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Reactions of Alkyl Diphenylphosphinates and Related Thio Esters with Some Nucleophiles. S_N2 (S) Reaction and Wittig Type Rearrangement

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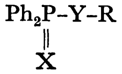
Reactions of alkyl diphenylphosphinates $Ph_2P(=X)YCHR^1R^2$ (X, Y=O,S) with organolithiums and Grignard reagents afforded different types of products depending on the combination of X and Y. When Y=O, the reagents (R^3M) mainly attacked the phosphorus atom to give $Ph_2P(=X)R^3$ and $R^1R^2CHO^-$ irrespective of X, while, when X=Y=S, the reaction occurred exclusively at the ester sulfur atom, $S_N2(S)$, to give $R^3SCHR^1R^2$ and $[Ph_2PS]^-$. When the X=O and Y=S, a Wittig type rearrangement of a carbanion $[Ph_2P(=O)SCR^1R^2]^-$ was observed along with attacks on the phosphorus (major) and the sulfur (minor) atoms. Reactions with some other nucleophiles (hydride, amide and alkoxide ions) are also described.

Substitution on the phosphoryl group with Grignard reagents[1] and organolithiums[2] has been used as a synthetic method. However, there seems to be no report on the reaction of alkyl diphenylphosphinates and related thio esters (**1**—**4**) with organolithiums or Grignard reagents.

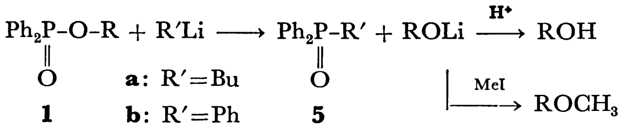


$$\underset{\underset{X}{\|}}{Ph_2P}\text{-Y-R}$$

1: X=Y=O **3**: X=O, Y=S
2: X=S, Y=O **4**: X=Y=S

The esters (**1**—**4**) have four reaction centers towards nucleophile, the phosphorus, Y atoms, and the α-carbon and α-hydrogen atoms of the R group. In the course of an investigation on the reactions of the esters (**1**—**4**) with some nucleophiles, we found two types of novel reactions in the case of Y=S (**3** and **4**), *viz.*, Wittig type rearrangement and S_N2 attack on the sulfur atom (S_N2 (S)).[3] This paper gives detailed results of the investigation.

Reactions of 1 (X=Y=O). Reactions of diphenylphosphinate esters (**1**) with nucleophiles such as butyl- and phenyllithiums, sodium hydride, and potassium *t*-butoxide were carried out in tetrahydrofuran (THF) under nitrogen. The results are summarized in Table 1.

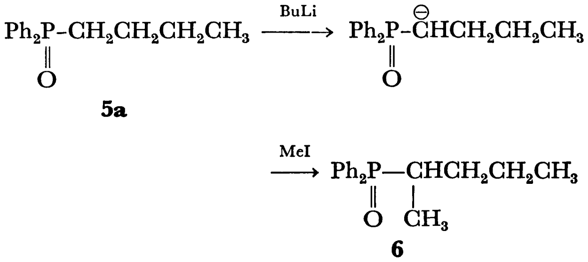


$$\underset{\underset{O}{\|}}{Ph_2P}\text{-O-R} + R'Li \longrightarrow \underset{\underset{O}{\|}}{Ph_2P}\text{-R'} + ROLi \xrightarrow{H^+} ROH$$

$$\xrightarrow{MeI} ROCH_3$$

1 **a**: R'=Bu **5**
b: R'=Ph

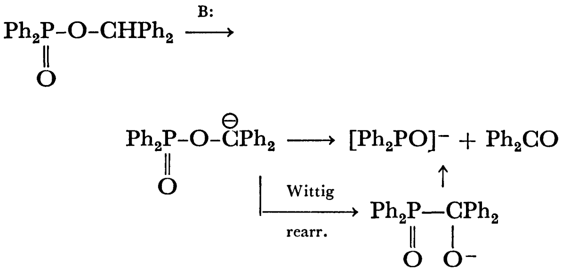
The formation of (1-methylbutyl)diphenylphosphine oxide (**6**) is attributed to methylation of butyldiphenylphosphine oxide (**5a**) initially formed by methyl iodide in the presence of excess butyllithium.



$$\underset{\underset{O}{\|}}{Ph_2P}\text{-}CH_2CH_2CH_2CH_3 \xrightarrow{BuLi} \underset{\underset{O}{\|}}{Ph_2P}\text{-}\overset{\ominus}{C}HCH_2CH_2CH_3 \xrightarrow{MeI} \underset{\underset{O}{\|}}{Ph_2P}\text{—}\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$$

5a **6**

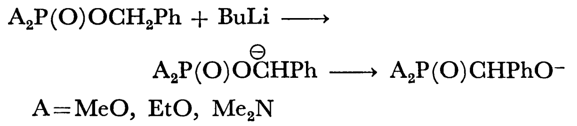
The formation of bis(diphenylmethyl) ether in the case of diphenylmethyl ester might be due to S_N2 attack on the α-carbon atom by diphenylmethoxide anion produced in the reaction. In the reaction with sodium hydride, benzophenone is considered to be formed in the following ways, $[Ph_2PO]^-$ being isolated as diphenylphosphinic acid because of the easy oxidation during the work-up.



$$\underset{\underset{O}{\|}}{Ph_2P}\text{-O-}CHPh_2 \xrightarrow{B:} \underset{\underset{O}{\|}}{Ph_2P}\text{-O-}\overset{\ominus}{C}Ph_2 \longrightarrow [Ph_2PO]^- + Ph_2CO$$

$$\underset{\underset{O}{\|}}{Ph_2P}\text{-O-}\overset{\ominus}{C}Ph_2 \xrightarrow[\text{rearr.}]{\text{Wittig}} \underset{\underset{O}{\|}}{Ph_2P}\text{—}\underset{\underset{O^-}{|}}{C}Ph_2 \longrightarrow Ph_2CO$$

The following example of Wittig type rearrangement has been reported.[4]



$$A_2P(O)OCH_2Ph + BuLi \longrightarrow A_2P(O)O\overset{\ominus}{C}HPh \longrightarrow A_2P(O)CHPhO^-$$

A=MeO, EtO, Me_2N

TABLE 1. REACTIONS OF **1** WITH NUCLEOPHILES (Nu) IN THF

R	Nu	Reaction temp (°C)	Reaction time (h)	Product (%)
$PhCH_2$	BuLi[a]	−78	0.5	**6** (60)[b]
Ph_2CH	BuLi[a]	−78	0.5	**6** (59),[b] ROMe (77)[b]
	PhLi	−78	0.5	**5b** (50), ROH (55)
	NaH	r. t.	6.0	$Ph_2P(O)OH$ (51), ROH (trace) Ph_2CO (59)
	t-BuOK[a]	r. t.	0.5	$Ph_2P(O)O$-*t*-Bu (19) ROMe (73),[b] ROR (14)

a) The reaction mixture was treated with methyl iodide. b) Methylated product.

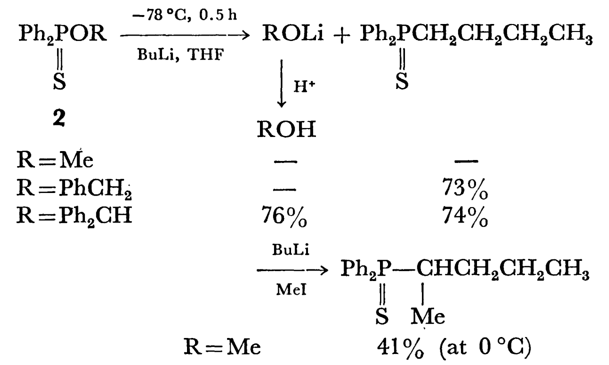
Examples of $S_N2(C)$ reaction has also been reported in the case of phosphate esters with Grignard reagents.[5] However, no reaction of this type was detected in the present system, *i.e.*, diphenylphosphinate esters with organolithiums.

$$(RO)_2P(O)OR + PhMgBr \longrightarrow (RO)_2P(O)O^- + R\text{-}Ph$$

The low yield of *t*-butyl diphenylphosphinates in the reaction with potassium *t*-butoxide is attributed to the easy S_N1 type hydrolysis on silica gel column during the work-up.

Therefore, the main reaction modes in **1** are S_N2 (P) and $S_N2(C)$ reactions.

*Reactions of **2** (X=S, Y=O).* The results of the reaction of *O*-alkyl diphenylphosphinothioates (**2**) with butyllithium are shown in the following scheme.



$$\underset{\substack{\| \\ S \\ \mathbf{2}}}{Ph_2POR} \xrightarrow[\text{BuLi, THF}]{-78\,^\circ C,\ 0.5\,h} ROLi + \underset{\substack{\| \\ S}}{Ph_2PCH_2CH_2CH_2CH_3} \qquad ROLi \xrightarrow{H^+} ROH$$

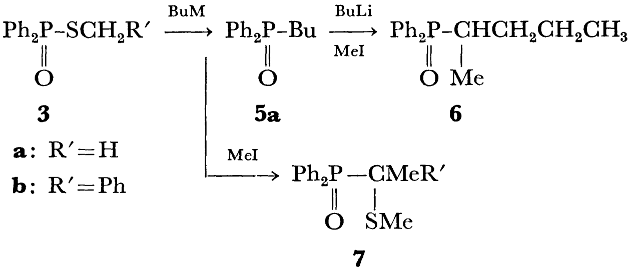
	ROH	$Ph_2P(S)CH_2CH_2CH_2CH_3$
R=Me	—	—
R=PhCH$_2$	—	73%
R=Ph$_2$CH	76%	74%

$$\xrightarrow[MeI]{BuLi} \underset{\substack{\| \quad | \\ S \quad Me}}{Ph_2P\text{—}CHCH_2CH_2CH_3}$$

R=Me 41% (at 0 °C)

Thus, $S_N2(P)$ pathway occurs mainly.

*Reaction of **3** (X=O, Y=S).* The results are given in Table 2.

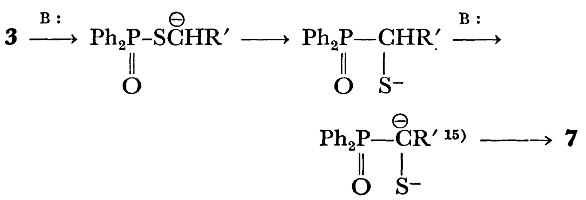


$$\underset{\substack{\| \\ O \\ \mathbf{3}}}{Ph_2P\text{-}SCH_2R'} \xrightarrow{BuM} \underset{\substack{\| \\ O \\ \mathbf{5a}}}{Ph_2P\text{-}Bu} \xrightarrow[MeI]{BuLi} \underset{\substack{\| \quad | \\ O \quad Me \\ \mathbf{6}}}{Ph_2P\text{-}CHCH_2CH_2CH_3}$$

$$\xrightarrow{MeI} \underset{\substack{\| \quad | \\ O \quad SMe \\ \mathbf{7}}}{Ph_2P\text{—}CMeR'}$$

a: R′=H
b: R′=Ph

Formation of (α-methylthioalkyl)diphenylphosphine oxide (**7**) is the first example of Wittig type rearrangement in **3**.



$$\mathbf{3} \xrightarrow{B:} \underset{\substack{\| \\ O}}{Ph_2P\text{-}S\overset{\ominus}{C}HR'} \longrightarrow \underset{\substack{\| \quad | \\ O \quad S^-}}{Ph_2P\text{—}CHR'} \xrightarrow{B:} \underset{\substack{\| \quad | \\ O \quad S^-}}{Ph_2P\text{—}\overset{\ominus}{C}R'}{}^{15)} \longrightarrow \mathbf{7}$$

Formation of benzyl methyl sulfide and methyldiphenylphosphine oxide from **3b** is attributed to methylation of α-toluenethiolate anion and $[Ph_2PO]^-$ produced by $S_N2(P)$ and $S_N2(S)$ pathway, respectively. The latter is of the same type as that in the reactions of **4** described below.

Thus, the main pathway is $S_N2(P)$ accompanied by $S_N2(S)$.

*Reactions of **4** (X=Y=S).* Reactions of diphenylphosphinodithioate esters (**4**) with butyllithium or butylmagnesium chloride were carried out in THF at −78 °C or under reflux. The reaction mixture was

Table 2. Reactions of **3** with nucleophiles (Nu) in THF

R′	Nu	Reaction temp (°C)	Reaction time (h)	Product (%)
H	BuMgCl	refl.	0.1	**5a** (93)[b]
	BuLi	−78	0.5	**5a** (48)
	LiN(*c*-C_6H_{11})$_2$	−78	0.5	**7a** (12)
Ph	BuLi[a]	−78	0.5	**6** (57), **7b** (11) $Ph_2P(O)Me$ (14), $PhCH_2SMe$ (54)

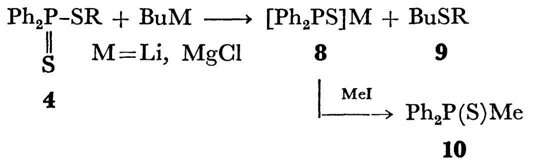
[a] The reaction mixture was treated with methyl iodide. [b] Mp 93.0—94.5 °C (lit,[14] 95 °C).

Table 3. Reactions of **4** with butyllithium and butylmagnesium chloride followed by methylation (in THE)

R	M	Reaction temp (°C)	Reaction time (h)	Product (%)[a]
Me	Li	−78	0.5	**10** (100)
	MgCl	refl.	0.5	**10** (47)
Ph	Li	−78	0.5	**10** (94), **9** (95)[b]
	MgCl	refl.	0.5	**10** (35)[b], recovered **4** (48)[b]
PhCH$_2$	Li	−78	0.5	**10** (84), **9** (39)[b]
	MgCl	refl.	0.5	**10** (10),[b] recovered **4** (74)[b]
CH$_2$=CHCH$_2$	Li	−78	0.5	**10** (62)
t-Bu	Li	−78	1/6	**18** (trace), $Ph_2P(S)CHMe\text{-}n\text{-}C_3H_7$ (main), $Ph_2P(S)SMe$ (minor)

[a] Determined by GLC unless noted otherwise. [b] Isolated by DCC.

then treated with methyl iodide. The results are summarized in Table 3.



$$\underset{\mathbf{4}}{\underset{\displaystyle S}{\overset{}{Ph_2\underset{\|}{P}\text{-}SR}}} + BuM \longrightarrow \underset{\mathbf{8}}{[Ph_2PS]M} + \underset{\mathbf{9}}{BuSR} \quad M{=}Li,\ MgCl$$

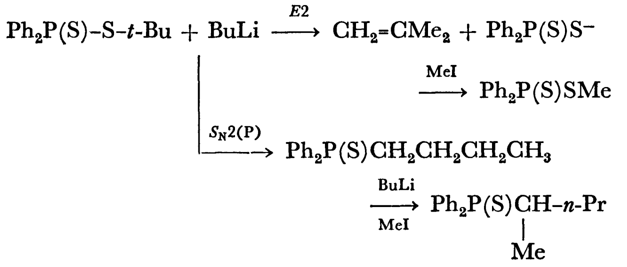
$$[Ph_2PS]M \xrightarrow{MeI} \underset{\mathbf{10}}{Ph_2P(S)Me}$$

The results show that the reactions of **4** with butyllithium in THF at −78 °C were fast, giving diphenylphosphinothioylide (**8**) and butyl sulfides (**9**) selectively in excellent yields. Thus, the reactions are utilized in preparation of unsymmetrical sulfides.[6]

On the other hand, the reactions with Grignard reagents were very slow. Phenylmagnesium bromide in particular did not react with methyl, phenyl, and benzyl esters to an appreciable extent even in refluxing THF for 3 h.

The reactions are the first example of S_N2(S) reaction in **4**. Since methyl diphenylphosphinodithioate is prepared easily and in a high yield from the Friedel-Crafts reaction of benzene and phosphorus pentasulfide followed by refluxing with methanol,[7] the reaction of methyl diphenylphosphinodithioate with butyllithium is used as a new method for preparation of **8**.

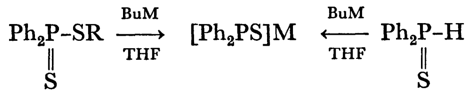
The S_N2(S) reaction did not occur in the case of *t*-butyl ester, because of steric hindrance, the reaction proceeding *via E*2 and S_N2(P) pathways as follows:



$$Ph_2P(S)\text{-}S\text{-}t\text{-}Bu + BuLi \xrightarrow{E2} CH_2{=}CMe_2 + Ph_2P(S)S^- \xrightarrow{MeI} Ph_2P(S)SMe$$

$$Ph_2P(S)\text{-}S\text{-}t\text{-}Bu + BuLi \xrightarrow{S_N2(P)} Ph_2P(S)CH_2CH_2CH_2CH_3 \xrightarrow[MeI]{BuLi} Ph_2P(S)\underset{\displaystyle Me}{\underset{|}{C}}H\text{-}n\text{-}Pr$$

The formation of **8** was also indicated by means of ^{31}P-NMR as shown below.



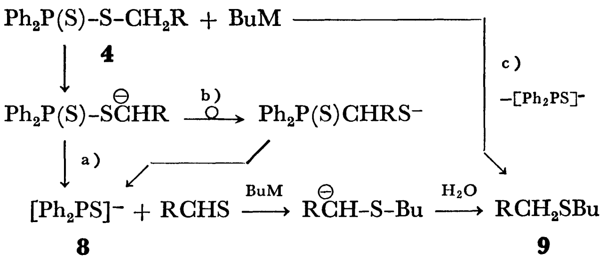
$$\underset{\displaystyle S}{\underset{\|}{Ph_2P}}\text{-}SR \xrightarrow[THF]{BuM} [Ph_2PS]M \xleftarrow[THF]{BuM} \underset{\displaystyle S}{\underset{\|}{Ph_2P}}\text{-}H$$

	δ_P		δ_P	δ_P
R=Me	−64.2	M=Li	−20.7	−20.8
Ph	−64.8	MgCl	−14.3	
$PhCH_2$	−62.9			
Et	−62.4			
$CH_2{=}CHCH_2$	−62.4			

In each case, the signal was observed at the same position, *i.e.*, at −20.7 or −14.3 ppm depending on M=Li or MgCl, respectively.[8]

In the reaction of allyl ester with butylmagnesium chloride, the signal due to $Ph_2P(S)SMgCl$ at −58.6 ppm was detected, indicating the existence of S_N2(C) pathway.

Evidence for S_N2*(S) Mechanism in **4**.* The following three pathways are possible for the formation of **8** and **9**.



$$Ph_2P(S)\text{-}S\text{-}CH_2R + BuM \ (\mathbf{4}) \longrightarrow Ph_2P(S)\text{-}S\overset{\ominus}{C}HR \xrightarrow{\text{b)}} Ph_2P(S)CHRS^-$$

$$Ph_2P(S)\text{-}S\overset{\ominus}{C}HR \xrightarrow{\text{a)}} \underset{\mathbf{8}}{[Ph_2PS]^-} + RCHS \xrightarrow{BuM} R\overset{\ominus}{C}H\text{-}S\text{-}Bu \xrightarrow{H_2O} \underset{\mathbf{9}}{RCH_2SBu}$$

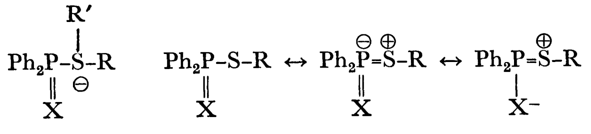
$$Ph_2P(S)\text{-}S\text{-}CH_2R + BuM \xrightarrow[-[Ph_2PS]^-]{\text{c)}} RCH_2SBu$$

Paths a) and b) involve the formation of the corresponding α-carbanion in the first step, followed by direct elimination of thioaldehyde (path a)) or by the Wittig type rearrangement followed by elimination (path b)). Path c) is a direct attack on the sulfur atom of **4** (S_N2(S) reaction). Paths a) and b) are ruled out in view of the following: 1) the reaction did not require two molar amounts of BuM, the yield of methyldiphenylphosphine sulfide (**10**) being 97 and 100% in the reactions of an equimolar and two molar amounts of butyllithium with methyl ester, respectively, 2) even phenyl ester reacted quantitatively in spite of the absence of α-hydrogen atom, and 3) reaction of benzyl ester with an equimolar amount of butyllithium at −78 °C afforded benzyl butyl sulfide containing no deuterium atom after quenching with D_2O (by MS and NMR).

Thus, it can be concluded that the formation of **8** and **9** takes place through S_N2(S) mechanism (path c)).

Reason for the Differences in Reaction Modes. In the case of **1** and **2** (Y=O), the main path is S_N2(P) reaction. On the other hand, in the case of **4** (X=Y=S), S_N2(S) reaction occurs selectively, and in the case of **3** (X=O, Y=S), the S_N2(P) pathway occurs along with S_N2(S).

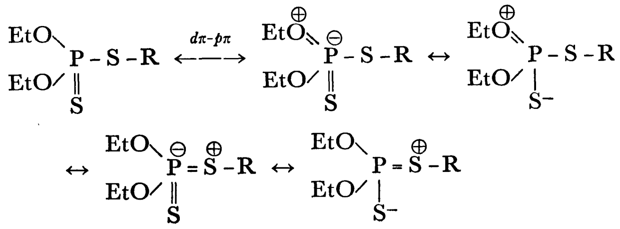
The fact that organometalloids R′M attack Y only when Y=S is explained in terms of the possible involvement of **A** as an intermediate (or transition state), since such a structure is impossible in the case of oxygen, S_N2(P) process being considered to occur irrespective of X when Y=O.



$$\underset{\mathbf{A}}{\underset{\displaystyle X}{\underset{\|\ \ominus}{Ph_2P}}\text{-}\overset{\displaystyle R'}{\overset{|}{S}}\text{-}R} \qquad \underset{\displaystyle X}{\underset{\|}{Ph_2P}}\text{-}S\text{-}R \leftrightarrow \underset{\mathbf{B}}{\underset{\displaystyle X}{\underset{\|}{Ph_2\overset{\ominus}{P}}}{=}\overset{\oplus}{S}\text{-}R} \leftrightarrow \underset{\mathbf{C}}{\underset{\displaystyle X^-}{\underset{|}{Ph_2P}}{=}\overset{\oplus}{S}\text{-}R}$$

Canonical structures such as **B** and **C** having a positive charge on sulfur may also make some contribution in the ground state of **4**, making the formation of **A** possible.

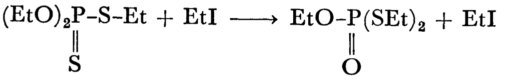
No S_N2(S) reaction was found to occur in the reaction of butyllithium with *S*-alkyl *O*,*O*-diethyl dithiophosphate, in which the following resonance structures are possible.



$$(EtO)_2\underset{\displaystyle S}{\underset{\|}{P}}\text{-}S\text{-}R \xleftrightarrow{d\pi\text{-}p\pi} (Et\overset{\oplus}{O})(EtO)\underset{\displaystyle S}{\underset{\|}{\overset{\ominus}{P}}}\text{-}S\text{-}R \leftrightarrow (Et\overset{\oplus}{O})(EtO)\underset{\displaystyle S^-}{\underset{|}{P}}\text{-}S\text{-}R$$

$$\leftrightarrow (EtO)_2\underset{\displaystyle S}{\underset{\|}{\overset{\ominus}{P}}}{=}\overset{\oplus}{S}\text{-}R \leftrightarrow (EtO)_2\underset{\displaystyle S^-}{\underset{|}{P}}{=}\overset{\oplus}{S}\text{-}R$$

Since the contribution of *dπ-pπ* interaction in the S–P bond is considered to be smaller than that in O–P bond, $S_{\rm N}2$(S) pathway cannot take place, since the ester sulfur atom does not carry such a positive charge as in **4** to accept organometalloids. The following reaction[9] might support the above interpretation.



$$(\mathrm{EtO})_2\underset{\underset{\displaystyle \mathrm{S}}{\|}}{\mathrm{P}}\text{–S–Et} + \mathrm{EtI} \longrightarrow \mathrm{EtO}\text{–}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{SEt})_2 + \mathrm{EtI}$$

It has been shown that the organolithiums possess a larger thiophilicity than the Grignard reagents, as indicated in the reactions with thioketones[10] and with 2-nitrosoimino-2,3-dihydrobenzothiazoles.[11] The results we obtained are in line with these facts.

The observation that **3** (X=O, Y=S) undergoes both $S_{\rm N}2$(P) and $S_{\rm N}2$(S) in contrast to the exclusive occurrence of $S_{\rm N}2$(S) in **4** (X=Y=S) is easily understandable in view of the well-known greater electrophilic reactivity of phosphinyl group than that of a thiophosphinyl group. For example, diphenylphosphinic chloride undergoes hydrolysis more easily than diphenylphosphinothioic chloride. Similarly, *S*-benzyl diphenylphosphinothioate undergoes hydrolysis more easily than benzyl diphenylphosphinodithioate (see Experimental).

Experimental

^{31}P-NMR spectra were measured with a Hitachi R-20B-R-204 PB spectrometer using 85% phosphoric acid as an external standard.

Materials. *S*-Methyl,[8] *S*-benzyl,[12] *O*-methyl,[12] *O*-benzyl diphenylphosphinothioates,[13] and *t*-butyl diphenylphosphinodithioate[7b] were prepared by the reported methods.

Methyl Diphenylphosphinodithioate. A mixture of sodium hydroxide (20 g, 0.5 mol) and diphenylphosphinodithioic acid (105 g, 0.42 mol) in THF (300 ml) was stirred at room temperature for 1 h. Methyl iodide (60 g, 0.42 mol) was added and the mixture was stirred at room temperature for 1 h. The reaction mixture was washed with water and extracted with benzene. After removal of the solvent from the dried extract, the residue was recrystallized from ethanol, mp 86—87 °C (lit,[7] 82—83 °C), yield 98 g (88%).

Diphenylmethyl Diphenylphosphinate. A mixture of diphenylphosphinic chloride (17.3 g, 73 mmol), diphenylmethanol (22.7 g, 123 mmol) and triethylamine (12 ml) in THF (80 ml) was refluxed for 2 h. The reaction mixture was treated similarly. Mp 138—139 °C (from 2-propanol), yield 20.6 g (73%). NMR (CDCl$_3$): δ 6.60 (d, 1H, $J_{\rm POCH}$=11 Hz, CH), 7.42 (s, 10H, 2Ph), and 7.30–8.10 (m, 10H, 2P-Ph); ^{31}P-NMR (THF): $\delta_{\rm P}$−29.5 ppm.

Benzyl Diphenylphosphinate. A mixture of diphenylphosphinic chloride (1.86 g, 79 mmol) and benzyl alcohol (20 ml) in THF (80 ml) was stirred for 1 h. The reaction mixture was washed with 10% aqueous sodium hydrogencarbonate and extracted with benzene. After removal of the solvent from the dried extract, the residue was recrystallized from ether, mp 82.5—83.5 °C, yield 17.1 g (71%). NMR (CDCl$_3$): δ 4.95 (d, 2H, $J_{\rm POCH}$=7 Hz, OCH$_2$), 7.22 (s, 5H, Ph), and 7.20—8.00 (m, 10H, 2P-Ph).

Found: C, 74.15; H, 5.65%. Calcd for $C_{19}H_{17}O_2P$: C, 74.02; H, 5.56%.

O-Diphenylmethyl Diphenylphosphinothioate. To a mixture of diphenylmethanol (10 g, 54 mmol) and sodium (1 g, 43 mmol) in THF (40 ml) was added diphenylphosphinothioic chloride (11.0 g, 45 mmol) in THF (50 ml), and the reaction mixture was treated in the usual way, mp 97—98 °C (from ethanol), yield 13.9 g (95%). IR (KBr): 980 (P-O) and 640 cm^{-1} (P=S); NMR (CDCl$_3$): δ 6.75 (d, 1H, $J_{\rm POCH}$= 13 Hz, CH), 7.20 (s, 10H, 2Ph), and 7.10—7.95 (m, 10H, 2P-Ph); ^{31}P-NMR (THF): $\delta_{\rm P}$−82.1 ppm.

Found: C, 75.06; H, 5.25; S, 8.13%. Calcd for $C_{25}H_{21}OPS$: C, 74.98; H, 5.29; S, 8.01%.

Benzyl Diphenylphosphinodithioate. To a mixture of diphenylphosphinodithioic acid (48 g, 0.19 mol) and sodium (4.6 g, 0.2 mol) in THF (200 ml) was added benzyl bromide (34.2 g, 0.2 mol), and the mixture was stirred for 3 h. After the usual work-up, the reaction mixture was subjected to column chromatography with CHCl$_3$ to give colorless viscous oil, yield 56 g (86%), which could not be distilled. NMR (CDCl$_3$): δ 4.05 (d, 2H, $J_{\rm PSCH}$=13 Hz, CH$_2$), 7.05 (s, 5H, Ph), and 7.15—8.05 (m, 10H, 2P-Ph); ^{31}P-NMR (THF): $\delta_{\rm P}$−62.9 ppm.

Found: C, 66.98; H, 5.06; S, 18.81%. Calcd for $C_{19}H_{17}PS_2$: C, 67.03; H, 5.03; S, 18.84%.

Phenyl Diphenylphosphinodithioate. To a mixture of benzenethiol (10 ml) and sodium (2.5 g, 0.11 mol) in THF (30 ml) was added diphenylphosphinothioic chloride (24 g, 0.095 mol), and the reaction mixture was stirred for 3 h. After the usual work-up, the product was distilled *in vacuo*, bp 229 °C/0.1 mmHg, mp 57—59 °C (from ethanol), yield 24 g (77%). ^{31}P-NMR (THF): $\delta_{\rm P}$−64.8 ppm.

Found: C, 66.14; H, 4.50; S, 19.57%. Calcd for $C_{18}H_{25}PS_2$: C, 66.23; H, 4.63; S, 19.65%.

Ethyl Diphenylphosphinodithioate. To a mixture of diphenylphosphinodithioic acid (50 g, 0.2 mol) and sodium hydroxide (8 g, 0.2 mol) in THF (150 ml) was added ethyl bromide (15 ml) under stirring at room temperature and the mixture was stirred for 1 h. The usual work-up afforded the ester (46 g, 83%), bp 166 °C/0.2 mmHg (lit,[7b] 166—167 °C/0.3 mmHg).

Allyl Diphenylphosphinodithioate. To a mixture of diphenylphosphinodithioic acid (29 g, 0.12 mol) and sodium hydroxide (6 g, 0.15 mol) in THF (100 ml) was added allyl bromide (10 ml), and the mixture was stirred for 3 h at room temperature. The usual work-up gave the ester (27 g, 80%), bp 160 °C/0.04 mmHg. NMR (CCl$_4$): δ 3.55 (dd, 2H, $J_{\rm PSCH}$=13 Hz, CH$_2$), 4.7—6.0 (m, 3H, CH=CH$_2$), and 7.2—8.2 (m, 10H, 2P-Ph); ^{31}P-NMR (THF): $\delta_{\rm P}$−62.4 ppm.

Found: C, 62.32; H, 4.92%. Calcd for $C_{15}H_{15}PS_2$: C, 62.02; H, 5.21%.

*Reactions of **1** with Nucleophiles.* Only some typical examples are described. Reactions were carried out under nitrogen or argon.

Reaction of Benzyl Diphenylphosphinate with Butyllithium. Butyllithium (3 mmol) in hexane (2 ml) was added to the ester (0.795 g, 2.6 mmol) in THF (30 ml) at −78 °C and the mixture was stirred at this temperature for 0.5 h. After addition of methyl iodide (1 ml), the reaction mixture was warmed to room temperature, washed with water, and extracted with chloroform. After removal of the solvent from the dried extract, the residue was subjected to dry column chromatography (DCC) (SiO$_2$, MeCO$_2$Et) to give **6** (0.419 g, 60%), mp 86—88 °C (from ether). NMR (CCl$_4$): δ 0.87 (t, 3H, Me), 1.17 (dd, $J_{\rm PCCH}$=14 Hz, $J_{\rm HH}$=7 Hz, 3H, Me), 1.27—1.70 (m, 4H, 2CH$_2$), 2.05—2.50 (m, 1H, CH), and 7.20—7.90 (m, 10H, 2P-Ph).

Found: C, 75.22; H, 7.61%. Calcd for $C_{17}H_{21}OP$: C, 74.98; H, 7.71%.

Reaction of Diphenylmethyl Diphenylphosphinate with Sodium Hydride. Sodium hydride (0.157 g, 6.5 mmol) was added to the ester (0.247 g, 0.64 mmol) in THF (15 ml) at room temperature, and the mixture was stirred for 6 h. After addition of methanol (1 ml), the mixture was acidified with dil. hydrochloric acid and extracted with benzene. Removal of benzene from the extract gave 71 mg (51%) of diphenylphosphinic acid and oily material, the latter being separated with DCC (SiO_2, $CHCl_3$; then SiO_2, hexane) to give benzophenone(69 mg, 59%) and diphenylmethanol (trace) which were identified by IR and NMR.

Reaction of O-*Methyl Diphenylphosphinothioate with Butyllithium.* Butyllithium (10.9 mmol) in hexane (7 ml) was added to a solution of the ester (1.467 g, 5.9 mmol) in THF (30 ml) at 0 °C and the mixture was stirred for 1 h. After addition of methyl iodide (1 ml), the mixture was stirred for 3 h. After the usual work-up, recrystallization of the residue from 2-propanol twice gave 0.699 g (41%) of (1-methylbutyl)diphenylphosphine sulfide, mp 114—115 °C. IR (KBr): 1430, 1105 (P–Ph), and 605 cm^{-1} (P=S); NMR ($CDCl_3$): δ 0.85 (t, 3H, $J_{HH}=7$ Hz, Me), 1.15 (dd, 3H, $J_{PCCH}=19$ Hz, $J_{HH}=7$ Hz, Me), 1.35—1.65 (m, 4H, $2CH_2$), 2.50—2.90 (m, 1H, CH), and 7.35—8.10 (m, 10H, 2P–Ph); MS: *m/e* 288 (M^+, 7%), 218 (Ph_2P^+SH, 100), and 185 (Ph_2P^+, 25).

Found: C, 70.84; H, 7.44; S, 11.12%. Calcd for $C_{17}H_{21}SP$: C, 70.80; H, 7.34; S, 11.12%.

Reaction of S-*Methyl Diphenylphosphinothioate with Lithium Dicyclohexylamide.* Butyllithium (12.5 mmol) in hexane (8 ml) was added to dicyclohexylamine (2.28 g, 12.6 mmol) in THF (25 ml) at −78 °C and the mixture was stirred at this temperature for 0.5 h. *S*-Methyl diphenylphosphinothioate (1.74 g, 7.0 mmol) in THF (25 ml) was then added to the mixture and the mixture was stirred at the same temperature for 0.5 h. After addition of methyl iodide (2 ml), the reaction mixture was warmed to room temperature, washed with aqueous citric acid, and extracted with benzene. The extract was dried, evaporated, and subjected to DCC (SiO_2, AcOEt) to give 0.229 g (12%) of **7a**, mp 185—187 °C (from ether). IR (KBr): 1438, 1120(P–Ph), and 1198 cm^{-1} (P=O); NMR ($CDCl_3$): δ 1.54 (dd, 3H, $J_{PCCH}=14$ Hz, $J_{HH}=7$ Hz, Me), 2.73 (s, 3H, SMe), 3.83 (dq, 1H, $J_{PCH}=14$ Hz, $J_{HH}=7$ Hz, CH–P), and 7.40—8.10 (m, 10H, 2P–Ph); MS: *m/e* 276 (M^+, 7%), 230 (M^+-SCH_2, 100), and 202 (Ph_2P^+OH, 78).

Found: C, 64.93; H, 5.66%. Calcd for $C_{15}H_{17}OPS$: C, 65.20; H, 6.20%.

Reaction of S-*Benzyl Diphenylphosphinothioate with Butyllithium.* Butyllithium (2.0 mmol) in hexane (1.3 ml) was added to the ester (0.354 g, 1.1 mmol) in THF (15 ml) at −78 °C and the mixture was stirred at this temperature for 0.5 h. Methyl iodide (0.5 ml) was added to the mixture at −78 °C. The temperature was then raised to room temperature. The reaction mixture was washed with water and extracted with chloroform. DCC (SiO_2, CCl_4) of the dried extract gave benzyl methyl sulfide (81 mg, 54%), methyldiphenylphosphine oxide (32 mg, 14%), **6** (168 mg, 57%) (by IR and NMR), and oily **7b** (42 mg, 11%).

7b: NMR ($CDCl_3$): δ 1.85 (d, 3H, $J_{PCCH}=14$ Hz, Me), 2.03 (s, 3H, SMe), 7.13 (s, 5H, Ph), and 7.22—8.10 (m, 10H, 2P–Ph).

Found: C, 71.48; H, 6.14; S, 9.03%. Calcd for $C_{21}H_{21}OPS$: C, 71.56; H, 6.01; S, 9.10%.

Reaction of Phenyl Diphenylphosphinodithioate with Butyllithium. Butyllithium (4.5 mmol) in hexane (3 ml) was added to a solution of the ester (0.496 g, 1.5 mmol) in THF (10 ml) at −78 °C and the mixture was stirred at this temperature for 0.5 h. After addition of methyl iodide (0.5 ml) at −78 °C, the mixture was stirred at room temperature for 0.5 h and determined by gas chromatography (GLC, at 210 °C, H 523 column). The yield of **10** was 94%. DCC (SiO_2, CCl_4) of the reaction mixture after the usual work-up gave butyl phenyl sulfide (0.240 g, 95%) (by IR and NMR).

Reaction of Benzyl Diphenylphosphinodithioate with Butyllithium Followed by Treatment with D_2O. A mixture of butyllithium (1.5 mmol) in hexane (1 ml) and the ester (1.06 g, 3.1 mmol) in THF (15 ml) was treated in a similar way to that above and the reaction mixture was quenched with D_2O (0.1 ml). DCC (SiO_2, $CHCl_3$) gave 0.25 g (1.4 mmol) of benzyl butyl sulfide. NMR ($CDCl_3$): C_6H_5 : CH_2-*n*-Pr= 5.3 : 2.0 (as average value of five measurements). MS: *m/e* 180 (M^+): 181 (M^++1): 182 (M^++2)=100 : 15 : 7 (calcd: 100 : 14 : 5).

Alkaline Hydrolysis. *1) Benzyl Diphenylphosphinodithioate*: The ester (1.295 g, 3.8 mmol) was stirred with 10% aqueous sodium hydroxide (30 ml) at 80 °C for 6 h. The reaction mixture was extracted with chloroform to remove unchanged ester. The extract was acidified with hydrochloric acid and extracted with chloroform. Evaporation of the dried extract gave diphenylphosphinothioic acid (11 mg, 1%), which was identified by IR.

2) S-*Benzyl Diphenylphosphinothioate*: The ester (0.512 g, 1.6 mmol) was treated in a similar way to that above with 10% aqueous sodium hydroxide (20 ml). The reaction products were diphenylphosphinic acid (0.304 g, 89%) and α-toluenethiol (72 mg, 37%) (by IR and NMR).

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