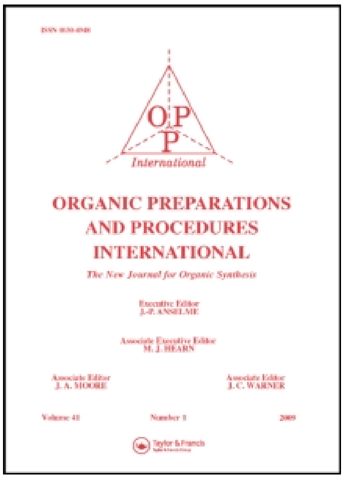

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COUPLING OF THIOLS AND SELENOLS CATALYZED BY TRIS[TRINITRATOCERIUM(IV)]PARAPERIODATE

Submitted by (03/07/94)

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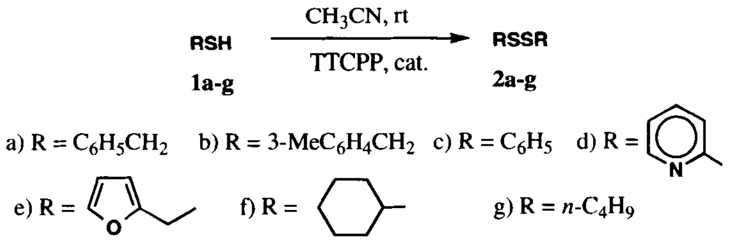
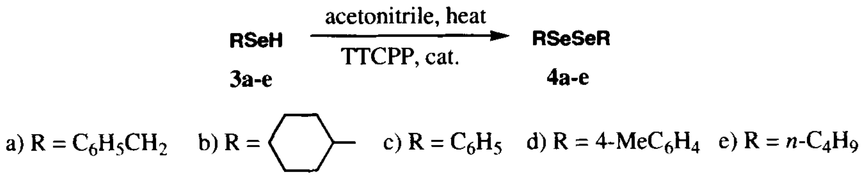
The dimerization of thiols and selenols to the corresponding disulfides and diselenides under mild and neutral conditions in organic media is of practical importance in organic synthesis. Since thiols and selenols are easily oxidizable and may thus be over oxidized, extensive studies have been carried out to discover procedures for the controlled oxidation of these two classes of functional groups.[1-12] As is usually the case, these reactions suffer from either one or more of the following disadvantages: a) availability,[4] b) preparation,[2] c) relatively long reaction time,[7-9] d) difficult work up,[7] e) highly poisonous reagents.[1] We have already described[13] the use of tris[trinitratocerium(IV)]-paraperiodate $[(NO_3)_3Ce]_3H_2IO_6$ (TTCPP) as a safe, easily prepared and stable oxidant for oxidation of different types of organic compounds in refluxing benzene. We now report that TTCPP can act as a very efficient catalyst for the dimerization of thiols in acetonitrile both at room temperature or under refluxing conditions (Table 1) in high yields.



The dimerization of selenols was also achieved in high yields in refluxing acetonitrile (Table 2).



The dimerization of thiols to disulfides has been shown to occur through a radical type reaction.[11] It is also known that Ce(IV) salts can initiate radical reactions by a one-electron oxidation of the hetero atom and conversion to Ce(III).[14-16] The catalytic nature of TTCPP reactions with both thiols and selenols could be due to the regeneration of Ce(IV) by the periodate moiety which is present as a co-oxidant in the catalyst. The above results indicates that this catalytic method could be a useful alternative to the available methodologies.

TABLE 1. Disulfides (**2a-g**) from Mercaptans in Acetonitrile

Disulfides	Time (min)	Yield[a] (%)	Time (min)	Yield[b] (%)	mp. or bp./Torr (°C) Found	lit.
2a	60	90	10	88	70-71	70-71[17]
2b	30	88	5	85	44-45	45[18-19]
2c	70	95	5	85	58-59	58-60[18]
2d	80	93	15	95	55-56	54-57[18]
2e	90	88	15	90	119-121/1	112-115/0.5[18]
2f	90	85	15	90	124-129	125-130[20]
2g	80	85	15	85	116-118/20	114-115/18[20]

a) At reflux; 0.1 molar ratio of TTCPP/RSH. b) At room temperature; 0.2 molar ratio of TTCPP/RSH.

EXPERIMENTAL SECTION

Products were characterized by comparison with authentic samples. Reactions were monitored by thin layer or gas chromatography.

TABLE 2. Diselenides (4a-e) from Selenols in Acetonitrile[a]

Disulfides	Time (min)	Yield[a] (%)	mp. or bp./Torr (°C) Found	lit.
4a	80	90	92-93	93[22]
4b	80	85	157-158/760	158/760[23]
4c	60	92	63	62[24]
4d	60	88	46-47	47[24]
4e	80	90	107-108/760	108/760[23]

a) At reflux; 0.15 molar ratio of TTCPP/RSeH.

Oxidative Coupling of Cyclohexanethiol (1f). Typical Procedure.- A stirred solution of cyclohexanethiol (1.16 g, 10 mmol) in acetonitrile (50 mL)was treated with TTCPP (2.4 g, 2 mmol) at room temperature; glc monitoring showed the reaction to be complete after 15 min. The solvent was evaporated, ether (100 mL) was added; the resulting solid was filtered off by gravity and washed with ether several times. Evaporation of the combined filtrates and washes gave the crude cyclohexyldisulfide (1.08g, 95%). Purification was achieved by column chromatography on silica-gel using n-hexane-CCl_4 (1:1) as eluent to give the pure product (1.03 g, 90%).

Oxidative Coupling of Benzyl Selenol (2a). Typical Procedure.- To a solution of benzyl selenol (1.7 g, 10 mmol) in acetonitrile (50 mL) was added (1.8 g, 1.5 mmol) of TTCPP and the mixture was heated at reflux for 80 min. The progress of reaction was monitored by t.l.c. The reaction mixture was filtered and the filter cake was washed three times with acetonitrile (50 mL). After evaporation of the combined filtrates and washes, water (80 mL) was added and the organic product was extracted with ether three times (3x30mL). The ethereal solution was dried with anhydrous $MgSO_4$ and filtered. Evaporation of solvent gave the pure product as a solid which according to its spectral and physical data was found to be dibenzyldiselenide (1.5 g, 90%).

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AN IMPROVED PROCEDURE FOR THE PREPARATION OF ARYLOXIRANES

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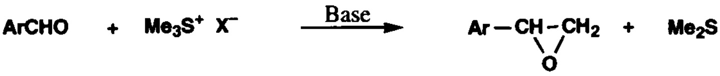
Oxiranes are reactive and versatile synthetic intermediates,[1] conveniently prepared by reaction of aldehydes and ketones with dimethylsulfonium methylide. While a method for generating the ylide under strong acid conditions has recently been reported,[2] strongly basic conditions are more usual.



$$\mathrm{ArCHO} + \mathrm{Me_3S^+\ X^-} \xrightarrow{\text{Base}} \mathrm{Ar{-}}\underset{\mathrm{O}}{\mathrm{CH{-}CH_2}} + \mathrm{Me_2S}$$

The original method in which the ylide was generated from trimethylsulfonium iodide with sodium hydride in anhydrous dimethyl sulfoxide,[3] was subsequently applied to a range of aromatic and heteroaromatic aldehydes to prepare intermediates in the synthesis of antimalarials.[4] Success has since been reported for phenyloxirane with conc. aqueous sodium hydroxide as base in two-phase systems, both with[5] and without[6] a phase-transfer catalyst. In aqueous conditions, the sulfonium salt counterion is stated to be important in ylide generation, with better results with the chloride (though less convenient to prepare) than iodide.[7] Under phase-transfer conditions, the sulfonium chloride gave a 60% yield of *p*-nitrophenyloxirane[8] and 15% yield of the 4-pyridinyl analog.[9]

In our hands, the phase-transfer reaction with trimethylsulfonium *iodide* and aqueous sodium hydroxide was quite successful when applied to benzaldehyde. With the more reactive 4-nitrobenzaldehyde, however, the Cannizzaro reaction was competitive and 4-nitrobenzyl alcohol