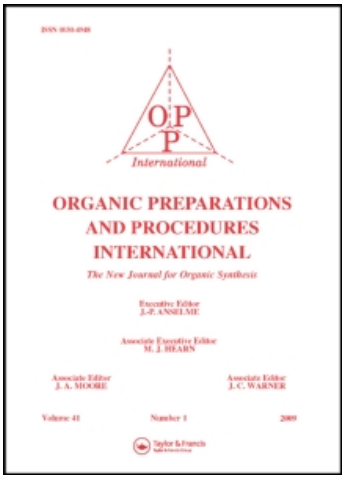

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SAMARIUM TRIIODIDE CATALYZED DITHIOACETAL AND DITHIOKETAL FORMATION

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SAMARIUM TRIIODIDE CATALYZED DITHIOACETAL AND DITHIOKETAL FORMATION

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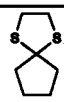
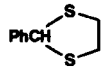
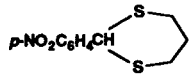
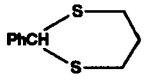
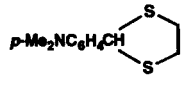
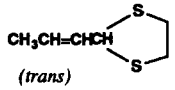
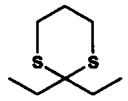
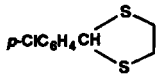
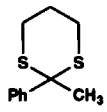
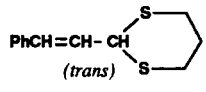
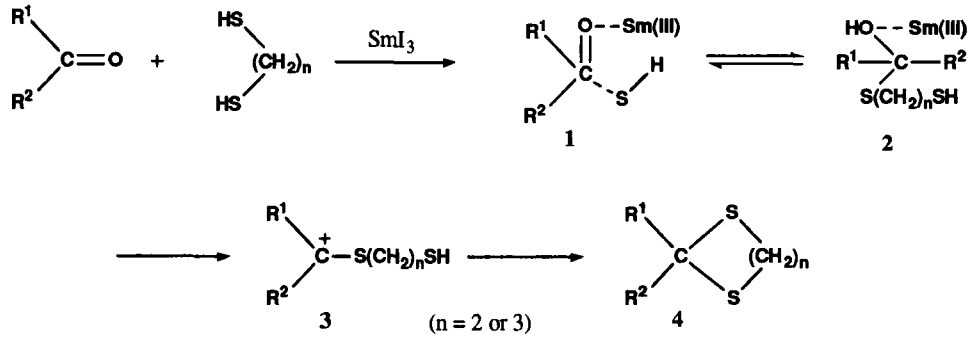
Recently, lanthanide compounds, in particular samarium (II) diiodide, have gained increasing popularity as versatile reagents in organic synthesis.[1] However as far as we know, little attention has been devoted to the application of samarium (III) compounds. Very recently, we have found that samarium triiodide promoted the efficient formation of the carbon-carbon double bond between α-haloketones and carbonyl compounds, and the opening of the tetrahydrofuran ring accompanied by the coupling with acyl chloride.[2] We now report the dithioacetalization or dithioketalization of carbonyl compounds in the presence of samarium triiodide.

At room temperature, most carbonyl compounds are satisfactorily dithioacetalized or dithioketalized by 1,2-dithioethane or 1,3-dithiopropane in anhydrous acetonitrile in the presence of two equivalents of samarium triiodide (Method A). Furthermore, satisfactory results were also obtained with catalytic amount of samarium triiodide (0.1 equiv.) with longer reaction time (Method B). Samarium triiodide is conveniently prepared from samarium powder and iodine either stepwise prior to the reaction or *in situ* in a one-pot reaction. In the case of sterically hindered ketones, such as benzophenone or α-bromocamphor, the desired dithioketals were not obtained probably because of

TABLE. Yield, Physical Constants and Spectra Data of Products[a]

No.	Product	Method	Time (hrs)	Yield (%)	mp. (°C) (lit.)	^{1}H NMR ($CDCl_3$/TMS) (ppm)
1		A B	1.5 2.5	92 87	oil[4]	3.40 (s, 4H), 1.5-2.12 (m, 8H).
2		A B	1.5 2.5	90 86	oil[4]	7.60-7.20 (m, 5H), 5.10 (s, 1H), 3.30 (s, 4H).
3		A	8	71	141.5-142 (141-142)[6]	8.20-7.20 (m, 4H), 5.60 (s, 1H), 3.50 (m, 4H) 2.30-1.70 (m, 2H).
4		A	1.5	87	72-73 (72)[6]	7.60-7.16 (m, 5H), 5.10 (s, 1H), 3.10-2.75 (m, 4H), 2.30-1.60 (m, 2H).
5		A	12	62	105-106 (107)[7]	7.50-6.50 (m, 4H), 5.60 (s, 1H), 3.40 (s, 4H).
6	 *(trans)*	A B	3 4	85 78	oil[7]	5.80-5.40 (m, 2H), 4.70 (d, 1H), 3.10 (s, 4H), 1.67-1.75 (d, 3H).
7		A B	1.5 3	90 88	oil[8]	3.40-3.60 (m, 4H), 3.10-2.90 (m, 2H), 2.85-2.75 (q, 4H), 1.65-1.45 (t, 6H).
8		A	2	89	120 (119)[7]	7.40-7.20 (q, 4H), 5.55 (s, 1H), 3.10 (m, 4H).
9		B	2.5	79	oil[7]	8.0-7.2 (m, 5H), 2.7 (m, 4H), 2.0 (m, 2H) 1.8 (s, 3H).
10	 *(trans)*	B	2.5	83	oil[7]	7.2 (s, 5H), 6.68 (s, 1H), 6.55 (s, 1H), 4.7-4.60 (d, 1H), 2.8 (m, 4H), 2.1 (m, 2H).

a) All products purified by column chromatography.



the low reactivity of the substrates. A possible reaction mechanism is as follows. As a Lewis acid, samarium triiodide weakens the carbon oxygen bond of the carbonyl compound by complexation with the oxygen atom, thus facilitating the conversion of **1** to **2** then to **3**; intermediate **3** reacts with the other thio group to give the product **4**.

Thioacetals or thioketals, which are widely used as protecting groups of carbonyl compounds[3] as well as synthons for acyl nucleophile,[4] are usually prepared from carbonyl compounds and thiols in the presence of anhydrous proton acids or Lewis acids. Although Garlaschelli and Vidari[5] have reported anhydrous $LaCl_3$ promoted thioacetalization of carbonyl compounds, the thioacetalization requires two equivalents of anhydrous $LaCl_3$. In contrast, the present method has the advantages of using the catalytic amount of Lewis acid and easily prepared *in situ* samarium triiodide and could be the method of choice for the preparation of dithioacetals and dithioketals.

EXPERIMENTAL SECTION

All melting points are uncorrected. ^1H NMR spectra were measured on a FX 90Q spectrometer using TMS as the internal reference.

Typical Procedure. Method A. - To a 25 mL Schlenk flask,[9] 3 mL CH_3CN, samarium powder (0.32 g, 2 mmol), iodine (0.75 g, 3 mmol), 1,2-ethanedithiol (0.44 g, 4 mmol), cyclohexanone (0.17 g, 2 mmol) were added, the reaction was carried out at room temperature under nitrogen. After stirring at room temperature for 1.5 hr, the mixture was diluted with 20 mL petroleum ether. The mixture was filtered and the filtrate was washed by 10% NaOH (2 x 10 mL) to remove the excess ethanedithiol. The organic phase was washed by water, brine, dried over anhydrous $MgSO_4$. Removal of solvent gave the crude product which was purified by chromatography (eluent, 3:1 petroleum ether-ethyl ether) on SiO_2 to yield 0.32 g (92%) of pure product.

Method B.- The amounts of samarium powder and I_2 added were 10% of the amounts used in Method A. The other operations were identical to those of Method A.

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A CONVENIENT SYNTHESIS OF 7-HYDROXY-3-HYDROXYMETHYL-4-PHENYL-2-NAPHTHOIC ACID, LACTONE FORM

Submitted by (09/09/92)

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1-Arylnaphthalene lignans have become interesting synthetic targets due to their wide range of biological activity.[1] We became interested in the synthesis of 7-hydroxy-3-hydroxymethyl-4-phenyl-2-naphthoic acid, lactone form (**4**) in connection with ongoing research in our laboratories. Previously reported procedures[2] for preparing compounds of this type include Diels-Alder reaction of 1-arylisobenzofurans,[3] tandem conjugate addition-aldol reaction involving aryl cyanohydrin anions