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DIRECT CONVERSION OF BENZYL ALCOHOLS INTO BENZYL SULFIDES WITH ORGANIC DISULFIDE/DIPHOSPHORUS TETRAIODIDE

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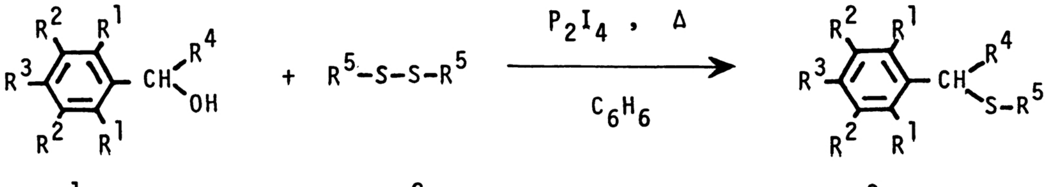
Organic disulfides react with diphosphorus tetraiodide in hot benzene to give an orange-colored solution, in which benzyl alcohols are readily converted into the corresponding benzyl sulfides in fair to good yields.

The commonly used methods for the preparation of organic sulfides are based on the alkylation of thiols, action of halides on alkali metal sulfides, decomposition of diazosulfides, addition of thiols to olefinic compounds, and cleavage of disulfides with organometallic compounds.[1] To our knowledge, however, there seem to be no practical methods that can convert alcohols into sulfides in one step. We now wish to report that various benzyl sulfides may be obtained directly from benzyl alcohols in fair to good yields when the alcohols are treated with organic disulfides and diphosphorus tetraiodide (P_2I_4) in hot benzene. The latter reagent is easily accessible by the disproportionation of phosphorus triiodide in dry ether.[2] It is an efficient deoxygenation agent for epoxides,[3] sulfoxides,[4] and amine N-oxides.[5]

The direct conversion of benzyl alcohols into benzyl sulfides can be carried out simply by heating an equimolar amount of disulfide 2 and P_2I_4 in benzene under gentle reflux to form an orange-colored solution, to which is added benzyl alcohol 1 and the mixture is heated further for 4-10 h. Ordinary work-up affords sulfide 3 in 24-95% yields.



1 2 3

The mechanism of this facile thiolation is not clear at present, although the transformations involved may be represented as in equations below:

$$\text{R-S-S-R} \quad + \quad P_2I_4 \xrightarrow{\qquad\qquad} 2\ \text{R-S-PI}_2$$

$$\text{R-S-PI}_2 \quad + \quad \text{R'-OH} \xrightarrow{\qquad\qquad} \text{R-S-R'} \quad + \quad \text{HPOI}_2$$

Table. Benzyl Sulfides Obtained from the Reaction of Benzyl Alcohols with Organic Disulfide/Diphosphorus Tetraiodide Reagent

Benzyl sulfide	R^1	R^2	R^3	R^4	R^5	Reaction time (h)	Mp ($^{\circ}$C)	Yield (%)[a]
3a	Me	H	Me	H	Ph	9	68-69	80
3b	Me	Me	H	H	Ph	4	128-129	77
3c	Me	Me	Me	H	Ph	9	145-146	95
3d	H	H	H	Me	Ph	8	—— [b]	30[c,d]
3e	Me	Me	Me	Me	Ph	10	—— [b]	31[c,d]
3f	Me	Me	H	H	*n*-Bu	8	31-32	24[d,e]
3g	H	H	Cl	H	*n*-Bu	7	—— [b]	6[d,e]

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a. The yields refer to the compounds isolated and are not optimized.
b. Low-melting solid.
c. Accompanied by the extensive formation of styrene polymers.
d. Purified by chromatography on silica gel using hexane as the eluant.
e. Benzyl iodide is obtained as the major product.

In view of the importance of sulfides as intermediate for organic synthesis, we feel that the thiolation procedure reported herein is a useful addition to the existing ones in terms of the direct functional group conversion, easy manipulation, and mild reaction conditions. Extension of the present method to other alcohols is in progress and its scope will be reported in due course.

In a representative procedure, a mixture of diphenyl disulfide (0.5 mmol), P_2I_4 (0.5 mmol), and benzene (10 ml) is heated under reflux for 10 min to give a bright orange-colored solution, to which is added in one portion a solution of 2,4,6-trimethylbenzyl alcohol (1.0 mmol) in the same solvent. The color immediately fades away and the resulting yellowish solution is heated under gentle reflux for 9 h, and then diluted by the addition of aqueous sodium sulfite. Organic layer is separated, washed with aqueous sodium hydroxide and water, dried over sodium sulfate, and evaporated *in vacuo* to leave an oily residue, which is chromatographed on alumina using a mixture of hexane and chloroform (8:2) as the solvent, giving sulfide 3c as white needles, mp 68-69 $^{\circ}$C. Yield, 80%.

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