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Facile Synthesis of Alkylthiophosphonium Salts of Tris(2,6-dimethoxyphenyl)phosphine and Their Reactions with Thiols

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Tris(2,6-dimethoxyphenyl)phosphine sulfide reacted with alkyl iodides or bromides under mild conditions to give stable alkylthiophosphonium salts, which reacted with thiols at room temperature in the presence of a catalytic amount of tris(2,6-dimethoxyphenyl)phosphine to give the tertiary phosphonium salt and unsymmetrical disulfides.

Although an alkylthiophosphonium salt is a key intermediate in the reactions or formation of organodisulfides,[1] its isolation from these reaction mixtures is generally very difficult.[2] It has now been found that tris(2,6-dimethoxyphenyl)phosphine sulfide [abbr. $(2,6)_3P=S$][3] reacts directly with common alkyl bromides and iodides under mild conditions to give the corresponding stable alkylthiophosphonium salts.

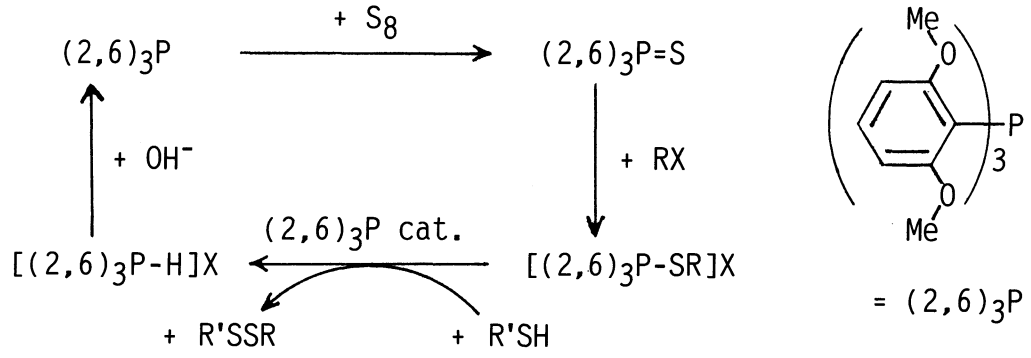
The compound $(2,6)_3P=S$ was easily prepared by the reaction of $(2,6)_3P$ and elemental sulfur at room temperature.[3] To a solution of $(2,6)_3P=S$ (1 mmol) in benzene (10-20 ml) was added an alkyl iodide (RI= MeI, EtI, n-BuI; a slight excess) with stirring at room temperature. The solution immediately formed white precipitates of $[(2,6)_3P\text{-}SR]I$ in 80-100% yields after 2 h stirring. The reactions with alkyl bromides were slower under

analogous conditions. Thus, a solution of $(2,6)_3P{=}S$ (1 mmol) and an alkyl bromide (EtBr, n-BuBr; a slight excess) in ethanol (10 ml) was heated at ca. 60 °C for 2 h. Addition of 60% aqueous perchloric acid (0.2 ml) followed by cooling to -30 °C resulted in the precipitation of $[(2,6)_3P\text{-}SR]ClO_4$ in 89% (R= Et) and 86% (n-Bu) yields. Under these conditions triphenylphosphine sulfide did not react with these alkyl halides. These alkylthiophosphonium salts were fully characterized by ^1H and ^{13}C NMR spectra, IR spectra, and elemental analysis (C,H).[4] They are thermally stable and were recovered after heating in ethanol at 80 °C for 24 h even in the presence of triethylamine. The inertness of the P-SR bond to alcoholysis can readily be explained by both the steric and electronic effects of the 2,6-methoxy substituents. However, the most attractive explanation involves the formation of an interaction between the phosphorus atom and one or more of the 2,6-methoxy oxygens in the phosphonium species. The presence of such interactions may interfere both sterically and electronically with additional coordination by oxy anions, a key step for P-SR bond cleavage.

Masui et al. recently reported that $[Ph_3P\text{-}SR]ClO_4$ could be prepared electrochemically from Ph_3P and RSSR and that their reaction with thiols in the presence of triethylamine gave Ph_3P and unsymmetrical disulfides.[5] We also found that $[(2,6)_3P\text{-}SR]I$ (R= Me, Et, n-Bu; 1 mmol) reacted with thiols R'SH (R'= C_8H_{17}, Ph, 4-MeC_6H_4; 1.1 mmol) in methanol (10 ml) containing a catalytic amount of $(2,6)_3P$ (0.1 mmol). The mixture was stirred at room temperature for 24 h under argon, and the tertiary phosphonium salt $[(2,6)_3P\text{-}H]I$[6] and the unsymmetrical disulfides (GLC) were obtained in quantitative yields (>95%).[8] We expected that in this reaction the catalyst $(2,6)_3P$ (pK_a 9.33)[7,10] worked as a base toward R'SH to form $[(2,6)_3P\text{-}H]SR'$, and that the anion $R'S^-$ thus formed reacted with the cation $[(2,6)_3P\text{-}SR]^+$ 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 $[Et_3NH]I$ and $(2,6)_3P$, as well as RSSR'. We observed no formation of

monosulfide RSR'. However, the formation of symmetrical disulfides was observed when the reactions were performed at elevated temperature or when the base was used in larger amount. In the absence of base, the reaction was very slow even at elevated temperature. 2,6-Dimethoxybenzenethiol[11] reacted much slower than the other thiols, due probably to the bulkiness.

Since $[(2,6)_3P\text{-}H]I$ can easily be deprotonated by aqueous alkali hydroxide,[6] we now obtained a reaction cycle as shown in Scheme 1. 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 1.

References

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4) $[(2,6)_3P\text{-}SMe]I$: mp 220 °C; ^1H NMR (270 MHz, $CDCl_3$, δ) 2.09 (3H, d, J_{HP}= 19 Hz); ^{13}C NMR (270 MHz, $CDCl_3$, δ) 15.1 (d, J_{CP}= 6 Hz); %C found 48.8 (calcd. 48.7) %H found 4.9 (calcd. 4.9). $[(2,6)_3P\text{-}SEt]I$: mp 206 °C; ^1H NMR 2.51 (2H, dq, J_{HP}= 10 Hz, J_{HH}= 7 Hz), 1.25 (3H, dt, J_{HP}= 2 Hz, J_{HH}= 7 Hz); ^{13}C NMR 27.4 (d, J_{CP}= 6 Hz), 14.3 (d, J_{CP}= 12 Hz); %C

49.5 (49.5) %H 5.1 (5.1). $[(2,6)_3P\text{-}SBu\text{-}n]I$: mp 175 °C; ^1H NMR 2.48 (2H, dt, J_{HP}= 10 Hz, J_{HH}= 7 Hz), 1.55 (2H, multiplet), 1.32 (2H, multiplet), 0.84 (3H, t, J_{HH}= 7 Hz); ^{13}C NMR 32.7 (d, J_{CP}= 6 Hz), 31.3 (d, J_{CP}= 12 Hz), 22.1 (s), 13.6 (s); %C 50.8 (51.1) %H 5.5 (5.5). $[(2,6)_3P\text{-}SEt]ClO_4$: IR (Nujol) 1100 cm^{-1}; %C 51.7 (51.8) %H 5.4 (5.4). $[(2,6)_3P\text{-}SBu\text{-}n]ClO_4$: IR 1100 cm^{-1}; %C 53.0 (53.0) %H 5.8 (5.8). The ^1H NMR spectra of $[(2,6)_3P\text{-}SR]X$ commonly showed resonances at δ 7.58 (1H, t, J_{HH}= 8 Hz, 4-H), 6.67 (2H, dd, J_{HH}= 8 Hz, J_{HP}= 6 Hz, 3,5-H), and 3.61 (18H, s, OCH_3). Their ^{13}C NMR spectra commonly showed resonances at δ 162.5 (s, 2,6-C), 136.2 (s, 4-C), 104.8 (d, J_{CP}= 7 Hz, 3,5-C), and 101.0 (d, J_{CP}= 99 Hz, 1-C).

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6) $[(2,6)_3P\text{-}H]I$ was isolated from the reaction mixture by evaporation of the solvent and washing the residue with benzene: mp 215-217 °C after recrystallization from water; ^1H and ^{13}C NMR spectra were identical with those of $[(2,6)_3P\text{-}H]ClO_4$.[7] A methanol (4 ml) solution of $[(2,6)_3P\text{-}H]I$ (1 mmol) was treated with diluted aqueous sodium hydroxide (a slight excess, 40 ml) to give the precipitates of $(2,6)_3P$[7] in 95% yield.

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8) The GLC retention times of unsymmetrical disulfides were measured separately with the samples obtained by exchange reaction of two symmetrical disulfides catalyzed by triphenylphosphine or $(2,6)_3P$. The procedure has been reported elsewhere.[9]

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