

## An Improved Method for the Synthesis of Sulfides

Philippe SAVIGNAC and Philippe COUTROT


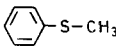
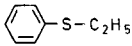
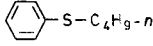
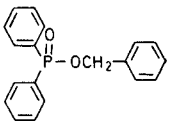
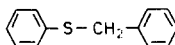
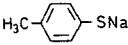
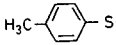
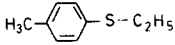
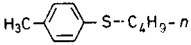
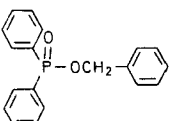
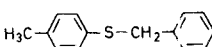
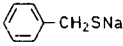
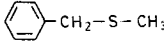
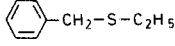
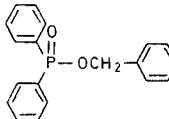
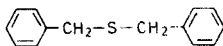
Laboratoire de Synthèse Organique, E.R.A. C.N.R.S. n° 31  
 Université Pierre et Marie Curie, tour 44 45, 3<sup>e</sup> étage,  
 4, Place Jussieu, 75230 Paris Cédex 05, France

The literature contains numerous methods for the preparation of sulfides. Unsymmetrical sulfides may be generally obtained by treatment of alkyl halides or alcohols with mercaptans; symmetrical sulfides may also be prepared by treatment of alkyl halides with sodium sulfide<sup>1</sup>.

Some dealkylations of phosphorus compounds have already been mentioned in connection with the preparation of mono-selenoacid salts<sup>2</sup>, monothiophosphate salts<sup>3</sup>, and trisubstituted phosphorothioate esters<sup>4</sup>. All of these reactions give also sulfides and suggest the synthetic utility of phosphorus compounds. The present communication describes an efficient route which gives sulfides in almost quantitative yields.

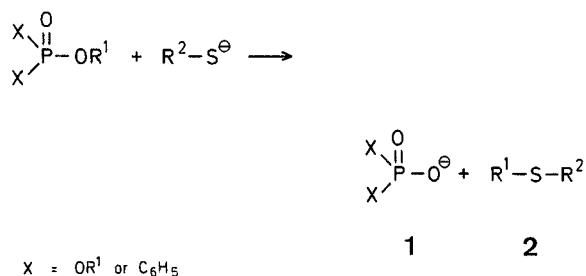
Previously, compounds of type **1** have been prepared by dealkylation of the appropriate di- or tri-substituted phosphates or phosphonates with sodium mercaptides<sup>5</sup>. In connection with this work, we applied this method to the preparation of sulfides **2**.

**Table.** Sulfides Prepared from Trialkyl Phosphates or Benzyl Diphenylphosphinate and Sodium Thiolates

Sodium thiolate	Phosphorus compound	Sulfide	Yield (%) <sup>a</sup>	B.p. or m.p.
<i>n</i> -C <sub>5</sub> H <sub>11</sub> SNa	(H <sub>3</sub> CO) <sub>3</sub> P=O	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -S-CH <sub>3</sub>	60	60°/20 torr
<i>n</i> -C <sub>4</sub> H <sub>9</sub> SNa	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> P=O	<i>n</i> -C <sub>4</sub> H <sub>9</sub> -S-C <sub>4</sub> H <sub>9</sub> - <i>n</i>	88	90°/30 torr
<i>n</i> -C <sub>5</sub> H <sub>11</sub> SNa	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> P=O	<i>n</i> -C <sub>5</sub> H <sub>11</sub> -S-C <sub>4</sub> H <sub>9</sub> - <i>n</i>	95	102°/25 torr
 -SNa	(H <sub>3</sub> CO) <sub>3</sub> P=O		85	30°/0.3 torr
	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P=O		94	37°/0.5 torr
	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> P=O		90	56°/0.5 torr
			90 <sup>b</sup>	m.p. 43°
 -SNa	(H <sub>3</sub> CO) <sub>3</sub> P=O		87	37°/0.3 torr
	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P=O		90	46°/0.3 torr
	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> P=O		97	70°/0.3 torr
			92 <sup>b</sup>	m.p. 43°
 -CH <sub>2</sub> SNa	(H <sub>3</sub> CO) <sub>3</sub> P=O		90	45°/0.3 torr
	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P=O		80	52°/0.3 torr
			91 <sup>b</sup>	m.p. 48°

<sup>a</sup> Yield after distillation except where noted.

<sup>b</sup> Solid product, yield after one crystallization from water/ethanol.



Our procedure has several advantages:

- It uses commercial reactants, the reaction being achieved in one step in mild and fast conditions;
- It gives phosphorus salt, **1**, which can easily be entirely removed by water extraction;
- It generates a variety of alkyl and aryl sulfides **2** in practically quantitative yields (see Table) and often in practically pure form.

Thiols can be oxidised by the reaction medium. Therefore it is advisable to work with a slight deficiency of the phosphate or phosphinate in order to prevent the presence of traces of the starting materials in the crude sulfides.

#### General Procedure:

Sodium ethoxide was prepared by dissolving sodium (0.1 g-atom) in methanol (100 ml) under nitrogen. The thiol (0.1 mol) was added and the mixture stirred for 15 min at room temperature. Pure trialkyl phosphate or phosphinate<sup>6</sup> (0.090 mol) was then added with stirring and the mixture heated under reflux for 3 h. The mixture was cooled and concentrated by evaporation to give a syrup. Water (50 ml) was added and the aqueous phase obtained extracted three times with ether (3 × 50 ml). The organic layer was separated, dried with magnesium sulfate, and evaporated. The product so obtained is the pure sulfide, the purity of which was tested by N.M.R. spectrometry.

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<sup>2</sup> P. Pishchimuka, *J. Prakt. Chem.* **84**, 746 (1911); *Zh. Fiz. Khim.* **44**, 1406 (1912).

<sup>3</sup> L. Carius, *Amer. Chem. Pharm.* **112**, 190 (1859).

<sup>4</sup> R. G. Harvey, H. I. Jacobson, E. V. Jensen, *J. Amer. Chem. Soc.* **85**, 1618 (1963).

<sup>5</sup> P. Savignac, G. Lavielle, *Bull. Soc. Chim. France* **1974**, 1506.

<sup>6</sup> J. E. Quick, D. L. Venezky, *J. Chem. Eng. Data* **15**, 377 (1970).