Some Unusual Properties of Tris(2,6-dimethoxyphenyl)phosphine Sulfide and the Related Compounds

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The title sulfide {2,6-$(MeO)_2C_6H_3$}$_3$P=S [abbr. $(2,6)_3$P=S] reacted with acids to form a novel mercaptophosphonium salt [$(2,6)_3$P–SH]X, solution thermolysis of which in the absence or presence of triphenylphosphine resulted in the unusual desulfurization to give the tertiary phosphonium salts [$(2,6)_3$P–OH]X. $(2,6)_3$P=S also reacted with alkyl iodides or bromides under mild conditions to give stable (alkylthio)phosphonium salts [$(2,6)_3$P–SR]X (R=Me, Et, n-Bu), which reacted with thiols at room temperature in the presence of a catalytic amount of the tertiary phosphine $(2,6)_3$P to give [$(2,6)_3$P–H]X and unsymmetrical disulfides.

Triphenylphosphines bearing methoxyl substituents at 2,6-positions of the phenyl groups, such as {2,6-$(MeO)_2C_6H_3$}$_3$P [abbr. $(2,6)_3$P, see Fig. 1], exhibit high basicities and nucleophilicities.[1–3] In our previous paper, we reported some unusual physical and chemical properties of the oxide $(2,6)_3$P=O.[4] In the present paper, we report the details of some unusual properties of its sulfide $(2,6)_3$P=S towards acids and alkyl halides. The preliminary results have been reported elsewhere.[5,6]

Results and Discussion

Preparation and Desulfurization of Mercaptophosphonium Salts. The tertiary phosphine $(2,6)_3$P reacted easily with elemental sulfur in toluene at room temperature to give its sulfide $(2,6)_3$P=S [step (1) of Scheme 1].

In contrast to triphenylphosphine sulfide Ph_3P=S, an addition of 60% $HClO_4$ to a solution of $(2,6)_3$P=S in acetone resulted in immediate precipitation of a novel mercaptophosphonium salt [$(2,6)_3$P–SH]ClO_4 [step (2)]. To our further surprise, when [$(2,6)_3$P–SH]ClO_4 was heated in 2-propanol, it was partly desulfurized to give an equilibrated mixture of [$(2,6)_3$P–H]ClO_4 and [$(2,6)_3$P–SH]ClO_4 in a ratio of 71 : 29 [step (3)]. Heating a solution of $(2,6)_3$P=S in ethyl methyl ketone (MEK) containing aqueous HCl also gave [$(2,6)_3$P–H]$^+$ salt (55% yield). Analogous results were obtained using methanol or 2-propanol as the solvent. The reversibility [step (3′)] was confirmed by treating [$(2,6)_3$P–H]Cl·2.5H_2O with sulfur in acetone.

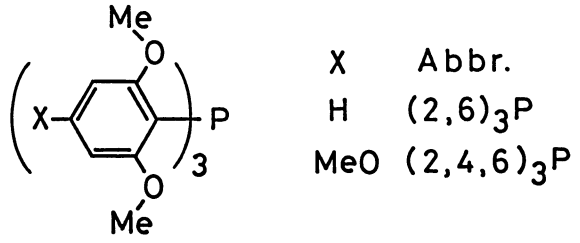
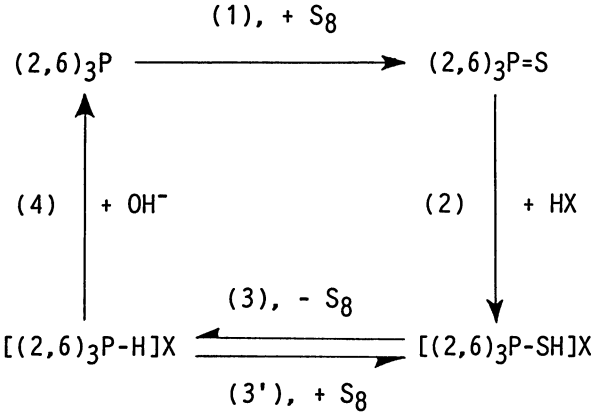


Fig. 1.



Scheme 1.

Since [$(2,6)_3$P–H]$^+$ salts are easily deprotonated by aqueous sodium hydroxide to give $(2,6)_3$P in quantitative yields [step (4)], the combination of these reactions [steps (2)–(4)] may be used to reduce $(2,6)_3$P=S to $(2,6)_3$P *without using any reaqent.*

Although other sulfides $(2,6)_2$PhP=S, $(2,6)Ph_2$P=S, and $(2\text{-}MeOC_6H_4)_3$P=S were prepared from the corresponding tertiary phosphine and elemental sulfur, we had no evidence for the formation of their mercaptophosphonium salts. These sulfides, as well as Ph_3P=S, were stable against the desulfurization in solutions containing HCl or $HClO_4$ even at 70 °C for 8 h. Tris(2,4,6-trimethoxyphenyl)phosphine sulfide $(2,4,6)_3$P=S [(2,4,6)= 2,4,6-$(MeO)_3C_6H_2$], on the other hand, gave a complex mixture containing 1,3,5-trimethoxybenzene, the protonation product at C(–P).

When $(2,6)_3$P=S was treated with Ph_3P in acetone containing HCl at 50 °C for 3 h, a mixture of [$(2,6)_3$P–H]Cl·2.5H_2O and Ph_3P=S was obtained both in quantitative yields. $(2,6)_2$PhP=S also reacted with Ph_3P in the presence of acid to give [$(2,6)_2$PhP–H]$^+$ salt[1] and Ph_3P=S, but $(2,6)Ph_2$P=S and $(2\text{-}MeOC_6H_4)_3$P=S were recovered almost unreacted.

Reactions of Triarylphosphine Sulfides with Alkyl Halides. Although an (alkylthio)phosphonium salt is a key intermediate in the reactions or formation of organodisulfides,[7] its isolation from these reaction mixtures is generally very difficult.[8] We found that $(2,6)_3$P=S reacted very easily with alkyl iodide (RI=MeI, EtI, *n*-BuI) in benzene at room temperature to give imme-

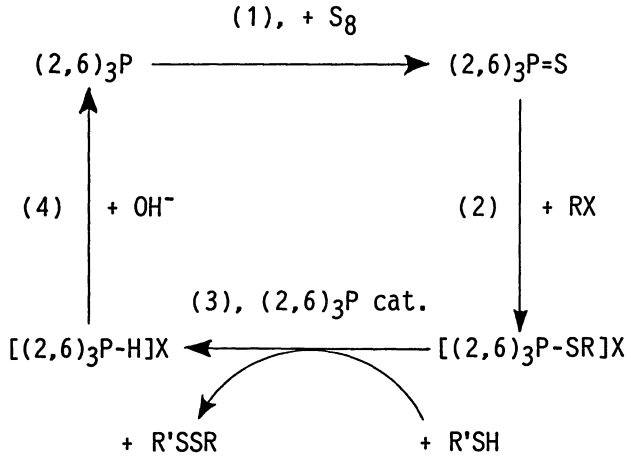
diately precipitates of $[(2,6)_3P–SR]I$ [step (2) of Scheme 2]. The reactions with alkyl bromides were slower under analogous conditions, but $(2,6)_3P=S$ reacted both with EtBr and BuBr in ethanol on heating at 60 °C for 2 h. $(2,6)_2PhP=S$ also reacted with methyl iodide at room temperature to give $[(2,6)_2PhP–SMe]I$, but neither $(2,6)Ph_2P=S$ nor $Ph_3P=S$ reacted with these alkyl halides under these conditions.

The bromides $[(2,6)_3P–SR]Br$ are soluble and stable in water, and an addition of 60% aqueous perchloric acid to the aqueous solution gave the precipitates of $[(2,6)_3P–SR]ClO_4$. These (alkylthio)phosphonium salts are thermally stable even in the presense of base. Thus, they were recovered almost unchanged after heating at 80 °C for 24 h in ethanol containing triethylamine.

The inertness of the P–SR bond to hydrolysis or to alcoholysis can readily be explained by both the steric and electronic effects of the 2,6-dimethoxyl substituents. However, the most attractive explanation involves the interaction between the phosphorus atom and one or more of the oxygen atoms on 2,6-positions in the phosphonium species. The presence of such interactions may interfere both sterically and electronically with additional coordination by oxide anions, a key step for P–SR bond cleavage. An analogous explanation has been cited for the unusual thermal reactions of (2-hydroxyalkyl)phosphonium salts $[(2,6)_3P–CH_2CRR'OH]X$.[2]

Reactions of (Alkylthio)phosphonium Salts with Thiols. Omelańczuk and Mikołajczyk prepared some-(methylthio)phosphonium salts by treating the phosphine sulfides with methyl triflate.[9] They also found that reaction of $[Ph_3P–SMe]^+$ salt with NaSEt gave exclusively triphenylphosphine and a mixture of dimethyl, diethyl, and methyl ethyl disulfides. Masui et al. reported that a variety of phosphonium salts $[Ph_3P–SR]ClO_4$ could be prepared electrochemically from Ph_3P and dialkyl (or diaryl) disulfide and that their reaction with thiols in the presence of triethylamine gave Ph_3P and unsymmetrical diorganodisulfides.[10] We also found that $[(2,6)_3P–SR]I$ (R=Me, Et, Bu) reacted with thiols R'SH (R'=Ph, 4-MeC_6H_4, n-C_8H_{17}), in methanol containing a catalytic amount of $(2,6)_3P$ [step (3)]. The mixture was stirred at room temperature for 24 h under argon, and it was worked up to give the tertiary phosphonium salt $[(2,6)_3P–H]I$ and the unsymmetrical disulfides selectively. 2,6-Dimethoxybenzenethiol[11] reacted with $[(2,6)_3P–SR]I$ much slower than the other thiols, due probably to the bulkiness. We expected that in these reactions the catalyst $(2,6)_3P$ (pK_a 9.33)[1,12] worked as a base toward R'SH to form $[(2,6)_3P–H]SR'$, and that the anion $R'S^-$ thus formed reacted with the cation $[(2,6)_3P–SR]^+$ to form RSSR' and to reproduce $(2,6)_3P$. In fact, triethylamine (pK_a 10.75) could be used in place of $(2,6)_3P$ to give triethylammonium iodide and $(2,6)_3P$, as well as RSSR'. The lack of formation of symmetrical disulfides at lower temperatures is astonishing, and it can be best explained as that the exchange of alkylthio group at phosphorus by $R'S^-$ anion[9] is sterically precluded in our compounds. However, the formation of symmetrical disulfides was observed when the reactions were performed at elevated temperatures or when the base was used in larger amounts. We observed no formation of monosulfide RSR' even under these conditions. In the absence of base, the reaction was very slow even at elevated temperatures, and it gave equilibrium mixtures of $[(2,6)_3P–SR]I$, $[(2,6)_3P–H]I$, R'SH, and RSSR'. The reversibility of the reaction could be used for the preparation of (phenylthio)phosphonium salt $[(2,6)_3P–SPh]ClO_4$ by the reaction of $[(2,6)_3P–H]Cl$ and PhSSPh, although the yield was poor.

Since $[(2,6)_3P–H]I$ can easily be deprotonated by aqueous alkali hydroxide, we now obtained a reaction cycle as shown in Scheme 2. This indicates that unsymmetrical disulfides can be prepared under mild conditions from elemental sulfur, alkyl halide, thiol, and aqueous alkali hydroxide using $(2,6)_3P$ as a reproducible reagent.



Scheme 2.

Experimental

Physical Measurements. ^1H and ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer operating at 270 and 67 MHz, respectively. IR spectra were recorded for Nujol mull using a Simadzu FTIR-4200 spectrophotometer. Gas–liquid chromatography was recorded on a Hitachi 263-30 gas chromatograph by means of a one m. Silicone gum rubber SE 30 column at 60—250 °C.

The ^1H NMR and ^{13}C NMR spectral data of new compounds are shown in Tables 1 and 2, respectively.

Triarylphosphines. Tris(2,6-dimethoxyphenyl)phosphine, $(2,6)_3P$, was obtained from the K. I. Kasei Co., Ltd. It was purified by washing with water followed by recrystallization from 2-propanol. Other tertiary phosphines, tris(2,4,6-trimethoxyphenyl)phosphine, $(2,4,6)_3P$, bis(2,6-dimethoxyphenyl)phenylphosphine, $(2,6)_2PhP$, (2,6-dimethoxyphenyl)-diphenylphosphine, $(2,6)Ph_2P$, and tris(2-methoxyphenyl)-phosphine, $(2\text{-}MeOC_6H_4)_3P$, were prepared as described previously.[1,12]

Table 1. ^{1}H NMR Spectral Data[a] for Organophosphorus Compounds

Compounds	4-H[b]	3,5-H[c]	2,6-MeO[d]	Other protons[e]
$(2,4,6)_3P{=}S$	—	6.03[f]	3.53	3.77s(4-MeO)
$(2,6)_3P{=}S$	7.22	6.49	3.53	
$(2,6)_2PhP{=}S$	7.27	6.47	3.47	8.06ddd[15]$_P$[6]$_H$[3]$_H$(2′,6′-H), 7.4—7.2m(3′,4′,5′-H)
$(2,6)Ph_2P{=}S$	—[g]	6.51	3.27	8.0—7.8m(4H) and 7.5—7.3m(7H) (Ph)
$[(2,6)_3P{-}SH]ClO_4$	7.56	6.65	3.66	
$[(2,6)_3P{-}SMe]I$	7.59	6.68	3.60	2.09d[19]$_P$(CH_3)
$[(2,6)_3P{-}SEt]I$	7.58	6.66	3.61	2.51dq[10]$_P$[8]$_H$(CH_2), 1.25dt[2]$_P$[7]$_H$(CH_3)
$[(2,6)_3P{-}SBu]I$	7.58	6.66	3.61	2.48dt[10]$_P$[7]$_H$(P-CH_2), 1.58—1.28m (CH_2CH_2), 0.84t[7]$_H$(CH_3)
$[(2,6)_3P{-}SPh]ClO_4$	7.44	6.52	3.63	7.27—7.13m(Ph)
$[(2,6)_2PhP{-}SMe]I$	7.67	6.73	3.61	2.12d[18]$_P$(CH_3), 7.84—7.58m(Ph)
$[(2,6)_3P{-}H]Cl\cdot 2.5H_2O$	7.61	6.69	3.71	8.48d[546]$_P$(P-H)
$[(2,6)_3P{-}H]I$	7.62	6.68	3.72	8.48d[546]$_P$(P-H)
$(2\text{-}MeOC_6H_4)_3P{=}S$	7.70ddd[16]$_P$[8]$_H$[2]$_H$(6-H), 7.44tdd[8]$_H$[2]$_H$[2]$_P$(5-H), 6.99tdd[8]$_H$[2]$_H$[1]$_P$(4-H), 6.89dd[8]$_H$[6]$_P$(3-H), 3.55s(OMe)			

a) In $CDCl_3$ (δ, s=singlet, d=doublet, t=triplet, m=multiplet, and q=quartet. b) Triplet with J_H 8—9 Hz. c) Double doublets with J_H 8—9 Hz and J_P 4—6 Hz. d) Singlet. e) The coupling constants J_P or J_H (in Hz) given in square brackets. f) Doublet with J_P 4 Hz. g) Overlapped with Ph proton resonances.

Table 2. ^{13}C NMR Spectral Data[a] for Organophosphorus Compounds

Compounds	δ (ppm) in $CDCl_3$
$(2,4,6)_3P{=}S$	—,[b] 162.4d[2], 91.9d[7], 162.7s, 56.0s, 55.2s
$(2,6)_3P{=}S$	—,[b] 161.6s, 105.1d[6], 130.9s, 55.9s
$(2,6)_2PhP{=}S$	114.7d[92], 161.1s, 105.0d[7], 129.5d[3], 55.7s
$(2,6)Ph_2P{=}S$	—,[b] 162.2s, 105.2d[6], 129.9d[4], 55.4s, 136.4d[90], 130.5d[10], 127.7d[12], 134.1s
$[(2,6)_3P{-}SH]ClO_4$	—,[b] 162.0s, 104.9d[8], 136.2s, 56.3s
$[(2,6)_3P{-}SMe]I$	101.0d[99], 162.5s, 104.8d[7], 136.2s, 56.4s, 15.1d[6]
$[(2,6)_3P{-}SEt]I$	101.0d[99], 162.5s, 104.8d[7], 136.2s, 56.4s, 27.4d[6], 14.3d[12]
$[(2,6)_3P{-}SBu]I$	101.0d[99], 162.5s, 104.8d[7], 136.2s, 56.4s, 32.7d[6], 31.3d[12], 22.1s, 13.6s
$[(2,6)_3P{-}SPh]ClO_4$	101.3s[100], 162.2s, 104.5d[4], 136.0s, 56.1s, 134.9d[6], 129.8d[4], 128.6s
$[(2,6)_2PhP{-}SMe]I$	98.3d[96], 162.3s, 105.5d[7], 133.4d[3], 56.7s, 15.05d[5], 124.9d[90], 131.9d[13], 129.3d[15], 137.8s
$[(2,6)_3P{-}H]Cl\cdot 2.5H_2O$	94.7d[105], 162.9s, 104.6d[7], 137.0s, 56.7s
$[(2,6)_3P{-}H]I$	94.8d[105], 162.9s, 104.8d[7], 137.0s, 56.9s
$(2\text{-}MeOC_6H_4)_3P{=}S$	121.7d[91], 160.9d[3], 134.4d[10], 132.8d[3], 120.4d[14], 111.9d[7], 55.6s

a) In the order of C-1, C-2,6, C-3,5, C-4, MeO-2,6, C-1′, C-2′, and others; s=singlet, d=doublet; J_P (in Hz) given in square brackets. b) The C-1 resonance could not be observed.

Preparation of Triarylphosphine Sulfides. $(2,6)_3P{=}S$. To a solution of $(2,6)_3P$ (4.425 g, 10 mmol) in toluene (100 ml) was added elemental sulfur (0.353 g, 11 mmol). The mixture was stirred at room temperature for 4 h. Unreacted sulfur was filtered off, and the filtrate was cooled to −30 °C to give crystals, which were dried at 120 °C for 2 h to give $(2,6)_3P{=}S$ in 88% yield. It can be purified by recrystallization from toluene, ethanol or acetone, followed by drying at 120 °C. Mp 206—208 °C. Anal. ($C_{24}H_{27}O_6PS$) C, H, S.

$(2,4,6)_3P{=}S$. To a solution of $(2,4,6)_3P$ (0.533 g, 1 mmol) in toluene (20 ml) was added elemental sulfur (0.032 g, 1 mmol) to give a clear solution in a few minutes. The mixture was stirred at room temperature for 1 h and was cooled to −30 °C to aid precipitation of the crystals of $(2,4,6)_3P{=}S$ in 70% yield. Mp 221 °C. Anal. ($C_{27}H_{33}O_9PS$) C, H, S.

$(2\text{-}MeOC_6H_4)_3P{=}S$. To a suspension of $(2\text{-}MeOC_6H_4)_3P$ (0.352 g, 1 mmol) in acetone (10 ml) was added elemental sulfur (0.032 g, 1mmol), and the mixture was stirred at room temperature for 3 h to afford the crystals of $(2\text{-}MeOC_6H_4)_3P{=}S$ in 87% yield, which were recrystallized from tetrahydrofuran to give the analytical sample. The melting point was not observed below 230 °C. Anal. ($C_{21}H_{21}O_3PS$) C, H.

$(2,6)_2PhP{=}S$ and $(2,6)Ph_2P{=}S$. Analogous treatments of $(2,6)_2PhP$ or $(2,6)Ph_2P$ as described above resulted in the formation of $(2,6)_2PhP{=}S$ (mp 170 °C) or $(2,6)Ph_2P{=}S$ (mp 159—160 °C) in 80—90% yields. Anal. ($C_{22}H_{23}O_4PS$) C, H, S and ($C_{20}H_{19}O_2PS$) C, H.

Preparation of Mercaptophosphonium Salt. To a solution of $(2,6)_3P{=}S$ (0.485 g, 1 mmol) in acetone (10 ml) was added with stirring 60% aqueous perchloric acid (0.4 ml). The resultant precipitates were filtered, washed with cold acetone, and dried in air to give $[(2,6)_3P{-}SH]ClO_4$ in 95% yield. Mp

181—182 °C. Anal. ($C_{24}H_{28}O_{10}ClPS$) C, H.

Desulfurization of $[(2.6)_3P\text{-}SH]^+$ Salts A suspension of $[(2,6)_3P\text{-}SH]ClO_4$ (0.338 g, 0.6 mmol) in 2-propanol (30 ml) was heated at 70 °C. Aliquots were taken at 1, 4, and 8 h of heating. The solvent was removed under reduced pressure, and the ^1H NMR spectra of the residue showed the presence of $[(2,6)_3P\text{-}SH]ClO_4$ and $[(2,6)_3P\text{-}H]ClO_4$[1] in 32 : 68, 29 : 71, and 29 : 71 ratios, respectively.

To a solution of $(2,6)_3P{=}S$ (0. 2 mmol) in MEK (15 ml) was added 6M HCl (2 ml) (1 M=1 mol dm^{-3}). The resultant suspension was heated at 70 °C for 4 h to give new crystals, which were found to be identical with those of $[(2,6)_3P\text{-}H]Cl\cdot 2.5H_2O$ (55% yield, see below).

Preparation of $[(2.6)_3P\text{-}H]Cl\cdot 2.5H_2O$. To a solution of $(2,6)_3P$ (2.212 g, 5 mmol) in MEK (50 ml) was added 12M HCl (1 ml) dissolved in MEK (4 ml). The resultant precipitates were recrystallized from acetone (120 ml) to give $[(2,6)_3P\text{-}H]Cl\cdot 2.5H_2O$ in 95% yield. Mp 170—187 °C, decomposed. Anal. ($C_{24}H_{33}O_{8.5}ClP$) C, H, Cl.

Reactions of Triarylphosphine Sulfides with Triphenylphosphine in the Presence of Acid. A mixture of $(2,6)_3P{=}S$ (3 mmol) and Ph_3P (0.800 g, 3.05 mmol) in acetone (30 ml) containing 6M HCl (1 ml) was heated at 50 °C for 3 h. The solvent was removed under reduced pressure, and the residual solid was treated with water (100 ml) to leave the crystals of $Ph_3P{=}S$ (92% yield). To the aqueous filtrate was added 60% aqueous perchloric acid (1 ml) to precipitate the crystals of $[(2,6)_3P\text{-}H]ClO_4$[1] in 99% yield.

$(2,6)_2PhP{=}S$ reacted with Ph_3P in analogous manner to give $[(2,6)_2PhP\text{-}H]ClO_4$[1] in 77% yield.

Preparations of (Alkylthio)phosphonium Salts. $[(2,6)_3P\text{-}SR]I$ (R=Me, Et, *n*-Bu) and $[(2,6)_2PhP\text{-}SMe]I$. To a solution of $(2,6)_3P{=}S$ (1 mmol) in benzene (10 ml) was added MeI (0.2 ml) to give immediately the precipitates of $[(2,6)_3P\text{-}SMe]I$ in quantitative yield. Mp 220 °C, decomposed. Anal. ($C_{25}H_{30}O_6IPS$) C, H.

Analogous treatments of $(2,6)_3P{=}S$ with RI (R=Et, Bu) resulted in the formations of $[(2,6)_3P\text{-}SEt]I$ (mp 206 °C) and $[(2,6)_3P\text{-}SBu]I$ (mp 175 °C) in 80 and 88% yields, respectively. Anal. ($C_{26}H_{32}O_6IPS$) C, H and ($C_{28}H_{36}O_6IPS$) C, H.

An analogous treatment of $(2,6)_2PhP$ with MeI resulted in the formation of $[(2,6)_2PhP\text{-}SMe]I$ in 84% yield. Mp 168—170 °C, decomposed. Anal. ($C_{23}H_{26}O_4IPS$) C, H.

$[(2,6)_3P\text{-}SR]Br$ and $[(2,6)_3P\text{-}SR]ClO_4$ (R=Et, Bu). To a solution of $(2,6)_3P{=}S$ (1 mmol) in ethanol (20 ml) was added EtBr (0.5 ml). The mixture was heated at 55 °C for 2 h. The volatile materials were removed under reduced pressure, and the residual solid was washed with benzene to give $[(2,6)_3P\text{-}SEt]Br$ in 91% yield; mp 194 °C. It was dissolved in water (0.100 g 10 ml) by heating, and 60% aqueous perchloric acid (0.1 ml) was added at room temperature to give the precipitates of $[(2,6)_3P\text{-}SEt]ClO_4$ in 82% yield. The perchlorate salt was served for the elemental analysis. The melting point was not observed below 230 °C. Anal. ($C_{26}H_{32}O_{10}ClPS$) C, H

An analogous treatment of $(2,6)_3P{=}S$ with BuBr resulted in the formation of $[(2,6)_3P\text{-}SBu]Br$ (74% yield, mp 174 °C) and $[(2,6)_3P\text{-}SBu]ClO_4$ (86%, the melting point was not observed below 230 °C. Anal. ($C_{28}H_{36}O_{10}ClPS$) C, H.

Reactions of $[(2,6)_3P\text{-}SR]I$ (R=Me, Et, *n*-Bu) with Thiols. A mixture of $[(2,6)_3P\text{-}SMe]I$ (0.308 g, 0.5 mmol), PhSH (0.1 ml, 0.55 mmol), and $(2,6)_3P$ (0.022 g, 0.05 mmol) in methanol (10 ml) was stirred under argon at room temperature for 24 h. An aliquot was analyzed by GLC to confirm the selective formation of MeSSPh. The mixture was acidified by addition of 1 M HCl (0.1 ml), the volatile materials were removed under reduced pressure, and the residue was treated with benzene (10 ml) to separate the excess PhSH and MeSSPh. The ^1H NMR and the IR spectra of the residue were identical with those for $[(2,6)_3P\text{-}H]I$ (94% yield). The GLC retention time of MeSSPh was measured separately with the sample obtained by exchange reaction[13] of two symmetrical disulfides catalyzed by Ph_3P or $(2,6)_3P$. When $[(2,6)_3P\text{-}SMe]I$ was reacted with $4\text{-}MeC_6H_4SH$ or $n\text{-}C_8H_{17}SH$ in analogous manners, the ^1H NMR spectrum showed that the residues contained mainly $[(2,6)_3P\text{-}H]I$ (95% yield) and small amounts (<2%) of unreacted $[(2,6)_3P\text{-}SMe]I$. The yields (>90%) of MeSSR were estimated by ^1H NMR or GLC.

Analogous results were obtained for $[(2,6)_3P\text{-}SEt]I$ and $[(2,6)_3P\text{-}SBu]I$, and they reacted with PhSH, $4\text{-}MeC_6H_4SH$, and $C_8H_{17}SH$ under the same conditions to give $[(2,6)_3P\text{-}H]I$ (>85% yields) and unsymmetrical disulfides (^1H NMR or GLC, >85% yields).

Preparation of $[(2,6)_3P\text{-}H]I$. $(2,6)_3P$ (3 mmol) was dissolved in water (150 ml) containing HCl (7 mmol). Addition of KI (0.548 g, 3.3 mmol) solution in water (3 ml) resulted in the precipitation of crystals, which were recrystallized from water to give $[(2,6)_3P\text{-}H]I$ in 80% yield. Mp 215—217 °C. Anal. ($C_{24}H_{28}O_6PI$) C, H, I.

Preparation of (Phenylthio)phosphonium Salt. A mixture of $[(2,6)_3P\text{-}H]Cl\cdot 2.5H_2O$ (1.572 g, 3 mmol) and PhSSPh (0.218 g, 1 mmol) in methanol (10 ml) was heated in a sealed glass tube at 80 °C for 24 h. The solvent was removed under reduced pressure, and the residue was extracted with benzene (10 ml)–water (45 ml). Addition of 1 M sodium hydroxide (3.5 ml) to the water layer resulted in the precipitation of $(2,6)_3P$ (2.36 mmol). To the filtrate was added 60% percloric acid to result in the precipitation of $[(2,6)_3P\text{-}SPh]ClO_4$ (0.3 mmol). The melting point was not observed below 230 °C. Anal. ($C_{30}H_{32}O_{10}ClPS$) C, H.

Reaction of $[(2,6)_3P\text{-}H]I$ with Base. To a methanol (4 ml) solution of $[(2,6)_3P\text{-}H]I$ (0.570 g, 1 mmol) was added 1 M sodium hydroxide (1.1 ml) to give light yellow precipitates, which were washed well with water and filtered to give $(2,6)_3P$ in 95% yield.

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