Free Radical Alkylthiylation of Hydridophosphoranes. Structure–Reactivity Factors Affecting the Reactions of Bicyclic Phosphoranyl Radicals with Disulfides

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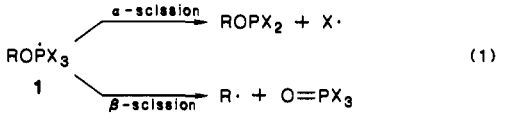
Abstract: The bicyclic hydridophosphorane **2** (Z_4PH) was shown to undergo UV-light-induced alkylthiylation reactions with a series of alkyl disulfides (RSSR, R = CH_3, *n*-Bu, neopentyl, *sec*-Bu, and *t*-Bu) to give the corresponding isolable thiaphosphoranes (Z_4PSR) in preparatively useful amounts (61–100%), except for *t*-BuSSBu-*t* which gave a poor yield of product. The reactions of the alkyl disulfides were all inhibited by α-methylstyrene. PhSSPh reacted with **2** even without light initiation in a process not inhibited by α-methylstyrene or galvinoxyl. The results for the alkyl disulfides are interpreted in terms of a two-step radical chain process: (1) $RS^\bullet + Z_4PH \rightarrow RSH + Z_4P^\bullet$ and (2) $Z_4P^\bullet + RSSR \rightarrow Z_4PSR + RS^\bullet$. *Intermolecular* competitions involving the presumed phosphoranyl radical intermediate, $Z_4P^\bullet$ (**16**), and the alkyl disulfides resulted in a reactivity order *t*-Bu:*sec*-Bu:neopentyl:*n*-Bu:CH_3 of 1:16:102:184:578. Evidently, the very large range of reactivities observed, compared to other S_H reactions of disulfides, arises from steric effects on the free energy of activation for the S_H attack of $Z_4P^\bullet$ (**16**) on disulfide sulfur. The *intramolecular* competition involving *sec*-BuSSBu-*sec* gave an *n*-BuS/*sec*-BuS reactivity ratio of 4.1:1. Kinetically controlled reactions of $Z_4P^\bullet$ (**16**) with *n*-BuSSPh and *sec*-BuSSPh led to nearly exclusive formation of the *n*-BuS and *sec*-BuS thiaphosphoranes. From *intermolecular* competitions for $Z_4P^\bullet$ (**16**) involving *n*-BuSSBu-*n* vs. *sec*-BuSSPh and *sec*-BuSSBu-*sec* vs. *n*-BuSSPh, 12- and 50-fold enhancements of the reactivities of *sec*-BuSSPh and *n*-BuSSPh, respectively, were found compared to their expected reactivities if only the steric factors noted for the RSSR reactions were operative. These enhancements are interpreted as most likely stemming from rate-determining sulfur–sulfur cleavage in one- or two-step S_H reactions of phosphoranyl radical **16** ($Z_4P^\bullet$) with the two RSSPh. The reactivities of phosphoranyl radicals toward disulfides are thus seen to be dependent on both steric factors and sulfur–sulfur bond strength considerations.

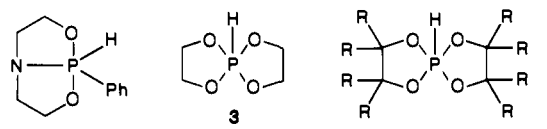
The scission reactions of phosphoranyl radicals, **1** (eq 1), have been thoroughly studied.[1] However, processes in which phosphoranyl radicals react as intact species to give stable products are much less well-understood. Phosphoranyl radicals which



(1)

undergo scission only relatively slowly, and thus potentially can be trapped by nonscission process, are typically spiro or bicyclic ones. These can be generated easily from pentacovalent precursors, for example, by abstraction of hydrogen from a hydridophosphorane, Z_4PH.[1]

We recently reported the reaction, initiated by AIBN or UV light, of hydridophosphorane **2** with *n*-butyl disulfide and suggested



that the free-radical chain sequence of eq 2 could readily account

$$Z_4PH + RS^\bullet \xrightarrow{a} Z_4P^\bullet + RSH$$

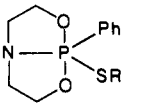
$$Z_4P^\bullet + RSSR \xrightarrow{b} Z_4PSR + RS^\bullet \qquad (2)$$

$$\overline{Z_4PH + RSSR \rightarrow Z_4PSR + RSH}$$

for the observed reaction.[2] Phosphorane **3** was seen to yield the corresponding CH_3S derivative on reaction with CH_3SSCH_3. However, **4** and **5** both proved to be either totally unreactive toward CH_3SSCH_3 or to give product only extremely slowly and/or in very low yields.[3] These results indicated that step 2b might be very sensitive to steric crowding in the radical $Z_4P^\bullet$, as exemplified by the reactions of **4** and **5**. This has led us to investigate the reactivity of **2**, and by implication $Z_4P^\bullet$ derived from it, toward a series of symmetrical, RSSR, and unsymmetrical disulfides, R^1SSR^2, to see what effects changes in the nature of R and in the sulfur–sulfur bond dissociation energy might have on step 2b. Indeed the rate of 2b (or sequence of reactions equivalent to 2b) appears to be greatly retarded by increases in the steric size of R and to be enhanced by the weakened sulfur–sulfur bond of certain aryl alkyl disulfides, RSSPh. This study is one of the first concerning the structure–reactivity considerations which govern the nonscission reactions of intact phosphoranyl radicals. Furthermore, this research provides new understanding of the rate-determining steps for S_H reactions of free radicals with disulfides.

Results

Product Studies. The photoinitiated reactions of **2** with a series of RSSR were monitored quantitatively by ^{31}P NMR with $(MeO)_3PO$ added as external standard. High NMR yields (81–93% except for **10**) were found (Table I). Preparative reactions were run on a 0.3–1.0 g scale with products **6–9** isolated



6; R = CH_3. **9**; R = neopentyl
7; R = *n*-Bu. **10**; R = *t*-Bu
8; R = *sec*-Bu. **11**; R = Ph

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‡ Visiting Professor, 1983–1984, from University of the Pacific.

(1) For reviews of the formation, structures, and reactions of phosphoranyl radicals, see: (a) Bentrude, W. G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: London, 1983; Vol. 3, pp 199–298. (b) Bentrude, W. G. *Acc. Chem. Res.* **1982**, *15*, 117. (c) Roberts, B. P. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Heyden and Sons: London, 1980; Vol. 6, pp 225–289.

(2) Kawashima, T.; Bentrude, W. G. *J. Am. Chem. Soc.* **1979**, *101*, 3981.
(3) Unpublished results from this laboratory.

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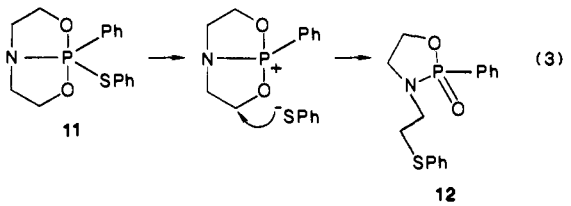
Table I. Yields of Thiaphosphoranes from Reactions of Alkyl Disulfides with **2** Determined by ^{31}P NMR[a]

RSSR	thiaphosphorane	% yield[b]
CH_3SSCH_3	**6**	93 (4)
n-BuSSBu-*n*	**7**	93 (4)
sec-BuSSBu-*sec*	**8**	82 (8)
neopentyl-SS-neopentyl	**9**	85 (4)
t-BuSSBu-*t*	**10**	37 (4)[c]
CH_3SSCH_3/*n*-BuSSBu-*n*	**6, 7**	81 (2)[d]
n-BuSSBu-*n*/*sec*-BuSSBu-*sec*	**7, 8**	85 (2)[d]
neopentyl-SS-neopentyl/*sec*-BuSSBu-*sec*	**9, 8**	89 (1)[d]

[a] Samples in C_6D_6 (0.5 mL). Starting amounts of **2**, 0.19–0.38 mmol. Total starting disulfide amounts, 0.53–2.8 mmol. [b] Determined relative to external $(CH_3O)_3P{=}O$ standard (see Experimental Section). Number of experiments averaged given in parentheses. [c] Sum of yields of **10** (21%) and **13** (16%). [d] Sum of yields of individual product thiaphosphoranes.

in 61–100% yields (Experimental Section). Rapid reaction with PhSSPh occurred at room temperature even in the dark. ^{31}P, ^1H NMR (Table II), and ^{13}C (Table III) NMR data along with mass spectrometry (Table IV) confirmed the structures.

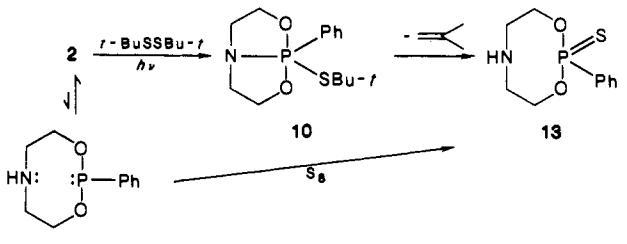
Product **11** was isolated in nearly pure form on solvent removal, as indicated by quantitative elemental analysis and spectroscopic criteria. However, it proved to be unstable toward heat on attempted bulb-to-bulb distillation. Rearranged material, **12**, was



(3)

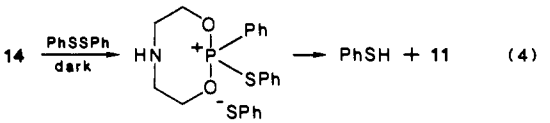
isolated. Its formation is most reasonably understood in terms of reaction sequence 3. The ionization of **11** is promoted by the relative stability of PhS^-. The ensuing displacement is of the normal Arbuzov type. Treatment of **11** with *n*-PrOH at room temperature quickly led to replacement of PhS by *n*-PrO and formation of the known *n*-propoxyphosphorane.[2]

t-BuSSBu-*t* reacted with **2** only very sluggishly. For example, under standard conditions in which 0.5 M solutions of **2** with excess *n*-BuSSBu-*n* showed total consumption of **2** in 20 min, no more than 50% of **2** had undergone reaction with excess *t*-BuSSBu-*t* in 2–3 h. Two major product peaks were observed in the ^{31}P NMR spectrum (C_6D_6) at δ −34.1 and 82.5 in an average ratio of 1.7/1.0. Capillary GLC revealed two major products as well. GC–MS of the product with the higher field ^{31}P shift did not show a molecular ion peak corresponding to the molecular weight of **10** but displayed a fragmentation pattern similar to those for **6–9** (Table IV). The second product (GLC and ^{31}P NMR) had a highest mass peak at m/e = 243 which could be the molecular ion of **13**. This product would arise from loss of isobutylene from **10**. Treatment of **2** with S_8 gave a compound identical (GLC and MS) with the by-product of reaction with *t*-BuSSBu-*t* (^{31}P shift of 82.6, C_6D_6). These results are consistent with the following scheme:



Inhibitor Studies. Since **2** is known to undergo reactions in its trivalent form **14**[4] and other hydridophosphoranes undergo both free-radical (PH form)[5] and polar additions (trivalent form) to conjugated alkenes,[5c,6] the truly radical chain character of each reaction was carefully tested. The reactions of the symmetrical alkyl disulfides, RSSR (R = CH_3, *n*-Bu, *sec*-Bu, neopentyl, *t*-Bu), and that of *sec*-BuSSBu-*n* were strongly inhibited by the addition of 5 mol % of α-methylstyrene. Thus, under conditions in which uninhibited solutions (initial RSSR/**2** $\simeq$ 2) had undergone at least 50% consumption of **2**, those containing 5% of α-methylstyrene (mol percentage based on excess RSSR) were completely unreacted (^{31}P NMR and GLC).

By distinct contrast, addition of as much as 20 mol % of α-methylstyrene gave no evidence of retarding the reaction with PhSSPh, even in the dark. (See Experimental Section for details.) Likewise, galvinoxyl (3 mol %) was ineffective as an inhibitor, suggesting the possible intervention of an ionic process



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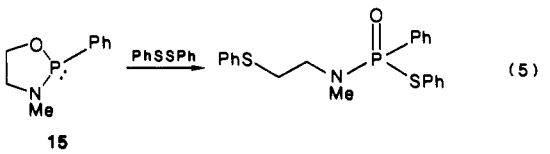
In fact ^1H NMR examination of the vinylic region of the α-methylstyrene containing samples before and after reaction gave no evidence of consumption of alkene. This discounts the possibility that the α-methylstyrene was quickly consumed in a very rapid free-radical process prior to subsequent free-radical reaction of the remaining PhSSPh with **2**. The 1,3,2-oxazaphospholane **15** also reacted very rapidly in the dark at room temperature with PhSSPh, presumably via sequence 5, although the product (δ ^{31}P = 43.6) was not characterized further.



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The reaction of *sec*-BuSSPh with **2** was fully inhibited by α-methylstyrene and required UV light initiation. *n*-BuSSPh likewise would not react with **2** in the dark, but the UV-light-initiated reaction was not inhibited by α-methylstyrene. Thus, the fully radical-chain character of the latter reaction could not be affirmed.

Since disulfides and thiols readily convert tricovalent phosphorus into the sulfide (P=S) under free radical conditions,[1] we irradiated a C_6D_6 solution of **2** with *n*-BuSH present in excess. After a 15-h irradiation, no reaction of **2** had occurred (^{31}P NMR). Formation of **13**, which might cyclize to the pentacovalent P(Ph)SH product and then give **1** by loss of H_2S on reaction with *n*-BuSH, was thereby excluded.

Intramolecular Competition Studies. Reactions of *n*-BuSSPh and *sec*-BuSSPh under UV light initiation were also monitored to see whether **11** or the alkylthio products, **7** or **8**, would result. ^{31}P NMR techniques showed that **7** and **8** were formed in ratios **7**/**11** and **8**/**11** of 97/3 and 95/5, respectively. To avoid formation of increased amounts of **11**, reactions had to be run to only 5–20% conversion of **2**. At longer reaction times, disproportionation of the disulfide (eq 6) gave PhSSPh which spontaneously yielded

$$2\text{RSSPh} \xrightarrow{h\nu} \text{RSSR} + \text{PhSSPh} \qquad (6)$$

11. (GLC showed the presence of RSSR. PhSSPh is evidently immediately consumed and was not detected.) Careful controls verified that rapid, kinetically controlled formation of **11**, followed by exchange with *n*-BuSH or *sec*-BuSH to form **7** or **8**, did not occur (Experimental Section).

The mixed disulfide *n*-BuSSBu-*sec* reacted cleanly to yield a conversion-independent **7**/**8** ratio of 4.1 ± 0.1 by ^{31}P NMR (3.9 ± 0.1 by GLC) in overall yield (**7** + **8**) of >90%.

Intermolecular Competition Studies. The reactions of **2** with various ratios of different disulfides present in large excess were studied (eq 7). The product ratios were determined by GLC and ^{31}P NMR methods. These efforts were aimed at determining the relative reactivities of various disulfides toward the presumed intermediate phosphoranyl radical **16**. By use of known ratios of excess disulfides, the relative *apparent* rate constants, k_{R^1S}/k_{R^2S},

Table II. ^1H and ^{31}P NMR Spectral Parameters for Thiaphosphoranes **6–9** and **11**

compd	^1H chemical shifts, δ[a] RS	N-CH_2[c]	OCH_2[c]	*m*, *p* H[c]	*o* H[c]	δ ^{31}P[b]
6[d]	2.16 (d, J_{HP} = 14.9 Hz CH_3)	3.12–3.35	3.79–4.04	7.30–7.45	7.69–7.89	−29.85
7[e]	0.83 (t, CH_3), 1.13–1.77 (m, CH_2CH_2), 2.47–2.87 (d of t, SCH_2)	2.93–3.37	3.60–4.07	7.13–7.47	7.53–7.93	−29.58
8[d]	0.94 (t, CH_3CH_2), 1.28 (d, CH_3CH), 1.42–1.76 (2 overlapping m, $CHCH_2CH_3$),[e] 3.20–3.40 (m, *CH*)	2.54–2.88	3.42–3.86	7.02–7.26	7.96–8.16	−29.37
9[d]	0.98 (s, CH_3), 2.71 (d, J_{PH} = 9.5 Hz, CH_2)	3.08–3.32	3.77–4.01	7.24–7.50	7.68–7.88	−29.89
11[c]	7.00–8.03[f]	2.83–3.47	3.47–3.93	7.00–8.03[f]		−30.39

[a] In ppm downfield from internal Me_4Si. Splitting patterns if discernable are in parentheses. Solvent is $CDCl_3$. [b] in ppm upfield (negative) of external H_3PO_4. In perdeuteriobenzene at 32.2 MHz. Chemical shift of **2** is −45.06 (C_6D_6) and of **10** is −34.07 (C_6D_6). [c] Unresolved multiplets. [d] 300 MHz. [e] 90 MHz. [f] SPh and PPh protons overlapped.

Table III. ^{13}C NMR Spectral Parameters for Thiaphosphoranes **6–9** and **11** in $CDCl_3$ at 75.4 MHz[a,b]

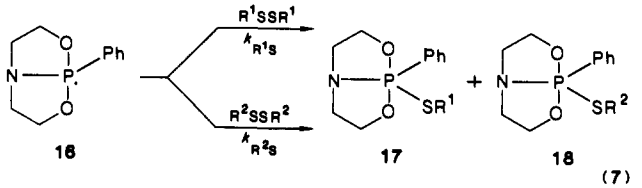
compd	δ (J_{CP})[c] N-CH_2	O-CH_2	RS		C_6H_5P
6	43.45 (17.6)	59.40 (3.1)	15.36 (5.7)	CH_3	141.94 (195.8) ipso
					129.20 (3.4) *p*
					127.79 (17.2) *o*, *m*
					129.93 (11.3) *o*, *m*
7	43.57 (18.1)	59.59 (0)	13.71 (0)	CH_3	142.75 (194.6) ipso
			22.06 (0)	CH_2–CH_3	129.47 (0) *p*
			32.00 (5.5)	S-CH_2	128.10 (16.6) *o*, *n*
			33.01 (7.1)	S-CH_2-CH_2	130.23 (11.1) *o*, *m*
8	43.30 (17.9)	59.26 (3.7)[e]	11.57 (0)	CH_3-CH_2	142.84 (194.0) ipso
		59.34 (3.6)[e]	22.76 (5.0)	CH_3-*CH*	128.80 (3.2) *p*
			31.10 (7.8)	CH_2	127.42 (16.9) *o*, *m*
			43.15 (6.0)	*CH*	129.83 (11.5) *o*, *m*
9	43.37 (17.4)	59.19 (3.2)	28.88 (0)	CH_3	141.85 (196.9) ipso
			31.85 (6.8)	$(CH_3)_3C$	128.88 (3.6) *p*
			45.29 (6.4)	CH_2-S	127.53 (17.0) *o*, *m*
					129.62 (11.0) *o*, *m*
11	43.49 (17.7)	59.38 (3.7)	134.09 (7.8)	ipso-SPh	141.90 (197.8) ipso
			135.11 (4.6)	*o*-SPh	
			127.61,[d] 127.73, 127.96, 128.20, 128.23		
			129.05, 129.37, 129.42, 130.56, 130.71		

[a] With the exception of compound **6** run at 20.0 MHz. [b] Assignments in compounds **7** and **8** checked by off-resonance spectra. [c] Chemical shifts are in ppm downfield of internal Me_4Si. ^{13}C–^{31}P coupling constants (Hz) in parentheses. [d] Aromatic peaks for both PhS and PhP moieties. Assignments of δ and J not made. [e] Carbons are diastereotopic.

Table IV. Mass Spectral Data for Thiaphosphoranes **6–9**

compd	*m/e* (rel intensity)
6	257 (0.7, M^+), 210 (32.7, M − CH_3S), 196 (75.5), 56 (100)
7	299 (0.3, M^+), 242 (5.1, M − Bu), 210 (47.6, M − BuS), 196 (94.9) 56 (100)
8	299 (0.2, M^+), 242 (5.9, M − Bu), 210 (100, M − BuS), 196 (28.9), 56 (42.7)
9	313 (0.4, M^+), 242 (3.3, M − $C_5H_{11}S$), 210 (100, M − $C_5H_{11}S$), 196.1 (51.6)
10	242 (94, M − Bu),[a] 210 (100, M − BuS), 196 (88), 56 (100)

[a] Molecular ion (*m/e*, 299) not observed.



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were readily derived from the measurable ratios of products. (See eq 8 and 9.) Table V records the results of these competitions

$$\frac{d[17]}{dt} = k_{R^1S}[16][R^1SSR^1]$$
$$\frac{d[18]}{dt} = k_{R^2S}[16][R^2SSR^2] \quad (8)$$

$$\frac{k_{R^1S}}{k_{R^2S}} = \frac{[R^2SSR^2][17]}{[R^1SSR^1][18]} \quad (9)$$

for alkyl disulfides. The relative constancy of k_{R^1S}/k_{R^2S} over a range of reactant disulfide ratios is gratifying, as is the agreement between ^{31}P NMR and GLC results. For the reactivity series which includes *t*-BuSSBu-*t*, the amount of product **10** was taken as the sum of **10** and presumed **13**.

In Table VI are results for analogous competitions of dialkyl sulfides with unsymmetrical alkyl phenyl disulfides. Again, reproducibility is excellent.

For the competitions between *n*-BuSSBu-*n* and *sec*-BuSSBu-*sec*, it was necessary to keep the conversions of **2** low, since the ratio $k_{n\text{-BuS}}/k_{s\text{-BuS}}$ decreased with time. This result clearly stems from scrambling of the reactant disulfides under free radical conditions. This was evidenced by the identification by GLC of *sec*-BuSSBu-*n* formed during the reaction. As noted above, the ratio of **7**/**8** (~4/1) from reaction of **16** with *n*-BuSSBu-*sec* is much reduced from that formed on reaction of a 1:1 ratio of *n*-BuSSBu-*n* to *sec*-BuSSBu-*sec* (~10/1). The change in apparent $k_{n\text{-BuS}}/k_{sec\text{-Bu}}$ with time is shown graphically in Figure 1 along with the buildup with time of *n*-BuSSBu-*sec* expressed as *n*-BuSSBu-*sec*/*n*-BuSSBu-*n*. The other competitions involving alkyl disulfides gave k_{R^1S}/k_{R^2S} ratios relatively insensitive to time and no evidence for buildup of R^1SSR^2. However, the competitions between *n*-BuSSBu-*n* and *sec*-BuSSPh or *n*-BuSSPh were sensitive to conversion. Therefore, values of k_{R^1S}/k_{R^2S} of Tables V and VI are for low conversions.

Discussion

The UV-light-initiated reactions of hydridophosphorane **2** with a variety of disulfides occur rapidly to yield the product pentacovalent compounds **6–10**. Reaction with PhSSPh to give **11** occurs even in the dark. Products **6–9** are easily isolable as pure materials by distillation. Thus the alkylation reactions are preparatively useful. Thiaphosphorane **11** undergoes thermal

Table V. Individual Competition Reactions of Symmetrical Alkyl Disulfides with **2** at 20 °C

R^1	R^2	$[R^1SSR^1]/[R^2SSR^2]$	% convrsn	k_{R^1S}/k_{R^2S}	k_{R^2S}/k_{R^1S}	av
CH_3	*n*-Bu	2.4	83	3.10[a]		
		2.1	10	3.28		
		0.98	18	3.23		
		0.63	35	2.96		
		0.21	90	3.11		3.14 ± 0.13[d]
sec-Bu	*n*-Bu	10.0	7.6		11.0[a]	
		6.0	14		11.0	
		4.0	39		10.0	
		3.0	4.0		12.9	11.2 ± 1.2
		10.2	12–17		11.3 (2)[b]	
		3.06	8–26		10.3 (4)	
		1.02	17		12.1 (1)	
		0.51	16		9.6 (1)	10.8 ± 1.1
sec-Bu	neopentyl	7.01	33		6.15[a]	
		2.99	42		6.28	
		1.44	56		6.27	
		0.90	78		6.20	6.23 ± 0.06
t-Bu	*sec*-Bu	10.0	29		17.7[a,c]	
		8.0	44		14.9	
		4.0	39		16.6	16.4 ± 1.4

[a] Followed by ^{31}P NMR by using gated decoupling. Amounts of **2**, 0.19–0.33 mmol. Total disulfide amounts, 1.1–3.9 mmol. Solvent is C_6D_6 (0.5 mL). [b] Followed by GLC. Amounts of **2**, 0.0244 and 0.0240 mmol. In *n*-decane (1 mL) solvent. Total disulfide amounts, 0.6–2.2 mmol. Number of separate reactions at same disulfide ratio averaged. [c] The amount of reaction of **2** with *t*-BuSSBu-*t* is found by adding the amounts of **10** and **13**. [d] Standard deviations.

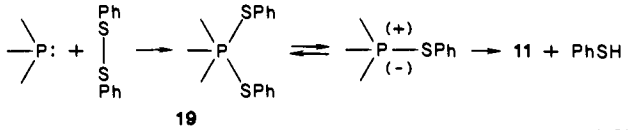
Table VI. Competitive Reactions of R^1SSR^1 and R^2SSPh with **2** at 20 °C. Relative Rate Constants Determined by ^{31}P NMR[a]

R^1	R^2	$[R^1SSR^1]/[R^2SSPh]$	% convrsn of **2**	k_{R^2S}/k_{R^1S}[b]
n-Bu	*sec*-Bu	3.0 (2)[c]	11–15	1.23
		1.0 (3)	6–10	1.15
		0.5 (2)	5–10	1.21
				av 1.20 ± 0.04[d]
sec-Bu	*n*-Bu	10.0	8	480
		3.0	4	500
				av 490

[a] In C_6D_6. See Experimental Section for concentrations of reactions. [b] Statistically corrected for one reaction site on RSSPh. [c] Number of replications in parentheses. [d] Standard deviation.

rearrangement. Product **10** is generated in only low yields.

From a mechanistic standpoint, the chain carrying reactions 2a and 2b account reasonably for the demonstrated free-radical chain nature of the reactions of all the disulfides except PhSSPh and possibly *n*-BuSSPh. (The possibility that reaction 2b involves more than one step will be addressed later.) Evidently PhSSPh undergoes reaction by a completely different mechanism, possibly as depicted in sequence 10. The weakness of the disulfide bond



19

(10)

of PhSSPh could make it susceptible to a nonradical biphilic attack similar to that postulated for reactions of dialkyl peroxides with tricovalent phosphorus.[7] This route would provide **19** as the initial adduct and precursor to the phosphonium intermediate in sequences 4 and 10. (The phosphonium intermediate may instead be formed initially.)

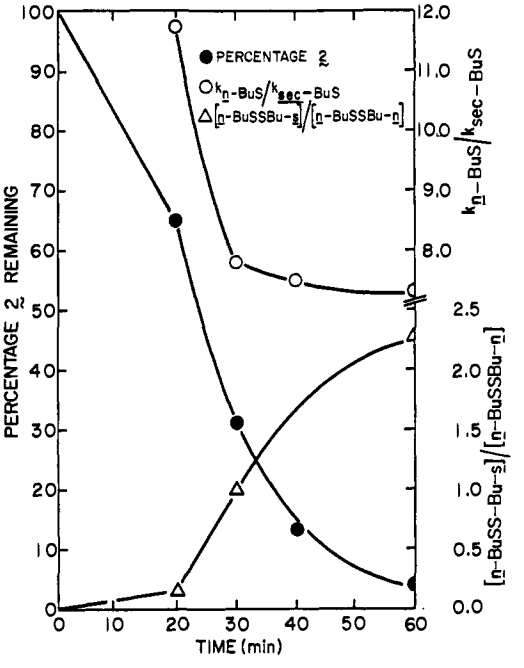


Figure 1. Effect of extent of conversion of **2** on the apparent $k_{n\text{-BuS}}/k_{sec\text{-BuS}}$ for the competition between *n*-BuSSBu-*n* and *sec*-BuSSBu-*sec* for presumed phosphoranyl radical **16** at 20 °C. (GLC method).

As to the failure of the light-initiated reaction with *n*-BuSSPh to be inhibited by α-methylstyrene or galvinoxyl, it can be suggested that perhaps the intermediate **16** in this case alone fails to be intercepted by α-methylstyrene (or even galvinoxyl) because of the rapidity of step 2b resulting from the low S–S bond dissociation energy and the steric ease of attack on sulfur with *n*-Bu attached. (See latter discussion.) Phosphoranyl radicals are known to be trapped by addition to alkenes.[8] Of course, PhS• are similarly captured.[9] However, if PhS• were the species trapped in competition with step 2a, α-methylstyrene should just as effectively inhibit the reaction of *n*-BuSSPh as that of *sec*-BuSSPh.[9]

(4) For an example of the reaction of **2** with metal carbonyls leading to coordination with trivalent nitrogen and phosphorus, see: Wachter, J.; Jeanneaux, I.; Riess, J. G. *J. Am. Chem. Soc.* **1980**, *103*, 4272.

(5) (a) Grechkin, N. P.; Gubanova, G. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 2803. (b) Laurenco, C.; Burgada, R. *Tetrahedron* **1976**, *32*, 2253. (c) Willson, M.; Burgada, R. *Phosphorus Sulfur* **1979**, *7*, 115.

(6) Burgada, R. *Bull. Soc. Chim. Fr. Ser. C* **1975**, 407. Burgada, R. *Phosphorus Sulfur* **1976**, *2*, 237. Burgada, R.; Mohri, A. *Phosphorus Sulfur* **1981**, *9*, 285.

(7) Lloyd, J. R.; Lowther, N.; Hall, C. D. *J. Chem. Soc., Perkin Trans. 2* **1985**, 245. Woz'niak, L.; Kowalski, J.; Chojnowski, J. *Tetrahedron Lett.* **1985**, 4965. Clennan, E. L.; Heath, P. C. *J. Org. Chem.* **1981**, *46*, 4105. Baumstark, A. L.; McCloskey, L. J.; Williams, T. E.; Chrisope, D. R. *J. Org. Chem.* **1980**, *45*, 3593. Denney, D. B.; Denney, D. Z.; Hall, C. D.; Marsi, K. L. *J. Am. Chem. Soc.* **1972**, *94*, 245.

(8) Griller, D.; Roberts, B. P. *J. Chem. Soc., Perkin Trans 2* **1973**, 1416.

(9) See: Abell, P. I. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 13.

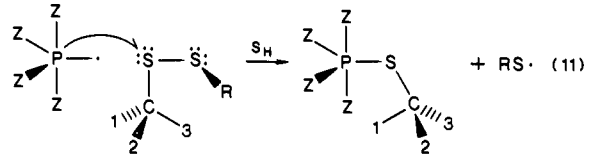
Table VII. Relative Rate Constants for Reactions of **2** with Alkyl Disulfides at 20 °C

disulfide	k_{rel}[a]
t-BuSSBu-*t*	1
sec-BuSSBu-*sec*	16.4
neopentyl-SS-neopentyl	102
n-BuSSBu-*n*	184
CH_3SSCH_3	578

[a] Determined from disulfide competitions followed by ^{31}P NMR.

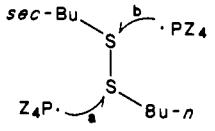
In this regard, step 2a may well be quite favorable thermodynamically. Sulfur–hydrogen bond dissociation energies for RSH are about 90 kcal/mol (92 ± 2 for CH_3SH).[10] While values for the PH bond of pentacovalent phosphorus are unknown, PH bonds are generally weak as exemplified by the bond dissociation energy for PH_3 of 77 kcal/mol.[11] However, although step **2b** is aided by the weakness of the sulfur–sulfur bond of disulfides (~70 kcal/mol; 74 for CH_3SSCH_3),[10] P–S bond dissociation energies are not generally available, though they are presumably less than those for PO bonds. The *average* PO bond strength in $(EtO)_3P$ is 84 kcal/mol.[12]

The large susceptibility of step 2b to the steric size of R may reflect a delicate balance between P–S and S–S bond energies and hence the overall thermodynamics of that process. Indeed, the near 600-fold range of reactivities seen in Table VII are most straight-forwardly interpreted as resulting from steric-derived variations in the transition-state free energy for attack of phosphoranyl radical **16** ($Z_4P^\bullet$) at sulfur. In the simplest (concerted) case (eq 11), carbon substituents 1, 2, or 3 partially block the



approach of the phosphorus center. The progression of apparent steric effects CH_3 < *n*-Bu < neopentyl < *sec*-Bu < *t*-Bu is readily explained. The *n*-Bu(R) group is equivalent to 1 = $CH_2CH_2CH_3$, 2 = 3 = H. Similarly, the neopentyl has but one carbon substituent at C-α, 1 = $C(CH_3)_3$, 2 = 3 = H; but the *t*-Bu group, being highly branched, has a larger effect than *n*-Pr. R = *sec*-Bu (1 = CH_3, 2 = CH_3CH_2, 3 = H) features two C-α substituents, while the R = *t*-Bu case (1 = 2 = 3 = CH_3) is triply methyl-substituted at the carbon α to sulfur. The *t*-Bu in particular is highly resistant to the approach of the phosphoranyl radical. Attack on sulfur of *t*-BuSSBu-*t* is equivalent to S_N2 attack at the CH_2 of a neopentyl group. The steric bulk in neopentylSSpentylneo is one carbon further removed from the reactive center.

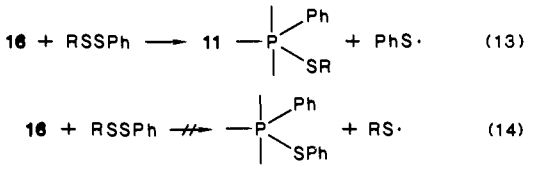
The reduced selectivity in the *intramolecular* competition involving *sec*-BuSSBu-*n* could mean that the steric size of *both* alkyl groups influences the rate of attack at a particular sulfur. Thus, according to the reactions of eq 12, attack via route a could be



(12)

reduced slightly in rate compared to that on *n*-BuSSBu-*n* by the remote *sec*-Bu. Likely, attack via route b would be marginally more favored than that on *sec*-BuSSBu-*sec* because of the reduced size of the more remote *n*-BuS. The importance of such remote effects would be influenced by the C–S–S–C dihedral angle at the moment of $Z_4P^\bullet$ attack. This angle in the lowest energy rotamer of disulfides is normally about 90°.[13] This reaction system does not undergo disulfide scrambling even at high conversions.

The reaction of **16** with the mixed phenyl alkyl disulfides, which controls verified reflects kinetically preferential attack, follows the thermodynamically more favored route (eq 13). In both equations 13 and 14, the thermodynamic component for cleavage



of the sulfur–sulfur bond is the same. The difference in the two pathways energetically is the greater strength at the PSR compared to the PSPh bond. (The analogy is seen in the reaction of R• with HBr to give RH, not RBr.) Evidently this thermodynamic difference is felt in the relative transition-state energies for the rate-determining steps of eq 13 and 14. This strongly suggests that phosphorus–sulfur bond formation (and by implication sulfur–sulfur bond breaking) is somehow involved in the rate-determining step. The simplest process, of course, involves concerted P–S bond formation and S–S bond cleavage, eq 11.

It also might be argued that the *regioselectivity* in the reactions with RSSPh, as with the RSSR competitions, arises from steric factors with *n*-Bu and *sec*-Bu being in fact smaller than phenyl. Contrary to this notion, space filling models show that rotation about the S–Ph bond gives rise to a conformation in which the sulfur adjacent to Ph is readily accessible to radical attack, more so than that next to *n*-Bu or *sec*-Bu. The above ratios of **7**/**11** and **8**/**11** (Results) are minimum values because of the formation PhSSPh which accompanies the reactions. It is unreasonable that the close to 2 kcal/mol difference in transition-state free energies would be derived primarily from steric considerations. Indeed the selectivity in the *n*-BuSSBu-*sec* case was only 4:1 (vide supra).

Even with *t*-BuSSPh, featuring the sterically large *tert*-butyl, clean attack on SPh to give **11** does not occur. Only a very sluggish reaction takes place which gives both **10** and **11**. Unfortunately, the reaction is so slow that *t*-BuSSBu-*t* and PhSSPh are formed via radical-induced disproportionation. Thus, one cannot accurately account for the origins of **10** and **11**. It is surprising that the steric bulk of the *tert*-butyl does not simply direct attack away from the *t*-BuS to the adjacent sulfur to yield **11**. Perhaps the bulk of the *tert*-butyl hinders even **11** formation. Alternatively, the overall thermodynamics of the displacement to yield **11** may be unfavorable as a result of the undoubtedly reduced strength of the P–SPh compared to the P–SR bond in the product phosphorane. (See above arguments regarding the potentially delicate balance of P–S and S–S bond dissociation energies.)

Interestingly, the degree of scrambling of the dialkyl disulfides in the competition experiments depends greatly on the disulfides in question. Only in the *n*-BuSSBu-*n*/*sec*-BuSSBu-*sec* case, in which a large *sec*-BuSSBu-*sec*/*n*-BuSSBu-*n* ratio is required, does extensive exchange occur. In the other competitions (RSSR; R = CH_3, *n*-Bu, neopentyl) reaction of **2** occurs rapidly with both disulfides. Evidently, retardation of step 2a or 2b when *sec*-BuS• or *sec*-BuSSBu-*sec* is the reactant allows disulfide exchange to compete, the key step of which is attack by R′S• on RSSR. Scrambling in competition with reaction of **2** is observed for all three RSSPh (R = *n*-Bu, *sec*-Bu, *t*-Bu). Likely the weakened sulfur–sulfur bond facilitates the formation of RSSR and PhSSPh.

The intermolecular competitions between *n*-BuSSBu-*n* and the

(10) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1977**, *9*, 295 and references therein.

(11) Based on ΔH_f^0 (298, g) of 1.3 kcal/mol for PH_3 (Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H.; NBS Technical Note 270-3; U.S. Government Printing Office: Washington, DC, 1968) and ΔH_f^0 (298, g) for $H_2P^\bullet$ (*JANAF Thermochemical Tables*; The Dow Chemical Company: Midland, Michigan). See: Bentrude, W. G. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 22.

(12) Based on ΔH_f^0 (298, g) of −195.9 kcal/mol for $(EtO)_3P$ (Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York and London, 1970), −6.7 kcal for EtO• (Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465), and 75.2 kcal/g atom for white phosphorus (standard state).

(13) Van Wart, H. E.; Scheraga, H. A. *J. Phys. Chem.* **1976**, *80*, 1812. Sugeta, H.; Go, A.; Miyazawa, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3407.

disulfides *n*-BuSSPh and *sec*-BuSSPh can be interpreted as evidence that the weakened sulfur–sulfur bond has enhanced the overall rate of attack by phosphoranyl radical **16** and that at least in the attack on RSSPh, sulfur–sulfur cleavage is in some way rate-determining. Thus, the relative reactivities of *n*-BuSSBu-*n* (**20**) and *sec*-BuSSPh (**21**) give *apparent* relative rate constants, $k_{21}/k_{20} \cong 0.6$ (Table VI). On the basis of the competition between *n*-BuSSBu-*n* and *sec*-BuSSBu-*sec* (Table V), attack next to *sec*-BuS should be about 10 times slower than that next to *n*-BuS, where steric factors alone are operative. Taking into account statistical factors, the ratio $k_{21}/k_{20} = 0.6$ amounts to an enhancement of (2 × 0.6 × 10) or 12-fold for **21** compared to *sec*-BuSSBu-*sec*. The competition involving *sec*-BuSSBu-*sec* and *n*-BuSSPh leads to an estimated 50-fold enhancement ((2 × 250)/10) for *n*-BuSSPh compared to *n*-BuSSBu-*n*. It seems extremely unlikely that this differential results primarily from the reduced steric size of the Ph remote to attack. (See earlier discussion of effects of the remote alkyl in the reaction of *n*-BuSSBu-*sec*.) This enhancement, if a result of the weakened S–S bond, *excludes* the possibility that both eq 15 and 16 involve rate-determining formation of a sulfuranyl radical (**22** or **23**). (Unless PhS somehow stabilizes **23** in some special fashion.)

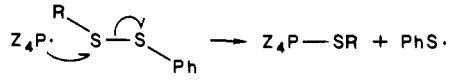
$$Z_4P\cdot + RSSR \xrightarrow{slow} Z_4P{-}\overset{R}{\underset{|}{\overset{|}{S}}}{\cdot}{-}SR \xrightarrow{fast} Z_4PSR + RS\cdot \quad (15)$$

22

$$Z_4P\cdot + RSSPh \xrightarrow{slow} Z_4P{-}\overset{R}{\underset{|}{\overset{|}{S}}}{\cdot}{-}SPh \xrightarrow[k_{16}]{fast} Z_4PSR + PhS\cdot \quad (16)$$

23

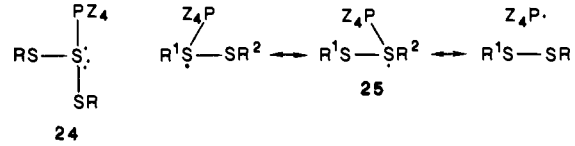
The most straightforward interpretation of the alkyl disulfide competitions, along with those involving *n*-BuSSPh and *sec*-BuSSPh, is via a concerted process depicted by eq 11. The weakened sulfur–sulfur bond in the reactions of RSSPh lowers the activating free energy



Both experimental[14] and theoretical[15] justifications are available for the notion that S_H displacements at heteroatoms are "inline", i.e., back side to the leaving radical with a preferred linear arrangement, in this case, of the attacking phosphorus and two sulfur atoms. The greater P–SR than P–SPh bond energy is also reflected in such a transition state accounting for the selective attack at RS. (See above.)

Evidence for the intermediacy of sulfuranyl radicals exists in the reactions of sulfides with various free radicals. Whether the weakness of the sulfur–sulfur bond precludes the existence of **22** and **23** is not known. The results of the present study are not inconsistent with eq 15 and 16 if **22** and **23**, the sulfuranyl radical intermediates, are formed rapidly and reversibly with subsequent slow k_{15} or k_{16}. (In this view the regioselectivity of step 16 is still rationalized in terms of the greater energy of the P–SR bond which is felt as the S–S bond is cleaved in the slow second step.) Indeed, reactions 15 and 16 even could have different rate-determining steps with the second step rate-determining in 15 and the first step slow and irreversible in 16 in which the sulfur–sulfur scission is much faster than in 15. This scission essentially traps the initial adduct or has become concerted with attack by $Z_4P\cdot$ **16**.

The sulfuranyl radical intermediate would likely be a T-shaped species with the odd electron in an orbital perpendicular (π radical) or in the plane (σ radical) of the substituents on sulfur.[16] This is depicted by **24**. A bridged, three-electron, three-centered



bonding description, **25**, may be more accurate. The above results that also could be rationalized in terms of **25** were evidence for its intermediacy to arise.

The magnitude of the steric effects observed for **2** and **16** is emphasized by comparisons of the *intermolecular* selectivities of Table VII with those for other free radicals on reaction with alkyl or phenyl disulfides. Thus, for the chain-transfer reaction of styryl radicals in styrene polymerization, the relative reactivities for the series of RSSR, R = *t*-Bu:*i*-Pr:*n*-Pr:Me, were 1:5:17:68.[17] The phenyl radical toward *t*-Bu, *n*-Pr, *i*-Pr, and CH_3 disulfides displayed reactivities in the ratio 1:8:22:112 at 60 °C.[18] The tri-*n*-butyl tin radical showed the reactivity order of *t*-Bu:$PhCH_2$:*n*-Bu:Ph of 1:9:14:114.[19] The intermolecular selectivity range displayed by phosphoranyl radical **16**, by comparison, is very great indeed, especially considering the reactivity of *t*-BuSSBu-*t* could in fact be only about half that given in Table VII. (Numbers in Table VII are based on the assumption that both products observed from *t*-BuSSBu-*t* are derived from **10**.)

The propionyl radical shows an *intramolecular* selectivity on reaction with *n*-BuSSPr-*i* of ≥7/2 in favor of *n*-Bu$SCOC_2H_5$ formation (cf. 4/1 for **16** on reaction with *sec*-BuSSBu-*n*). Acetyl radical gives no *t*-Bu$SCOCH_3$ from attack on *t*-BuSSEt.[20] Significantly, and consistent with our findings,[3] the kinetics of the bimolecular decay of ESR signals for phosphoranyl radicals derived from, e.g., **3** and **4** (presumed dimerization) are sensitive to steric factors in the phosphoranyl radical.[21] Moreover, the addition of phosphoranyl radicals from **3** to alkenes is strongly retarded by bulky substitution on the double bond. The highly substituted phosphoranyl radical from **4** does not add to terminal olefins at all.[8] *One must conclude that the reactions of phosphoranyl radicals as intact entities are very sensitive to steric bulk both in the phosphoranyl radical and in the trapping species*, e.g., alkenes or disulfides.

Interestingly, **2** reacts readily with both EtOOEt and *t*-BuOOBu-*t* under UV light irradiation conditions. The apparent lack of major steric factors in this system could reflect the operation of an electron-transfer step to give $[Z_4P^+][ROR^{\cdot-}]$ prior to oxygen–oxygen scission and formation of Z_4POR. These processes will merit further investigation.

Experimental Section

General Methods. *n*-Butyl, *sec*-butyl, and *tert*-butyl disulfides (Aldrich) were distilled and stored over 4Å molecular sieves. Phenyl disulfide (Aldrich) was used without further purification. The hydridophosphorane **2** was prepared from bis(dimethylamino)phenylphosphane by the method of Wolf.[22] Neopentyl alcohol and sodium hydrogen sulfide (Aldrich) were used without further purification. Tosyl chloride (Eastman) was recrystallized by the method of Pelletier.[23] *n*-Decane

(14) At sulfur: Kampmeier, J. A.; Jordan, R. B.; Liu, M. S.; Yamanaka, H.; Bishop, D. J. In *Organic Free Radicals*; Pryor, W. A., Ed.; American Chemical Society: Washington, DC 1978; Chapter 16. Bentrude, W. G.; Khan, W. A.; Murakami, M.; Tan, H.-W. *J. Am. Chem. Soc.* **1974**, *96*, 5566. Nakanishi, A.; Bentrude, W. G. *J. Am. Chem. Soc.* **1978**, *100*, 6271. At oxygen: Porter, N. A.; Cudd, M. A.; Miller, R. W.; McPhail, A. T. *J. Am. Chem. Soc.* **1980**, *102*, 415. At phosphorus: Bentrude, W. G., Moriyama, M.; Mueller, H. D.; Sopchik, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 6053. In the last reference inversion occurs at phosphorus even though the potential exists for the formation of a four-covalent phosphoranyl radical which need not give inversion at phosphorus.

(15) Bonacic-Koutecky, V.; Koutecky, J.; Salem, L. *J. Am. Chem. Soc.* **1977**, *99*, 842.

(16) See: Chatgilialoglu, C.; Castelhana, A. L.; Griller, D. *J. Org. Chem.* **1985**, *50*, 2516 and references given therein. Pyramidal σ^* radical structures also have been proposed for sulfuranyls.

(17) Pryor, W. A.; Pickering, T. L. *J. Am. Chem. Soc.* **1962**, *84*, 2705.

(18) Pryor, W. A.; Smith, K. *J. Am. Chem. Soc.* **1970**, *92*, 2731.

(19) Spanswick, J.; Ingold, K. U. *Int. J. Chem. Kinet.* **1970**, *2*, 157.

(20) Takagi, M.; Goto, S.; Tazaki, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1982.

(21) Griller, D.; Roberts, B. P.; Davies, A. G.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 554.

(22) Houlla, D.; Mouheich, T.; Sanchez, M.; Wolf, R. *Phosphorus* **1975**, *5*, 229.

(23) Pelletier, S. W. *Chem. Ind.* **1953**, 1034.

(Aldrich) was distilled and then stored over 4Å molecular sieves. Perdeuteriobenzene (Cambridge Isotope, KOR Isotope, Aldrich) was used as received. Unsymmetrically substituted disulfides were synthesized by the method of Harpp et al.[24] from the appropriate thiols and sulfenimide derivatives.[25] Photolyses were carried out by using a medium-pressure 450-W Hanovia mercury lamp housed in a quartz cooling jacket. Samples for irradiation and the quartz cooling jacket were immersed in a water bath kept at 20 °C. GLC analyses were carried out by using an internal standard to follow formation of thiaphosphorane **6–9**, RSH formation (except CH_3SH), or disulfide consumption on either a Hewlett-Packard Model 5840 gas chromatograph equipped with a 0.33-μm cross-linked methyl silicone, 0.20 mm × 12 m fused-silica column or a Varian Model 3300 gas chromatograph equipped with a 0.25-μm DB-1, 0.32 mm × 10 m fused-silica column. Both instruments were equipped with a split injector and flame ionization detector and used helium as the carrier gas. Continuous wave ^1H NMR spectra were obtained on a Varian EM 390 instrument. Routine FT ^{31}P, ^{13}C, and ^1H NMR spectra were taken on Varian XL-300, SC-300, and FT-80 spectrometers. Quantitative determinations of ratios of pentacovalent thiaphosphoranes (**6–11**) by ^{31}P NMR were made on the Varian XL-300 instrument by using gated decoupling and a 20-s pulse delay. Quantitations of yields were accomplished by ^{31}P NMR on the Varian XL-300 with a 20-s pulse delay without proton decoupling. Quantitative elemental analyses were run by Galbraith Laboratories, Knoxville, TN. Electron ionization mass spectra were done on a VG Micromass 7070-E double-focusing, high resolution mass spectrometer with a VG Data System 2000. Melting points are uncorrected.

Competition Reactions Followed by GLC. The reaction of the hydridophosphorane **2** with *n*-butyl and *sec*-butyl disulfides is typical. An aliquot (100 μL) of a standard decane solution containing hydridophosphorane (21.3×10^{-3} mmol) and internal standard eicosane (2.96×10^{-3} mmol) in decane was mixed with *n*-butyl disulfide (100 μL, 0.53 mmol), *sec*-butyl disulfide (300 μL, 1.6 mmol), and *n*-decane (2 mL) in a Pyrex reaction thimble. The thimble was fitted with a septum-capped three-way glass stopcock valve. The solution was deaerated by bubbling argon through the liquid for about 10 min by means of a stainless steel needle. The reaction thimble was suspended in a water bath and a zero-time sample was removed after which the lamp was turned on. Aliquots of the reaction solution were withdrawn at intervals via a gastight syringe, transferred to septum-capped sample vials, and frozen in liquid nitrogen prior to analysis by GLC. *n*-Butyl and *sec*-butyl thiol formation could be followed by GLC by using *n*-octane as an internal standard. Disulfide consumption was followed by GLC by using tetradecane as the standard.

Hydridophosphorane/Disulfide Reactions Monitored by ^{31}P NMR. The hydridophosphorane (0.0651 g, 0.309 mmol) was dissolved in perdeuteriobenzene (0.50 mL) contained in a screw-top 5-mm NMR tube. The unsymmetrical *n*-butyl–*sec*-butyl disulfide (200 μL, 0.91 mmol) was added, and the NMR tube was sealed with a screw cap fitted with a Teflon/buta-rubber seal. Argon was bubbled through the solution for 5 min by means of a 9-in. inlet needle and a shorter exhaust needle. The needles were removed. The cap was covered with Parafilm to ensure a good seal, and the sample was placed in the photolysis apparatus. The sample was irradiated for 6.5 min and then immediately analyzed by ^{31}P NMR. Duplicate acquisitions gave ratios of **7**/**8** of 4.18 and 4.16. All competitions between symmetrical and unsymmetrical disulfides were run in this manner.

Yields of Hydridophosphorane/Disulfide Reactions by ^{31}P NMR. For example, hydridophosphorane **2** (0.0457 g, 0.216 mmol) was dissolved in perdeuteriobenzene (0.5 mL) contained in a screw-top, 5-mm NMR tube. A sealed capillary tube containing trimethyl phosphate (0.592 molar in perdeuteriobenzene) was placed in the NMR tube. Duplicate proton-coupled ^{31}P NMR spectra were run to determine the ratio of hydridophosphorane to trimethyl phosphate. *n*-Butyl disulfide (200 μL, 1.05 mmol) was added; the tube was sealed and deaerated as above. The solution was irradiated for 20 min, and the ^{31}P NMR spectra were taken immediately. Duplicate proton-coupled spectra gave PSBu-*n* **7** to trimethyl phosphate ratios from which yields of 89% and 95% were determined.

Reaction of *tert*-Butyl Disulfide with Hydridophosphorane 2. Hydridophosphorane (0.0550 g, 0.261 mmol) was dissolved in perdeuteriobenzene (0.5 mL). A capillary tube containing $(CH_3O)_3P{=}O$ in benzene was placed in the NMR tube, and the ^1H-coupled ^{31}P NMR spectrum was taken. *tert*-Butyl disulfide (200 μL, 1.02 mmol) was added. The sample was deaerated as above and then irradiated for 100 min (very sluggish reaction). The ^{31}P NMR spectrum was retaken, and yields of 16.8% of **13** (82.5 ppm) was 7.7% of **10** (−34.1 ppm) were obtained. A third peak was observed in the ^{31}P NMR spectrum (−24 ppm). Although this peak was not definitely assigned, a GC–MS spectrum of a similar reaction showed a compound with molecular ion corresponding to that of the pentacovalent P(Ph)Bu-*t* compound: MS (**13**), *m/e* (rel intensity) 243 (13), 157 (22), 77 (26), 70 (36), 69 (100), 68 (57), 56 (88).

Attempted Inhibition of the Reaction of Phenyl Disulfide with Hydridophosphorane 2. Phenyl disulfide (0.146 g, 0.671 mmol) and α-methylstyrene (4.6 μL, 0.0354 mmol, 5.2% relative to phenyl disulfide) were dissolved in perdeuteriobenzene (0.25 mL) in a 5-mm NMR tube. The solution was frozen, and the hydridophosphorane (0.0644 g, 0.0305 mmol) in perdeuteriobenzene (0.25 mL) was added. The NMR tube was then sealed without thawing the solution. The sample was thawed and mixed. The ^{31}P NMR spectrum taken in less than 30 min showed the phosphorane to be completely converted to **11**. A ^1H NMR spectrum showed that the α-methylstyrene was still present (methyl and olefinic proton resonances clearly detectable and unchanged).

Reactions were run in a similar manner with 10% and 20% (relative to phenyl disulfide) α-methylstyrene and also 5% galvinoxyl. None of these reactions exhibited detectable inhibition.

Dark Reaction of Hydridophosphorane 2 with Phenyl Disulfide. A benzene solution of phenyl disulfide and hydridophosphorane was prepared as above except the NMR tube was wrapped in aluminum foil and minimal lighting was used in the laboratory. The sample was unwrapped and placed in the NMR probe. The probe was covered with aluminum foil. No difference between this and the "light exposed" reactions was observed.

α-Methylstyrene Inhibition of the Reaction of Alkyl Disulfides with Hydridophosphorane 2 Followed by GLC. As an example a solution of hydridophosphorane **2** (0.0320 mmol), *tert*-butyl disulfide (50 μL, 0.255 mmol), and α-methylstyrene (1.6 μL, 0.0123 mmol, 4.8% relative to disulfide) in decane (2 mL) was deaerated and irradiated. At 50% consumption of hydridophosphorane in the control, the α-methylstyrene inhibited sample had not produced detectable products. Similar inhibitions were noted with *n*-BuSSBu-*n*, *sec*-BuSSBu-*sec*, *sec*-BuSSBu-*n*, *sec*-BuSSPh, and MeSSMe.

α-Methylstyrene Inhibition of the Reaction of Methyl Disulfide with Hydridophosphorane 2 Followed by NMR. Hydridophosphorane (0.0376 g, 0.178 mmol), methyl disulfide (50 μL, 0.56 mmol), and α-methylstyrene (2 μL, 0.015 mmol, 2.7% relation to disulfide) were dissolved in perdeuteriobenzene and deaerated. The sample was irradiated for 6.5 min. A ^{31}P NMR spectrum of the sample showed that no reaction of **2** had occurred. A control sample containing similar amounts of reagents (except α-methylstyrene) run at the same time had gone to over 80% completion. Similar reactions were carried out with *n*-butyl, *sec*-butyl, *tert*-butyl, and neopentyl disulfide. In each case the reaction of hydridophosphorane was completely inhibited with about 3% α-methylstyrene while control reactions which did not contain α-methylstyrene went to over 50% completion.

Inhibition of Reaction of Hydridophosphorane 2 with Galvinoxyl. Hydridophosphorane **2** (0.0646 g, 0.306 mmol), *n*-butyl disulfide (100 μL, 0.53 mmol), and galvinoxyl (0.0065 g, 0.015 mmol, 2.8% relative to disulfide) were mixed and deaerated as above. The sample was then irradiated for 15 min. A ^{31}P NMR (121 MHz) spectrum of the sample showed *no* reaction had occurred. A control reaction (run without galvinoxyl) had proceeded to over 80% conversion of **2** to **7**.

Preparation of *n*-BuS Derivative 7. A solution of hydridophosphorane (0.613 g, 2.901 mmol), *n*-butyl disulfide (2 mL), and benzene (2 mL) in a Pyrex tube was deaerated by bubbling argon through the solution. The sample tube was irradiated for 2 h. The benzene and *n*-butyl thiol (byproduct) were stripped off by using a rotary evaporator. Kugelrohr distillation of the remaining material yielded the GLC pure *n*-butylthiaphosphorane **7** bp 140–150 °C at 0.2 mmHg (0.604 g, 2.02 mmol, 69.5%), as a colorless oil. Anal. Calcd for $C_{14}H_{22}NO_2PS$: C, 56.17; H, 7.41; N, 4.68; P, 10.35. Found: C, 56.12; H, 7.33; N, 4.63; P, 10.66.

Preparation of *sec*-BuS Derivative 8. A solution of hydridophosphorane (0.645 g, 3.05 mmol), *sec*-butyl disulfide (2 mL), and benzene (3 mL) was prepared in the same manner as the *n*-butyl analogue. The reaction solution was irradiated for 5.5 h. After the photolysis, during which some polymeric material had precipitated, the benzene was stripped off. The remaining liquid was Kugelrohr distilled. The second and third fractions contained the desired GLC pure *sec*-butylthiaphosphorane **8** (0.55 g, 1.87 mmol, 61% yield) as a colorless oil. Anal. Calcd for $C_{14}H_{22}NO_2PS$: C, 56.17; H, 7.41; N, 4.68; P, 10.35. Found: C, 55.45; H, 7.62; N, 4.71; P, 10.66.

Preparation of neopentylS Derivative 9. A solution of hydridophosphorane (0.341 g, 1.61 mmol), neopentyl disulfide (0.437 g, 2.12 mmol), and benzene (3 mL) was prepared as above and then irradiated for 4 h. The benzene was stripped off on a rotary evaporator. The remaining material was Kugelrohr distilled. The second fraction (bp

(24) Harpp, D. N.; Ash, D. K.; Back, T. G.; Gleason, J. G.; Orwig, B. A.; Van Horne, W. F.; Snyder, J. P. *Tetrahedron Lett.* **1970**, 3551.

(25) Behforowz, M.; Kerwood, J. E. *J. Org. Chem.* **1969**, *34*, 51.

135–150 °C, 0.6 mmHg), a colorless oil, was the phosphorane **9** (0.417 g, 1.33 mmol, 83% yield), pure by GLC. Anal. Calcd for $C_{15}H_{24}O_2PNS$: C, 57.49; H, 7.72; P, 10.21. Found: C, 57.35; H, 7.75; P, 10.12.

Preparation of MeS Derivative 6. Hydridophosphorane **2** (1.30 g, 6.2 mmol) and methyl disulfide (0.58 g, 6.2 mmol) were dissolved in 20 mL of dry benzene. The solution was deoxygenated with a 5-min nitrogen purge and then irradiated for 1 h. Rotary evaporation removed the benzene after which Kugelrohr distillation at less than 1-mm pressure gave a colorless oil which turned solid on standing in the refrigerator: yield 0.590 g, 2.3 mmol, 37%, mp 46 °C; MS (CI, isobutane), 258 (M + 1, 65), 210 (M – MeS, 100). Anal. Calcd for $C_{11}H_{16}O_2NPS$: C, 51.35; H, 6.27; N, 5.45. Found: C, 51.30; H, 6.59; N, 5.40. (Similarly, irradiation of **2** (2.37 g, 11.2 mmol) in 40 mL of benzene for 2 h followed by removal of solvent and all volatiles gave 2.80 g (100% yield) of crystalline material, mp 46 °C, pure by ^{31}P NMR.)

Preparation of 11. Hydridophosphorane (0.410 g, 1.94 mmol) and phenyl disulfide (0.425 g, 1.95 mmol) were dissolved in benzene (20 mL). After 1 h the solvent was stripped on a rotary evaporator. High vacuum (1.5 mmHg) was applied for 2 h to remove the product phenyl thiol leaving **11** (yield 0.615 g, 1.92 mmol).

Preparation of 12. Hydridophosphorane **2** (2.50 g, 11.8 mmol) and PhSSPh (2.58 g, 11.8 mmol) were mixed without solvent and placed in a Kugelrohr distillation apparatus. Heating at 70 °C under 0.1-mm pressure resulted in complete consumption of **2** (GLC). Column chromatography on SiO_2 with ethyl acetate as eluting solvent gave **12** as a yellow oil which was largely free of PhSSPh and PhSH. Molecular distillation (240°, 0.05 mm) gave an oil which was only slightly yellow colored: ^1H NMR ($CDCl_3$, 90 MHz) δ 2.88–3.60 (m, 4 H, NCH_2CH_2S); 3.27–3.60 (m, 2 H, OCH_2CH_2N), 4.04–4.62 (m, 2 H, OCH_2CH_2N); 7.00–7.92 (m, 10 H, PhS, PhPO); ^{31}P NMR (C_6D_6, 32.20 MHz) 33.4. Anal. Calcd for $C_{16}H_{18}NO_2SP$: C, 60.18; H, 5.68. Found: C, 60.12; H, 5.79.

Synthesis of Neopentyl Disulfide. Neopentyl mercaptan (6.34 g, 60.9 mmol),[26] prepared by the method of Courtin et al.,[27] was dissolved in a stirred mixture of 10% potassium bicarbonate (40 mL) and methylene chloride (20 mL) cooled to ice bath temperature. Bromine (3.8 g) in methylene chloride was added dropwise.[28] One-half hour after the addition was complete, the organic layer was separated, washed with water, and dried over magnesium sulfate. The solution was filtered, and the methylene chloride was stripped away. The remaining material solidified on standing. Recrystallization, from methanol, gave the desired neopentyl disulfide (3.83 g, 18.6 mmol, 61% yield) in two crops, mp 42–43 °C; ^1H NMR (80 MHz, $CDCl_3$) δ 0.99, (s, 9 H, CH_3), 2.75 (s, 2 H, CH_2); ^{13}C NMR (20 MHz, $CDCl_3$) δ 55.96 (CH_2), 32.44 (Cq), 28.84 (CH_3); MS, *m/e* (rel intensity) 206.0 M^+ (26.1), 136.2 (6.8), 131.0 (5.6), 87.0 (12.4), 71 (100). Anal. Calcd for $C_{10}H_{22}S_2$: C, 58.19; H, 10.74. Found: C, 58.47; H, 10.63.

General Procedure for Preparation of Unsymmetrical Disulfides. *n*-Butyl thiol (4.5 g, 50 mmol), *N*-phenylthiaphthalimide (12.1 g, 50 mmol), and benzene (100 mL) were mixed in a 200-mL round-bottom flask equipped with a magnetic stirring bar and a reflux condensor. The mixture was heated at reflux for 24 h, then cooled, and filtered (to remove phthalimide product), and the volume was reduced by two-thirds. Pentane (15 mL) was added resulting in the precipitation of more phthalimide. This mixture was filtered, and the solvent was stripped. The remaining liquid was distilled bp 126 °C (0.17 mmHg), 6.44 g, 32.5 mmol, 65%: ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J = 7.3 Hz, 3 H, CH_3), 1.35 (m, 2 H, CH_2–CH_3), 1.62 (m, 2 H, –CH_2–CH_2–CH_2), 2.70 (t, J = 7.3 Hz, 2 H, CH_2–S), 7.18 (t, 1 H, *p*), 7.29 (t, 2 H, *m*), 7.52 (d, 2 H, *o*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.59 (CH_3), 21.53 (CH_2–CH_3), 30.77 (CH_2–CH_2–CH_2) 38.51 CH_2–S), 126.34 (*p* C), 127.06 (*m* C), 128.65 (*o* C), 137.44 (ipso C). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11. Found: C, 60.42; H, 7.26.

***sec*-Butyl Phenyl Disulfide.** This disulfide was prepared similarly. ^1H NMR ($CDCl_3$, 90 MHz) δ 0.92 (t, 3 H, CH_3–CH_2, 1.24 (d, 3 H, CH_3–CH), 1.34–1.87 (m, 2 H, CH_2), 2.58–3.07 (m, 1 H, CH), 6.97–7.65 (m, 5 H, Ar); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 11.40 (CH_3–CH_2–), 19.83 (CH_3–CH), 28.68 (CH_2), 48.16 (CH), 126.08 (*p* C), 126.73 (*m* or *o* C), 128.51 (*m* or *o* C), 138.07 (ipso C); yield >90%; bp 72–73 °C (0.1 mmHg). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11. Found C, 60.90; H, 6.76.

***tert*-Butyl Phenyl Disulfide.** A parallel procedure gave this product: ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 9 H, $(CH_3)_3C$), 7.13 (t, 1 H, *p*), 7.27 (t, 2 H, *m*), 7.55 (d, 2 H, *o*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.74 (CH_3), 48.97 ((CH_3)$_3C$), 125.95 (*p* C), 126.50 (*m* C), 128.40 (*o* C), 138.48 (ipso C); yield >90%; bp 65 °C (0.5 mmHg). Anal. Calcd for $C_{10}H_{14}S_2$: C, 60.56; H, 7.11. Found: C, 59.93; H, 7.08.

***n*-Butyl *sec*-Butyl Disulfide.** This product was prepared similarly in >90% yield, bp 75–76 °C (0.5 mmHg): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J = 7.2 Hz, 3 H, CH_3CH_2), 0.98 (t, J = 7.6 Hz, 3 H, CH_3CH_2), 1.29 (d, J = 6.7 Hz, 3 H, CH_3CH), 1.40–1.86 (m, 6 H. CH_2CH, CH_2CH_2), 2.75 (t, J = 6.7 Hz, 2 H, SCH_2), 2.71 (m, 1 H, CHS); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 11.5 ($CH_3CH_2CHCH_3$), 13.7 ($CH_3CH_2CH_2CH_2$), 20.2 ($CH_3CHCH_2CH_3$), 21.7 ($CH_3CH_2CH_2CH_2$), 28.9 ($CH_3CH_2CHCH_3$), 31.4 ($CH_3CH_2CH_2CH_2$), 39.7 ($CH_3CH_2CH_2$-CH_2), 47.9 ($CH_3CHCH_2CH_3$). Anal. Calcd for $C_8H_{18}S_2$: C, 53.88; H, 10.18. Found: C, 53.80; H, 9.97.

Stability of Thiaphosphorane 8. A deaerated solution of hydridophosphorane **2** (0.0213 mmol) and *sec*-butyl disulfide (19 μL, 18.1 mg, 0.10 mmol) in *n*-decane (1 mL) was irradiated as described above for 1.5 h. About 5% of hydridophosphorane remained. *n*-Butyl disulfide (20 μL, 18.8 mg, 0.10 mmol) was added, and the solution was irradiated again for 0.5 h. GLC analysis of the solution showed that no detectable change in product composition had occurred. *n*-Butyl thiol (20 μL, 16.8 mg, 0.19 mmol) was added, and irradiation was continued for another 0.5 h. GLC analysis again showed no change in product composition.

Stability of Thiaphosphorane 11. Hydridophosphorane **2** (37.0 mg, 0.175 mmol) and phenyl disulfide (45.1 mg, 0.207 mmol) were dissolved in perdeuteriobenzene (0.5 mL) in a screw-capped NMR tube. After 30 min the ^{31}P NMR (32.2 MHz) spectrum of the sample showed that no starting material remained, and only the resonance for **11** (–30 ppm) was observed. *n*-Butyl thiol (15 μL, 14 mg, 0.016 mmol) was then added via a syringe, and the sample was irradiated for 30 min. The ^{31}P NMR (32.2 MHz) spectrum was unchanged from that spectrum before the addition of thiol.

Alcoholysis of 11. To 0.04 mL of a 0.9 M solution of **11** in C_6H_6 was added 5 μL of *n*-PrOH. GLC analysis of the reaction mixture taken 24 h after mixing showed the thiaphosphorane **11** to be totally converted to the known *n*-propoxyphosphorane. Its formation was confirmed by the presence of an absorption at δ –39.4 in the ^{31}P NMR spectrum.

Stability of Phosphorane 11 by ^{31}P NMR. Hydridophosphorane **2** (43.6 mg, 0.207 mmol) was dissolved in perdeuteriobenzene (0.5 mL) in a screw-top NMR tube. A capillary tube containing a benzene solution of trimethyl phosphate was inserted as an external standard. Duplicate ^1H-coupled ^{31}P NMR spectra were recorded to determine the ratio of **2** to $(CH_3O)_3PO$. Phenyl disulfide (20.7 mg, 0.095 mmol) was added to the NMR tube. After all the disulfide had reached (0.5 h) the ^1H-coupled ^{31}P spectrum was run again, and the ratios of **2** and **11** to $(CH_3O)_3P{=}O$ were found. Phenyl *n*-butyl disulfide (50 μL, 0.24 mmol) and *n*-butyl thiol (10 μL, 9.3 mg, 0.13 mmol) were then added to the tube. The sample was irradiated for 10 min. ^1H-coupled ^{31}P NMR spectra showed that none of the originally generated **11** was consumed under conditions that give exclusively **7** from the reaction of **2** and *n*-BuSSPh.

Stability of 8 by ^{31}P NMR. Hydridophosphorane **2** (48.6 mg, 0.230 mmol) was dissolved in perdeuteriobenzene (0.5 mL) in a screw-top NMR tube. A capillary containing $(CH_3O)_3PO$ standard solution was inserted. *s*-Butyl disulfide (20 μL, 19 mg, 0.11 mmol) was added to the tube. The sample was irradiated for 35 min. Gated proton decoupled ^{31}P NMR spectra were taken, and the ratio of **8**:$(CH_3O)_3PO$ was determined (0.49, average of two spectra). *n*-Butyl disulfide (100 μL, 94 mg, 0.533 mmol) and more *sec*-butyl disulfide (300 μL, 270 mg, 1.59 mmol) were added. The sample was irradiated for an additional 30 min. The gated decoupled ^{31}P spectra gave average (of two) ratios of **8**:$(CH_3O)_3PO$ and of **7**:$(CH_3O)_3PO$ of 1.31 and 1.80, respectively, with no **2** remaining. Subtracting the relative amount of **8** initially formed from the final amount a relative rate constant ratio ($k_{n\text{-BuSSBu-}n}/k_{sec\text{-BuSSBu-}sec}$) of 11.0 can be obtained. This is consistent with the rate constant ratio found in the standard competition reactions and therefore shows that **8** is stable under the competition reaction conditions.

Attempted Reaction of Hydridophosphorane 2 with *n*-Butyl Thiol. Hydridophosphorane **2** (0.0511 g, 0.242 mmol), *n*-butyl thiol (50 μL, 42 mg, 0.47 mmol), and perdeuteriobenzene (0.5 mL) were mixed and deaerated in an NMR tube as above. The sample was irradiated for 15 h, and a ^{31}P NMR spectrum taken. It showed that no reaction had occurred.

Reaction of 2 with Sulfur. The hydridophosphorane **2** (42.0 mg, 0.199 mmol), sulfur (S_8) (28.2 mg, 0.881 mmol), and perdeuteriobenzene (0.5 mL) were mixed together in a 5-mm NMR tube at room temperature. A ^{31}P NMR (32.2 MHz) spectrum taken after 1 h showed peaks at 94.04, 82.56, and 71.47 with *no* peak at –45 ppm for **2**. After 5 h another ^{31}P NMR spectrum (121 MHz) was taken with one large peak at 83.92 and two small peaks at +95 and +73 ppm: ^1H NMR (90 MHz, $CDCl_3$) δ 2.67–3.40 (m, 4 H, N–CH_2), 3.60–4.23 (m, 4 H, O–CH_2), 4.30–4.77 (m, 1 H, N*H*), 7.17–7.60 (m, 3 H, *m* and *p*), 7.60–8.03 (m, 2 H, *o*); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 43.49 (s, CH_2–N–CH_2), 68.69 (d, J_{CP} =

(26) Contaminated by approximately 2% of $CH_3OCH_2CH_2OH$.

(27) Courtin, A.; Tobel, H.-R. V.; Auerbach, G. *Helv. Chim. Acta* **1980**, *63*, 1412.

(28) Method of Drabowicz, J.; Mikolajczyk, M. *Synthesis* **1980**, 32.

8.3 Hz, CH_2O), 131.63 (d, J_{CP} = 3.2 Hz, *p* C), 133.78 (d, J_{CP} = 163.8 Hz, ipso C), 128.00 (d, J_{CP} = 15.1 Hz, *o* or *m* C) 129.90 (d, J_{CP} = 11.0 Hz, *o* or *m* C); MS, *m/e* (rel intensity) 243.0, M^+ (3.8), 156.9 (6.6), 69.0 (100.0), 56.1 (26.9).

Reaction of 15 with PhSSPh. Bis(dimethylamino)phenylphosphine (1.08 g, 5.51 mmol) and 2-(methylamino)ethanol (0.48 g, 6.4 mmol) were dissolved in dry *p*-xylene (30 mL) under argon. The solution was heated to 120–130 °C for 3 h and then allowed to cool. The *p*-xylene was removed, and the residue was Kugelrohr distilled under high vacuum. The desired 2-phenyl-1,3,2-oxazaphospholidine (**15**) was found in two fractions along with its polymer (110–120 °C, 120–140 °C, 0.2 mmHg, lit. 64–66, 0.03 mmHg[29]): yield 0.530 g, 2.93 mmol (53% determined by ^{31}P NMR, 32.2 MHz, $CDCl_3$) resonance of monomer at 143.1 ppm.[30]

Phenyl disulfide (0.20 g, 0.92 mmol) was then added to one of the fractions (0.256 g, 1.41 mmol) and dissolved in ~0.5 mL of $CDCl_3$. The ^{31}P NMR spectrum of this solution, taken within 15 min, showed that the peaks for the monomer *and* polymer had greatly diminished, and a new peak at +43.59 ppm had appeared.

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(29) Mitsunobu, O.; Ohashi, T.; Kikuchi, M.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 214.
(30) Robert, J. B.; Weichmann, H. *J. Org. Chem.* **1978**, *43*, 3031.

Communications to the Editor

Dioxygen-Copper Reactivity: EXAFS Studies of a Peroxo-Dicopper(II) Complex

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As part of our efforts in establishing the relevant coordination chemistry of copper proteins[2,3] which bind and/or activate dioxygen,[4] we previously reported the preparation and preliminary characterization of a dioxygen-copper complex, III[5] (Figure 1). This was formed in the reaction of dioxygen ($Cu:O_2$ = 2:1) with the phenoxo-bridged dicopper(I) compound II in dichloromethane at -80 °C. Complex III exhibits a band at 803 cm^{-1} in a resonance Raman experiment which has been assigned to the O–O stretch of a bound peroxide moiety. The binding of O_2 to II is quasi-reversible[4,6] [i.e., $Cu(I)_2L + O_2 \rightleftharpoons Cu(II)_2L(O_2^{2-})$], and complex III therefore serves as a prototype of the proposed dioxygen–copper intermediates in proteins including the O_2 carrier hemocyanin[7] and the monooxygenases tyrosinase[7,8] and dopamine-β-hydroxylase.[8,9]

A knowledge of the structure of III and other related dioxygen adducts[10] would aid considerably our understanding of the factors controlling functional variations among the copper enzyme systems. Since the temperature sensitivity ($T < -60$ °C) of these dioxygen adducts has thus far precluded crystallization, structural characterization must rely on low-temperature spectroscopic methods. Here, we report preliminary findings of extended X-ray absorption fine structure (EXAFS) studies on the dioxygen–copper complex III. As an aid to the interpretation, we have also examined the related X-ray crystallographically characterized precursor dicopper(I) compound II and the phenoxo and hydroxo doubly bridged complex I (Figure I). We find that the Cu···Cu distance in III is 3.31 ± 0.04 Å, which sets limits on the possible dioxygen binding modes in this system.

EXAFS data were collected on stations 7.1 and 9.2 at the SRS, S.E.R.C. Daresbury Laboratory, operating at 2.0 GeV and maximum currents of 300 mA. For the peroxo complex, III, data were collected as the fluorescence excitation spectrum at 10 K (frozen glass). Compounds I and II were measured as solids in transmission mode at 77 K. Raw data were background subtracted and analyzed with the program EXCURVE[11] by methods previously described.[12] The Fourier transforms of the raw data for all the

Table I. Parameters Used To Simulate the Theoretical EXAFS Fits Shown in the Figure[a]

shell	R_{EXAFS}, Å	R_{av}(cryst), Å	$2\sigma^2$, Å^2
	Compound I		
2 O	1.96	1.962	0.009
2 N	2.03	2.023	0.007
1 N	2.27	2.204	0.013
4 C	2.91		0.007
Cu–Cu	3.08	3.082	0.006
3 C	3.32 (6)		0.011
	Compound II		
2 N(py)	1.97	1.969	0.004
1 O(phen)	2.07 (5)	2.031	0.006
1 N(amino)	2.25 (8)	2.171	0.035
4 C	2.90		0.013
3 C	3.3 (15)		0.06
	Compound III (Peroxo Complex)		
1 O	1.93		0.006
3 N	2.08 (4)		0.012
4 C	2.99		0.011
Cu–Cu	3.31		0.015

[a] Unless otherwise indicated (by parentheses), estimated errors are ± 0.03 Å for inner-shell and ± 0.04 Å for outer-shell distances.

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(2) *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, 1984; Vol. 1–3.
(3) (a) *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, New York, 1983. (b) *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, New York, 1986; Vol. 1–2.
(4) Karlin, K. D.; Gultneh, Y. *J. Chem. Educ.* **1985**, *62*, 983–990.
(5) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 3372–3374.
(6) Karlin, K. D. and co-workers, manuscript in preparation.
(7) Solomon, E. I. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 41–108.
(8) Lerch, K. *Met. Ions Biol. Syst.* **1981**, *13*, 143–186.
(9) Miller, S. M.; Klinman, J. P. *Biochemistry* **1985**, *24*, 2114–2127.
(10) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Gultneh, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5828–5829.

(11) EXCURVE is a nonlinear least-squares minimization program which calculates the theroetical EXAFS by using the spherical wave approximation. Phase shifts are obtained from ab initio calculations and refined by using appropriate model compounds. (a) Lee, P. A.; Pendry, J. B. *Phys. Rev. B.* **1975**, *11*, 2795–2811. (b) Perutz, M. F.; Hasnain, S. S.; Duke, P. J.; Sessler, J. L.; Hahn, J. E. *Nature (London)* **1982**, *295*, 535–538.

0002-7863/87/1509-1235$01.50/0