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Thiol elimination from tris[2-(phenylthio)ethyl]phosphine oxide: a convenient route to trivinylphosphine oxide

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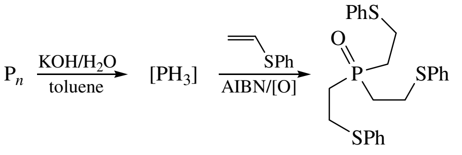
Tris[2-(phenylthio)ethyl]phosphine oxide reacts with sodium amide to afford trivinylphosphine oxide in a good yield. The reaction involves the generation of phosphoryl-stabilised carbanions, which further eliminate benzene thiolate anions.

Trivinylphosphine oxide is a prospective cross-linking agent for non-flammable materials and a reactive building block, which is used, particularly, as a reagent for the preparation of P-stereogenic phosphine oxides with three different alkenyl groups *via* a cross-metathesis reaction.[1] Conventional syntheses of trivinylphosphine oxide are based on phosphorus chlorides[1,2] or triphenyl phosphite[3] and organometallics.

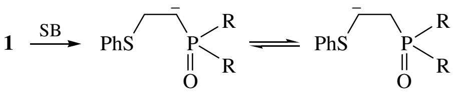
Here we describe a novel convenient approach to the synthesis of trivinylphosphine oxide from tris[2-(phenylthio)ethyl]phosphine oxide **1**. Tris[2-(organylthio)ethyl]phosphine oxides like compound **1**, which were efficiently synthesised[4] from elemental phosphorus (*via in situ* generated phosphine), and available organyl vinyl sulfides[5] (Scheme 1) represent rewarding objects for a study of the competitive P and S stabilization of the adjacent carbanion, as well as promising synthetic intermediates.



AIBN = 2,2′-azobisisobutyronitrile **1**

Scheme 1

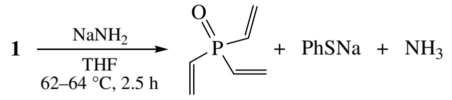
Under the action of a strong base (SB) in the 2-[(phenylthio)ethyl]phosphoryl moiety of **1**, two equilibrium carbanions **A** and **B** should be generated (Scheme 2), which can undergo elimination or be further employed in reactions with appropriate electrophiles.



A **B**

Scheme 2

In this case, the predominant formation of carbanion **A** due to a stronger electron-withdrawing effect of the phosphoryl group would be expected. Therefore, a synthetically attracting route to trivinylphosphine oxide through the benzene thiolate anion elimination from **A** is here envisaged. The expectations came true: the reaction of phosphine oxide **1** with an excess of sodium amide in THF (62–64 °C, 2.5 h) does afford trivinylphosphine oxide **2** (Scheme 3) in a good yield. The benzene thiolate anion is identified (GC/MS) as methyl phenyl sulfide when methyl iodide is added to the reaction mixture.



2

Scheme 3

Although the ^{31}P NMR spectrum shows no P-containing products other than **2**, its highest isolated yield[†] obtained so far is 62%. Still taking into account that phosphine oxide **1** and phenyl vinyl sulfide are now readily available, this novel route to trivinylphosphine oxide appears to be worthy for further optimization.

Apart from its synthetic meaning, this reaction is an unambiguous answer to a fundamental question: which of the two heteroatomic functions stabilises the adjacent carbanion better? Indeed, the result obtained indicates intermediate α-phosphorus-containing carbanions to be exclusively generated in this reaction.

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[†] To a solution of phosphine oxide **1** (0.23 g, 0.5 mmol) in 15 ml of absolute THF, sodium amide (0.1 g, 2.6 mmol) was added under an argon atmosphere. The reaction mixture was stirred at 62–64 °C for 2.5 h and cooled to room temperature; the precipitate obtained was filtered off. The filtrate was passed through a layer of silica gel (~1 cm); THF was removed under reduced pressure to give 0.04 g (62% yield) of phosphine oxide **2**, which was purified by vacuum sublimation; white hygroscopic crystals, mp 96–98 °C (lit.,[1] 96–98 °C).

^{1}H, ^{13}C and ^{31}P NMR spectra were measured on a Bruker DPX 400 (400.13, 101.61 and 161.98 MHz, respectively) spectrometer. IR spectra were recorded on a Bruker IFS-25 spectrometer in KBr pellets. GC/MS analyses (EI, 70eV) were performed on a Hewlett-Packard HP 5971A instrument. NMR-spectroscopic data are identical to those of samples described in earlier publications.[1,3] IR (ν/cm^{-1}): 3082, 3033, 3004, 2964 ($\nu_{=CH_2}$), 1604 ($\nu_{C=C}$), 1396 ($\delta_{=CH_2}$), 1154 ($\nu_{P=O}$), 980 ($\delta_{=CH}$), 772, 749 (δ_{C-P-C}), 609 ($\delta_{P-C=C}$). MS (EI), *m*/*z* (%): 128 (26, [M]$^+$), 113 (8, [M – Me]$^+$), 102 (17, [M – C$_2$H$_2$]$^+$), 101 (18, [M – C$_2$H$_3$]$^+$), 100 (11, [M – C$_2$H$_4$]$^+$), 85 (30, [(C$_2$H$_3$)$_2$P]$^+$), 83 (43), 81 (9), 79 (12), 75 (20), 74 (6), 73 (5), 71 (12), 66 (18), 57 (23), 56 (6), 55 (24), 54 (42), 53 (8), 49 (31), 48 (20), 47 (100, [P=O]$^+$), 46 (8), 45 (12), 43 (6), 41 (14), 39 (14).