A New Approach to the Reduction of Sulfoxides to Sulfides with 1,3-Dithiane in the Presence of Electrophilic Bromine as Catalyst

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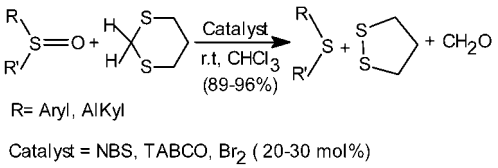
A new, mild, and novel method is described for the efficient deoxygenation of sulfoxides to their corresponding sulfides with 1,3-dithiane at room temperature in the presence of catalytic amounts of *N*-bromosuccinimide (NBS), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TABCO), or Br_2 as the source of electrophilic bromine.

Introduction

Reduction of sulfoxides to the corresponding sulfides is an important organic[1] and biological reaction[2] and has found wide applications in various synthetic transformations as well as asymmetric synthesis.[3] d-Block metals have been widely used as low-valent oxophilic reagents in deoxygenation of various types of organic substrates as well as sulfoxides.[1f,g,4−11] Very recently, we have reported the use of WCl_6/NaI as another example of a d-block metal reductive system.[12]

An alternative approach to the reduction of sulfoxides is the use of sulfur compounds, e.g., thiols;[13a] hydrogen sulfide;[13b] carbodithionic acids;[13c] thiophosphinic, thiophosphonic, and thiophosphoric acids;[13d] sulfides;[14,15] sulfenyl, sulfinyl, and sulfonyl chlorides;[16] disulfides;[17a] elemental sulfur (S_8);[17b] and thionyl chloride.[17c] However, the reduction of sulfoxides with these compounds sometimes suffers from serious disadvantages, such as use of an expensive reagent, difficult workup procedures, harsh acidic conditions (e.g., mixture of CF_3SO_3H and CF_3CO_2H, H_2SO_4 in refluxing acetic acid and or aqueous 4 M HCl or 4−6 M $HClO_4$ [1a,13a]), very high reaction temperatures (200−280 °C),[1a,17b] and long reaction times.[13]

Scheme 1



In this work, we report a new, novel, and efficient reduction of sulfoxides to their corresponding sulfides using 1,3-dithiane, a commercially available sulfur compound and catalytic amounts of *N*-bromosuccinimide (NBS), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TABCO),[18,19] or molecular bromine as the source of electrophilic halogen (Scheme 1).

Results and Discussion

In the course of our studies on the dethioacetalization of carbonyl compounds with NBS, TABCO, and Br_2 in DMSO, we observed that DMSO was reduced to dimethyl sulfide. This finding encouraged us to develop a simple method for the reduction of sulfoxides to their corresponding sulfides. To optimize the reaction conditions, we first studied the reduction of dibenzyl sulfoxide using 1,3-dithiane as the sulfur compound and different quantities of compounds carrying electrophilic holonium ions such as NBS, NCS (*N*-chlorosuccinimide), TABCO, and TCCA (trichlorocyanuric acid) as well as molecular bromine and iodine in dry chloroform. The results are shown in Table 1.

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Table 1. Conversion of Dibenzyl Sulfoxides (1.0 mmol) to Dibenzyl Sulfide with 1,3-Dithiane (1.1 mmol) in the Presence of Different Catalysts (NBS, NCS, TABCO, TCCA, Br_2, and I_2) in $CHCl_3$ at Room Temperature

entry	catalyst/ molar equiv	time (min)	% yield[a]	entry	catalyst/ molar equiv	time (min)	% yield[a]
1	NBS/0.05	250	94	12	NCS/0.2	55	92
2	NBS/0.1	110	93	13	TCCA/0.1	250	89
3	NBS/0.15	45	95	14	TCCA/0.15	200	92
4	NBS/0.2	30	94	15	TCCA/0.2	120	90
5	TABCO/0.05	300	90	16	Br_2/0.1	50	96
6	TABCO/0.1	100	95	17	Br_2/0.2	20	95
7	TABCO/0.15	71	94	18	I_2/0.1	24h	10
8	TABCO/0.2	35	92	19	I_2/0.15	24h	15
9	NCS/0.05	460	91	20	I_2/0.2	24h	25
10	NCS/0.1	180	92	21	I_2/0.3	24h	30
11	NCS/0.15	120	94	22	I_2/1.2	12h	40

[a] Isolated yield.

Table 2. Reduction of Dibenzyl Sulfoxide (1.0 mmol) Catalyzed with NBS, TABCO, and Also Br_2 (0.2 mmol) Using Cyclic and Acyclic Dithioacetals (1.1 mmol) in $CHCl_3$ at Room Temperature

entry	reagent	catalyst	time (min)	% yield[a]
1	2,2-dimethyl-1,3-dithiane	NBS	85	83
2	2,2-dimethyl-1,3-dithiane	Br_2	60	84
3	2,2-dimethyl-1,3-dithiane	TABCO	130	81
4	1,3-dithiane	NBS	30	94
5	1,3-dithiane	Br_2	20	95
6	1,3-dithiane	TABCO	35	92
7	1,3-dithiolane	NBS	30	90
8	1,3-dithiolane	Br_2	30	91
8	1,3-dithiolane	TABCO	45	90
10	acetone diethylthioacetal	NBS	60	82
11	acetone diethylthioacetal	Br_2	50	83
12	acetone diethylthioacetal	TABCO	65	81

[a] Isolated yield.

Among the catalysts we used for this reduction, those compounds carrying electrophilic bromine (NBS and TABCO; Table 1, entries 1−8) were found to be more efficient than those having electrophilic chlorine (NCS and TCCA; Table 1, entries 9−15). The reduction in the presence of catalytic amounts of molecular bromine was found to be as fast as using NBS and TABCO (Table 1, entries 16, 17); however, the reactions using molecular iodine as catalyst were found to be very slow and uncompleted, even when excess of iodine was used (Table 1, entries 18−22).

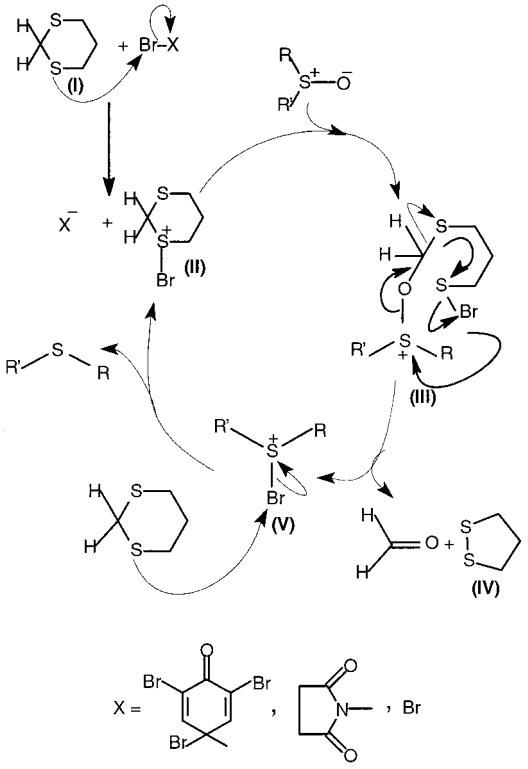
To observe the effect of different sulfur compounds on the rate and the yield of this reduction, we choose NBS, TABCO, and Br_2 (20 mol %) as preferred catalysts and continued our study by using structurally different cyclic and acyclic dithioacetals for reduction of dibenzyl sulfoxide. The results obtained for this reduction using different dithioacetals are compared in Table 2.

According to the results of Table 2, the reactions with 1,3-dithiane and 1,3-dithiolane are somewhat faster and with higher yields in comparison with the reactions when other thioacetals are used. Due to better availability of 1,3-dithiane, we choose it as the preferred sulfur compound and continued our study on the reduction of different sulfoxides.

Using this method, efficient deoxygenation of dibenzyl, dialkyl, benzyl alkyl, phenyl alkyl, and benzyl phenyl sulfoxides to their sulfides was achieved in excellent yields at room temperature (Table 3).

The formation of 1,2-dithiacyclopetane as a product of the reaction can be easily removed from the reaction

Scheme 2



mixture, due to its ease of polymerization to an unidentified polymer upon concentrating of the reaction mixture.[21]

A mechanism has been proposed to show the catalytic role of the electrophilic bromine in these reactions (Scheme 2). The bromination of 1,3-dithiane (**I**) produces an intermediate (**II**), which reacts with a molecule of sulfoxide to give another intermediate (**III**). Sulfenyl halides have been reported to dissociate in polar solvents to sulfonium and halide ions.[20] In our proposed mechanism, intermediate **III** could produce formaldehyde, 1,2-dithiacyclopetane (**IV**), and intermediate **V** as another source of electrophilic bromine in this catalytic cycle. For this reaction, dry solvent should be used. When we used wet choroform in this reaction, a water molecule attacks intermediate **II** instead of sulfoxide and results in the formation of formaldehyde, 1,2-dithiacyclopetane, and HBr in the reaction mixture. 1,2-Dithiacyclopetane (**IV**) was detected in the crude reaction mixture and identified by comparison of its ^1H and ^{13}C NMR spectral data to that reported in the literature.[21] In addition, its spectral data and GC retention time were also compared with those of a known sample obtained from intramolecular coupling of 1,3-propandithiol.[22]

To show that formaldehyde has been formed in this reaction, we have studied the reduction of dibenzyl sulfoxide in the presence of 2-phenyl-1,3-dithiane, which should produce benzaldehyde (according to the proposed mechanism) in the process of the reaction. In fact, benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone derivative in 96% yield from the reaction mixture.

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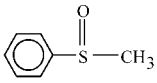
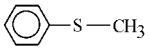
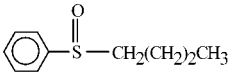
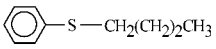
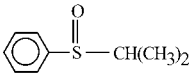
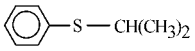
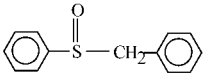
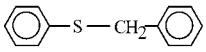
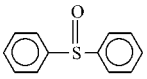
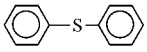
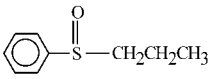
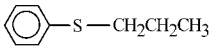
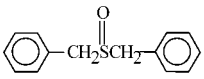
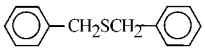
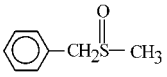
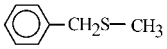
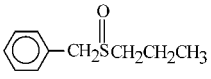
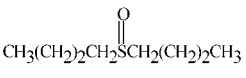
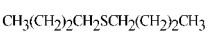
(22) Harpp, D. N.; Gleason, J. G.; Snyder, J. P. *J. Am. Chem. Soc.* **1968**, *90*, 4181. Spectral data for 1,2-dithiacyclopetane is as follows: UV absorption band at 330 nm (ϵ 147); ^1H NMR (δ, ppm) 2.81 (t, 4H), 2.01 (m, 2H); ^{13}C NMR (δ, ppm) 29.9, 26.6.

Table 3. Reduction of Sulfoxides to Sulfides with 1,3-Dithiane in the Presence of TABCO (A), NBS (B), or Br_2 (C) in $CHCl_3$ at Room Temperature

Entry	Substrate	Products	Catalyst [a]	Time (min)	Yield [c]
1			A	15	94
			B	12	94
			C	10	95
2			A	40	90
			B	30	92
			C	25	92
3			A	50	90
			B	40	90
			C	35	91
4			A	40	90
			B[b]	20	91
			C	25	90
5			A[b]	55	93
			B[b]	40	94
			C[b]	35	95
6			A	35	85
			B	30	89
			C	20	90
7			A	35	92
			B	30	94
			C	20	95
8			A	35	91
			B	30	93
			C	20	94
9			A	45	89
			B	35	91
			C	25	94
10			A	12	94
			B	10	96
			C	8	96

[a] The ratio of sulfoxide/1,3-dithiane/catalyst is 1/1.1/0.2, unless otherwise stated. [b] The ratio of sulfoxide/1,3-dithiane/catalyst is 1/1.2/0.3. [c] Isolated yield. The products were purified by column chromatography and were identified by the comparison of their melting point, IR, MS, and NMR data with those reported in the literature.[4−17,23,24]

Table 4. Reduction of Sulfoxides to Sulfides in the Presence of Compounds Having Different Functional Groups with 1,3-Dithiane and NBS as Catalyst in $CHCl_3$ at Room Temperature[a]

Entry	Substrate 1 Substrate 2	Product 1 Product 2	Time (min)	Yield (%)
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		98
1	$H_2N\overset{\overset{O}{\|}}{C}NH_2$	$H_2N\overset{\overset{O}{\|}}{C}NH_2$	35	100
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		98
2	$H_2N\overset{\overset{S}{\|}}{C}NH_2$	$H_2N\overset{\overset{S}{\|}}{C}NH_2$	40	100
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		97
3	$PhC\overset{\overset{O}{\|}}{N}H_2$	$PhC\overset{\overset{O}{\|}}{N}H_2$	45	100
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		98
4	$C_2H_5O\overset{\overset{O}{\|}}{C}NH_2$	$C_2H_5O\overset{\overset{O}{\|}}{C}NH_2$	50	100
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		99
5	$PhC\overset{\overset{O}{\|}}{O}C_2H_5$	$PhC\overset{\overset{O}{\|}}{O}C_2H_5$	35	100
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		99
6			40	100
	$PhCH_2\overset{\overset{O}{\|}}{S}CH_2Ph$	$PhCH_2SCH_2Ph$		2
7	PhSH	PhSSPh	2	10

[a] Yields based on NMR and GC (*n*-heptane was used as an internal standard).

This is strong evidence in support of the formation of aldehydes when 1,3-dithianes are used as reducing agents in these reactions.

To show the scope and limitation of this method for the reduction of sulfoxides, the reduction of dibenzyl sulfoxide in the presence of urea, thiourea, benzamide, ethylcarbamate, and carbonyl groups was studied. The results of this study (Table 4) indicate that the reduction of the sulfoxide in the presence of these functional groups performs well with a slight decrease in the rate of the reaction. This decrease in the rate of the reaction in the presence of −NH− containing compounds (Table 4, entries 1−4) could be due to the possibility of bromine exchange between NBS and the −NH− functionality. However, this reduction in the presence of the −SH functionality could not occur, due to the ready coupling of thiol to its corresponding disulfide (Table 4, entry 7).

In summary, we have presented a new and novel method for the reduction of sulfoxides with electrophilic bromine as catalyst in the presence of dithioacetals as the sulfur compound. High yields of the desired products, short reaction times, easy workup, and mild reaction conditions in comparison with the other sulfur-based reduction methods are the strong points of the presented procedure.

Experimental Section

All yields refer to isolated products. The products were purified by column chromatography, and the purity determination of the products was accomplished by GLC on a Shi-

madzu model GC-8A instrument or by TLC on silica gel polygrams SIL G/UV254 plates. Chloroform was dried by refluxing over anhydrous calcium chloride for 48 h, followed by distillation, and stored over 4A molecular sieve. Mass spectra were run on a Shimadzu GC MS-QP 1000EX at 20 or 75 eV. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument. Melting points were determined in open capillary tubes in a Buchi-510 circulating oil melting point apparatus and are uncorrected.

General Procedure for the Reduction of Sulfoxides to the Corresponding Sulfides with 1,3-Dithiane Using a Catalytic Amount of Electrophilic Halogens in Chloroform.

Sulfoxide (1.0 mmol) was added to a stirred solution of the appropriate catalyst (NBS, TABCO, or Br_2; 0.2−0.3 mmol) in dry chloroform (3 mL). Then, 1,3-dithiane (1.1 mmol) was added to the resulting solution and stirring was continued for the appropriate time (Table 3). The reaction was monitored by TLC on a silica gel plate using *n*-hexane as eluent. After completion of the reaction, $CHCl_3$ (25 mL) was added to the reaction mixture and the mixture was washed with a solution of NaOH (5%, 2 × 10 mL), brine solution (10 mL), and H_2O (2 × 10 mL) subsequently. The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated. Further purification was performed using chromatography over a short column of silica gel using *n*-hexane as eluent. The sulfides were characterized by comparison of their physical data (melting point and IR, ^{1}H NMR, ^{13}C NMR, and MS spectra) with those of known samples.[4−17,23,24]

Typical Procedure for the Reduction of Dibenzyl Sulfoxide to Dibenzyl Sulfide with 1,3-Dithiane Using Catalytic Amounts of TABCO.

Dibenzyl sulfoxide (1.0 mmol) was added to a stirred solution of TABCO (0.2 mmol) in dry $CHCl_3$ (3 mL). 1,3-Dithiane (1.1 mmol) was then added to the resulting solution and the mixture was stirred for 35 min. After completion of the reaction, $CHCl_3$ (25 mL) was added to the reaction mixture and washed with a solution of NaOH (5%, 2 × 10 mL), brine solution (10 mL), and H_2O (2 × 10 mL). The organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was purified by column chromatography on silica gel using *n*-hexane as an eluent. Dibenzyl sulfide was isolated in 92% yield (Table 3, entry 7): mp 48 °C (lit.[23] mp 49−50 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) (δ, ppm) 7.27 (s, 10H), 3.59 (s, 4H); ^{13}C NMR ($CDCl_3$, 62 MHz) (δ, ppm) 138.1, 128.9, 128.3, 126.8, 35.5; MS (75 eV), *m*/*z*: 214 (M^+, 28), 123 (23), 92 (21), 91 (100); IR (KBr) (ν, cm^{-1}) 3083, 3059, 3039, 3026, 2953, 2920, 1493, 1453, 1412, 1073, 704, 696.

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(23) Tenca, C.; Dossena, A.; Marchelli, R. *Synthesis* **1981**, 141.

(24) Selected spectral data for some sulfides. (a) Methyl phenyl sulfide (Table 3, entry 1): ^{1}H NMR (δ, ppm) 7.24−7.10 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (δ, ppm) 138.4, 128.7, 126.5, 124.9, 15.6; MS (75 eV) 124 (M^+, 100), 109 (34), 91 (26), 78 (31). (b) Benzyl phenyl sulfide (Table 3, entry 4): ^{1}H NMR (δ, ppm) 7.44−7.00 (m, 10H), 4.09 (s, 2H); ^{13}C NMR (δ, ppm) 137.4, 136.4, 129.7, 128.7, 128.3, 127.0, 126.2, 38.9; MS (75 eV) 200 (M^+, 24), 91 (100); IR (cm^{-1}) 3061, 3047, 3031, 1686, 1571, 1495, 1481, 1454, 1438, 1091, 1070, 1023, 730, 716, 701, 694, 687. (c) Diphenyl sulfide (Table 3, entry 5): ^{1}H NMR (δ, ppm) 7.44−7.08 (m, 10H); ^{13}C NMR (δ, ppm) 135.8, 131.0, 129.1, 126.9; MS (75 eV) 187 (M + 1, 16), 186 (M^+, 100), 185 (66), 184 (25); IR (cm^{-1}) 3073, 3059, 3020, 1580, 1476, 1439, 1081, 1068, 1024, 749, 738, 689. (d) Benzyl methyl sulfide (Table 3, entry 8): ^{1}H NMR (δ, ppm) 7.45−7.04 (m, 5H), 3.64 (s, 2H), 1.96 (s, 3H); ^{13}C NMR (δ, ppm) 138.2, 128.7, 128.3, 126.8, 38.2, 14.7; MS 138 (M^+, 31), 91(100); IR (cm^{-1}) 3084, 3062, 3028, 2972, 2916, 1602, 1494, 1453, 1436, 1426, 1240, 1072, 1029, 979, 771, 726, 699, 677, 666. (e) Dibutyl sulfide (Table 3, entry 10): ^{1}H NMR (δ, ppm) 2.5 (tt, 4H), 1.55 (m, 4H), 1.41 (m, 4H), 0.92 (tt, 6H); ^{13}C NMR (δ, ppm) 31.95, 22.13, 13.74; MS (20 eV) 146 (M^+, 37), 61 (94), 56 (100), 41 (40), 29 (38); IR (cm^{-1}) 2961, 2931, 2874, 2862, 1462, 1467, 1379, 1272, 1222.