Hydrothiophosphorylation of Vinyl Sulfoxides: First Examples

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Abstract: The first examples of facile hydrothiophosphorylation of organyl vinyl sulfoxides are described. Nucleophilic addition of $P,S$-ambident secondary phosphine sulfides $1$ and $2$ to organyl vinyl sulfoxides $3–6$ with potassium hydroxide at room temperature proceeds chemo- and regioselectively to give the corresponding bis(2-organylethyl)[2-(organylsulfinyl)ethyl]phosphine sulfides $7a–e$ in high isolated yields.

Key words: hydrothiophosphorylations, vinyl sulfoxides, secondary phosphine sulfides, nucleophilic additions

Tertiary phosphine sulfides are important ligands in the design of new metal complex catalysts; in some catalytic processes they have shown even better results than the corresponding tertiary phosphines. Over recent years, of increasing interest have been polydentate ‘hemilabile’ phosphorus- and sulfur-containing ligands, such as $R_2P(X)CH_2CH_2S(O)_nR$ (where $X$ is absent: $n = 0$; $X = O$: $n = 0$; $X = S$: $n = 0$). For example, ligands consisting of tertiary phosphines and phosphine oxides with sulfinyl moieties were successfully applied in palladium-catalyzed asymmetric allylic substitution reactions, and complexes of the $P,S$-ligands with Tc-99m are used in myocardial imaging. At the same time, the synthetic routes to such phosphorus- and sulfur-containing ligands are usually labor-intensive and involve multistep reactions. Therefore, the search for new convenient approaches to the synthesis of compounds with vicinal disposition of phosphorus and sulfur atoms of different coordination remains a challenging synthetic task.

In this context, additions of secondary phosphines and phosphine chalcogenides to sulfur-containing alkenes such as vinyl sulfides, sulfoxides, and sulfones represent a convenient and efficient approach to C–P bond formation and the synthesis of functionalized tertiary phosphines and phosphine chalcogenides.

Herein, we report, for the first time, on the hydrothiophosphorylation of available vinyl sulfoxides with secondary phosphine sulfides $1$ and $2$. The latter have been easily prepared from elemental sulfur and the corresponding secondary phosphines, which, in turn, recently became readily accessible through direct phosphorylation of styrene or vinylpyridine with elemental phosphorus. It is commonly believed that $P,S$-ambident diorganylphosphine sulfides, such as $1$ and $2$, can exist in two tautomeric forms (Scheme 1).

Using multinuclear NMR and IR spectroscopy, as well as X-ray diffraction analysis for sulfide $1$ (Figure 1), we have shown that the phosphorus atom in secondary phosphine sulfides $1$ and $2$ is four-coordinate. This conclusion agrees with the reactivity of phosphine sulfides $1$ and $2$, which add to vinyl sulfoxides $3–6$ (KOH, THF, r.t., 1 h) chemo- and regioselectively to give bis(2-organylethyl)[2-(organylsulfinyl)ethyl]phosphine sulfides $7a–e$ in 62–86% yield (Table 1).

Without using potassium hydroxide or under radical initiation (AIBN, $65 \degree C$, 5 h), the hydrothiophosphorylation of vinyl sulfoxides $3–6$ fails, thus confirming its nucleophilic character.

Hence, the addition of secondary phosphine sulfides to vinyl sulfoxides represents a facile straightforward atom-economic route to products $7$, potent ligands, special solvents, cocatalysts and convenient models for studying the competing reactivity of carbanions in vicinal...
The 1H, 13C, and 31P NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 100.69, and 161.98 MHz, respectively) in CDCl3 solutions and referenced to internal HMDS (1H NMR) and external 85% H3PO4 (31P NMR). IR spectra were run on a Bruker IFS 25 instrument in KBr pellets. UV spectra were recorded on a Perkin-Elmer Lamda 35 spectrometer in MeCN solutions.

**Bis(2-phenylethyl)phosphine Sulfide (1):**

Colorless plates; yield: 2.44 g (89%); mp 58 °C.

**Bis-[2-(2-pyridyl)ethyl phosphine Sulfide (2):**

Viscous straw-colored oil; yield: 2.21 g (80%).

**Bis[2-(2-pyridyl)ethyl][2-(2-methylsulfinyl)ethyl]phosphine Sulfide (3):**

Yield: 2.73 g (72%); mp 88–89 °C.

**Bis(2-phenylethyl)[2-(ethylsulfinyl)ethyl]phosphine Sulfide (4):**

Produced pressure, and the residue was recrystallized (hexane).

**Synthesis of Sulfinyl-Substituted Tertiary Phosphine Sulphides 7a–e:**

<table>
<thead>
<tr>
<th>Phosphine Sulfide</th>
<th>X</th>
<th>R</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH</td>
<td>Et</td>
<td>7a</td>
<td>72</td>
</tr>
<tr>
<td>1</td>
<td>CH</td>
<td>n-Pr</td>
<td>7b</td>
<td>86</td>
</tr>
<tr>
<td>1</td>
<td>CH</td>
<td>n-Bu</td>
<td>7c</td>
<td>65</td>
</tr>
<tr>
<td>1</td>
<td>CH</td>
<td>Ph</td>
<td>7d</td>
<td>69</td>
</tr>
<tr>
<td>2</td>
<td>N</td>
<td>Ph</td>
<td>7e</td>
<td>62</td>
</tr>
</tbody>
</table>

- After recrystallization.

**Analytical Data:**

- IR (KBr): 1019 (S=O), 612 cm⁻¹ (P=S).
- 1H NMR (400.13 MHz, CDCl₃): 8 = 2.86–2.33, 2.49–2.60 (2 m, 4 H, CH₂P), 3.16–3.20 (m, 4 H, pyCH₂), 6.47 (d, 1 H, J₆PC = 442.3 Hz, CH₂P), 7.12–7.19 (m, 10 H, Ph).
- 13C NMR (100.69 MHz, CDCl₃): 8 = 28.67 (d, J₆PC = 2.2 Hz, CH₂P), 31.62 (d, J₆PC = 50.4 Hz, CH₂P), 126.52 (p-c), 128.15 (m-C), 136.60 (C-4 (py)), 149.35 (C-6 (py)), 159.15 (d, J₆PC = 3.7 Hz, C-2 (py)).

**Bis-2-(2-pyridyl)phosphine Sulfide (7a):**

Yield: 2.73 g (72%); mp 88–89 °C.

**Bis(2-phenylethyl)[2-(butylsulfinyl)ethyl]phosphine Sulfide (7b):**

Yield: 2.64 g (65%); mp 65–67 °C.

**Bis(2-phenylethyl)[2-(ethylsulfinyl)ethyl]phosphine Sulfide (7c):**

Yield: 2.73 g (72%); mp 88–89 °C.

**Bis(2-phenylethyl)[2-(butylsulfinyl)ethyl]phosphine Sulfide (7d):**

Yield: 2.64 g (65%); mp 65–67 °C.

**Bis(2-(2-pyridyl)ethyl)phosphine Sulfide (7e):**

Yield: 2.64 g (65%); mp 65–67 °C.
Bis(2-phenylethyl)[2-(phenylsulfinyl)ethyl]phosphine Sulfide (7d):

Yield: 2.94 g (69%); mp 78–79 °C.

Anal. Calcd for C24H27OPS2: C, 67.57; H, 6.38; P, 7.26; S, 15.03.

References

(1) The positions of resonance in the 1H, 13C and 31P NMR spectra of compounds 1 and 2 which reflect magnetic interaction of the phosphorus atom (1P) with its immediate neighborhood (1H, 13C), as well as doublets in 1H spectra of phosphine sulfides which reflect absorption bands of stretching vibrations at 567–570 (P=S) and 2330–2363 cm–1 (P–H), and vibrations at 567–570 (P=S) and 2330–2363 cm–1 (P–H).

Acknowledgment

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References


X-ray crystal analysis was performed on an Enraf Nonius CAD4 diffractometer (graphite monochromator $\omega$-scanning Mo K$_\alpha$ radiation). The crystal structure was solved by direct methods using the SHELXS-97 program package and refined anisotropically by the full matrix least square method for all nonhydrogen atoms using the SHELXL-97 program, see: Sheldrick, G. M. *SHELXS-97, SHELXL-97, Programs for Crystal Structure Determination and Refinement*; Göttingen University: Germany, 1997, the absorption correction was applied. The coordinates of the H atoms were determined by Fourier synthesis and refined isotropically; $R$ factor is 0.047, $a = 6.304$ (1) Å, $b = 9.329$ (2) Å, $c = 13.220$ (3) Å, $\alpha = 88.65$ (3)$^\circ$, $\beta = 89.03$ (3)$^\circ$, $\gamma = 77.89$ (3)$^\circ$, triclinic $P\overline{1}$, $Z = 2$, $D_{\text{calc}} = 1.20$ g·cm$^{-3}$; $P(1)$–$S(1)$ 1.957 (1) Å, $P(1)$–$C(1)$ 1.811 (2) Å, $P(1)$–$C(9)$ 1.811 (2) Å, $P(1)$–$H(1)$ 1.31 (2) Å. CCDC 269206 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 (1223)336033; E-mail: deposit@ccdc.cam.ac.uk).