Oxidation Using Quaternary Ammonium Polyhalides. IV.1) Selective Oxidation of Sulfides to Sulfoxides with Benzyltrimethylammonium Tribromide

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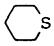
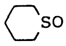
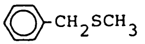
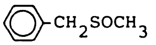
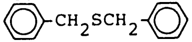
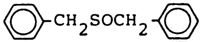
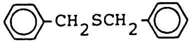
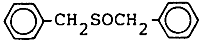
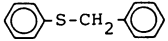
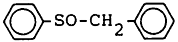
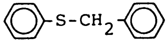
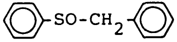
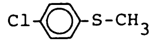
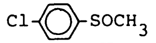
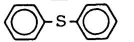
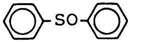
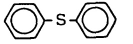
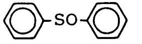
Synopsis. The reaction of sulfides with a stoichiometric amount of benzyltrimethylammonium tribromide and aqueous sodium hydroxide in dichloromethane at room temperature or in 1,2-dichloroethane under reflux gave the corresponding sulfoxides in good yields.

The usual methods of oxidation of sulfides (**1**) to sulfoxides (**2**) were occasionally found to be unsatisfactory. One of the difficulties is the relative ease of further oxidation of **2** to sulfone. However, the selective oxidation of **1** to **2** can be brought about by several reagents. For example, 30% hydrogen peroxide in acetone,2) chromic acid in pyridine,3) manganese dioxide in light petroleum,3) liquid dinitrogen tetroxide under cooling by alcohol-solid carbon dioxide,4) some organic hydroperoxides in appropriate solvent in sealed tube,5) and dimethyl sulfoxide under heating at 160—175 °C6) have been used. For the same purpose, some halogenating agents such as NBS,7) the addition complex of 1,4-diazabicyclo[2.2.2]octane with bromine,8) iodine with potassium iodide,9) *t*-butyl hypochlorite,10) and sodium bromite11) are also used.

In connection with our further investigation on the synthetic utility of quaternary ammonium polyhalides, we have found that benzyltrimethylammonium

Table 1. Oxidation of Sulfides (**1**) with BTMA Br_3/NaOH aq

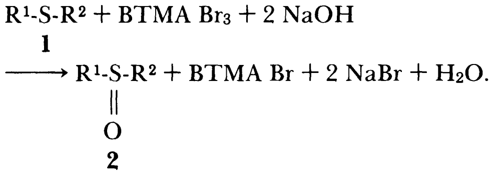
	Substrate **1**	Solvent	Reaction conditions Time/h	Temp/°C	Product^a) **2**	Yield^b) /%
a	$(CH_3CH_2CH_2)_2S$	CH_2Cl_2	1	rt	$(CH_3CH_2CH_2)_2SO$	89
b	$[(CH_3)_2CH]_2S$	CH_2Cl_2	1	rt	$[(CH_3)_2CH]_2SO$	94
c	$[CH_3(CH_2)_3]_2S$	CH_2Cl_2	1	rt	$[CH_3(CH_2)_3]_2SO$	98
d	$[(CH_3)_2CHCH_2]_2S$	CH_2Cl_2	1	rt	$[(CH_3)_2CHCH_2]_2SO$	95
e	$[C_2H_5(CH_3)CH]_2S$	CH_2Cl_2	1	rt	$[C_2H_5(CH_3)CH]_2SO$	76
f	$[(CH_3)_3C]_2S$	CH_2Cl_2	0.2	rt	$[(CH_3)_3C]_2SO$	20^c)
g	$[CH_3(CH_2)_5]_2S$	CH_2Cl_2	1	rt	$[CH_3(CH_2)_5]_2SO$	98
h	$[CH_3(CH_2)_6]_2S$	CH_2Cl_2	1.5	rt	$[CH_3(CH_2)_6]_2SO$	98
i	$[CH_3(CH_2)_7]_2S$	CH_2Cl_2	1	rt	$[CH_3(CH_2)_7]_2SO$	97
j	$[CH_3(CH_2)_{11}]_2S$	CH_2Cl_2	1.2	rt	$[CH_3(CH_2)_{11}]_2SO$	96
k	$[CH_3(CH_2)_{15}]_2S$	CH_2Cl_2	2.5	rt	$[CH_3(CH_2)_{15}]_2SO$	98
l	$[CH_3(CH_2)_{17}]_2S$	CH_2Cl_2	2	rt	$[CH_3(CH_2)_{17}]_2SO$	96
m	$C_2H_5S(CH_2)_2CH_3$	CH_2Cl_2	1	rt	$C_2H_5SO(CH_2)_2CH_3$	85
n	$CH_3(CH_2)_3SC_2H_5$	CH_2Cl_2	1	rt	$CH_3(CH_2)_3SOC_2H_5$	98
o	$CH_3(CH_2)_7SCH_3$	CH_2Cl_2	1.3	rt	$CH_3(CH_2)_7SOCH_3$	98
p	$CH_3(CH_2)_9SCH_3$	CH_2Cl_2	1.5	rt	$CH_3(CH_2)_9SOCH_3$	95
q		CH_2Cl_2	1	rt		66
r	$ClCH_2CH_2SC_2H_5$	CH_2Cl_2	1	rt	$ClCH_2CH_2SOC_2H_5$	47
s		CH_2Cl_2	1	rt		97
t		CH_2Cl_2	2	rt		84
u		$ClCH_2CH_2Cl$	0.5	Reflux		87
v		CH_2Cl_2	3	rt		53
w		$ClCH_2CH_2Cl$	4	Reflux		80
x		CH_2Cl_2	3	rt		66
y		CH_2Cl_2	6	rt		32
z		$ClCH_2CH_2Cl$	4	Reflux		73

a) Products were characterized by comparing ^1H NMR spectra and mp or bp with those of authentic samples or reported data. b) Yield of isolated product. In the cases of run r, v, and y, products **2r**, **2v**, and **2y** were isolated by column chromatography on silica gel. c) Yield was based on its ^1H NMR spectrum.

tribromide (BTMA Br_3) is a useful oxidizing agent. In this paper we wish to report on a selective synthesis of **2** from **1** by the use of BTMA Br_3 in aqueous sodium hydroxide.

Results and Discussion

The reaction of **1** with a calculated amount of BTMA Br_3 and aqueous sodium hydroxide in dichloromethane at room temperature or in 1,2-dichloroethane under reflux gave **2** in good yields. The results are summarized in Table 1, and the reaction scheme can be represented as



$$\underset{\mathbf{1}}{R^1\text{-S-}R^2} + \text{BTMA Br}_3 + 2\,\text{NaOH} \longrightarrow \underset{\mathbf{2}}{R^1\text{-}\underset{O}{\underset{\|}{S}}\text{-}R^2} + \text{BTMA Br} + 2\,\text{NaBr} + H_2O.$$

Aliphatic and aromatic sulfides **1a—z** have readily been oxidized to the corresponding **2a—z**. Our method, using BTMA Br_3, has a merit in that this stable reagent (orange red) can be treated safely and stoichiometrically. Furthermore, the end-point of the reaction can be recognized by decolorization of its initial orange color.

As a limitation of the procedure, attempts at the preparation of an unsaturated **2**, such as allyl phenyl sulfoxide and benzyl styryl sulfoxide, were unsuccessful, since the double bond underwent bromine addition under these conditions.

Experimental

Dihexyl Sulfoxide (2g); Typical Procedure: BTMA Br_3 (4.68 g, 12 mmol) was added to a mixture of dihexyl sulfide (**1g**) (2.02 g, 10 mmol) in dichloromethane (30 ml) and sodium hydroxide (1.1 g, 27.5 mmol) in water (15 ml), and the mixture was stirred at room temperature for 1 h. The orange color of the solution gradually faded and then completely decolorized during the period. To the reaction mixture was added a 20% aq solution of $NaHSO_3$ (10 ml); the organic layer was then separated. The aqueous layer was extracted with dichloromethane (10 ml×2) and the combined solution of dichloromethane was dried over $MgSO_4$ and evaporated in vacuo to give **2g** as colorless crystals; yield 2.14 g (98%); mp 57—58 °C (lit,[12] mp 60 °C).

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