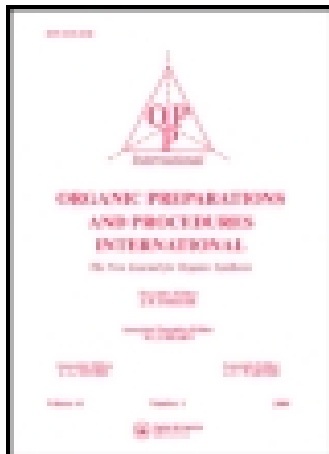


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DE(MONOTHIO)ACETALIZATION INDUCED BY HYPERVALENT IODINE AND SODIUM IODIDE

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**DE(MONOTHIO)ACETALIZATION INDUCED BY
HYPERVALENT IODINE AND SODIUM IODIDE**

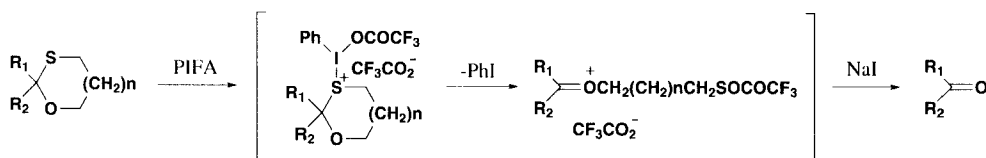
Submitted by
(4/20/99)

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
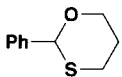

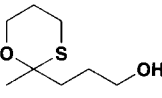
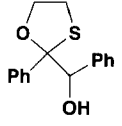
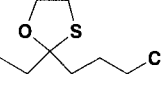
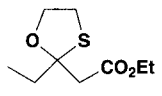
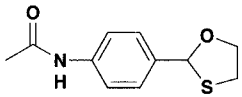
1,3-Oxathiane is a versatile reagent for carbon-carbon bond formation involving an acyl anion equivalent.¹ It was established by Eliel² and Utimoto³ that 1,3-oxathiane could be used in the enantioselective synthesis of α -hydroxyaldehydes. This procedure has been applied to a synthesis of (R)-(-)-mevalonolactone.⁴ In contrast to the many deprotection methods⁵ for 1,3-dithiolanes and 1,3-dithianes, only a few methods are known for 1,3-oxathiolanes or 1,3-oxathianes. Deprotection of 1,3-oxathiolanes and 1,3-oxathianes using Raney nickel requires harsh conditions and in some cases the products are contaminated with radical-derived by-products.⁶ Hydrolysis by mineral acids requires drastic conditions and gives the ketones only in moderate yields.⁷ Reactions using isoamyl nitrite⁸ or chloramine-T⁹ afford the parent carbonyl compound under mild reaction conditions, but only isolated examples of simple 1,3-oxathiolanes are documented. Recently, it has been shown that thioacetals can be cleaved to carbonyl compounds in high yields by treatment with phenyliodo(III) bis(trifluoroacetate) (PIFA);¹⁰ however, this method requires 6 h for the de(monothio)acetalization.¹¹ These facts prompted us to search for a more effective method for the deprotection of monothioacetals. The present work describes a rapid and simple method for de(monothio)acetalization under non-aqueous conditions.



When a monothioacetal was treated with PIFA and sodium iodide in dichloromethane at room temperature under N_2 atmosphere for 15 minutes, a rapid reaction occurred to give the parent carbonyl compound efficiently.

As illustrated in Table 1, the procedure is applicable for the selective deprotection of either 1,3-oxathiolanes or 1,3-oxathianes and is compatible with a variety of other functional groups such as alcohols, halides, ester and secondary amides.¹² Since certain functionalities are unstable under aqueous conditions, this method should find application in the synthesis of molecules with differentially protected carbonyl groups.

TABLE 1. Transformation of Monothioacetals to Carbonyl Compounds

Entry	Monothioacetal	Product	Yield (%)
a		Ph ₂ CO	91
b		PhCHO	87
c		PhCOCH ₃	86
d		CH ₃ COCH ₂ CH ₂ CH ₂ OH	90
e		PhCOCH(Ph)OH	84
f		CH ₃ COCH ₂ CH ₂ CH ₂ Cl	92
g		CH ₃ COCH ₂ CO ₂ Et	85
h		AcNHC ₆ H ₄ CHO	92

Typical Procedure.- To a solution of 2,2-diphenyl-1,3-oxathiane (Table 1, entry a) (362 mg, 1.40 mmol) and sodium iodide (231 mg, 1.54 mmol) in dry dichloromethane (8 mL), was gradually added PIFA (663 mg, 1.54 mmol) as a solid under N₂ atmosphere at room temperature. The reaction mixture was stirred for 15 min. at room temperature, quenched with water (30 mL) and extracted with dichloromethane (3 5 15 mL). The iodine color was discharged by shaking the organic solution with 10% aqueous Na₂S₂O₅. The dichloromethane layer was separated and dried over magnesium sulfate. Evaporation of the solvent gave an oily residue, which was purified by column chromatography on silica gel with chloroform as eluent to give benzophenone in 91% yield. The identity of the purified compounds was confirmed by comparison with authentic samples.

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