

Highly Selective Sulfur Transfer Reaction in the Solid State

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Benzyltriethylammonium tetrathiomolybdate **1** reacts readily with benzyl halides, alkyl iodides and acyl halides in the solid state to give the corresponding disulfides in good yields and with remarkable selectivity.

An increasing number of solid-state reactions have been reported in recent years some of which are superior in terms of yield and selectivity to their solution counterparts.¹ The absence of solvent and high volume efficiency make these reactions of particular interest.^{2–12}

Results and Discussion

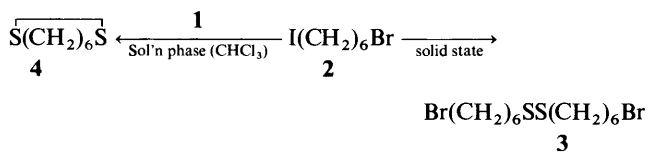
During our studies on new sulfur transfer reagents¹³ we found that benzyltriethylammonium tetrathiomolybdate **1** reacts readily (5–30 min) in the solid state with benzyl halides, alkyl iodides and acyl halides to afford the corresponding disulfides in good yields.

A mixture of benzyl or acyl halides when ground with **1** (1.1 equiv.) in an agate pestle and mortar, changed colour from dark red to black to give initially a viscid mass that became powdery within minutes. Extraction of this with dichloromethane or diethyl ether furnished the product.

Scanning electron microscopy was used to follow the conspicuous morphological changes which occurred as the reagent was ground with alkyl halides (Fig. 1).

Benzyl halides and acyl halides reacted smoothly to give the corresponding disulfides (entries 1–4 in Table 1) whilst α -chloroethyl acetate and a α -bromoethyl acetate gave a mixture of the corresponding mono- and di-sulfides (entries 7 and 8). Tributyltin chloride yielded the monosulfide as the sole isolable product (entry 5) whilst phenylmercuric bromide was converted into diphenylmercury (entry 6) *via* the corresponding monosulfide as has been reported earlier.¹⁴ Whereas most of the earlier reported solid-state reactions have taken place at higher temperatures (50–60 °C), and with longer reaction times (3–72 h), our reaction occurs rapidly (5–30 min) at room temperature (28 °C).

The selectivity achievable in such solid-state reactions complements that achievable in solution. Whereas butyl bromide failed to react with **1** in the solid state even after 48 h, in solution it reacted to give dibutyl disulfide in 96% yield. In contrast, butyl iodide reacted readily in the solid state with **1** to give dibutyl disulfide (entry 10). 1-Bromo-6-iodohexane **2** also reacted chemoselectively: thus on treatment with **1** in the solid state it yielded exclusively the corresponding dibromo disulfide **3** whilst in solution (CHCl₃) it gave the eight-membered cyclic disulfide **4**.



When in competition experiment, a mixture of 1-bromobutane and benzyl bromide was treated with **1** (2 equiv.) in the solid state, dibenzyl disulfide was produced selectively. To the

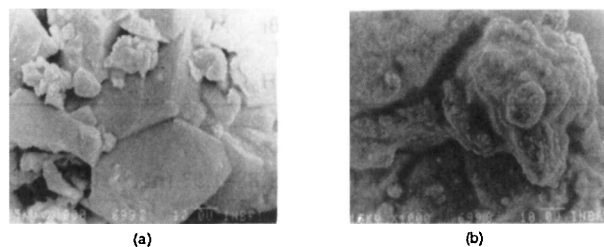


Fig. 1 (a) Scanning electron micrograph of benzyltriethylammonium tetrathiomolybdate **1** and (b) after grinding **1** with benzyl bromide

best of our knowledge this is the first report of a sulfur transfer reaction in the solid state.

Experimental

M.p.s and b.p.s are uncorrected. ¹H NMR spectra were recorded on JEOL FXQ 90 MHz and Hitachi 60 MHz FT spectrometers in CDCl₃. IR spectra were recorded on a Perkin Elmer model-781 spectrometer. Mass spectra and HRMS were recorded on a JEOL JMSD-300 spectrometer.

General Procedures.—Reaction of compound 2 with benzyltriethylammonium tetrathiomolybdate 1 in the solid state. 1-Bromo-6-iodohexane **2** (0.29 g, 1 mmol) was added in one portion to benzyltriethylammonium tetrathiomolybdate (1.4 g, 2.2 mmol) in an agate mortar and the mixture was ground continuously for 5 min. The colour of the mixture changed immediately from dark red to black and the initial viscid product became powdery within minutes. The mixture was ground occasionally for 20 min and then extracted with dichloromethane or diethyl ether; flash column chromatography of the extract on silica gel gave the product **3** as a viscous oil (0.10 g, 52%), δ_{H} (90 MHz; CDCl₃) 3.43 (t, 4 H), 2.60 (t, 4 H) and 2.00–1.30 (m, 16 H); *m/z* 392 (M⁺), 313, 281, 83 and 55 (Found M⁺, 391.9677. Calc. for C₁₂H₂₄Br₂S₂: M, 391.9665).

Reaction of p-bromobenzyl bromide with the tetrathiomolybdate 1. *p*-Bromobenzyl bromide (0.25 g, 1 mmol) was added in one portion to the tetrathiomolybdate **1** (0.67 g, 1.1 mmol) in an agate mortar and the solid mixture was ground continuously for 15 min. The resulting solid mass was extracted with diethyl ether to afford the corresponding disulfide as the only product (0.14 g, 71%), m.p. 95–96 °C (lit.,¹⁵ 95–96 °C).

Reaction of compound 2 with the tetrathiomolybdate 1 in chloroform. Compound **2** (0.29 g, 1 mmol) in chloroform (5 cm³) was added to a solution of **1** (1.4 g, 2.2 mmol) in chloroform (15 cm³) and the reaction mixture was stirred at room temperature (28 °C) for 3 h. After this the solvent was distilled off under reduced pressure and the residue was extracted with diethyl ether (4 × 20 cm³). Evaporation of the extract gave a residue which was purified by flash chromatography on silica gel to yield the cyclic disulfide **4** as an oil (0.11 g, 72%). δ_{H} (90

Table 1 Sulfur transfer reactions with tetrathiomolybdate 1 in the solid state

Entry	Substrate	Reaction time (min)	Product	Ref.	Yield (%)
1	PhCH ₂ Br	15	(PhCH ₂ S) ₂	13	72
2	<i>p</i> -BrC ₆ H ₄ CH ₂ Br	15	(<i>p</i> -BrC ₆ H ₄ CH ₂ S) ₂	15	71
3	PhCOCl	5	(PhCOS) ₂	16	70
4	<i>p</i> -MeC ₆ H ₄ COCl	5	(<i>p</i> -MeOC ₆ H ₄ COS) ₂	16	78
5	Bu ₃ SnCl	10	(Bu ₃ Sn) ₂ S	13	90
6	PhHgBr	30	(Ph ₂ Hg) ₂ S	14	78
7	ClCH ₂ CO ₂ Et	30	(EtO ₂ CCH ₂) ₂ S + (EtO ₂ CCH ₂ S) ₂ (1.6:1)	13	47
8	BrCH ₂ CO ₂ Et	10	(EtO ₂ CCH ₂) ₂ S + (EtO ₂ CCH ₂ S) ₂ (3.4:1)		67
9	BuBr	2880	No reaction		—
10	BuI	20	(BuS) ₂		74
11	I(CH ₂) ₄ I	20	S(CH ₂) ₄ S	17	72

MHz; CDCl₃) 2.56 (dt, 4 H) and 1.88–1.53 (m, 8 H); *m/z* 148 (M⁺), 115 and 83 (Found: M⁺ 148.0397. Calc. for C₆H₁₂S₂: *M*, 148.0381).

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