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SHORT COMMUNICATIONS

Coupling of Thiols Catalyzed by Trinitratocerium(IV) Bromate*

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Oxidative coupling of thiols to disulfides under neutral and mild conditions is important from both biological and practical viewpoints [1]. Thiols are compounds which can be overoxidized; therefore, extensive studies have been carried out on their controlled oxidation [2–16]. All reagents presently used for this purpose are characterized by one or more of the following disadvantages: relatively long reaction time [8, 16], low accessibility [15], difficult preparation [14], laborious isolation procedure [14]. We have already described the use of trinitratocerium(IV) bromate $(NO_3)_3CeBrO_3$ (TNCB) as a safe, easily obtainable, and stable oxidant with respect to benzyl alcohols and acyloins in boiling acetonitrile [17]. We now report that TNCB can act as a very efficient reagent for oxidation of thiols to disulfides in boiling acetonitrile, which ensures high yields of the products (Table 1).

To illustrate the efficiency of the proposed procedure, Table 2 compares some our results with published data [8]. The easy experimental and isolation procedure, short reaction time, and excellent yields of the products make the proposed procedure a useful supplement to the existing methods.

Typical procedure for oxidation of thiols with trinitratocerium(IV) bromate. A solution of 1 mmol of thiol in 3 ml of acetonitrile was treated with 0.2 equiv of TNCB, and the mixture was heated for 0.16–4.5 h under reflux. The progress of the reaction was monitored by TLC and GLC. When the reaction was complete, the mixture was filtered, and the solid precipitate was filtered off and washed with 10 ml of acetonitrile. The filtrate was evaporated, and the residue was subjected to column chromatography on silica gel. The products were identified by the melting points and IR and NMR spectra, which were compared with published data for authentic samples.

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Table 1. Oxidation of thiols with trinitratocerium(IV) bromate in boiling acetonitrile

Substrate	Product	Time, h	Yield,[a] %
C_6H_4SH	$(C_6H_5S_{-})_2$	0.25	92
p-ClC_6H_4SH	(*p*-$ClC_6H_4S)_2$	0.3	95
p-MeC_6H_4SH	(*p*-$MeC_6H_4S)_2$	0.16	90
o-HSC_6H_4COOH	(*o*-$HOCOC_6H_4S)_2$	4.5	0
$C_6H_5CH_2SH$	$(C_6H_5CH_2S)_2$	0.25	90
cyclo-$C_6H_{11}SH$	$(C_6H_{11}S)_2$	0.42	95
2-Mercaptopyridine	2,2′-Dithiopyridine	0.75	89
Ethane-1,2-dithiol	–	0.42[b]	–

[a] Yield of the isolated product.
[b] Polymerization occurred.

Table 2. Oxidation of thiols with trinitratocerium(IV) bromate (A), bis[trinitratocerium(IV) bromate] (B) [8], and pyridinium chlorochromate (C) [8]

Substrate	Oxidant (oxidant-to-substrate ratio)	Time, h	Yield, %
C_6H_5SH	A (0.2)	0.25	92
C_6H_5SH	B (2)	4	90
C_6H_5SH	C (1)	0.03	85
cyclo-$C_6H_{11}SH$	A (0.2)	0.42	95
cyclo-$C_6H_{11}SH$	B (2)	6	80
cyclo-$C_6H_{11}SH$	C (1)	2	0

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