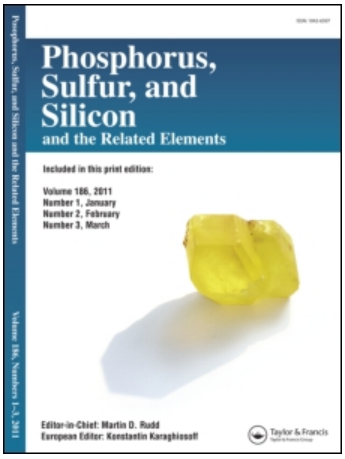

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SOME CHEMISTRY OF 2,8-DIOXA-5-AZA-1-PHOSPHABICYCLO[3.3.0] OCTANE AND 2,10-DIOXA-6-AZA-1-PHOSPHABICYCLO[4.4.0] DECANE. FURTHER EVIDENCE FOR THE BIPHILIC INSERTION MECHANISM

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SOME CHEMISTRY OF 2,8-DIOXA-5-AZA-1-PHOSPHABICYCLO[3.3.0] OCTANE AND 2,10-DIOXA-6-AZA-1-PHOSPHABICYCLO[4.4.0] DECANE. FURTHER EVIDENCE FOR THE BIPHILIC INSERTION MECHANISM

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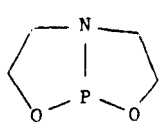
2,8-Dioxa-5-aza-1-phosphabicyclo[3.3.0] octane, **1**, and 2,10-dioxa-6-aza-1-phosphabicyclo[4.4.0] decane, **2**, both react with diethyl peroxide to give phosphoranes containing two ethoxy groups. The reactivities of **1** and **2** towards diethyl peroxide are very different. The reaction of **1** at 0°C in methylene chloride is complete after 7 days whereas **2** and diethyl peroxide in methylene chloride require 30 days at room temperature for 89% reaction. The opposite reactivity of **1** and **2** are found in their reactions with diphenyl disulfide. These data strongly support a direct insertion by phosphorus into the oxygen–oxygen bond of the peroxide. Compounds, **1** and **2** were allowed to react with trifluoroethoxy benzenesulfenate and 1,1,1,3,3,3-hexafluoroisopropoxy benzenesulfenate. Dioxyphosphoranes were formed in all cases. The structures of these materials are discussed. Products of condensation reactions of **1** and **2** were also obtained and structural features are noted.

Recently the interesting compounds **1** and **2** became available.[1] A number of phosphoranes derived from them were prepared and their structures and ligand reorganizations were studied by variable temperature NMR. It has been pointed out that **1** and methyl substituted derivatives have little interaction between the *p*-electrons on nitrogen and vacant orbitals on phosphorus. The structural constraint forces the nitrogen to remain pyramidal, and this leads to restoration of the nitrogens donor properties.[2] In general nitrogens adjacent to phosphorus are sp^2 hybridized and the lone pair in the *p*-orbital is not basic.[3] Derivatives of **1** form bis-adducts with borane, and one of these has had its structure determined by X-ray analysis. The structure of the adduct supports the suggestion that the nitrogen is sp^3 hybridized.



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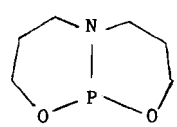


2

Recently, experimental results and theoretical calculations have indicated that in tricoordinated phosphorus compounds containing P—N bonds that there is a

correlation between $J_{^{31}P-^{15}N}$ and the hybridization at the nitrogen.[4] This interesting development must be viewed with caution and new examples are needed.

Over the years considerable evidence has accumulated that many trivalent phosphorus compounds react with a variety of peroxides by a direct insertion process which has been dubbed "biphilic insertion".[5] Much of the evidence for this mechanism has arisen from structure reactivity studies. The biphilic insertion mechanism involves tricoordinate phosphorus proceeding directly to pentacoordinate phosphorus via a transition state which has pentacoordinate character. If the tricoordinated compound contains a sterically strained ring then the possibility of loss of ring strain is present in this type of conversion. On the other hand if the reaction involves a change from tricoordinate phosphorus to tetracoordinate then increased strain in the ring may be found in the conversion.

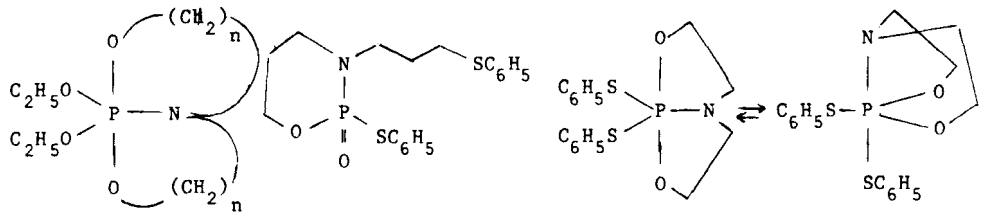
There is considerable evidence that the rings in **1** are strained. The compound is very unstable and it undergoes ring opening polymerization rapidly at room temperature. This process is probably catalyzed by traces of moisture. Compound, **2**, does not polymerize and it can be handled without difficulty.

It was the purpose to this work to study the chemistry and several reactions and the products of the reactions of **1** and **2**.

RESULTS AND DISCUSSION

The NMR spectral data for the compounds studied are collected in Tables I and II. The $J_{^{31}P-^{15}N}$ coupling constants of **1** and **2** are 62 Hz and 74 Hz respectively. The coupling in **1** is that expected for a nitrogen which is very nearly sp^3 hybridized. A value of $J_{^{31}P-^{15}N}$ of ca. 50 Hz has been assigned for sp^3 nitrogen and ca. 91 Hz for sp^2 hybridized nitrogen.[4] The J value found for **2** indicates that it is much closer to sp^2 hybridization than **1**. This result is not unexpected. There is considerably more flexibility in this molecule than is present in the rigid **1**. It is interesting to note that the preferred conformation of trivalent phosphorus P—N compounds where free rotation is possible about the P—N bond has the *p*-orbital on nitrogen orthogonal to the orbital with the lone pair on phosphorus. Clearly the rings of **2** preclude this arrangement.

The reactions of **1** and **2** with diethyl peroxide have now been conducted. The products of the reactions are assigned the structures **3** and **4** on the basis of NMR spectral data. In particular the ^{31}P NMR chemical shifts are those expected. The ^{1}H NMR data suggest the indicated structures. Rapid intramolecular ligand reorganization cannot be ruled out. A more quantitative investigation of these reactions has now been conducted. Reaction of **1** with highly purified diethyl peroxide in methylene chloride at 0°C proceeded smoothly and after 7 days an 88% yield of **3** was obtained. Compound, **2**, and diethyl peroxide in methylene chloride at the same concentration used with **1** required 30 days at room temperature to form 89% of **4**. The same reactants in the absence of solvent took 7 days at room temperature to yield 95% of **4**. These results strongly support the biphilic insertion mechanism for the reactions of **1** and **2** with diethyl peroxide. It should be noted that there are two possible modes of entry by the two oxygens. For the reaction of **1**, either equatorial-equatorial or apical-equatorial. Compound, **2**, could in principle have the two



3 n = 2

4 n = 3

5 6 6a

oxygens entering the two apical positions. This is extremely unlikely for **1**. Both rings would be required to be diequatorial and considerable strain would be introduced.

The above conclusion would be supported if it could be shown that **2** is a much better nucleophile than **1**, i.e., the P(III) to P(IV) transformation is faster for **2** than **1**.

When **2** was allowed to react with diphenyl disulfide at room temperature in solution the thiophosphate, **5**, was produced in seconds. This compound is that expected if **2** attacks upon a sulfur to form an intermediate phosphonium salt and thiophenoxide ion. Collapse of this salt by nucleophilic attack on one of the oxygen-bearing carbons yields **5**. This overall mechanism has received abundant support from many sources.[6] Compound, **1**, was heated with diphenyl disulfide at 58°C for 1 hr. At that time the ^{31}P NMR spectrum had a major resonance at δ-19. This is attributed to the phosphorane **6** which was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as with mass spectrometry. The same material was obtained by heating **1** and diphenyl disulfide under reflux in tetrahydrofuran for 10.5 hr. Under these conditions two other components were formed. These results strongly support the supposition that **2** is more nucleophilic than **1**. They do not prove that **6** was formed via an ionic path. They are suggestive that such a sequence is favored. It is interesting to note that **6** appears to be the only phosphorane ever isolated with two sulfurs bonded to phosphorus that are not in a ring. Previous attempts to prepare such materials have always yielded a tricoordinated phosphorus compound and a disulfide.[7] The NMR spectral data require that **6** be present as an intermediate or transition state. Whether **6a** is in equilibrium with **6** cannot be delineated from the data.

Compounds, **1** and **2**, have been allowed to react with trifluoroethoxy benzenesulfenate, **7**, and 1,1,1,3,3,3-hexafluoroisopropoxy benzenesulfenate, **8** to give the phosphoranes, **9**, **10**, **11** and **12**. In the case of **9** and **10** two trigonal bipyramidal structures, TBP, need to be considered, the pairs **9**, **9a** and **10**, **10a**. In the case of **11** and **12** three TBP structures must be considered eq. **11**, **11a**, **11b**, etc. In principle SP structures require consideration. These molecules do not have those special features which are present in phosphoranes that have been shown to favor square pyramidal, SP, structures in the low energy form.[8]

The ^{1}H NMR spectra of all four of these compounds require that structures **9**, **10**, **11**, **12** or **11a**, **12a** be present as transition states or intermediates. For example the CH_2O hydrogens are equivalent in **9** as are the CH_2N hydrogens. That is not the

TABLE I

^{31}P, ^{19}F and ^{1}H NMR Data[a]

Compound	^{31}P	^{1}H				°C	^{19}F
1	139.0[b,c]	2.43–3.84 (m)[d]					
2	128.9[b]	0.89–1.86 (m) 4H	2.40–3.38 (m) 4H	3.52–4.35 (m)[b] 4H			
3	−43.5[e]	1.22 (t) 6H J_{HCCH} = 7.0	3.15 (d of t) 4H J_{HCNP} = 11.4 J_{HCCH} = 6.0	3.85 (d of t) 4H J_{HOCP} = 12.0 J_{HCCH} = 6.0	3.95 (d of q)[e] 4H J_{HOCP} = 11.0 J_{HCCH} = 7.0		
4	−69.9[f]	1.17 (d of t) 6H J_{HCCH} = 7.0 J_{HCCOP} = 2.0	1.52–2.18 (m) 4H	2.80–3.40 (m) 4H	3.50–4.19 (m)[f] 8H		
5	22.3[b]	1.36–2.52 (m) 4H	2.70–3.79 (m) 6H	3.96–4.60 (m) 2H	7.26–8.06 (m)[b] 10H		
6	−19.2[d]	2.62 (d of t) 4H J_{HCNP} = 13.5 J_{HCCH} = 7.0	3.42 (d of t) 4H J_{HCOP} = 12.0 J_{HCCH} = 7.0	6.96–7.65 (m)[d] 10H			
9	−43.3[b]	3.13 (d of t) 4H J_{HCCH} = 6.0 J_{HCNP} = 12.0	3.97 (d of t) 4H J_{HCOP} = 12.0 J_{HCCH} = 6.0	4.33 (d of q)[b] 4H J_{HCCF} = 9.0 J_{HCOP} = 9.0		25 −60	−81.77 (t)[b] J_{FCCH} = 8.6 −81.19 (t) J_{FCCH} = 8.0

10	−46.5[b]	3.10 (d of t) 4H J_{HCNP} = 11.6 J_{HCCH} = 7.1	3.99(d of t) 4H J_{HCOP} = 13.1 J_{HCCH} = 6.8	5.44 (m)[b] 2H		25	−80.99 (d)[b] J_{FCCH} = 5.9
11	−72.2[b]	1.21–1.81 (m) 4H	2.4–3.0 (m) 4H	3.81 (d of t) 4H J_{HCOP} = 17.0 J_{HCCH} = 7.5	4.15 (d of q)[d] 4H J_{HCCF} = 8.5 J_{HCOP} = 6.5	25 −72	−83.20 (t)[b] J_{FCCH} = 9.0 −79.8 (t) J_{FCCH} = 8.8
12	−77.1[b,g]	1.8 (m) 4H	2.9 (m) 4H	3.90 (d of t) 4H J_{HCCH} = 7.0 J_{HCOP} = 1.7	5.5 (m)[b,g] 2H	25	−80.8 (d)[b,g] J_{FCCH} = 6.2
13	−41.6[d]	1.43–4.60 (m) 12H	1.82 (s)[b] 6H				
14	−41.2[f]	1.70–4.60 (m) 12H	7.2–7.8 (m)[f] 10H				
15	−36.5[f]	1.00–4.70 (m) 12H	7.0–8.3 (m)[f] 8H				

[a]See Experimental for details of NMR experiments.
[b]Solvent is $CDCl_3$.
[c]Lit[1a] 139.6.
[d]Solvent is C_6D_6.
[e]Solvent is CH_2Cl_2(ext. lock).
[f]Solvent is CD_2Cl_2.
[g]Spectrum was run at −10°.

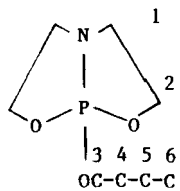
TABLE II

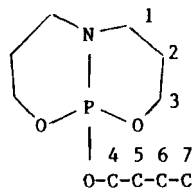
^{13}C NMR Data[a]

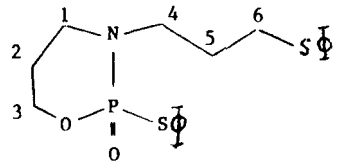
Compound/ Carbon[b]	1	2	3	4	5	6	7	8
1[c]	53.7 (d) J_{CNP} = 6.0	67.5 (d) J_{COP} = 10.0						
2[d]	46.3 (d) J_{CNP} = 5.5	24.1 (d) J_{CCOP} = 6.5	62.3 (d) J_{COP} = 1.8					
3[e]	42.9 (d) J_{CNP} = 22	58.3 (s)	62.67 (d) J_{COP} = 7.1	16.6 (d) J_{CCOP} = 8.4				
4[e]	51.6 (d) J_{CNP} = 3.2	27.6 (d) J_{CCOP} = 4.4	60.8 (d) J_{COP} = 9.8	63.1 (d) J_{COP} = 12.0	16.5 (d) J_{CCOP} = 8.3			
5[d]	47.6 (d) J_{CNP} = 1.9	26.4 (d) J_{CCOP} = 4.9	69.7 (s)	47.2 (s)	27.9 (d) J_{CCNP} = 1.9	30.8 (s)	plus resonances in the 125–135 range	
6[e]	42.4 (d) J_{CNP} = 20.1	61.1 (d) J_{COP} = 5.7	133.5 (d) J_{CSP} = 5.7	134.5 (d) J_{CCSP} = 4.7	127.6 (s)	128.5 (s)		
9[d]	41.7 (d) J_{CNP} = 22.7	58.4 (s)	63.8 (d of q) J_{CCF} = 35.9 J_{COP} = 7.8	127.2 (d of q) J_{CF} = 273.1 J_{CCOP} = 5.9				
10[d]	41.9 (d) J_{CNP} = 22.5	59.5 (d) J_{COP} = 0.9	72.6 (d of h) J_{COP} = 9.3 J_{CCF} = 34.5	121.1 (q) J_{CF} = 279.9				
11[d]	51.5 (d) J_{CNP} = 2.4	27.1 (d) J_{CCOP} = 5.4	62.3 (d) J_{COP} = 10.6	64.8 (d of q) J_{COP} = 11.2 J_{CCF} = 34.8	123.4 (d of q) J_{CF} = 274.6 J_{CCOP} = 12.5			
12[d,f]	51.53 (d) J_{CNP} = 3.4	27.2 (d) J_{CCOP} = 5.3	63.6 (d) J_{COP} = 10.5	72.5 (d of h) J_{COP} = 12.7 J_{CCF} = 33.9				
13[e]	48.5 (d) J_{CNP} = 5.1	25.9 (d) J_{CCOP} = 2.7	65.9 (d) J_{COP} = 10.1	128.8 (s)	10.8 (d) J_{CCOP} = 12.4			
13[e,g]	48.5 (d) J_{CNP} = 5.1	25.9 (d) J_{CCOP} = 2.7	65.9 (d) J_{COP} = 10.1	not visible	10.8 (d) J_{CCOP} = 12.4			
13[e,h]	46.9–47.1	22.3–24.4	64.9–65.3	130.9 (d) J_{COP} = 3.8 124.1 (d) J_{COP} = 2.5	9.9–10.5			

14[c]	48.1 (d) J_{CNP} = 5.5	25.4 (d) J_{CCOP} = 2.9	66.6 (d) J_{COP} = 9.9	133.3 (s)	131.7 (d) J_{CCOP} = 12.7	126.2 (s)	128.2 (s)	127.2 (s)
14[e,i]	48.1 (d) J_{CNP} = 5.5	25.4 (d) J_{CCOP} = 2.9	66.0 (d) J_{COP} = 9.9	not visible	131.7 (d) J_{CCOP} = 12.7	126.2 (s)	128.2 (s)	127.2 (s)
14[e,j]	Broad resonances in the 25–66 range		128.5 (d) J_{COP} = 2.3 135.6 (d) J_{COP} = 3.8	130.3 (d) J_{CCOP} = 12.7			Broad resonances in the 126–128 range	
15[e]	48.3 (d) J_{CNP} = 5.4	25.3 (d) J_{CCOP} = 3.1	66.7 (d) J_{COP} = 10.4	134.8 (s)	122.4 (d) J_{CCOP} = 13.8		plus resonances in the 120–126 range	
15[e,k]	48.3 (d) J_{CNP} = 5.4	25.3 (d) J_{CCOP} = 3.1	66.7 (d) J_{COP} = 10.4	not visible	not visible		plus resonances in the 120–126 range	
15[e,j]	Broad resonances in the 25–66 range			131.2 (s) 137.8 (d) J_{COP} = 7.7	121.8 (d) J_{CCOP} = 14.2 122.2 (d) J_{CCOP} = 13.1		Broad resonances in the 120–126 range	

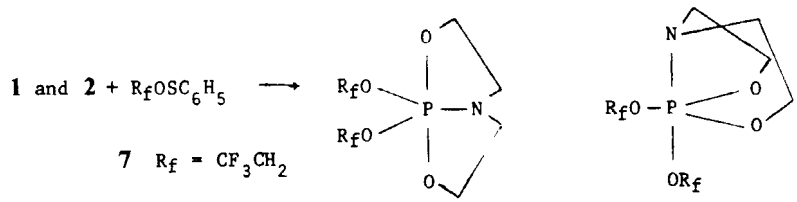
[a] See Experimental for details of NMR experiments.
[b] The numbering systems are as follows:

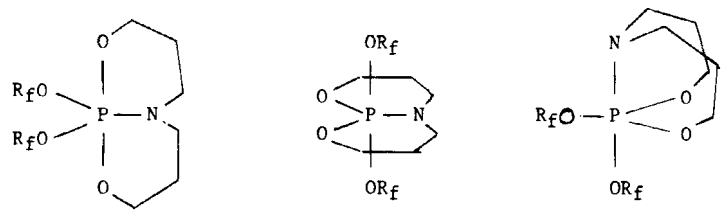






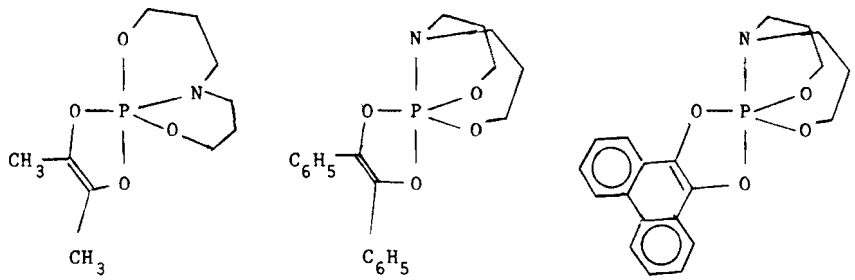
[c] Solvent is C_6D_6.
[d] Solvent is $CDCl_3$.
[e] Solvent is CD_2Cl_2.
[f] Spectrum was run at −10°C.
[g] Spectrum run at −63°C.
[h] Spectrum run at −85°C.
[i] Spectrum run at −34°C.
[j] Spectrum run at −80°C.
[k] Spectrum run at −45°C.





case in **9a**. This does not mean that **9a** cannot be present. Of considerable interest are the various coupling constants found for selected nuclei of these materials. Compounds, **9** and **10** have J_{HCOP} = 12 Hz and 13 Hz respectively for the ring hydrogens while those of **11** and **12** are 17 Hz. In general larger couplings are associated with H—C—O—P equatorial.[9] A similar trend has been noted for P—F couplings.[10] Compounds, **9** and **10** have J_{POC} < 1 Hz for the ring carbons whereas those for **11** and **12** are 10.5 Hz. The structural implications of these latter findings are certainly indicative of significantly different geometries for the pairs of the two series. A satisfactory explanation of these results is found if **9** and **10** are the major contributors in that series and **11a** and **12a** are the favored structures in the other series. The greater apicophilicities of the fluorinated ligands over the ring CH_2O groups accounts for **11a** and **12a** as the favored structures. Analogous structures from **9** and **10** are not favored because the 5-membered rings are forced into the highly strained diequatorial disposition. Variable temperature ^{19}F NMR studies of **9** and **11** showed no changes over the temperature range investigated 25 to −60 and −72°C respectively and thus no statement concerning intramolecular ligand reorganization can be made.

The condensation product, **13**, of **2** and biacetyl was shown by variable temperature NMR studies to have the structure depicted with one 6-membered ring spanning two equatorial position.[1b] The condensation products of **2** with benzil and phenanthrenequinone, **14** and **15** respectively have now been prepared. The variable temperature ^{13}C NMR spectra of **14** show that below −34°C there are nonequivalent olefinic carbons δ 135.6 (J_{POC} = 3.8 Hz) and δ 128.5 (J_{POC} = 2.3 Hz). The $\Delta G^{\ddagger}$



13 14 15

for the process that renders them equivalent is 11 kcal/mole. The pairs of carbons of the bicyclic moiety remained equivalent to $-80°C$. Similar ^{13}C NMR behavior was found for **15**. The olefinic and ipso carbons adjacent to the olefinic carbons became nonequivalent, $\Delta G^{\ddagger} = 11$ kcal/mole. The carbons of the bicyclic ring system remained as equivalent pairs. This behavior is totally different from that found for **13** and it implies structures **14** and **15** as written. There is a SP structure which fits the ^{13}C NMR data. It requires that the 6-membered ring span from apical to basal positions. This is more strained than the structures illustrated and there seems to be no reason to consider it further. The interesting thing about **14** and **15** is that they violate the observation that nitrogen favors an equatorial position i.e. its apicophilicity is less than oxygen. This effect is of course found in **13**. A tentative explanation for this reversal is that nonbonding electrons on the apical oxygen are delocalized into the aromatic ring system and that this delocalization is promoted by further delocalization of the non-bonding pair on the apical nitrogen towards phosphorus. This suggestion is currently being tested by appropriate experiments.

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). All ^{19}F chemical shifts are reported in parts per million relative to trichlorofluoromethane. ^{13}C chemical shifts are reported in parts per million relative to tetramethylsilane. 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. All spectra were recorded at probe temp. (24°C) unless stated otherwise.

All manipulations were carried out in an inert atmosphere. All solvents were freshly distilled and scrupulously dried.

Preparation of 2,8-Dioxa-5-aza-1-phosphabicyclo[3.3.0]octane, **1**. This was prepared according to the method of Denney *et al.*[1b]

Preparation of 2,10-Dioxa-6-aza-1-phosphabicyclo[4.4.0]decane, **2**. This was prepared according to the method of Denney *et al.*[1b]

Reaction of **1** *with Diethyl Peroxide.* To a stirred solution of **1** (0.49 g, 0.0037 mol) of **1** in dichloromethane at 0°C was added diethyl peroxide (0.41 g, 0.0046 mol). The reaction mixture was allowed to warm to room temp and after two hours the P(III) to P(V) ratio was 25 : 75. The reaction mixture was stored at 0°C for 5 days, at this point the P(III) to P(V) ratio was 90 : 10. All attempts to isolate the product **3** failed. The spectral data were obtained on the solution of the product.

Reaction of **2** *with Diethyl Peroxide.* To a solution of **2** (0.32 g, 0.002 mol) in dichloromethane-d_2 (2 ml) was added diethyl peroxide (0.18 g, 0.002 mol) in dichloromethane (1 ml). The reaction mixture was sealed in a 10 mm NMR tube and the course of the reaction was monitored by ^{31}P NMR spectroscopy. The ratio of P(III) to P(V) at selected times is as follows: 1 day, 98.2; 5 days, 73 : 27; 9 days, 67 : 33, 19 days, 31 : 69; 30 days, 11 : 89. When the reactants were allowed to react in the absence of solvent the ratios were: 3.7 days, 41 : 59; 5.8 days, 7 : 93, 7 days, 5 : 95.

The phosphorane, **4**, was isolated by molecular distillation (block 50°C, 0.02 mm).

Reaction of **1** *with Diphenyl Disulfide*

Reaction A. Diphenyl disulfide (0.37 g, 0.0017 mol) and **1** (0.22 g, 0.0016 mol) were mixed at room temp. The reaction mixture was heated at 58°C for 1 hr. The ^{31}P NMR spectrum at this time showed only one absorption at δ −19.2 (C_6D_6).

Reaction B. To a solution of **1** (0.34 g, 0.0025 mol) in tetrahydrofuran (2 ml) at room temp. was added a solution of diphenyl disulfide (0.55 g, 0.0025 mol) in tetrahydrofuran (2 ml). The reaction mixture was heated to reflux. The progress of the reaction was monitored by observing the ^{31}P NMR spectrum of the reaction mixture: 1 hr, δ −28.6 (1%), δ −18.0 (4%), δ +138.0 (95%); 7 hr, δ −28.6 (20%), δ −18.0 (63%), δ −12.6 (2%), δ +138.0 (12%); 10.5 hr, δ −28.6 (18%), δ −18.0 (58%), δ −12.6 (17%).

Preparation of 2,2,2-Trifluoroethyl Benzenesulfenate, **7**. This was prepared according to the method of Denney *et al.*[11]

Preparation of **5**. This was prepared by the method of Denney *et al.*[1b]

Reaction of **1** *with 2,2,2-Trifluoroethyl Benzenesulfenate.* To a stirred solution of 2,2,2-trifluoroethyl benzenesulfenate (4.16 g, 0.02 mol) in pentane (30 ml) at −30°C was added **1** (1.33 g, 0.01 mol) dissolved in pentane (10 ml). The reaction mixture was allowed to warm to room temp. After having been stirred for two hours the reaction mixture was cooled to −20°C and it was filtered. The filtrate was concentrated at reduced pressures to yield a solid. This solid was purified by sublimation (65°C, 0.005 mm) to yield 1.8 g (54.4%) of **9**, m.p. 67–68°C.

Reaction of **2** *with 2,2,2-Trifluoroethyl Benzenesulfenate.* To a stirred solution of 2,2,2-trifluoroethyl benzenesulfenate (4.16 g, 0.02 mol) in pentane (30 ml) at −30°C was added **2** (1.61 g, 0.01 mol) in pentane (10 ml). The reaction mixture was allowed to warm to room temp. It was stirred for 0.5 hr. The reaction mixture was cooled to −40°C and it was filtered. The filtrate was concentrated at reduced pressures and the residual oil was purified by molecular distillation (62°C, 0.01 mm) to give 1.50 g (41.5%) of **11**.

Preparation of **10**. To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propanol (2.69 g, 0.016 mol) and triethylamine (1.62 g, 0.016 mol) in pentane (40 ml) at −78°C was added benzenesulfenyl chloride (2.31 g, 0.016 mol). The reaction mixture was allowed to warm to room temp. and it was stirred for 1 hr. The solid was removed by filtration. The filtrate was cooled to −78°C and to this was added **1** (0.53 g, 0.004 mol). The reaction mixture was allowed to warm to room temp. and it was stirred for 1 hr. It was then cooled to −78°C and the solid was separated by filtration. The filtrate was concentrated at reduced pressures and the residual oil was purified by molecular distillation (55°C, 0.05 mm).

Preparation of **12**. To a solution of 1,1,1,3,3,3-hexafluoro-2-propanol (2.69 g, 0.016 mol) and triethylamine (1.62 g, 0.016 mol) in pentane (40 ml) at −78°C was added benzenesulfenyl chloride (2.31 g, 0.016 mol). The reaction mixture was allowed to warm to room temp. and it was stirred for 1 hr. The solid was removed by filtration. The filtrate was cooled to −78°C and to this was added **2** (0.64 g, 0.004 mol). The reaction mixture was stirred at this temp. for 1 hr and it was then filtered. The filtrate was concentrated at reduced pressures at 0°C to yield an oil which was unstable at room temp. If stored at room temp. for 12 hr the ^{31}P NMR spectrum of the material showed one absorption at δ 3.85 ($CDCl_3$).

Preparation of **13**. This was reported previously.[1b]

Preparation of **14**. To a stirred solution of **2** (0.322 g, 0.002 mol) in dichloromethane-d_2 (1.5 ml) was added benzil (0.42 g, 0.002 mol) in dichloromethane-d_2 (2 ml). The reaction mixture was stirred at room temp. for 10 min. All attempts to purify the material failed.

Preparation of **15**. To a stirred solution of **1** (0.322 g, 0.002 mol) in dichloromethane-d_2 (2 ml) at −15°C was added phenanthrenequinone (0.416 g, 0.002 mol) in dichloromethane-d_2. The mixture was allowed to

warm to room temp. and it was centrifuged. All spectral data were obtained using the supernatant liquid. Attempts to purify this material failed.

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