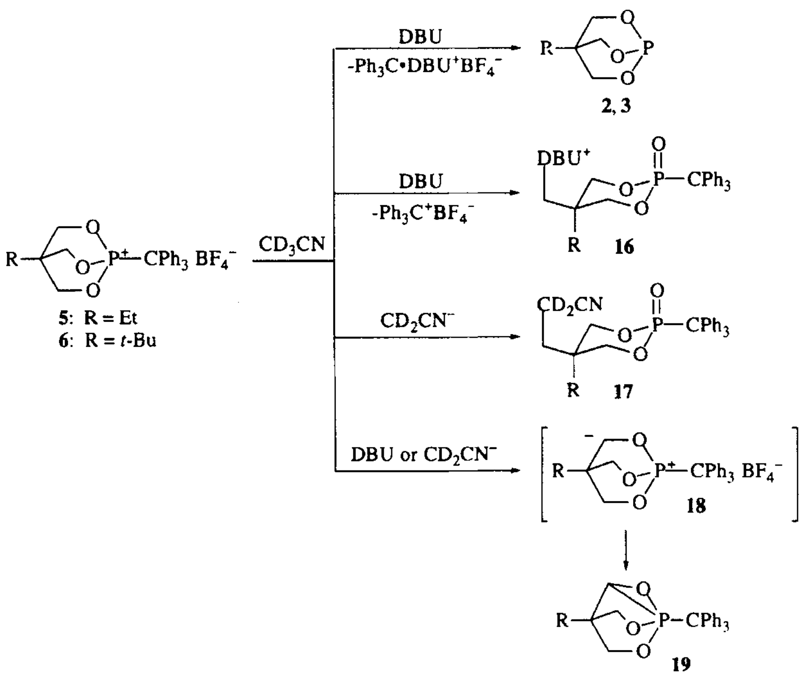


FIGURE 3 Computer drawing of **14** with ellipsoids drawn at the 50% probability level

When compound **6** was reacted with one equivalent of DBU, only one peak at 19.07 ppm appeared besides the peak at 53.66 ppm corresponding to the starting material **6**. When excess DBU was added, the peak at 53.66 ppm disappeared, indicating that all the starting material **6** was consumed. The peak at 19.07 increased with the appearance of new peaks at –4.86 ppm and 96.82 ppm, the latter corresponding to **3**.

These puzzling observations may stem from the somewhat unexpected nucleophilicity of DBU coupled with its strong basicity. Possible reaction paths are shown in Scheme 1 in which the first reaction records the remarkable P-C bond cleavage observed with DBU. Compounds **16** and **17** are the result of nuclophilic attack of DBU or CD_2CN^-, respectively, and such species could be associated with the peaks at *ca.* 20 ppm. Upon deprotonation of **5** or **6** by DBU or CH_2CN^-, the zwitterionic intermediate **18** formed could produce (the highly strained) phosphorane **19** which would be expected to give rise to an upfield ^{31}P chemical shift (e.g., the peak observed at –4.86 ppm).

When acyclic compounds **7** or **8** were treated with one equivalent of DBU, phosphonates **9** and **10**, respectively, were detected by ^{31}P NMR spectroscopy.



SCHEME 1

Reactions of salts with DBU and water

Salt **4** upon reaction with one equivalent of DBU followed by excess water gave a product whose ^{1}H, ^{13}C and ^{31}P NMR spectra are identical to those of compound **14**. Similarly, the product from salt **6** was identified as compound **15** by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, although there were some impurities which depressed the melting point. The same reaction with salts **7** and **8** gave ^{31}P NMR results analogous to those described above for pyridine/water reactions in which **9** and **10**, respectively, were produced.

In Table I are summarized some qualitative comparisons of reaction rates of salts **4**, **6**, **7** and **8** at room temperature. Bicyclic **4** is compared with its acyclic analogue **7** and the more sterically hindered bicyclic **6** is compared with its acyclic analogue **8**. In general, reactions with the less sterically congested bicyclic/acyclic pair require more time to proceed appreciably (if they proceed at all) than those with the more sterically hindered bicyclic/acyclic pair of substrates. Notably, the bicyclic salts are considerably more stable than their acyclic counterparts to water and to pyridine. This is also borne out by the competition reactions of **6** and **8** versus **4** and **7** in pyridine shown in Table II. Here no reaction of **6** or **8** is observable after 15 min., while some **7** does react. With DBU, **4** is slower to react than **7**, but bicyclic **6** appears to react somewhat faster than acyclic **8**. This observation is also substantiated in Table II where it is seen that **4** remains intact while **7** is almost totally converted to **9**. On the other hand **6** is attacked by DBU/CD_3CN forming **17/18** (Scheme 1) while **8** appears to remain intact. The decreased susceptibility of **8** versus **6** here may be associated with the notion that the rather bulky DBU molecule finds **8** to be effectively more sterically hindered than **6** in view of the constrained nature of **6**. In a DBU/H_2O mixture, we see from the data in Table I that acyclic **7** is converted to **9** more rapidly than bicyclic **4** is transformed to **14**, while in the case of **6** and **8**, bicyclic **6** is attacked to the virtual exclusion of **8**. This is also supported by the data in Table II.

TABLE I Qualitative reaction rate data taken at ambient NMR probe temperature

substrate	*reagent*	*time (min.)*	*^{31}P resonance^a (integration) after reaction*		
			substrate	*identifiable product*	*unknown product*
4	H_2O^b	15	52.65		
7	H_2O^b	15	32.37(1.00)	27.02(0.32) **9**	24.98(0.13)
6	H_2O^b	50	53.10		
8	H_2O^b	50	33.11 (1.00)	26.00(0.13) **10**	
4	DBU^c	20	52.37(1.00)		21.53(0.32)
7	DBU^c	20	32.35(1.00)	26.92(4.80) **9**	18.61(0.24)^d **16,17?**
6	DBU^c	40	53.10(1.00)		18.72(0.17)^e
8	DBU^c	40	33.16(1.00)	25.89(0.06) **10**	**16,17?**

substrate	*reagent*	*time (min.)*	*^{31}P resonance^{a} (integration) after reaction*		
			substrate	*identifiable product*	*unknown product*
4	DBU^{c}-H$_2$O^{b}	15	52.38(1.00)	21.72(5.83)	
7	DBU^{c}-H$_2$O^{b}	15	32.35(1.00)	14	
				26.76(28.6) **9**	
6	DBU^{C}-H$_2$O^{b} .	45		19.23, **15**	
8	DBU^{c}-H$_2$O^{b}	45	33.11(1.00)	26.07(0.13)	
				10	
4	pyridme^{c}	15	52.37		
7	pyridine^{c}	15	32.35(1.00)	26.80(8.3) **9**	
6	pyridine^{c}	30	53.12		
8	pyridine^{c}	30	33.16(1.00)	25.90(0.06)	9.32 (0.03)
				10	

[a]in CD$_3$CN. [b]excess. [c]one equivalent. [d]R= Me [e]R=*t*-Bu.

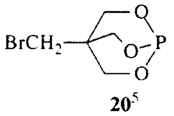
TABLE II Competition reaction rate data taken over 15 minutes at ambient probe temperature

substrate	*reagent*	*^{31}P resonance^{a} (integration)*	
		substrate	*product*
4 +**7**	pyridine^{b}	52.37(1.00) **4**, 32.35(0.06) **7**	26.77(0.77) **9**
6 + **8**	pyridine^{b}	53.11 (0.70) 6, 33.16(1.00) **8**	
4 + **7**	DBU^{b}	52.38(1.00) **4**, 32.36(0.16) **7**	26.76(0.98) **9**
6 + **8**	DBU^{b}	53.11(0.71) **6**,	18.74(0.17)^{c} **16, 17?**
		33.16(1.00) **8**	
4 + **7**	DBU^{b}-H$_2$O^{d}	52.37(1.00) **4**,	26.87(1.05) **9**
		32.35(0.23) **7**	
6 + **8**	DBU^{b}-H$_2$O^{d}	33.12(1.00) **8**	21.21(0.06)^{c} **16, 17**
			19.22(1.53) **15**

[a]in CD$_3$CN. [b]one equivalent. [c]R = *t*-Bu. [d]excess.

Structural considerations

The data collection and reduction information for **4**, **12** and **14** are collected in Table III. The molecular structure determined here for the cation of **4** is the first for a bicyclic phosphite cation and we now compare its bond angles with those of **20** and **25**. (The bond distances within the cage are very comparable among these compounds.) In progressing from **20** to the group of compounds **21–25**, the OPO and POC bond angles remain quite constant within 3σ (~101° and 118°, respectively). In **25**, however, the OPO angle opens to 103.7(6)° and in response the POC bond angle closes to 115.2(1)°. This observation suggests that the positive charge on phosphorus, which is virtually zero in **19** and much less than +1 on average in **21–24**, is perhaps actually larger in **25** indicating substantial ylide character in **25**. In accord with this notion, the OPO angle in **4** is the largest (107.7(2)°) and its POC angle is the smallest (111.1(3)°) among this group of compounds. These trends are in agreement with the idea that positive charge buildup on an atom (surrounded by an electron octet) to the point of true "onium" ion formation, results in sp^3hybridization on that atom in the absence of stereoelectronic constraints.



20[5]

$Co[P(OCH_2)_3CCH_3]_5^+$

21[6]

$\{Ni[P(OCH_2)_3CCH_3]_3(NO)\}^+$

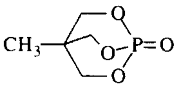
22[7]

$Ag[P(OCH_2)_3CCH_3]_4^+$

23[8]

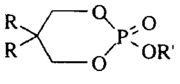
$Ni[P(OCH_2)_3CCH_3]_5^{2+}$

24[9]



25[10]

The structures of **12** and **14** confirm the stereochemistry expected from the normal pathway for nucleophilic attack of **5** and **4**, respectively. Thus both structures possess *cis* phosphoryl and attacking-nucleophile substituents and the sterically bulky CPh_3group occupies an equatorial site in both. The bond angles and lengths in both molecules are unremarkable and they also compare well to those in similar ring systems such as **26–28**[11] even though the OR′ substituent on phosphorus is more electronegative than the CPh_3 group in **12** and **14**. When the bulky CPh_3 is forced to occupy an axial site as in **29**, the OPO portion of the ring is flattened and the POC angle (127.5°) is about 8° larger than in other phosphorinane ring systems.[12]



	R	R′
26	H	H
27	Me	H
28	H	Ph

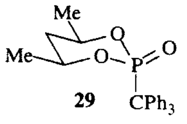


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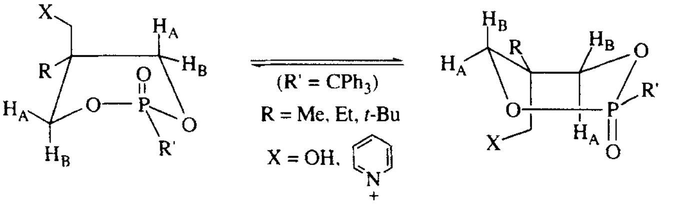
TABLE III Crystallographic data for **4**, **12** and **14**

	4	*12*	*14*
formula	$C_{27}H_{30}BF_4O_3P$	$C_3OH_{31}BF_4NO_3P$	$C_{48}H_{50}O_4P_2$
fw	520.29	571.34	816.88
color, habit	clear, rectangular	clear, triangular	colorless
crystal size (mm)	0.3 × 0.15 × 0.07	0.4 × 0.3 × 0.125	0.40 × 0.21 × 0.24
space group	$P2_1/n$	P1	$P2_1/c$
a (Å)	9.092(2)	9.2580(10)	19.026(4)
b (Å)	28.636(6)	9.4710(10)	14.146(3)
c (Å)	10.012(2)	18.616(2)	16.793(3)
α(°)	90	91.540(10)	-
β(°)	94.11(3)	97.770(10)	115.00(2)
γ(°)	90	118.400(10)	-
V(Å^3)	2600.0(9)	1414.9(3)	4096(2)
Z	4	2	4
d_{calcd} (g cm^{-3})	1.329	1.341	1.325
data collecn instrument	Siemens P4RA	Siemens P4	Enraf-Nonius CAD4
temp, K	293(2)	293(2)	294(1)
data collecn range, 2θ, (°)	3.09–57.47	2.41–56.84	0–50
scan method	ω	θ-2θ	0–2θ
R^a	0.0860	0.582	0.0741
R_ω^{b}	0.1920	0.1542	0.0941

$^a R = \Sigma \, ||F_o| - |F_c|| / \Sigma |F_o|$. $^b [\Sigma[\omega(F_o^2 - F_c^2)^2] / \Sigma[\omega(F_o^2)^2]]^{0.5}$.

Although the X-ray structures clearly indicate chair forms for the 1,3,2-dioxaphosphorinane rings in **12** and **14**, these conformations are not retained in solution. For the biased chair conformations of a series of 2-oxo-1,3,2-dioxaphosphorinanes $^3J(H_{ax}P)$ is 1–3 Hz and $^3J(H_{eq}P)$ is 19–26 Hz[13] while in our 1,3,2-dioxaphosphorinane derivatives the values of these corresponding vicinal coupling constants are similar as in **11**, **12** and **15**, or identical as in **14**. We suggest that these data reflect rapid equilibria of the boat conformations depicted below. In these boat conformations the bulkiest groups occupy the pseudoequatorial sites while repulsive interactions between H_B and the oxygens lone pair are minimal.



(8)

TABLE IV Selected bond lengths and angles in **4**

	bond lengths (A)		
P-O(3)	1.537(4)	P-O(1)	1.543(4)
P-O(2)	1.548(4)	P-C(9)	1.815(6)
	bond angles (°)		
O(3)-P-O(2)	107.3(2)	C(1)-O(1)-P	111.4(3)
O(3)-P-O(1)	107.3(2)	C(2)-O(2)-P	110.2(3)
O(2)-P-O(1)	106.6(2)	C(3)-O(3)-P	111.7(2)

TABLE V Selected bond lengths and angles in **12**

	bond lengths (A)		
P(1)-O(3)	1.461(2)	P(1)-O(1)	1.587(2)
P(1)-O(2)	1.586(2)	N(1)-C(6)	1.481(4)
	bond angles (°)		
O(2)-P(1)-O(1)	102.68(12)	C(25)-C(12)-P(1)	110.3(2)
O(3)-P(1)-C(12)	114.9(2)	C(19)-C(12)-P(1)	109.7(2)
C(1)-O(1)-P(1)	115.1(2)	C(13)-C(12)-P(1)	105.4(2)
C(3)-O(2)-P(1)	115.7(2)		

TABLE VI Selected bond lengths and angles in **14**

	bond lengths (A)		
P(1)-O(1)	1.470(6)	P(1)-O(3)	1.576(7)
P(1)-O(2)	1.564(8)	O(4)-C(5)	1.41(1)
	bond angles (°)		
O(2)-P(1)-O(3)	103.6(5)	P(1)-C(1)-C(21)	104.0(6)
O(1)-P(1)-C(1)	114.1(4)	P(1)-C(1)-C(31)	110.0(5)
P(1)-O(2)-C(2)	114.8(5)	P(1)-C(1)-C(11)	109.7(7)
P(1)-O(3)-C(3)	114.6(5)		

CONCLUSIONS

Various nucleophiles (H_2O, pyridine, DBU) attack tritylphosphonium salts of acyclic and bicyclic phosphites at CH_2OP sites regioselectively, thus giving rise to single products **9** and **10** when acyclic salts **7** and **8** are used. Structures of products obtained from bicyclic salts depend on the nucleophilicity and/or basicity of the reagents employed. No reaction with water was observed for **4–6**, while in the presence of pyridine or DBU, water cleanly cleaves the CH_2-OP bond in **4** and **6** to afford high yields of **14** and **15**, respectively. Excess dry pyridine transforms bicyclic salts into their respective pyridinium salts **11–13**, but with excess DBU complex transformations of **4** and **5** were noticed, including P-C bond cleavage.

EXPERIMENTAL SECTION

General methods

NMR spectra were recorded at 20 °C on a Varian VXR 300 or a Bruker AC 200 machine with deuterated solvent as an internal lock. ^1H NMR (300 MHz, VXR 300) and ^{13}C NMR (50 MHz, Bruker AC 200) spectra were referenced to the deuterated solvent. ^{31}P NMR spectra (81 MHz, Bruker AC 200) were externally referenced to 85% H_3PO_4. High-resolution (EI, 70 eV) mass spectra were recorded on a Kratos MS-50 instrument. The masses are reported for the most abundant isotope present. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Melting points (uncorrected) were measured with a Thomas-Hoover capillary apparatus. X-ray data collection and structure solutions were conducted at the Iowa State Molecular Structure Laboratory.

All reactions that required dry conditions were carried out under a nitrogen atmosphere. Acetonitrile (including CD_3CN), pyridine, CH_2Cl_2, acetone, and DBU were dried over and distilled from CaH_2 under nitrogen. Diethyl ether, THF and pentane were dried over and distilled from Na/benzophenone under nitrogen. Hexamethyl phosphorous triamide was purchased from Aldrich and distilled before use. Compound **1** was prepared according to the literature procedure[2] from trimethyl phosphite and 1,1,1-tris(hydroxymethyl)ethane both of which were purchased from Aldrich. Compound **2** was purchased from Lancaster. 2-*t*-Butyl-2-hydroxymethyl-1,3-propanediol was prepared according to literature procedures.[4,14] Triethyl phosphite, purchased from Aldrich, was treated with Na and distilled before use. Trineopentyl phosphite was prepared from neopentyl alcohol (Aldrich) and phosphorus trichloride according to a literature procedure.[15]

4-*t*-Butyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane (3)

This compound can be synthesized by the transesterification of trimethyl phosphite with $(HOCH_2)_3CC(CH_3)_3$ in the presence of triethylamine in 53% yield.[3] Here we report a modified method with a higher yield. 4-*t*-Butyl-2-hydroxymethyl-1,3-propanediol (6.336 g, 39.06 mmol) was mixed with hexamethyl phosphorous triamide (7.10 mL, 39.1 mmol) in 25 mL of THF and the reaction mixture was refluxed overnight. After the solvent was evaporated in vacuo, the white solid was sublimed (20 mtorr/100 °C) to give ^1H NMR-spectroscopically pure **3** in 74% yield.

4-Methyl-1-trityl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane tetrafluoroborate (4)

This compound was prepared in a manner similar to that described earlier by us,[16]with the modification that triphenylmethyl tetrafluoroborate was used instead of chlorotriphenylmethane followed by silver tetrafluoroborate. Here we also report complete NMR spectroscopic data for **4**: mp 210 °C (dec.); ^{1}H NMR (CD_3CN) δ 0.99 (s, 3 H, CH_3), 4.94 (d, *J* = 5.4 Hz, 6 H, CH_2OP), 7.12–7.51 (m, 15 H, C_6H_5); ^{13}C NMR (CD_3CN) δ 13.04 (s, CH_3), 37.68 (d, *J* = 35.4 Hz, C_4), 62.52 (d, *J* = 115.8 Hz, C-P), 82.95 (d, *J* = 6.3 Hz, CH_2OP), 130.30, 130.58, 131.18 (d, *J* = 8.2 Hz), 135.46 (d, *J* = 5.1 Hz) C_6H_5; ^{31}P NMR (CD_3CN) δ 52.37.

4-Ethyl-1-trityl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane tetrafluoroborate (5)

This compound was prepared in 79% yield analogously to the preceding procedure, using compound **2** and triphenylmethyl tetrafluoroborate: mp 211 °C (dec.); ^{1}H NMR (CD_3CN) δ 0.84 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.46 (q, *J* = 7.8 Hz, 2 H, CH_2), 4.97 (d, *J* = 5.4 Hz, 6 H, CH_2OP), 7.13–7.49 (m, 15 H, C_6H_5); ^{13}C NMR (CD_3CN) δ 7.33 (s, CH_3), 22.13 (d, *J* = 1.4 Hz, CH_2), 40.40 (d, *J* = 32.7 Hz, C_4), 62.50 (d, *J* = 115.5 Hz, C-P), 82.31 (d, *J*= 6.4 Hz, CH_2OP), 130.30, 130.56 (d, *J* = 2.7 Hz), 131.19 (d, *J* = 7.5 Hz), 135.46 (d, *J* = 5.6 Hz) C_6H_5; ^{31}P NMR (CD_3CN) δ 52.47.

4-*t*-Butyl-1-trityl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane tetrafluoroborate (6)

This compound was prepared in 89% yield analogously to the preceding two procedures, using compound **3** and triphenylmethyl tetrafluoroborate: mp 230 °C (dec.); ^{1}H NMR (CD_3CN) δ 0.94 (s, 9 H, CH_3, 5.12 (d, *J*= 6.0 Hz, 6 H, CH_2OP) 7.12–7.51 (m, 15 H, C_6H_5); ^{13}C NMR (CD_3CN) δ 25.26 (s, CH_3), 34.95 (s, CCH_3, 44.99 (d, *J* = 22.0 Hz, C_4), 62.36 (d, *J* = 114.9 Hz, CP), 80.85 (d, *J* = 6.3 Hz, CH_2OP), 130.30, 130.58, 131.18 (d, *J* = 8.3 Hz), 135.41 (d *J* = 6.2 Hz) C_6H_5; ^{31}P NMR (CD_3CN) δ 53.12.

Triethoxytritylphosphonium tetrafluoroborate (7)

This compound was synthesized according to a literature method.[17] Here we provide complete NMR spectral data: mp 158–159 °C, 143 °C[17]) ; ^{1}H NMR (CD_3CN) δ 1.17 (dt, *J*= 7.2 Hz, *J* = 1.5 Hz, 9 H, CH_3), 4.30 (dq, *J*= 6.6 Hz, 6 H, CH_2OP), 7.19–7.48 (m, 15 H, C_6H_5); ^{13}C NMR (CD_3CN) δ 15.76 (d, *J*= 6.4 Hz, CH_3), 64.85 (d, *J*= 131.9 Hz, CP), 73.95 (d, *J*=

10.7 Hz, CH_2OP), 129.99, 130.14, 131.13 (d, *J*= 6.8 Hz), 137.39 (d, *J* = 6.6 Hz) C_6H_5; ^{31}P NMR (CD_3CN) δ 32.35.

Trineopentoxytritylphosphonium tetrafluoroborate (8)

Triphenylmethyl tetrafluoroborate (1.07 g, 3.25 mmol) was dissolved in 20 mL of CH_2Cl_2. A solution of trineopentyl phosphite (1.15 g, 3.93 mmol) in 8 mL of CH_2Cl_2 was added at 0 °C. After stirring at room temperature for 30 minutes, the solvent was removed in vacuo. Pentane (50 mL) was added and the reaction mixture was stirred for another 30 minutes. The white solid product (1.7 g, 85%) was obtained after filtration and washing with pentane: mp 93 °C; ^1H NMR (CD_3CN) δ 0.8 (s, 27 H, CH_3), 3.96 (d, *J*= 2.7 Hz, CH_2), 7.17–7.50 (m, 15 H, C_6H_5); ^{13}C NMR (CD_3CN) δ 25.56 (s, CH_3), 33.24 (d, *J* = 6.9 Hz, CCH_3), 85.60 (d, *J*= 12.4 Hz, CH_2OP), 130.21, 130.37, 131.13 (d *J* = 6.9 Hz), 137.19 (d, *J* = 6.8 Hz) C_6H_5; ^{31}P NMR (CD_3CN) δ 33.11. This compound is unstable and must be made immediately prior to use.

Reaction of 4 with dry pyridine; preparation of 11

Compound 4 (308 mg, 0.644 mmol) was dissolved in 6 mL of pyridine at 65 °C. After cooling the solution to room temperature and concentrating it *in vacuo*, **11** (344 mg, 95.8%) was obtained as a white solid after filtration and washing with diethyl ether: mp 293–295 °C (dec.); ^1H NMR (DMSO-d_6) δ 0.69 (s, 3 H CH_3), 3.54 (t, *J* = 12.0 Hz, 2 H, H_ACOP), 4.37 (dd, *J*= 8.7 Hz, *J*= 11.1 Hz, 2 H, H_BCOP), 4.75 (s, 2 H, CH_2N), 7.33–7.38 (m, 15 H, C_6H_5), 8.15–8.87 (m, 5 H, pyridine-protons); ^{13}C NMR (DMSO-d_6) δ 16.39 (s, CH_3), 37.23 (d, *J*= 8.0 Hz, C_5), 62.29 (d, *J* = 132.1 Hz, CP), 62.89 (s, CH_2N), 71.76 (d, *J*= 7.1 Hz, CH_2OP), 127.40, 128.17, 128.42, 130.25 (d, *J* = 6.6 Hz), 140.16 (d *J* = 5.0 Hz), 145.72, 146.35 aromatic carbons; ^{31}P NMR (DMSO-d_6) δ 23.02.

Reaction of 5 with dry pyridine; preparation of 12

Compound **5** (603 mg, 1.22 mmol) was dissolved in 12 mL of pyridine at 50 °C. After cooling the solution to room temperature and concentrating it in vacuo, **12** (637 mg, 91.0%) was obtained as a white solid by fractional crystallization as pyridine was evaporated: mp 237–238 °C; ^1H NMR (CD_3CN) δ 0.69 (t, *J*= 7.5 Hz, 3 H, CH_3), 1.11 (q, *J* = 7.5 Hz, 2H, CH_2), 3.49 (dd, *J* = 12.0 Hz, *J*= 7.5 Hz, 2 H, H_ACOP), 3.94 (t, *J* = 12.0 Hz, 2 H, H_BCOP), 4.86 (s, 2 H,CH_2N), 7.35–7.43 (m, 15 H, C_6H_5), 8.06–8.65 (m, 5 H, pyridine protons); ^{13}C NMR (CD_3CN) δ 6.98 (s, CH_3), 23.27 (s, CH_2), 41.84 (d, *J*= 10.1 Hz, C_5), 62.50 (s, CH_2N), 64.43 (d, *J*= 133.8 Hz, C-P), 72.31 (d, *J*= 8.5 Hz, CH_2OP), 128.49, 129.21, 129.82, 131.53 (d, *J* = 6.8 Hz), 141.43 (d, *J* = 5.2 Hz), 146.70, 147.81 aromatic carbons; ^{31}P NMR (CD_3CN) δ 20.13; Anal. calcd for $C_{30}H_{31}BF_4NO_3P$: C, 63.07; H, 5.47. Found: C, 63.33; H, 5.58.

Reaction of 7 with dry pyridine; preparation of 9

Compound **7** (497 mg, 1.00 mmol) was dissolved in 3 mL of dry pyridine. After stirring at room temperature for 20 hours, the reaction mixture was evaporated to dryness. The residue was extracted with diethyl ether (3 x 20 mL). The ether extracts were combined, filtered and then evaporated in vacuo. The yellowish solid residue was decolorized by dissolving it in CH_3OH, adding activated charcoal, filtering and evaporating the filtrate *in vacuo* to give **9** (320 mg, 84.0%) as a white solid: mp 118–119 °C; ^1H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.2 Hz, 6 H, CH_3), 3.76–3.89 (m, 2 H, CH_AOP), 3.95–4.08 (m, 2 H, CH_BOP), 7.26–7.33 (m, 15 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 16.09 (d, *J*= 6.2 Hz, CH_3), 62.89 (d, *J*= 135.7 Hz, CP), 63.21 (d, *J*= 8.4 Hz, CH_2OP), 126.83, 127.75, 130.65 (d, *J*= 6.7 Hz), 141.57 (d, *J*= 6.2 Hz) C_6H_5; ^{31}P NMR ($CDCl_3$) δ 26.48; HRMS calcd. for $C_{23}H_{25}O_3P$ 380.15413, found 380.15389.

Reaction of 8 with dry pyridine; preparation of 10

Compound **8** (718 mg, 1.15 mmol) was dissolved in 5 mL of pyridine. After stirring at room temperature for 18 hours, the reaction mixture was evaporated to dryness in vacuo and the residue was extracted with diethyl ether (2 x 30 mL). The combined ether layer was decolorized by adding activated charcoal, then filtered and evaporated *in vacuo* to give **10** (534 mg, quantitative) as a white solid: mp 147–148 °C; ^1H NMR ($CDCl_3$) δ 0.738 (s, 18 H, CH_3), 3.38 (dd, *J* = 3.0 Hz, *J* = 9.3 Hz, 2 H, H_ACOP), 3.65 (dd, *J* = 4.5 Hz, *J*= 9.3 Hz, 2 H, H_BCOP), 7.26–7.36 (m, 15 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 25.93 (s, CH_3), 31.90 (d, *J*= 7.0 Hz, CCH_3), 63.05 (d, *J*=

136.8 Hz, C-P), 76.47 (d, *J*= 10.0 Hz, CH_2OP), 126.77, 127.76, 130.71 (d, *J*= 6.0 Hz), 141.65 (d, *J*= 5.2 Hz) C_6H_5; ^{31}P NMR ($CDCl_3$) δ 25.75; HRMS calcd. for $C_{29}H_{37}O_3P$ 464.24803, found 464.24896. Anal. calcd for $C_{29}H_{37}O_3P$: C, 74.97; H, 8.02. Found: C, 74.79; H, 7.91.

Reaction of 4 with wet pyridine; preparation of 14

Compound **4** (199 mg, 0.416 mmol) was dissolved in a mixture of pyridine (5 mL) and water (0.05 mL). After stirring the reaction mixture at room temperature for 30 mimutes, the solvent was evaporated *in vacuo* and the residue was chromatographed on silica gel with CH_2Cl_2/CH_3OH (30:1) to give **14** (159 mg, 93.6%) as white crystals after recrystallization from CH_2Cl_2/OH_3OH by evaporating the solvents in the open atmosphere: mp 213 °C ; ^1H NMR ($CDCl_3$) δ 0.68 (s, 3 H, CH_3), 3.25 (s, 1 H, OH), 3.32 (t, *J* = 10.8 Hz, 2 H, H_ACOP), 3.67 (s, 2 H, CH_2OH), 4.30 (t, *J* = 10.8 Hz, 2 H, H_BCOP), 7.29–7.47 (m, 15 H, C_6H_5) ; ^{13}C NMR ($CDCl_3$) δ 17.35 (s, CH_3), 37.87 (d, *J*= 8.6 Hz, C_5), 63.16 (d, *J*= 135.3 Hz, CP), 64.28 (s, CH_2OH), 73.33 (d, *J*= 7.9 Hz, CH_2OP), 127.17, 127.96, 130.77 (d, *J*= 6.5 Hz), 140.58 (d, *J*= 5.2 Hz) C_6H_5; ^{31}P NMR ($CDCl_3$) δ 20.91; HRMS calcd. for $C_{24}H_{25}O_4P$ 408.14905, found 408.14986; Anal. calcd for $C_{24}H_{25}O_4P$: C, 70.58; H, 6.17. Found: C, 70.77; H, 6.04.

Reaction of 6 with wet pyridine; preparation of 15

Compound **6** (111 mg, 0.213 mmol) was dissolved in a mixture of pyridine (2 mL) and water (0.05 mL). After stirring at room temperature overnight, H_2O (5 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried over Na_2SO_4 and evaporated to give **15** (96 mg, quantitative) as a white solid: mp 212 °C; ^1H NMR ($CDCl_3$) δ 0.72 (s, 9 H, CH_3), 2.77 (s, 1 H, OH), 3.48 (dd, *J*= 11.1 Hz, *J*= 7.8 Hz, 2 H, H_ACOP), 4.02 (s, 2 H, CH_2OH), 4.08 (t, *J* = 11.4 Hz, 2 H, H_BCOP), 7.30–7.51 (m, 15 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 25.65 (s, CH_3), 34.42 (s, CCH_3), 44.66 (d, *J*= 7.8 Hz, C_5), 61.69 (s, CH_2OH), 63.57 (d, *J*= 135.4 Hz, CP), 70.86 (d, *J*= 8.6 Hz, CH_2OP), 127.10, 128.00, 130.79 (d, *J*= 6.7 Hz), 140.68 (d, *J* = 5. 1 Hz) C_6H_5 ; ^{31}P NMR ($CDCl_3$) δ 20.53; HRMS calcd. for $C_{27}H_{31}O_4P$ 450.19600, found 450.19543.

Reaction of 5 with DBU

Compound **5** (13 mg, 0.026 mmol) was dissolved in 0.7 mL of CD_3CN in an NMR tube under N_2. DBU (4.0 μL, 1.0 equivalent) was injected through a micro syringe. The reaction mixture turned yellow and the ^{31}P NMR spectrum was taken. Succeeding spectra were recorded upon further additions of DBU.

Reaction of 6 with DBU

Compound **6** (25 mg; 0.048 mmol) was dissolved in 0.7 mL of CD_3CN in an NMR tube under N_2. DBU (7.2 μL, 1.0 equivalent) was injected through a micro syringe. The reaction mixture turned yellow and a ^{31}P NMR spectrum was taken. Succeeding spectra were recorded upon further additions of DBU.

Reaction of 4 with DBU and water; preparation of 14

Compound **4** (252 mg, 0.527 mmol) was dissolved in 6 mL of CH_3CN. DBU (79.0 μL, 0.527 mmol) was added, followed by the addition of 0.05 mL H_2O. After stirring at room temperature for 1 day, solvent was removed in vacuo and the residue was chromatographed on silica gel with an ethyl acetate/hexane eluent (6:1) to give **14** (169 mg, 79%) as a white solid; mp 208–209 °C.

Reaction of 6 with DBU and water; preparation of 15

Compound **6** (326 mg, 0.627 mmol) was dissolved in 5 mL of CH_3CN. DBU (94.0 μL, 0.627 mmol) was added, followed by the addition of 0.1 mL of H_2O. After stirring the reaction mixture at room temperature overnight, H_2O (10 mL) was added and then the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried over Na_2SO_4 and evaporated to give a white solid which was recrystallized by dissolving it in CH_2Cl_2, then adding hexane and evaporating the solvent in the atmosphere to give **15** as white crystals (233 mg, 82.5%).

X-ray crystallographic structure solution of 4

A crystal of the compound was mounted on a glass fiber on the Siemens PARA for a data collection at 293(2) ± 1K. The cell constants for the data collection were determined from reflections found using the hemispherical search routine in XSCANS.[18] Twenty-five reflections in the range of 10.814–27. 518° θ were used to determine precise cell constants. Lorentz and polarization corrections were applied. A nonlinear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for this specimen, though no absorption correction was applied to the data. The absorption coefficient for the compound is small enough not to warrant a correction. The space group $P2_1/n$ was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct-methods solution[19] and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map and were refined with anisotropic displacement parameters. All hydrogens were treated as riding atoms with individual isotropic displacement parameters. Final refinements were done with SHELXL-93.[20,21] The significant amount of disorder found for the BF_4^- counter ion was modeled as a partial occupancy in one of the fluorine atoms. The occupancy ratio F(1)/F(1′) is 60.4%/39.6%. The thermal parameters for all of the fluorine atoms were observed to be large. A low temperature data set was collected on the sample. The refinement did not improve due to slightly poorer overall crystal quality. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELXTL-Plus[19] and SHELXL-93.[20]

X-ray crystallographic structure solution of 12

A crystal of **12** compound was mounted on a glass fiber on the Siemens P4 for a data collection at 293(2) ± 1K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. Twenty-five reflections in the range of 16–33° θ were used to determine precise cell constants. Lorentz and polarization corrections were applied. A correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for this specimen and a semi-empirical absorption correction was applied to the data. The space group P1 was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct-methods solution[19] and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map and were refined with anisotropic displacement parameters. All hydrogens were treated as riding atoms with individual isotropic displacement parameters. Final refinements were done with SHELXL-93.[20,21] The temperature factors on the fluorine atoms of the BF_4^- group are large but the disorder is not significant. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using the SHELXTL- PLUS[19]and SHELXL-93.[20]

X-ray crystallographic structure solution of 14

A crystal approximately 0.1 × 0.1 × 0.1 mm was mounted in a 0.2 mm diameter thin-walled capillary tube, sealed with wax, and attached to a standard goniometer head. The crystal was aligned on a four-circle DATEX X-ray diffractometer. Four preliminary ω-oscillation photographs were taken at various ϕ settings. The approximate positions of 15 reflections were selected from the photographs and were used as input to an automatic indexing program.[22] The resulting reduced cell and reduced cell scalars indicated a primative monoclinic lattice. The predicted layer spacings for this cell were observed, within experimental error, on three axial ω-oscillation photographs. Accurate unit cell parameters were obtained by carefully centering ten independent high-angle reflections on the diffractometer and using the $\pm 2\theta$ values of these reflections as input to a least-squares fitting program. The data were collected at room temperature. No decay of the standard reflections was observed. The systematic absences uniquely indicated space group $P2_1/a$. The positions of the non-hydrogen atoms were determined as follows: Patterson superpositions were carried out using the a-glide phosphorus-phosphorus Harker vector, followed by the 2_1 phosphorus-phosphorus Harker vector. The resulting superposition map showed a quartet of large peaks, which were taken to represent phosphorus atoms. Further analysis showed a second quartet of peaks, also quite large in the original Patterson, which had the same relationships among themselves as did the initial quartet of peaks. This implied the presence of two paralellograms of phosphorus atoms. From these two quartets, the positions of two non-symmetry-related phophorus atoms were determined. The positions of the remaining non-hydrogen atoms were determined from successive structure factor and electron density map calculations.[23] The initial positional and isotropic thermal parameters were refined using a block-matrix least-squares procedure. The positional and anisotropic thermal parameters were refined to their final values using a full-matrix least-squares procedure.[24] The positions of approximately two-thirds of the hydrogens were determined from a difference electron density map and the rest of the hydrogen positions were calculated. None of the hydrogen positions were refined.

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References

[1] (a) Verkade, J. G. *Pure and Applied Chemistry* **1980**, *52*, 1131. (b) Verkade, J. G. *Phosphorus and Sulfur* **1976**, *2*, 251. (c) Verkade, J. G. *Coord. Chem. Rev.*, **1972**, *9*, 1.

[2] Huttemann, T. J.; Foxman, B. M.; Sperati, C. R. and Verkade, J. G. *Inorg. Chem.* **1965**, *4*, 950.

[3] Edmundson, R. S.; Forth, C. I. *Phosphorus and Sulfur,* **1980**, *8*, 315.

[3] Milbrath, D. S.; Engel, J. L.; Verkade, J. G. Casida, J. E. *Toxicology and applied pharmacology*. **1979**, *47*, 287.

[5] Milbrath, D. S.; Springer, J. P.; Clardy, J. C. and Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5493.

[6] Albright, J. O.; Clardy, J. C. and Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 1575.

[7] Meiners, J. H.; Rix, C. J.; Clardy, J. C. and Verkade, J. G. *Inorg. Chem.* **1975**, *14*, 705.

[8] Ugro, J.; Jacobson, R. A., unpublished results.

[9] Riedel, E. F.; Jacobson, R. A. *Inorg. Chim. Acta* **1970**, *4*, 407.

[10] Nimrod, D. M.; Fitzwater, D. R. and Verkade, J. G. *J. Am Chem. Soc.* **1968**, *90*, 2780.

[11] Verkade, J. G. *Bioinorg. Chem.* **1974**, *3*, 165 and references therein.

[12] Milbrath, D. S.; Springer, J. P.; Clardy, J. C. and Verkade, J. G. *Phosphorus and Sulfur* **1981**, *11*, 19.

[13] Bentrude, W. G. and Setzer, W. N., in "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis", Ed. Verkade, J. G., Quin, L. D., VCH Publishers, Inc., Deerfield Beach, FL, 1987; pp. 365–389.

[14] Eliel, E. L.; Hutchins, R O.; Knoeber, M. Sr. *Org. Synth.* **1970**, *50*, 38.

[15] Avila, L. Z.; Bishop, P. A.; Frost, J. W. *J. Am Chem Soc.* **1991**, *113*, 2242.

[16] Verkade, J. G.; Huttemann, T. J.; Fung, M. K.; King, R. W. *Inorg. Chem.* **1965**, *4*, 83.

[17] Dimroth, K.; Nurrenbach. A. *Chem. Ber.,* **1960**, *93*, 1649.

[18] XSCANS, Siemens Analytical Xray, Inc., Madison, WI.

[19] SHELXTL-PLUS, Siemens Analytical Xray, Inc., Madison, WI.

[20] Sheldrick, G. M., SHELXL-93, Program for the Refinement of Crystal Strutures, University of Göttingen, Germany.

[21] All X-ray scattering factors and anomalous dispersion terms were obtained from the "International Tables for Crystallography", Vol. C, pp.4.2.6.8 and 6.1.1.4.

[22] Jacobson, R. A., *J. Appl. Crystallog.* **1976**, *9*, 115.

[23] Lapp, R. L.; Jacobson, R. A. "ALLS: A Generalised Crystallographic Least-Squares Program", U.S. DOE Report, IS-4708, Iowa State University, Ames, IA, 1979.

[24] Powell, D. R.; Jacobson, R. A. "FOUR: A Generalized Crystallographic Fourier Program", U.S. DOE Report IS-4737, Iowa State University, Ames, IA, 1980.