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A NOVEL SYNTHESIS OF ORGANIC SULFIDES FROM ORGANOLITHIUMS AND PHOSPHINODITHIOATE ESTERS

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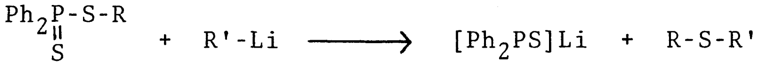
n-Butyl or phenyl sulfides were synthesized by the reactions of n-butyl- or phenyllithium and diphenylphosphinodithioates in tetrahydrofuran in excellent yields.

There is no report on the application of phosphinodithioates to synthesis of sulfur-containing compounds.

We have found that alkyl diphenylphosphinodithioate (1) reacted with n-butyllithium in tetrahydrofuran (THF) at -78°C under nitrogen to afford diphenylphosphinothioylide anion and alkyl n-butyl sulfide (2) in nearly quantitative yields, and that the reaction proceeded through S_N2 attack on the sulfur atom, because the reaction proceeded almost quantitatively even with an equimolar mixture of the two reagents and, in the case of benzyl ester (1, R=$PhCH_2$), benzyl n-butyl sulfide did not contain any deuterium after quenching with deuterium oxide.$^{1)}$



$$Ph_2\underset{\overset{\|}{S}}{P}\text{-S-R} + \text{R}'\text{-Li} \longrightarrow [Ph_2PS]Li + \text{R-S-R}'$$

1 2

This paper describes the application of the above reaction to preparation of sulfides (2).

The results are shown in the Table. A typical procedure is as follows. n-Butyllithium (4.5 mmol) in n-hexane (3 ml) was added dropwise to 1 (R=Ph, 0.50 g, 1.52 mmol) in THF (20 ml) at -78°C under nitrogen and the mixture was stirred for 30 min at -78°C. After usual work-up, the reaction mixture was chromatographed using a silica gel dry column with carbon tetrachloride to afford n-butyl phenyl

Table. Yields of sulfides (2)

1 R	R'-Li	Temp. (°C)	Yield of 2 (%)
Me	n-BuLi	-78	98
Et	n-BuLi	-78	88
Ph	n-BuLi	-78	95*
$PhCH_2$	n-BuLi	-78	86
$CH_2=CH-CH_2$	n-BuLi	-78	63
Me	PhLi	r.t.	95
Et	PhLi	r.t.	89
Ph	PhLi	r.t.	90
$PhCH_2$	PhLi	r.t.	60*
$PhCH_2$	PhLi	-78	79*
$CH_2=CH-CH_2$	PhLi	r.t.	72*

* By isolation. The others were determined by glc.

sulfides (2, R=Ph, R'=n-Bu) (0.24 g, 95%).

Recently, it has been reported that the sulfides are prepared from alkyl phosphinates and thiolates in excellent yields.²⁾ However, the present method may be useful in the following points: 1) the esters (1) are prepared easily from diphenylphosphinodithioic acid (3) and alcohols or alkyl halides, except for aryl esters,³⁾ 2) the anion $[Ph_2PS]^-$ thus formed is converted into 3 by treatment with sulfur and can recycle, 3) a use of thiols is avoided, except for preparation of diaryl sulfides, and 4) this method is applicable to preparation of diaryl sulfides, although arenethiols are required in the preparation of the aryl esters (1).

The low yields in the allyl ester are attributable to a contribution of Wittig type rearrangement through the allylic carbanion.

Application of 1 as a sulfur-transfer agent is under way.

References

1) Unpublished results.
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3) T. R. Hopkins and P. W. Vogel, J. Amer. Chem. Soc., 78, 4447 (1956).

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