The Reduction of Sulfoxides with *t*-Butyl Bromide

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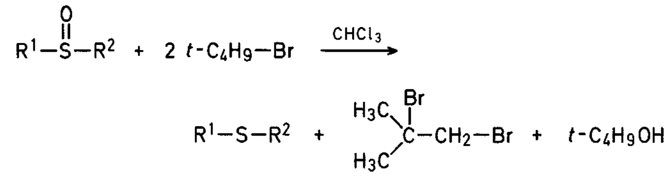
We have previously reported that *t*-butyl bromide acts as a particularly effective dimethyl sulfoxide activator in reactions with nucleophiles, leading to Pummerer-type reactions[1].

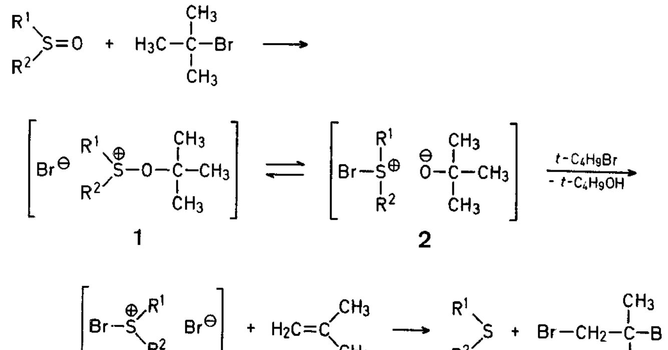
The considerable interest in the reduction of sulfoxides prompts us to report that *t*-butyl bromide deoxygenates sulfoxides to yield the corresponding sulfides under neutral conditions. Many deoxygenation procedures of sulfoxides have recently been reviewed[2] and studied[3]; however, only few take place in high yields, under mild conditions, and with the use of common, inexpensive laboratory reagents.

When alkyl, aryl, and aralkyl sulfoxides are heated under reflux (80 °C) with *t*-butyl bromide, in the presence of chloroform (various amounts) the corresponding sulfides are obtained in excellent yields (Table).



An inspection of the data reported in the Table reveals that the present procedure for the preparation of sulfides offers the following advantages: (a) a wide variety of sulfides are prepared in excellent yields, even dibenzyl sulfide and aryl sulfides which are normally difficult to synthesize; (b) low cost because of the use of common grade *t*-butyl bromide; (c) very simple work-up procedure, since the products may be obtained by percolation of the mixture on a silica gel column or directly distilled; (d) no concomitant formation of undesired halogenated sulfides.

The reaction mechanism can be represented as shown below.



The unstable alkoxysulfonium intermediate **1** may give rise to a more or less separated ion pair **2**. The *t*-butoxide anion, although present in a small quantity (the equilibrium is obviously driven to the left), catalyses elimination of *t*-butyl bromide, leading to *t*-butyl alcohol, isobutene, and a bromosulfonium bromide species **3**, which can brominate isobutene, thus forming 1,2-dibromo-2-methyl propane and the sulfide. *t*-Butyl alcohol has been actually detected by G.L.C. and mass spectrometry, together with the dibromo derivative. No bromosulfides are formed under the conditions employed.

Actually, it has been previously[6] shown that dimethyl sulfoxide is reduced in low yield to dimethyl sulfide in the presence of catalytic amounts of bromine and/or hydrobromic acid at 100 °C for several hours (5–240 h). It is suggested that an oxidation-reduction cycle is taking place, proceeding essentially through the addition of hydrobromic acid to dimethyl sulfoxide and developing bromine. Under our conditions, hydrogen bromide does not seem to be directly involved in the

Table. Deoxygenation of Sulfoxides with *t*-Butyl Bromide

Substrate and Product R^1	R^2	Amount of $CHCl_3$ (ml)	Reaction time (h)	Yield [%][a,b]	m.p. or b.p./torr	Lit. m.p. or b.p./torr
$C_6H_5CH_2$	$C_6H_5CH_2$	7	5	80[d]	48–49 °C	49–50 °C[4]
C_6H_5	C_6H_5	2	20	100	99–102 °C/0.1	296 °C/760[4]
4-H_3C—C_6H_4	4-H_3C—C_6H_4	2	20	97	56 °C	57.3 °C[5]
4-Cl—C_6H_4	4-Cl—C_6H_4[c]	7	28	96	94 °C	95 °C[5]
n-C_4H_9	*n*-C_4H_9	0	2	92	182–185 °C/760	185–185.5 °C/760[4]
n-C_3H_7	*n*-C_3H_7	0	2	90	139–141 °C/760	142 °C/760[4]
CH_3	C_6H_5	0	4	96	193 °C/760	193 °C/760[4]

[a] Yields are based on isolated products of purity ≥97% as determined by microanalyses.

[b] All sulfides are known compounds and gave correct physical and spectral (N.M.R., mass) characteristics.

[c] In this case 60 mmol of *t*-butyl bromide were used.

[d] In this case a 15% of benzaldehyde was recovered.

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process, since we never observe mono-brominated products when using other olefins (cyclohexene, styrene) as scavengers.

Both starting materials and products are known. They all displayed physical and spectral properties in agreement with literature values.

Deoxygenation of Sulfoxides with *t*-Butyl Bromide; General Procedure: *t*-Butyl bromide (40 mmol) is added to a solution of sulfoxide (10 mmol) in chloroform (various amounts: see the Table). The mixture is heated at reflux (80 °C) until completion of the reaction as detected by T. L. C., then percolated on a silica gel column, using hexane as eluent, or directly distilled to yield the pure sulfide.

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