Mild and Efficient Deoxygenation of Sulfoxides to Sulfides with Triflic Anhydride/Potassium Iodide Reagent System

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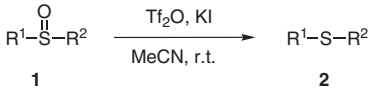
Abstract: It was found that the combination of triflic anhydride/potassium iodide was an effective promoter for the deoxygenation of sulfoxides and gave the corresponding sulfides in excellent yield in acetonitrile at room temperature. It is worth mentioning that this reagent system is chemoselective and tolerates various functional groups, such as alkene, ketone, ester, aldehyde, acid, and oxime.

Key words: deoxygenation, sulfoxide, sulfide, chemoselective, triflic anhydride

The deoxygenation of sulfoxides to the corresponding sulfides is an important reaction that has found considerable utility in biochemical reactions.[1] Although there are a good number of methodologies available for the deoxygenation of sulfoxides to the corresponding sulfides,[2–5] there remain the important problems of reaction conditions, for example, the use of reagents that are difficult to handle, functional group incompatibility, difficult workup procedures, or harsh reaction conditions, such as high temperatures or long reaction times. Therefore, a search for readily available reagents and operationally simple procedures for the deoxygenation of sulfoxides is still a worthwhile goal.

In continuation of our recent works on the deoxygenation of sulfoxides[6] and also the use of triflic anhydride in organic transformations,[7] we describe the successful use of the triflic anhydride/potassium iodide system as a method to deoxygenate sulfoxides **1** to the corresponding sulfides **2** (Scheme 1).

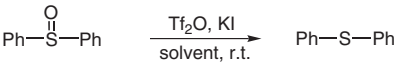
The optimum solvent was studied by using diphenyl sulfoxide (**1a**) as the substrate (Table 1). Among the solvents that were examined, acetonitrile was proved to be satisfactory in terms of rate and yield of the reaction (Table 1, entry 1).



R^1, R^2 = alkyl, aryl

Scheme 1

Table 1 Effects of Solvent on the Deoxygenation of Diphenyl Sulfoxide with Triflic Anhydride/Potassium Iodide



Entry	Solvent	Time (min)	Isolated yield[a] (%)
1	MeCN	5	98
2	*n*-hexane	5	10
3	$CHCl_3$	5	20
4	MeOH	5	80

[a] Ratio sulfoxide/Tf_2O/KI, 1:1:2.5.

Table 2 Effect of Increasing Amounts of Triflic Anhydride and Potassium Iodide on the Deoxygenation of Diphenyl Sulfoxide[a]

Entry	Tf_2O (mmol)	KI (mmol)	Isolated yield (%)
1	0.5	1	60
2	0.7	1.5	70
3	0.8	2	80
4	0.9	2.5	85
5	1	2.5	98

[a] **1a** (1 mmol), MeCN, r.t., 5 min.

The optimum molar ratio of sulfoxide to triflic anhydride to potassium iodide (1:1:2.5) is found to be ideal for the complete conversion of sulfoxide **1a** into sulfide **2a** in acetonitrile at room temperature, while with lesser amounts the reaction remains incomplete (Table 2).

To extend the scope of the reaction and to generalize the procedure, we investigated the deoxygenation of diaryl, dibenzyl, aryl benzyl, dialkyl, and cyclic sulfoxides **1a–x** under the optimized reaction conditions. The results are presented in Table 3.

As shown, all the reactions were complete within a short time and the sulfides **2a–x** were obtained in almost quantitative yields as the sole deoxygenation products.

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Table 3 Deoxygenation of Sulfoxides to the Corresponding Sulfides Using Triflic Anhydride/Potassium Iodide

Entry	R^1	R^2	Time (min)	Product[a]	Yield[b] (%)	Ref. for data
1	Ph	Ph	5	**2a**	98	8a
2	Bn	Bn	3	**2b**	98	8b
3	4-$BrC_6H_4CH_2$	Bn	4	**2c**	94	8c
4	Ph	Bn	3	**2d**	97	8b
5	Ph	4-$MeC_6H_4CH_2$	3	**2e**	97	8b
6	Ph	4-$FC_6H_4CH_2$	3	**2f**	97	8d
7	Ph	4-$BrC_6H_4CH_2$	4	**2g**	96	8d
8	Ph	4-$O_2NC_6H_4CH_2$	3	**2h**	93	8b
9	4-MeC_6H_4	Bn	2	**2i**	96	8b
10	4-MeC_6H_4	4-$BrC_6H_4CH_2$	2	**2j**	96	9a
11	4-MeC_6H_4	4-$MeC_6H_4CH_2$	4	**2k**	96	9b
12	4-MeC_6H_4	4-$O_2NC_6H_4CH_2$	3	**2l**	96	9b
13	4-ClC_6H_4	Bn	3	**2m**	95	8d
14	4-ClC_6H_4	4-$O_2NC_6H_4CH_2$	3	**2n**	95	9a
15	4-BrC_6H_4	Bn	3	**2o**	96	8d
16	4-BrC_6H_4	4-$BrC_6H_4CH_2$	5	**2p**	96	8d
17	4-BrC_6H_4	4-$MeC_6H_4CH_2$	3	**2q**	93	9c
18	naphth-1-yl	Bn	3	**2r**	96	9d
19	Ph	Me	2	**2s**	92	10a
20	Ph	CH_2CO_2Me	5	**2t**	91	10b
21	Ph	$CH_2CH{=}CH_2$	6	**2u**	93	10c
22	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$	5	**2v**	95	10d
23	2-$C_6H_4C(O)$-2-C_6H_4		5	**2w**	90	10e
24	Bu	Bu	5	**2x**	92	8b

[a] The products were characterized by comparison of their spectroscopic and physical data with those reported in the literature.[8–10]
[b] Yields refer to pure isolated products.

The sulfoxides possessing ester, alkene, and ketone functionalities were chemoselectively reduced to the corresponding sulfides in excellent yields without affecting these groups (Table 3 entries 20–23).

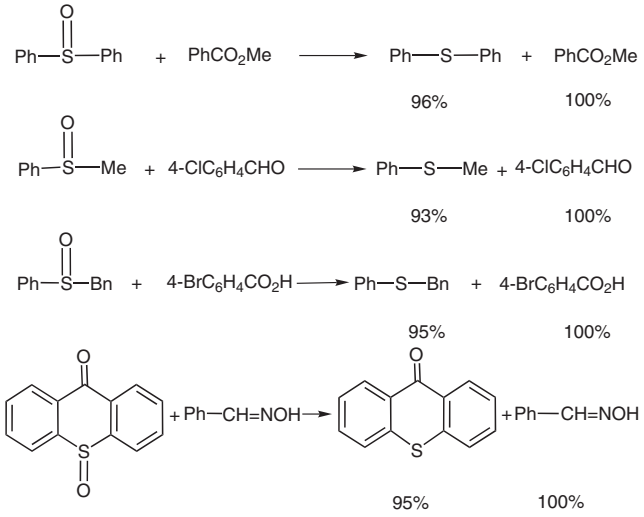
We also have monitored competitive deoxygenation of sulfoxides in the presence of ester, aldehyde, acid, and oxime groups (Scheme 2).

These observations clearly show that the method is applicable for the selective deoxygenation of sulfoxides in the presence of the previously mentioned functional groups and can be considered as a useful practical achievement for this transformation. Finally, sulfones failed to react under the present reaction conditions.

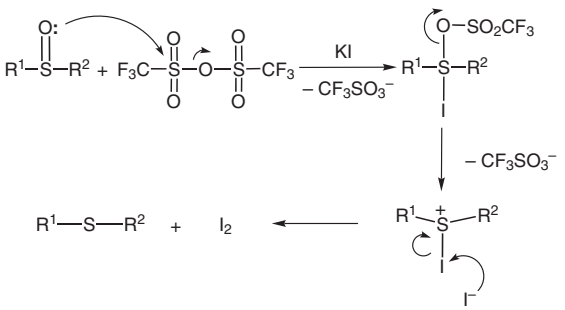
A possible mechanism is shown in Scheme 3. Firstly, coordination of triflic anhydride to the oxygen proceeds to make the attack of iodide anion feasible. The resultant iodinated species is in turn attacked by another iodide anion to give the deoxygenated sulfide.

In order to show the efficiency of this method, the results of the deoxygenation of dibenzyl sulfoxide (**1b**) to dibenzyl sulfide (**2b**) by our method are compared with those reported by other methods. The results show that this method is superior to some previously reported methods in terms of yields, reaction times, and the amount of the reagent used for successful deoxygenation (Table 4).

In summary, we have found that the triflic anhydride/potassium iodide system is an excellent and convenient



Scheme 2 *Reagents and conditions*: ratio substrate/Tf_2O/KI (1:1:1:2.5), MeCN, r.t.



Scheme 3 Proposed mechanism for the deoxygenation of sulfoxides to the corresponding sulfides with triflic anhydride/potassium iodide system

deoxygenation reagent for sulfoxides. The present procedure shows good chemoselectivity, and, under these conditions, the reaction is rapid and equally applicable to dialkyl, aryl alkyl, and diaryl sulfoxides. Thus, the use of the triflic anhydride/potassium iodide system is a good addition to the existing methodologies for the deoxygenation of sulfoxides.

Melting points were determined in a capillary tube and are not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-200 NMR spectrometer using TMS as internal standard.

Sulfides; General Procedure

To a flask containing a stirred mixture of sulfoxide (1 mmol) in MeCN (5 mL), Tf_2O (0.17 mL, 1 mmol) and KI (2.5 mmol, 0.42 g) were added. The mixture was stirred magnetically at r.t. and monitored by TLC. On completion of the reaction, the solvent was evaporated and then sat. aq $NaHCO_3$ (10 mL) was added to destroy the unreacted Tf_2O. The mixture was extracted with EtOAc (4 × 5 mL) and the extract dried (anhyd $MgSO_4$). The filtrate was evaporated and the corresponding sulfide was obtained as the sole product (Table 3). Spectral and physical data for selected compounds follow.

Table 4 Comparison of the Deoxygenation of Dibenzyl Sulfoxide to Dibenzyl Sulfide by the Triflic Anhydride/Potassium Iodide System with the Literature

Reagent	Temp	Time	Yield (%)
Tf_2O, KI, MeCN	r.t.	3 min	98
$NiCl_2/NaBH_4$ (3:9), THF	0 °C	2 h	81[11]
$PhSiH_3$, MoO_2Cl_2, toluene	reflux	20 h	95[12]
2,6-dihydroxypyridine, MeCN	reflux	4 h	98[13]
Ph_3P, $TiCl_4$ THF	r.t.	2 h	96[14]
TiI_4, MeCN	0 °C	10 min	85[15]
$BF_3{\cdot}OEt_2$, NaI, MeCN	r.t.	20 min	98[16]
BBr_3, CH_2Cl_2	–23 to 0 °C	40 min	91[17]

Diphenyl Sulfide (2a)

Pale yellow liquid (Lit.[8a] pale yellow liquid).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.32–7.25 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.0, 131.1, 129.5, 127.0.

Benzyl 4-Chlorophenyl Sulfide (2m)

Pale pink solid; mp 52–53 °C (Lit.[8d] 51–52 °C).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.30–7.25 (m, 9 H), 4.1 (s, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.3, 134.8, 132.4, 131.5, 129.0, 128.7, 128.6, 127.5, 39.3.

Dibutyl Sulfide (2x)

Colorless oil (Lit.[8b] colorless oil).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.60–0.41 (m, 18 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 46.1, 45.8, 29.7, 8.9.

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