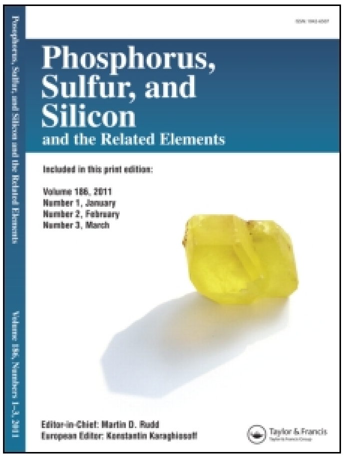


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PREPARATION AND STRUCTURAL STUDIES OF A NUMBER OF HETEROCYCLIC PHOSPHORANES

Donald B. Denney[a]; Dorothy Z. Denney[a]; Lun-Tsu Liu[a]
[a] Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey

To cite this Article Denney, Donald B. , Denney, Dorothy Z. and Liu, Lun-Tsu(1985) 'PREPARATION AND STRUCTURAL STUDIES OF A NUMBER OF HETEROCYCLIC PHOSPHORANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 22: 1, 71 — 84

To link to this Article: DOI: 10.1080/03086648508073356

URL: http://dx.doi.org/10.1080/03086648508073356

Phosphorus and Sulfur, 1985, Vol. 22, pp. 71–84
0308-664X/85/2201-0071/$20.00/0

PREPARATION AND STRUCTURAL STUDIES OF A NUMBER OF HETEROCYCLIC PHOSPHORANES

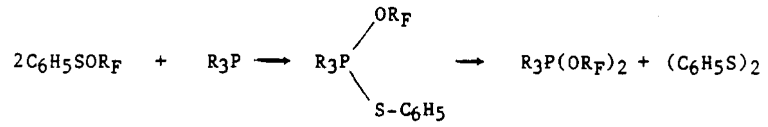
DONALD B. DENNEY,* DOROTHY Z. DENNEY and LUN-TSU LIU

Contribution from the Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

(*Received July 25, 1984; in final form August 23, 1984*)

A series of monocyclic five-membered ring containing trivalent phosphorus compounds with oxygen, nitrogen and sulfur bonded to phosphorus, in various combinations has been allowed to react with trifluoroethyl and 1,1,1,3,3,3-hexafluoroisopropyl benzenesulfenates. In some cases, pentacoordinated phosphorus compounds resulted. These materials have been studied by various NMR techniques. The same trivalent phosphorus compounds were allowed to react with 3,4-(bistrifluoromethyl)1,2,dithiete. In some cases phosphoranes were formed and they were also studied by NMR.

It has been well established that 5-membered ring containing phosphoranes are usually more stable than the corresponding acyclic substances. Initial studies focused on these materials because of their stability and this seminal work provided valuable insights into the chemistry of phosphoranes.[1] Most of these studies concerned 5-membered ring containing compounds with oxygen bonded to phosphorus. More recently studies of compounds containing nitrogen and sulfur bonded to phosphorus have been reported.[1e] Recently it has been shown that trifluoroethyl benzenesulfenate, **1**,[2a] and 1,1,1,3,3,3,-hexafluoroisopropyl benzenesulfenate,[2b] **2**, usually react with tricoordinated phosphorus compounds to give mixed thiophenoxyalkoxyphosphoranes, **3** and **4**. These materials often further react with another mole of **1** and **2** to give dialkoxyphosphoranes, **5** and **6**.



$$2C_6H_5SOR_F + R_3P \longrightarrow R_3P{\genfrac{}{}{0pt}{}{OR_F}{S\text{-}C_6H_5}} \longrightarrow R_3P(OR_F)_2 + (C_6H_5S)_2$$

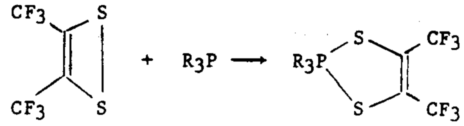
1 $R_F = CH_2CF_3$
2 $R_F = CH(CF_3)_2$
3 $R_F = CH_2CF_3$
4 $R_F = CH(CF_3)_2$
5 $R_F = CH_2CF_3$
6 $R_F = CH(CF_3)_2$

It has also been demonstrated that the dithiete, **7**, often reacts with trivalent phosphorus compounds to give phosphoranes, **8**, which contain a 5-membered ring with two sulfurs bonded to phosphorus.[3] All of these reactions take place under

---

*Author to whom all correspondence should be addressed.

quite mild conditions and thus it has been possible on many occasions to intercept otherwise quite unstable phosphoranes.

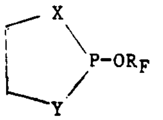


7 **8**

It has been the purpose of this work to study the reactions of a variety of tricoordinated phosphorus compounds containing one 5-membered ring and containing various heteroatoms with **1**, **2** and **7**.

RESULTS AND DISCUSSION

The various starting materials were prepared by conventional means and these are outlined in the Experimental Section. The compounds studied are illustrated below. Their ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectral data are collected in Tables I and II.



9 $X=Y=NCH_3$; $R_F=CH_2CF_3$

10 $X=Y=NCH_3$; $R_F=CH(CF_3)_2$

13 $X=Y=S$; $R_F=CH_2CF_3$

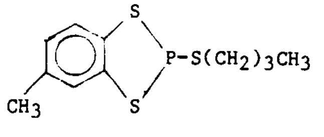
14 $X=Y=S$; $R_F=CH(CF_3)_2$

11 $X=NCH_3$; $Y=O$; $R_F=CH_2F_3$

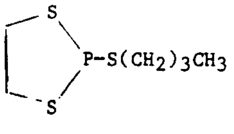
12 $X=NCH_3$; $Y=O$; $R_F=CH(CF_3)_2$

15 $X=S$; $Y=O$; $R_F=CH_2CF_3$

16 $X=S$; $Y=O$; $R_F=CH(CF_3)_2$



17



18

Reaction of **9** with two moles of **1** gave a distillable material, **19**, whose ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectral data are collected in Tables I and II. That this substance is a phosphorane containing a single 5-membered ring is strongly supported by the ^{31}P chemical shift, δ -58. The structure of **19**, a trigonal bipyramid, TBP, is assigned as illustrated with the provision that rapid ligand reorganization is occurring which renders the various groups equivalent. Such a process is not unexpected

TABLE I

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

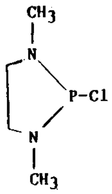
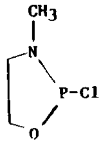
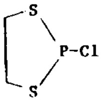
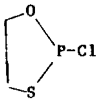
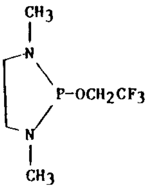
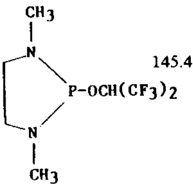
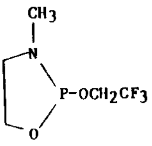
Compound	^{31}P	^{1}H				^{19}F	
						T °C	
	165.0[b,i]	2.63(d) 6H J_{HCNP} = 14.8		2.66–2.96(m)[b] 4H			
	168.3[b]	2.78(d) 3H J_{HCNP} = 15.0	2.33–3.45(m) 2H	4.23–4.70(m)[c] 2H			
	168.1[b]	3.43–4.00(m)[c]					
	204.2[b]	2.93–3.70(m) 2H	4.27–5.10(m)[c] 2H				
9 	140.7[b]	2.73(d) 6H J_{HCNP} = 13.0	2.93–3.57(m) 4H	2.93 (d of q)[c] 2H J_{HCCF} = 7.0 J_{HCOP} = 7.0		26	−81.51 (d of t)[c] J_{FCCH} = 8.7 J_{FCCOP} = 4.3
10 	145.4[c]	2.70(d) 6H J_{HCNP} = 13.0	3.0–3.4(m) 4H	4.23–4.80(m)[c] 1H		26	−80.68 (d of d)[c] J_{FCCH} = 5.9 J_{FCCOP} = 5.9
11 	140.8[b]	2.75(d) 3H J_{HCNP} = 12.0	2.93–3.30(m) 2H	3.97 (d of q) 2H J_{HCCF} = 8.0 J_{HCOP} = 8.0	3.9–4.5(m)[c]	26	−81.63 (d of t)[c] J_{FCCH} = 8.6 J_{FCCOP} = 5.3

TABLE I (*Continued*)

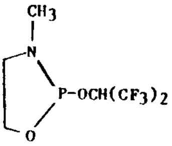
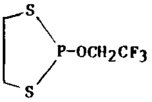
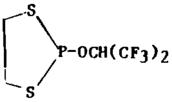
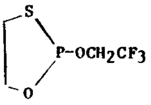
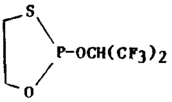
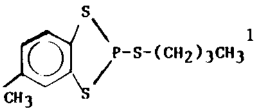
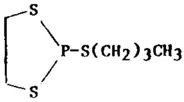
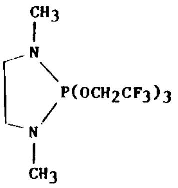
Compound	^{31}P	^{1}H					^{19}F	
							T °C	
12 	147.2^{c}	2.75(d) 3H J_{HCNP} = 12.0	2.93–3.30 2H	3.90–4.76^{c} 3H			26	−75.24(m)^{c}
13 	153.4^{d}	3.92 (d of q) 2H J_{HCCF} = 8.0 J_{HCOP} = 8.0	3.22–3.57(m)^{c} 4H				26	−86.3 (d of t)^{c} J_{FCCH} = 8.4 J_{FCCOP} = 2.0
14 	177.7^{e}	3.10–3.80(m) 4H	4.50(heptet)^{c} 1H J_{HCCF} = 6.0				26	−74.20 (d of d)^{c} J_{FCCH} = 8.3 J_{FCCOP} = 5.9
15 	173.4^{d}	2.63–3.30(m) 2H	3.83–4.68(m) 2H	4.05 (d of q)^{c} 2H J_{HCCF} = 8.0 J_{HCOP} = 8.0			26	−81.0 (d of t)^{c} J_{FCCH} = 8.6 J_{FCCOP} = 4.2
16 	185.7^{e}	2.80–3.40(m) 2H	4.50(heptet) 1H J_{HCCF} = 6.0	4.30–5.00(m)^{c} 2H				−75.20 (d of d)^{c} J_{FCCH} = 6.7 J_{FCCOP} = 6.7
 **17**	108.0^{c}	0.80(m) 3H	1.33(m) 4H	2.25(s) 3H	2.63 (d of t) 2H J_{HCCH} = 7.0 J_{HCSP} = 7.0	6.70–7.50(m)^{c} 3H		
18 	108.0^{c}	0.90(m) 3H	1.60(m) 4H	2.70 (d of t) 2H J_{HCCH} = 6.0 J_{HCSP} = 11.0	3.4(m)^{c} 4H			
19 	−57.8^{c}	2.53(d) 6H J_{HCNP} = 10.0	2.88(d) 4H J_{HCNP} = 12.0	4.25 (d of q)^{c} 6H J_{HCCF} = 8.5 J_{HCOP} = 8.5			26 −60	−81.50(t)^{c} J_{FCCH} = 8.7 −80.64(t)^{c} J_{FCCH} = 8.8

TABLE I (*Continued*)

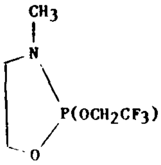
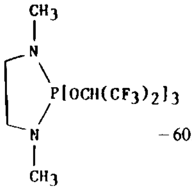
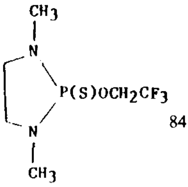
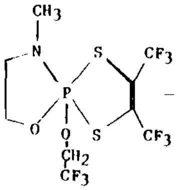
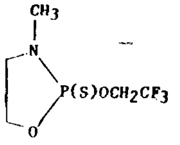
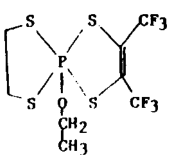
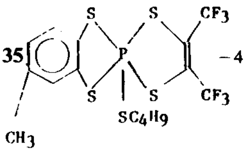
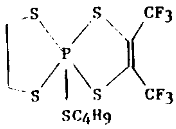
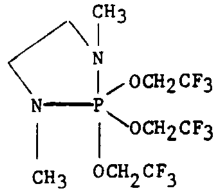
Compound		^{31}P	^{1}H				^{19}F	
							T °C	
20		−63.1[c]	2.90(d) 3H J_{HCNP} = 9.0	2.6–3.3(m) 2H	3.6–4.6(m) 2H	4.2 (d of q)[c] 6H J_{HCCF} = 8.0 J_{HCOP} = 8.0	26	−78.4 (d of t) J_{FCCH} = 8.6
							−60	−81.83(t)[c] J_{FCCH} = 8.5
24	$(C_6H_5\text{-}S\text{-}S\text{-}CH_2)_2$		2.98(s) 4H	7.1–7.6(m)[c] 10H				
27		−60.8[f]	2.10–3.10(m) 4H	2.78(d) 6H J_{HCNP} = 14.0	5.2 (heptet)[f] 3H J_{HCCF} = 7.0		26	−76.60(d)[f] J_{FCCH} = 7.5
29		84.1[c]	2.68(d) 6H J_{HCNP} = 12.5	3.00–3.60(m) 4H	4.36 (d of q)[c] 2H J_{HCCF} = 8.5 J_{HCOP} = 11.0		26	−80.81(t)[c] J_{FCCH} = 8.5
30		−10.7[f]	3.03(d) 3H J_{HCNP} = 13.0	3.26–3.70(m) 4H	3.86–4.73[c] 2H		63	−81.12(t)[g] J_{FCCH} = 8.3 −59.77(s)
							37	−81.1(t)[g] J_{FCCH} = 8.3 −60 (mound)
							−30	−79.77(t)[f] J_{FCCH} = 8.4 −59.68(q) J_{FCCCF} = 12.0 −57.64 (d of q) J_{FCCCF} = 12.0 J_{FCCSP} = 4.4
31		85.0[c]	2.75(d) 3H J_{HCNP} = 13.0	3.20–3.68(m) 2H	4.1–4.68(m) 2H	4.4 (d of q)[c] 2H J_{HCCF} = 8.0 J_{HCOP} = 2.0	26	−80.84(t)[c] J_{FCCH} = 8.6

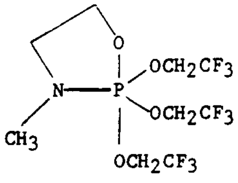
TABLE I (*Continued*)

							^{19}F	
Compound	^{31}P	^{1}H					T °C	
34 	20.3^{c}	3.3(s) 2H	3.63(s) 2H (broad)	4.61^{c} 2H $J_{HCCF} = 8.0$ $J_{HCOP} = 14.0$			26 −73	$-80.28(t)^{c}$ $J_{FCCH} = 8.0$ $-60.47(d)$ $J_{FCCSP} = 2.3$ $-79.90(t)$ $J_{FCCH} = 7.8$ $-60.10(d)$ $J_{FCCSP} = 2.3$
35 	-4.4^{f}	0.87(m) 3H	1.42(m) 4H	2.28(s) 3H	2.95 (d of t) 2H $J_{HCCH} = 7.3$ $J_{CS} = 27.9$	$7.14(m)^{f}$ 3H	26 −70	$-57.6(s)^{f,h}$ $-57.3(s)$
36 	-7.0^{c}	0.97(t) 3H $J_{HCCH} = 6.4$	1.6(m) 4H	3.1 (d of t) 2H $J_{HCCH} = 7.6$ $J_{HCSP} = 24.2$	3.39(s) 2H	$3.63(d)^{i}$ 2H $J_{HCSP} = 1.7$	26 −80	$-58.80(d)^{f}$ $J_{FCCSP} = 1.8$ $-58.70(d)$ $J_{FCCSP} = 1.8$

[a] See experimental for details of nmr experiments.
[b] Solvent is benzene-d_6.
[c] Solvent is chloroform-d.
[d] Solvent is dichloromethane, lock is external.
[e] Material is neat, lock is external.
[f] Solvent is dichloromethane-d_2.
[g] Solvent is toluene-d_8.
[h] The ^{19}F NMR of this sample, run on a Varian 200 MHz spectrometer, shows a single resonance, ht 1/2 = 0.43 Hz.
[i] Lit −167.3 (neat), F. Ramirez, A. V. Patwardhan, H. J. Kugler and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967).



19



20

and is demanded by the various NMR data. In particular the equivalence of the trifluoromethyl groups in the ^{19}F NMR spectrum is a sensitive detector. Variable temperature ^{19}F NMR studies showed no change down to −60°C and it is tempting to conclude that ligand permutation remains rapid on the ^{19}F NMR time scale. Negative evidence of this type can always be explained by a static **19** in which there

TABLE II

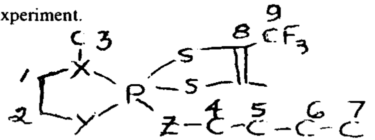
^{13}C NMR data[a]

Cpd.	Carbon 1	2	3	4	5	6	7	8	9	10
9[e]	53.5(d) $J_{CNP} = 10.5$		33.8(d) $J_{CNP} = 24.8$	61.9 (d of q) $J_{CCF} = 25.2$ $J_{COP} = 2.8$	125.0 (d of q) $J_{CF} = 273.7$ $J_{CCOP} = 1.7$					
11[e]	49.5(d) $J_{CNP} = 4.7$	69.7(d) $J_{COP} = 10.5$	31.1(d) $J_{CNP} = 21.8$	61.6 (d of q) $J_{CCF} = 35.1$ $J_{COP} = 11.8$	124.8 (d of q) $J_{CF} = 273.6$ $J_{CCOP} = 2.8$					
12[f]	49.1(d) $J_{CNP} = 5.4$	70.1(d) $J_{COP} = 10.1$	30.8(d) $J_{CNP} = 19.8$	70.1 (d of h) $J_{CCF} = 28.6$ $J_{COP} = 16.8$	122.7 (d of q) $J_{CF} = 281.4$ $J_{CCOP} = 3.4$					
13[f]	42.7(s)			61.8(q) $J_{CCF} = 35.4$	123.7(q) $J_{CF} = 273.7$					
14[f]	41.7(s)			73.9 (d of h) $J_{CCF} = 24.2$ $J_{COP} = 11.7$	121.7 (d of q) $J_{CF} = 283.5$ $J_{CCOP} = 2.2$					
15[f]	31.9(s)	75.2(d) $J_{COP} = 16.2$		62.6 (d of q) $J_{CCF} = 36.1$ $J_{COP} = 7.6$	123.9 (d of q) $J_{CF} = 277.8$ $J_{CCOP} = 4.0$					
16[f]	31.9(s)	75.2(d) $J_{COP} = 15.3$		74.7(m)	121.8 (d of q) $J_{CF} = 277.7$ $J_{CCOP} = 2.0$					
17[e]	138.6(s) $J_{CSP} = 2.3$	135.1(d) $J_{CSP} = 2.3$		32.9(d) $J_{CSP} = 24.3$	33.3(d) $J_{CCSP} = 3.8$	22.1(s)	13.9(s)	Plus resonances at δ 21.1 (s, ring CH_3), 126.1 (d, $J_{CCSP} = 5.7$), 127.49(s), 136.39(s) 125.27(d, CSSP = 5.1)		
18[e]	41.1(s)			34.5(d) $J_{CSP} = 18.4$	33.7(d) $J_{CCSP} = 4.9$	22.3(s)	14.3(s)			
19[e]	41.8(d) $J_{CNP} = 13.8$		37.4(s)	64.7 (d of q) $J_{CCF} = 35.7$ $J_{COP} = 10.4$	122.6 (d of q) $J_{CF} = 278.1$ $J_{CCOP} = 9.3$					
20[e]	48.8(d) $J_{CNP} = 22.6$	58.1(s)	36.5(s)	63.7 (d of q) $J_{CCF} = 35.4$ $J_{COP} = 9.3$	126.2 (d of q) $J_{CF} = 274.0$ $J_{CCOP} = 9.0$					
29[e]	47.9(d) $J_{CNP} = 9.4$		31.9(d) $J_{CNP} = 4.8$	63.3 (d of q) $J_{CCF} = 28.7$ $J_{COP} = 2.3$	[c]					
30[g]	53.0(d) $J_{CNP} = 15.7$	61.6(d) $J_{COP} = 2.0$	35.3(d) $J_{CNP} = 6.4$	66.1 (d of q) $J_{CCF} = 36.3$ $J_{COP} = 12.7$	[c]			[c]	[c]	
31[e]	49.9(d) $J_{CNP} = 13.1$	65.8(d) $J_{COP} = 5.6$	31.9(d) $J_{CNP} = 7.1$	64.6 (d of q) $J_{CCF} = 36.7$ $J_{COP} = 3.9$	[c]					
34[h]	41.1(d) $J_{CSP} = 3.1$			65.7 (d of q) $J_{CCF} = 37.3$ $J_{COP} = 12.7$	[c]			[c]	121 (d of q)[i] $J_{CF} = 264$ $J_{CCSP} = 16$	
35[g]	135.6(d) $J_{CSP} = 2.1$	131.9(d) $J_{CSP} = 1.9$		43.2(d)[j] $J_{CSP} = 9.3$	32.5(d)[j] $J_{CCSP} = 4.9$	22.0(s)	13.4(s)	[c]	120.5(q) $J_{CF} = 278.0$	[d]
36[e]	41.6(s)			42.5(d) $J_{CSP} = 9.0$	32.3(d) $J_{CCSP} = 6.1$	22.2(s)	13.8(s)	[c]	120.6(q) $J_{CF} = 270.9$	

---

[a] See Experimental for details of nmr experiment.

[b] Numbering systems are as follows.



[c] Impossible to assign either a chemical shift or a coupling constant.

[d] Additional resonances in the aromatic region plus an absorption at δ 21.0 due to the aromatic-CH_3 carbon.

[e] The solvent is chloroform-d.

[f] The sample is neat, the lock is external.

[g] The solvent is dichloromethane $-d_2$.

[h] The solvent is chloroform $-$d, the temp is $-20°$.

[i] The data are not as accurate as would be possible because of the instability of the compound.

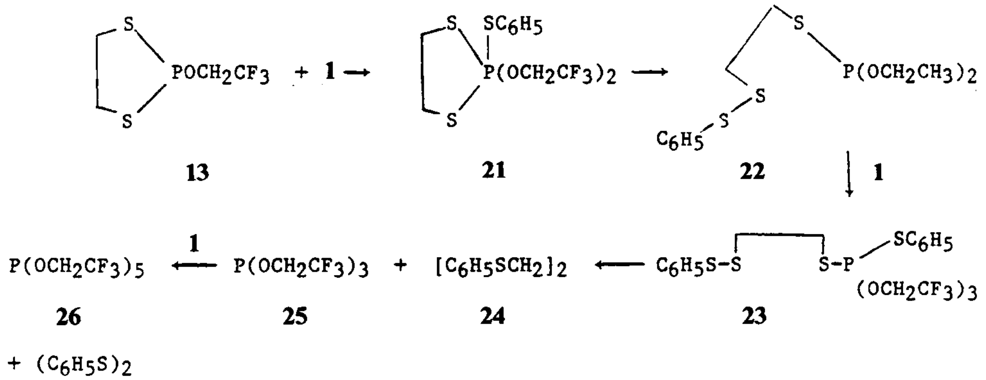
[j] These assignments may be reversed.

[k] Additional resonances in the aromatic region.

are accidental identical shift values. It should also be noted that a square pyramidal, SP, structure is not acceptable unless the above mentioned conditions are met. SP structures have only been found with phosphoranes containing two 5-membered rings.

Reaction of **11** with 2 moles of **1** affords a material whose NMR spectral data are in agreement with a phosphorane, **20**. Once again rapid ligand reorganization is indicated and this process is not apparently slowed on cooling.

Compound, **13**, reacted with 2 moles of **1** to give as the isolated products pentakis(trifluoroethoxy) phosphorane, **26**, diphenyl disulfide and the compound, **24**. These products can be accounted for by a sequence of reactions in which P—S bonds are broken in intermediates **21** and **23** with the formation of disulfide linkages. Such reactions are not unknown and they have been discussed, recently.[4]



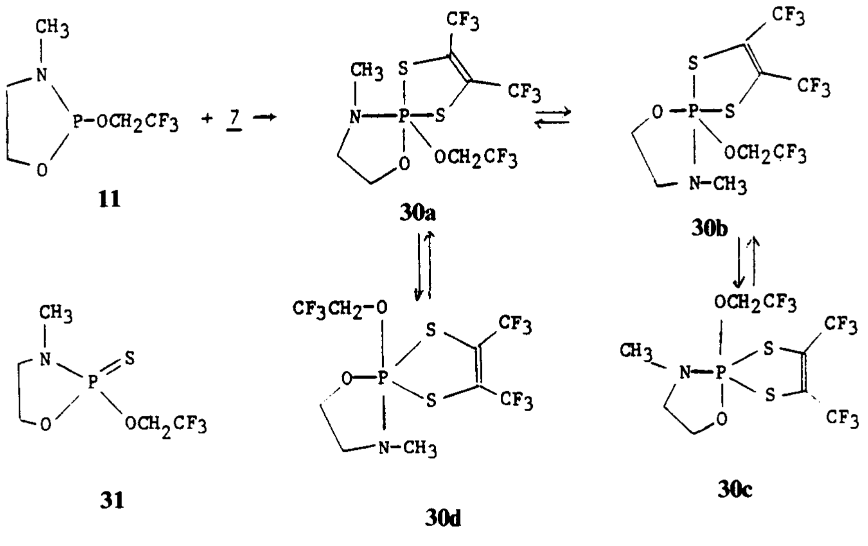
Compound, **15**, reacted with two moles of **1** to give an unstable material with a broad absorption in its ^{31}P NMR spectrum at δ -21. Because of the inherent instability of this material no further studies have been conducted.

Compound, **10**, reacted with two moles of **2** to give an unstable material with δ ^{31}P -61. This substance decomposed on attempted isolation. It seems likely that it is the appropriate phosphorane, **27**. Other NMR data for this substance are collected in Table I. Similarly, **12**, **14**, and **16** reacted with **2** to give materials that were too unstable to be isolated. In the case of **14** attempted isolation yielded the phosphorane, $C_6H_5P(OCH(CF_3)_2)_4$, **28**. This material has been obtained earlier from the reaction of tris(1,1,1,3,3,3-hexafluoropropyl) phosphite and **2**.[2b] A sequence similar to that used to explain the formation of **16** and **24** accounts for the production of **28**.

The results of this portion of the investigation indicate that the hexafluoroisopropoxy phosphoranes are less stable than the corresponding trifluoroethoxy compounds. Part of the instability is due to steric strain in these more highly congested molecules. In some cases the greater acidity of the hydrogen on the carbon bonded to oxygen may also contribute to the compounds inherent instability.

The reaction of **9** with **7** did not yield a phosphorane. The only phosphorus containing product was the thiophosphoryl derivature of **9**, compound **29**. This material was also prepared by another procedure. The pertinent NMR spectral data are collected in Tables I and II.

The reaction of **11** with **7** yielded the phosphorane, **30**, 88% and the thiophosphoryl compound, **31**, 12%. The variable temperature ^{19}F NMR spectra of **30** showed that below 37°C there are two nonequivalent trifluoromethyl groups bonded to the 5-membered ring. The $\Delta G^{\ddagger}$ for the process that renders them equivalent is 14.5 kcal/mol. Within the Berry mechanism for pseudorotation,[5] equivalence of the trifluoromethyl groups can be achieved by placing the 5-membered ring containing the two sulfurs in a diequatorial disposition. Either **30c** or **30d** are possible; **30c** is of lower energy than **30d**. There are two oxygens in apical positions of **30c** and the nitrogen is in the preferred equatorial position. It is interesting to compare the activation energy for this process to that for the **32a** ⇄ **32b** conversion.[6] The $\Delta G^{\ddagger}$ is 11 kcal/mole. The lower energy for this process is probably due to a higher energy of **32a** relative to that of **30a**. In **32a** both oxygens are in equatorial positions and the nitrogen is apical. In **30a** only the trifluoroethoxy group is not in a preferred apical position. It should be noted that a trifluoroethoxy group is undoubtedly more apicophilic than a regular alkoxy group. A further comparison with **33** is instructive. The $\Delta G^{\ddagger}$ for placing the sulfur containing ring diequatorial is 22.3 kcal/mole.[7] In the case of **33** there are no compensating driving forces present which can aid in lowering the activation energy for placing the ring diequatorial. There is always one oxygen in an equatorial position. There might be some difference in apicophilicity between phenoxy and alkoxy but it probably is not great. The structural modifications in the series **30**, **32** and **33** are illustrative of the real differences in activation energies that arise with relatively modest variation in structure.



11

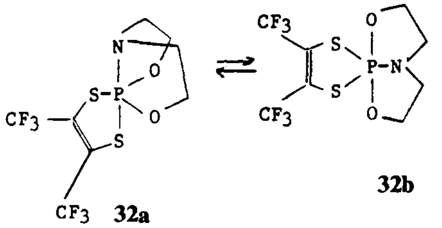
30a

30b

31

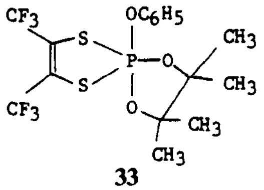
30d

30c



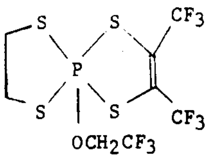
32a

32b

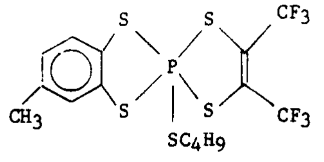


33

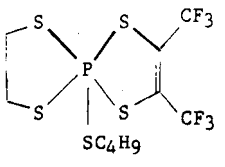
The reaction of compound, **15**, with **7** gave a complicated mixture of phosphorus containing compounds.



34



35



36

Compounds, **13**, **17** and **18** reacted with **7** to give phosphoranes, **34**–**36**. The variable temperature ^{19}F NMR spectra of **34** showed no change on cooling to $-73°C$. This could be due to rapid ligand reorganization between TBP structures or alternatively a SP structure with the two rings spanning basal positions can account for the data.

Compound, **35**, has δ -4.4 in its ^{31}P NMR spectrum which is in the region expected for a phosphorane. There was no change in its ^{19}F NMR spectrum to $-80°C$. Compound, **35**, may be undergoing ionization with ring opening of the ring bearing the trifluoromethyl groups. This possibility is raised because no PSCCF coupling was observed. Compound, **36**, has such coupling and it is a true phosphorane. There was no change in its ^{19}F NMR spectrum at $-80°C$. Rapid ligand reorganization or a SP structure similar to that discussed for **34** explain this observation.

Compound, **36**, appears to be the first phosphorane with five sulfurs bonded to phosphorus. Previous attempts to prepare such materials have yielded disulfides and trivalent phosphorus compounds.[4,8]

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 tetramethylislane. ^{13}C, ^{31}P, and ^{19}F NMR spectra were run on a Varian Model FT-80 spectrometer equipped with a 10-mmn, 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 are recorded at probe temp (26°) unless stated otherwise. A negative value of the chemical shift implies a nucleus shielded with respect to the standard.

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

Preparation of $\left[{}^{X}_{Y}\!\!>\!P\text{—}Cl;\ X=Y=N(CH_3);\ X=Y=S;\ X=N\text{—}CH_3,\ Y=O;\ X=S,\ Y=O.\right.$ To a solution of phosphorus trichloride (41.2 g, 0.3 mol) in ether (200 mL) at $-40°C$ was added a solution of triethylamine (60.6 g, 0.6 mol) and the appropriate, $HXCH_2CH_2YH$, compound (0.3 mol) in ether (50 mL). After having been stirred at $-40°$ for 15 min the reaction mixture was allowed to warm to room temp. The solid was removed by filtration and the filtrate was concentrated at reduced pressures. The residual oil was distilled, see Table III.

Preparation of **9**–**16**. To a solution of the appropriate phosphorochloridite (0.1 mol) in ether cooled to $-40°C$ was added a solution of the appropriate fluoroalcohol (0.1 mol) and triethylamine (10.1 g, 0.1 mol) in ether (50 ml). The reaction mixture was allowed to warm to room temp. and it was stirred for an

TABLE III

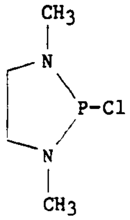
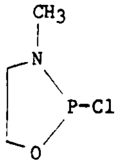
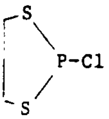
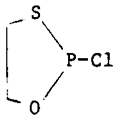
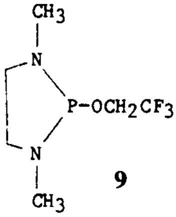
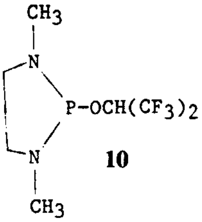
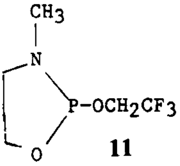
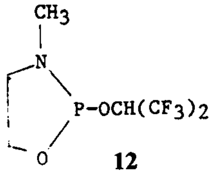
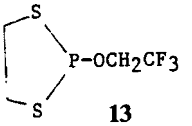
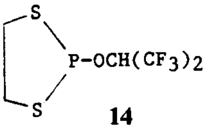
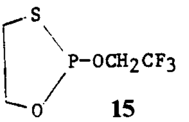
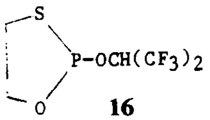
Compound	b.p. (°C/mm Hg)	Yield %
	55/0.5 lit. 70/0.2[a]	44
	52/2.4 lit. 57–58/2[b]	24
	84/2.0[c]	31
	42/0.5[d]	35
 **9**	45/2.5	60
 **10**	47/2.0	65
 **11**	41/1.0	43

TABLE III (*Continued*)

Compound	b.p. (°C/mm Hg)	Yield %
 **12**	48/4.0	62
 **13**	60/0.5	71
 **14**	47/0.5	67
 **15**	52/2.2	62
 **16**	46/3.0	69

---

[a] F. Ramirez, A. V. Patwardhan, H. J. Kugler, C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 6276 (1967).

[b] I. V. Marlynov, Y. L. Kruglyakand and S. I. Malekin, *Zr. Obshch. Khim.*, **38**, 2343 (1968).

[c] C. A. **73**, 3470 (1973).

[d] C. A. **69**, 96736 (1968).

additional hour. The solid was removed by filtration and the filtrate was concentrated at reduced pressures. The residual oil was distilled, see Table III.

Preparation of **17**. To a solution of the appropriate phosphorochloridite[8] (1.28 g, 0.0058 mol) in pentane (30 mL) at −78°C was added a solution of *n*-butanethiol (0.52 g, 0.0058 mol) and triethylamine (0.59 g, 0.0058 mol) in pentane (10 mL). The reaction mixture was allowed to warm to room temp and it was stirred for 2 hr. The solid was removed by filtration and the filtrate was concentrated at reduced pressures. No further attempts were made to purify the residual oil, 1.27 g (80%).

Preparation of **18**. To a solution of the appropriate phosphorochloridite (1.68 g, 0.011 mol) in ether 30 (mL) at −78°C was added butanethiol (0.95 g, 0.011 mol) and triethylamine (1.11 g, 0.011 mol). The reaction mixture was allowed to warm to room temp and it was stirred for 2 hrs. The solid was removed by filtration and the filtrate was concentrated at reduced pressures. The residue was molecularly distilled (65°, 0.05 mm) to yield 1.77 g (75.6%) of an oil **18**.

Preparation of **19**. To a solution of 2,2,2-trifluoroethyl benzenesulfeante (4.16 g, 0.02 mol) in pentane (30 mL) at −50°C was added **9** (2.16 g, 0.01 mol) in pentane (10 mL). The reaction mixture was allowed to warm to room temp and it was stirred for 30 min. It was cooled to −78°C and the solid was removed by filtration. After having concentrated the filtrate at reduced pressures the residual oil was molecularly distilled (52°C, 0.01 mm) to yield 1.64 g (39.6%) of a colorless oil, **19**.

Preparation of **20**. To a solution of 2,2,2-trifluoroethyl benzenesulfenate (4.16 g, 0.02 mol) in pentane (30 mL) at −40°C was added **11** (2.03 g, 0.01 mol) in pentane (10 mL). The reaction mixture was allowed to warm to room temp and it was stirred for 1 hr. It was cooled to −70°C and the solid was removed by filtration. After having concentrated the filtrate at reduced pressure, the residual oil was molecularly distilled (60°, 0.005 mm) to yield 1.61 g (40.1%) of a colorless oil, **20**.

Synthesis of **24**. Compound **24** was synthesized according to the method of Hayash, *et al.*,[9] to yield a solid material m.p. 39–40° (lit[9] 40°).

Reaction of **13** *with* **1**. To a solution of **13** (1.11 g, 0.005 mol) in pentane (30 mL) at −70° was added 2,2,2-trifluoroethyl benzenesulfenate **1** (2.08 g, 0.001 mol). The mixture was allowed to warm to room temp and it was stirred for one hr. The reaction mixture was cooled to −70°C and the solid was removed by filtration. This material (m.p. 58–60°) proved to be identical in all respects to diphenyl disulfide. The filtrate was concentrated at reduced pressures. The residual oil was molecularly distilled (70°, 0.5 mm) to yield material which was identical in all respects to **26**. The residue was recrystallized from pentane to yield a solid (m.p. 38–39°) which was identical to **24**.

Preparation of **27**. To a stirred solution of 1,1,1,3,3,-hexafluoro-2-propanol (2.69 g, 0.016 mol) and triethylamine (1.62 g, 0.016 mol) in pentane (13 mL) at −30°C was added benzenesulfenyl chloride (2.319, 0.016 mol). The mixture was allowed to warm to room temp and it was then stirred for 1 hr. The solid was removed by filtration. The filtrate was cooled to −78°C and to this was added **10** (1.136 g, 0.004 mol) in pentane (15 mL). The solution was allowed to warm to room temp and it was stirred for 1 hr. The reaction mixture was cooled to −20°C and the solid was removed by filtration. The filtrate was concentrated to yield an oil which decomposed on distillation.

Preparation of **29**. To a stirred solution of **9** (0.65 g, 0.003 mol) in benzene (15 mL) was added sulfur (0.19 g, 0.006 mol). The reaction mixture was heated under reflux for 12 hr. The solvent was removed at reduced pressures and the residual oil was molecularly distilled (88°, 0.25 mm) to yield **29**.

Reaction of **9** *with Dithiete* **7**. To a stirred solution of **9** (0.432 g, 0.002 mol) in dichloromethane (2 mL) at −70°C was added **7** (0.452 g, 0.002 mol). The reaction mixture was allowed to warm to room temp. The solvent was removed at reduced pressures to yield an oil which could be molecularly distilled (90°, 0.25 mm) to yield **29**. Anal. Calcd for $C_6H_{12}F_3N_2OPS$: C, 29.03; H, 4.83. Found: C, 28.90; H, 4.76.

Reaction of **11** *with Dithiete* **7**. To a solution of **11** (1.22 g, 0.006 mol) in dichloromethane (10 mL) at −70°C was added dithiete, **7**, (1.49 g, 0.0066 mol). The reaction mixture was allowed to warm to room temp. The ^{31}P NMR spectrum of this mixture showed two absorptions; at δ −13.7 (88%) and at $\delta + 82.2$ (12%). After having concentrated the solution at reduced pressure, the residual oil was molecularly distilled (42°, 0.25 mm) to yield **31**. Anal. Calcd for $C_5H_9F_3NO_2PS$: C, 25.53; H, 3.80. Found: C, 25.45, H, 3.40. All attempts to isolate **30** failed.

Synthesis of **31**. To a solution of **11** (0.406 g, 0.002 mol) in benzene (5 mL) was added sulfur (0.12 g, 0.004 mol). The reaction mixture was heated under reflux for twelve hrs. The solvent was removed at reduced pressure and the residual oil was molecularly distilled (55°, 0.3 mm).

Reaction of **13** *with Dithiete* **7**. To a stirred solution of **13** (0.45 g, 0.002 mol) in dichloromethane (5 mL) at −70°C was added dithiete (0.904 g, 0.004 mol). The reaction mixture was allowed to warm to room temp. All volatiles were removed at reduced pressure. Attempts to purify this material, **34**, by sublimation or recrystallization failed.

Reaction of **17** *with Dithiete* **7**. To a stirred solution of **17** (0.55 g, 0.002 mol) in dichloromethane (2 mL) at −78°C was added dithiete (0.9 g, 0.004 mol). The reaction mixture was allowed to warm to room temp and it was stirred for an additional 30 min. The mixture was cooled to −78°C. The yellow solid which crystallized from solution was separated by filtration at low temp. This material, **35**, had a m.p. of 52–54°C.

Reaction of **18** *with Dithiete* **7**. To a stirred solution of **18** (0.42 g, 0.002 mol) in dichloromethane (2 ml) at −78°C was added dithiete (0.9 g, 0.004 mol). The reaction mixture was stirred at that temp for an additional 30 min. after which it was allowed to warm to room temp. All attempts is isolate and purify **36** failed.

ACKNOWLEDGMENTS

This research has been supported by the National Science Foundation and by the Public Health Research Grant GM 26428. We also wish to thank the Mobil Chemical Co. for funds which aided in the purchase of NMR equipment. L.T.L. wishes to thank the Peoples Republic of China for financial support.

REFERENCES AND NOTES

1. (a) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (b) F. Ramirez, *ibid.*, **1**, 168 (1968); (c) R. Luckenbach, "Dynamic Stereochemistry of Pentaco-ordinated Phosphorus and Related Elements, George Thieme, Stuttgart, 1973; (d) W. S. Sheldrick, Penta- and Hexacoordinate Phosphorus Derivatives, Topics in Current Chemistry, Springer-Verlag Berlin, 1978, Vol. 73; (e) Organophosphorus Chemistry, Specialist Periodical Reports, Royal Society of Chemistry, Burlington House, London W1V0BN, Vols. 1–12, S. Trippett Chap. 2; (f) R. R. Holmes, Pentacoordinated Phosphorus, American Chemical Soc., Washington, D.C., ACS Monograph 176, 1980, Vols. I and II; (g) F. Ramirez, *Bull. Soc. Chim. France*, 3491 (1970); (h) F. Ramirez, A. V. Patwardhan, H. J. Kugler and C. P. Smith, *Tetrahedron*, **24**, 2275 (1968); (i) F. Ramirez, A. S. Gulati and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 6238 (1967); (j) F. Ramirez, M. Nagabushanam and C. P. Smith, *Tetrahedron*, **24**, 1785 (1968); (k) P. Narayanan, H. M. Berman, F. Ramirez, J. F. Marecek, Y. F. Chaw and V. A. V. Prasad, *J. Am. Chem. Soc.*, **99**, 3336 (1977).
2. (a) D. B. Denney, D. Z. Denney, P. J. Hammond and Y. Wang, *J. Amer. Chem. Soc.*, **103**, 1875 (1981); (b) D. B. Denney, D. Z. Denney, P. J. Hammond, L. T. Liu and Y. P. Wang, *J. Org. Chem.*, **48**, 2159 (1983).
3. B. C. Burros, N. J. De'Ath, D. B. Denney, D. Z. Denney and I. J. Kipnus, *J. Amer. Chem. Soc.*, **100**, 7300 (1978) and references therein.
4. D. B. Denney, D. Z. Denney and D. M. Gavrilovic, *Phosphorus and Sulfur*, **11**, 1 (1981).
5. See in particular ref. 1c.
6. D. B. Denney, D. Z. Denney, P. J. Hammond, C. Huang and K. Tseng, *J. Am. Chem. Soc.*, **102**, 5073 (1980).
7. S. A. Bone, S. Tripett and P. J. Whittle, *J.C.S. Perkin 1*, 80 (1977).
8. D. B. Denney, D. Z. Denney and L-T. Liu, *Phosphorus and Sulfur*, **13**, 1 (1982).
9. S. Hayashi, M. Furukawa, J. Yamaoto and K. Hamamura, *Chem. Pharm. Bull.* (*Tokyo*), **15**, 1310 (1967).