

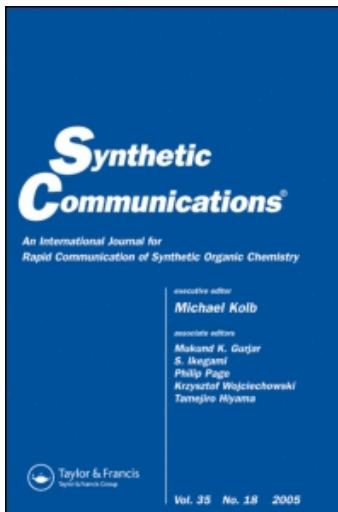
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BENZYLTRIETHYLMONIUM TETRATHIOMOLYBDATE: AN IMPROVED SULFUR TRANSFER REAGENT FOR THE SYNTHESIS OF DISULFIDES

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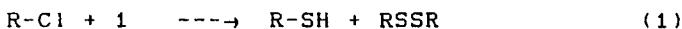
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ABSTRACT: Benzyltriethylammonium tetrathiomolybdate has been found to be a superior reagent for the conversion of alkyl halides to the corresponding disulfides in chloroform at room temperature.

The chemistry of molybdenum-sulfur compounds has attracted much attention in the past, particularly with respect to their implications in bioinorganic chemistry and catalysis.^{1,2} Though the simplest binary Mo-S moiety, MoS_4^{2-} anion has been known for many years, its chemical reactivity has only recently been appreciated and relatively few studies have been reported on reactivity towards organic reagents.³ We have begun a systematic study of such an investigation of the reactivity of tetrathiomolybdate with organic/ organometallic halides.

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Earlier work from our laboratories has shown that piperidinium tetrathiotungstate, $(C_8H_{12}N)_2WS_4$ 1 is an effective sulfur transfer reagent employed in the conversion of alkyl halides and sulfonyl derivatives to the corresponding disulfides.⁴ Although this reagent has been novel in terms of reactivity, the main disadvantage was that, of necessity, the reaction had to be performed in polar aprotic solvents like DMF and the workup procedure on a larger scale was cumbersome. Additionally, the reaction of alkyl halides with 1 in DMF invariably led to the formation of substantial amounts of the corresponding thiols as byproducts apart from the disulfides(eq-1).



In order to increase the scope and utility of this sulfur transfer reaction, we have now a modified reagent, benzyltriethylammonium tetrathiomolybdate, $(PhCH_2NEt_3)_2MoS_4$ 2.

This quaternaryammonium molybdate 2 is soluble in chloroform or methylene chloride and on treatment of 2 (1.1 mole eq.) with a variety of organic and organo-metallic halides in chloroform at room temperature(28°C) afforded the corresponding disulfides in very good yield (Table).

In contrast to piperidinium tetrathiotungstate 1 , the tetrathiomolybdate 2 on reaction with benzyl chloride yielded exclusively the corresponding disulfide 4 in good yield (entry 2). In general, primary benzylic bromides

TABLE
SULFUR TRANSFER REACTIONS WITH BENZYLTRIETHYLLAMMONIUM TETRAETHIOMOLYBDATE $\underline{\underline{\underline{\underline{2}}}}$

Entry	Substrate	Time h	Product ^a	Yield ^b %	m.p./b.p. °C
1.	PhCH_2Br	<u>3</u>	$\text{CPhCH}_2\text{S}-\text{J}_2$	<u>4</u>	88 71-72 ⁶
2.	PhCH_2Cl	<u>5</u>	<u>8</u>	<u>4</u>	85 ---, ---
3.	PhCH_2OTs	<u>6</u>	<u>16</u>	<u>4</u>	81 ---, ---
4.	$p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$	<u>7</u>	$\text{Cp-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}-\text{J}_2$	<u>8</u>	80 124-125 ⁷
5.	$m\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$	<u>9</u>	<u>2</u>	$\text{Cm-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{S}-\text{J}_2$	<u>10</u> 76 69-71
6.	$p\text{-NCC}_6\text{H}_4\text{CH}_2\text{Br}$	<u>11</u>	<u>1</u>	$\text{Cp-NCC}_6\text{H}_4\text{CH}_2\text{S}-\text{J}_2$	<u>12</u> 86 146-148 ⁸
7.	$n\text{-BuBr}$	<u>13</u>	<u>10</u>	$\text{Cn-BuS}-\text{J}_2$ $\text{CEtO}_2\text{CCH}_2\text{S}-\text{J}_2$	<u>14</u> <u>16a</u> 96 135-37/1 mm ⁹ 10
8.	$\text{ClCH}_2\text{CO}_2\text{Et}$	<u>15</u>	<u>6</u>	$\text{CEtO}_2\text{CCH}_2\text{S}-\text{J}_2$	85 110-121 mm ¹¹
9.	$\text{C}_6\text{H}_{11}\text{Br}$	<u>17</u>	<u>10</u>		

... continued.

Table continued

Entry	Substrate	Time(h)	Product ^a	Yield ^b (%)	m. p./°C. p. C
10.		<u>19</u>	<u>8</u>		<u>20</u>
11.	n-Bu ₃ SnCl	<u>21</u>	<u>1</u>	(n-Bu ₃ Sn) ₂ S	<u>22</u>
12.	PhHgBr	<u>23</u>	<u>1^c</u>	(Ph) ₂ S	<u>24</u>
13.	PhBr	<u>25</u>	<u>12^c</u>	(PhS) ₂	<u>26</u>
14.		<u>27</u>	<u>8^c</u>		<u>28</u>

a) The products exhibited expected spectral data and were compared with authentic samples.

b) Yield refers to pure isolated products.

c) The reaction was performed in DMF at 70 °C.

reacted faster than the simple primary and secondary alkyl bromides (entries 1, 4-6, 7&9). Interestingly, α -chloroethyl acetate 15 gave a mixture of the corresponding disulfide 16a and sulfide 16b (entry 8). Tri-n-butyltinchloride 21 on treatment with 2 afforded the bis(tributyltin)sulfide 22 as the only product (entry 11). Phenyl mercuric bromide on the otherhand gave the corresponding sulfide 24 (entry 12). Although bromobenzene and hexachloro benzene do not react with 2 in chloroform under the normal reaction conditions, when the reaction was performed in DMF at 70°C (8-12 h) diphenyldisulfide 26 and pentachlorothiophenol 28 respectively were formed in poor yields (20-33 %).

Thus, in this study, we have been able to demonstrate the enhanced utility of this modified sulfur transfer reagent-benzyltriethylammonium tetrathiomolybdate-for new carbon-sulfur bond forming reactions.

EXPERIMENTAL

Benzyltriethylammonium tetrathiomolybdate⁵

Ammonium molybdate (10 g) was dissolved in water (20 ml) and ammonium hydroxide (60 ml, sp.gr. 0.91) was added. This solution was filtered and hydrogen sulfide was passed at room temperature for 10 min and at 60°C for 1 h. The reaction mixture was cooled to 0°C, and the solid product was filtered, washed successively with

isopropyl alcohol(20 ml) and ether(20 ml). The brick red crystals (13.5 g) of ammoniumtetrathiomolybdate were dried under vacuum.

To a solution of ammoniumtetrathiomolybdate(13 g) in water (20 ml) was added a solution of benzyltriethylammoniumchloride(23.3 g) in water(50 ml) and the reaction mixture was stirred at room temperature for 2 h. The solid that separated was filtered, washed with isopropyl alcohol(30 ml) and ether(30 ml) and dried under high vacuum. The dark red crystalline benzyltriethylammonium tetrathiomolybdate 2 (24 g, 80 %) m.p 150°C(decomp.) was stored in a desiccator. UV/Vis(DMF): λ_{max} (ϵ) 472(11,850), 320(16,750), 274(24,700) nm.

General procedure for the reaction of 2 with alkyl halides:

To a solution of 2 (2.0 g, 3.3 mmol) in chloroform(8 ml) was added the alkyl halide(3 mmol) in chloroform(6 ml) over a period of 10 min. After stirring for 1 h at room temperature(28°C) the solvent was removed under vacuum and the black residue was extracted with ether(2x 30 ml). The crude product after evaporation of solvent was purified by flash chromatography on silica gel to reveal the pure product.

Compound 10: IR(Nujol):2914, 1617, 1584, 1380, 1317 cm^{-1} ;
 ^1H NMR:(CDCl_3) δ , 3.70(s, 4H), 7.4-7.72(m), 8.0-8.28(m);
 ^{13}C NMR:(CDCl_3), δ , 148.5, 139.5, 135.5, 125.5, 129.7, 124.2, 122.7, 42.3.

Compound 20:

IR(Nujol): 3358, 1614, 1596, 1506, 1260, 744 cm^{-1} ;
 ^1H NMR: (CDCl₃), δ , 2.9-3.2(t, 4H), 4.2-4.48(t, 4H), 5.88
(s, 2H), 6.72-7.04(m, 8H); ^{13}C NMR : (CDCl₃), δ , 146.1, 145.3,
122.4, 120.2, 115.2, 112.7, 67.4, 37.9; MS: 338(M⁺), 229,
169, 109, 93.

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