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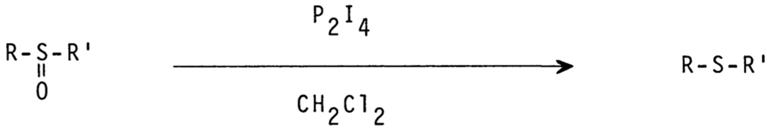
DIPHOSPHORUS TETRAIODIDE AS A MILD AND EFFICIENT REAGENT FOR THE DEOXYGENATION OF SULFOXIDES

Hitomi SUZUKI,* Naofumi SATO, and Atsuhiro OSUKA
Department of Chemistry, Faculty of Science,
Ehime University, Bunkyo-cho, Matsuyama 790

By treatment with diphosphorus tetraiodide in dichloromethane at room temperature, sulfoxides are rapidly deoxygenated to the corresponding sulfides in high yields.

Reduction of sulfoxides to the corresponding sulfides has recently received considerable attentions and a number of methods have been developed to effect such a conversion.[1] In a previous paper,[2] we reported a convenient use of diphosphorus tetraiodide (P_2I_4) as an efficient deoxygenating agent for epoxides. As an extension, we wish now to communicate the application of this reagent to the reduction of sulfoxide to sulfide.



$$\underset{\underset{O}{\|}}{R\text{-}S\text{-}R'} \xrightarrow[CH_2Cl_2]{P_2I_4} R\text{-}S\text{-}R'$$

1 2

When a solution of sulfoxide in dichloromethane is added to a well stirred suspension of diphosphorus tetraiodide in the same solvent, the reaction occurs immediately. After 5-10 min, the reaction mixture is quenched with water and worked up as usual, giving the corresponding sulfide in 84-98% yield. The product shows high purity on T.L.C. and spectral analyses. The phosphorus-containing product of deoxygenation is water-soluble and easily removed. Many functional groups including amino, carbonyl, halogen, nitro, and double bond are stable toward the action of this reagent under the conditions employed.[2]

Our method is advantageous in terms of the mild reaction conditions, the ease of performance, and the ready availability and inexpensiveness of the reagent. The results are summarized in the Table.

Diphosphorus tetraiodide is easily accessible by the disproportionation of phosphorus triiodide in dry ether[3,4] and, when protected from light and air, it can be stored without considerable deterioration. It can also effect the dehydration of aldoximes to nitriles.[2] Few organic reagents have been known so far which can be used efficiently for both deoxygenation and dehydration purposes.

Table. Deoxygenation of Sulfoxides with Diphosphorus Tetraiodide

Sulfoxide 1 R	Sulfoxide 1 R'	Isolated yield of sulfide 2 (%)*
$C_6H_5CH_2$	$C_6H_5CH_2$	94
C_6H_5	C_6H_5	98
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	93
C_6H_5	CH_3	90
$-(CH_2)_4-$		84
n-C_4H_9	*n*-C_4H_9	90

* In all cases, products are identified by direct comparison of IR and NMR spectral data with those from authentic samples.

Ketoximes are slow to react with this reagent, but on prolonged treatment they undergo the Beckmann rearrangement or dehydroxyimination.[5] Secondary and tertiary alcohols bearing hydroxyl group at activated position react with diphosphorus tetraiodide, giving either the corresponding iodides or olefins depending on the conditions employed.[4] In some cases it may be used in combination with branched alcohols to convert pyridine into N-alkylpyridinium iodides.[4] Diphosphorus tetraiodide seems to possess the combined property of phosphine and phosphorus triiodide and its development to be an interesting reagent for organic synthesis is expected.

Typical Procedure: To a stirred suspension of diphosphorus tetraiodide (0.84 g; 1.47 mmol) in dichloromethane (20 ml), diphenyl sulfoxide (0.298 g; 1.47 mmol) in the same solvent (10 ml) is added in one portion. The brisk reaction immediately takes place. After 5-10 min, the reaction mixture is quenched by the addition of water, and the organic layer is separated, washed with dilute aqueous sodium sulfite, and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gives practically pure diphenyl sulfide (0.270 g; 1.45 mmol; 98%).

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