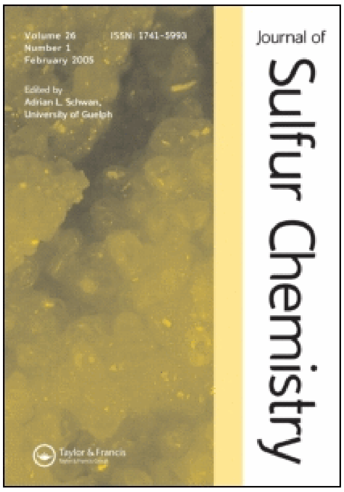

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$ZrCl_4$/NaI and $ZrOCl_2 \cdot 8H_2O$/NaI as effective systems for reductive coupling of sulfonyl chlorides and chemoselective deoxygenation of sulfoxides

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$ZrCl_4/NaI$ and $ZrOCl_2 \cdot 8H_2O/NaI$ as effective systems for reductive coupling of sulfonyl chlorides and chemoselective deoxygenation of sulfoxides

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Zirconium tetrachloride/sodium iodide ($ZrCl_4/NaI$) and $ZrOCl_2 \cdot 8H_2O/NaI$ conduct effective reductive coupling of sulfonyl chlorides to their corresponding disulfides and chemoselective reduction of sulfoxides to their thioethers in high yields.

Keywords: Deoxygenation; Sulfoxide; Reductive coupling; Sulfonyl chloride; Zirconium tetrachloride; Zirconium(IV) oxide chloride octahydrate

1. Introduction

Oxophilic d-block metals have become important in deoxygenation of different organic molecules [1–12]. $ZrCl_4$ and $ZrOCl_2 \cdot 8H_2O$ which are commercially available solid compounds [13] are good candidates to be used for the reductive reactions in the presence of an electron source such as NaI. Due to their low toxicity (LD 50 [$ZrCl_4$, oral rat] = 1688 mgKg) [14], low costs, ease of handling, high activity, the zirconium (IV) compounds can be considered as potential green catalysts or reagents. $ZrCl_4$ has been used for the reduction of varieties of functional groups in the presence of $NaBH_4$ [15–17], *ortho*-Fries rearrangement [18], direct ester condensation [19], arylether rearrangement [20], thioacetalization of carbonyl compounds [21], ring-opening of epoxides [22], Diels Alder reactions [23], *trans*-allylstannylation of acetylenes [24], acetylation reactions [25], catalyzing the Jacobsen reaction [26], synthesis of aminophosphonates [27]. Some of the important reactions mediated by $ZrCl_4$ are spotlighted very recently [28].

Organic disulfides are important from both biological [29], and industrial [30], points of view. They are also valuable precursors for the synthesis of a variety of sulfenyl [31], sulfinyl [32, 33], and the other valuable compounds [34–37].

Preparation of disulfides by the oxidation of thiols is an easy and well known procedure [38]. However, structurally different thiols are not always available and sometimes not easy

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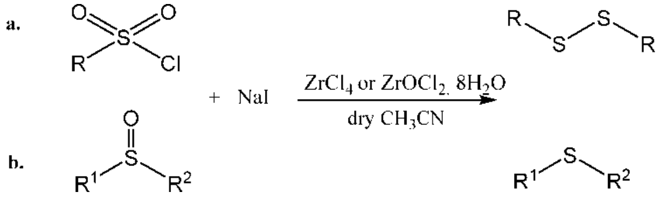
to prepare. In addition, thiols are very odorous compounds and their handling in laboratories need special precaution. Reductive coupling of sulfonyl chlorides is an operationally simple alternative protocol for the preparation of disulfides. Although, a variety of reagents are known for this purpose [9, 11, 39–47], still a safe, simple and high yielding procedure is of demand.

In the course of our research on new applications of $ZrCl_4$ in organic synthesis, we have explored it as an effective catalyst for highly chemoselective transthioacetalization of acetals [48, 49]. Very recently, we have employed $ZrCl_4/NaI$ as an efficient reagent for chemoselective iodination of alcohols [50], and deoxygenation of epoxides [51]. Now, we introduce $ZrCl_4/NaI$ and $ZrOCl_2 \cdot 8H_2O/NaI$ as expedient reagents for rapid reductive coupling of sulfonyl chlorides to the corresponding disulfides under mild reaction conditions (scheme 1a). We have also applied $ZrCl_4/NaI$ and $ZrOCl_2 \cdot 8H_2O/NaI$ for the chemoselective reduction of sulfoxides to their sulfides under mild conditions (scheme 1b). Reduction of sulfoxides which are used as chiral auxiliaries for the synthesis of chiral organic molecules is also an important transformation [52–59].



SCHEME 1

2. Result and discussion

$ZrCl_4$ and $ZrOCl_2 \cdot 8H_2O$ are two commercially available compounds having safe and easy handling. The only reservation about the use of $ZrCl_4$ is its mild hygroscopicity requiring to be kept under dried atmosphere whereas, $ZrOCl_2 \cdot 8H_2O$ is a highly stable compound and its storage does not need special precautions. First, we studied the reductive coupling of phenylsulfonyl chloride as a model compound in the presence of $ZrCl_4/NaI$ system in CH_3CN at reflux. We have found that the optimized molar ratio of the substrate with respect to $ZrCl_4$ and NaI was 1/1/4 which under such conditions the reaction was completed in 3 min. We have also optimized the reaction conditions for $ZrOCl_2 \cdot 8H_2O$ system with respect to phenylsulfonyl chloride as a model compound. We have found that in refluxing CH_3CN the molar ratio of the substrate with respect to $ZrOCl_2 \cdot 8H_2O$ and NaI was 1/2/4 leading to the completion of the reaction within 7 min. Then we applied similar conditions to structurally different sulfonyl chlorides. All the reactions proceeded well and the corresponding disulfides were isolated in excellent yields. The results of our studies are tabulated in table 1. Our results show that replacement of $ZrCl_4$ with $ZrOCl_2 \cdot 8H_2O$ in these reactions demands longer reaction times and requires two molar ratios of $ZrOCl_2 \cdot 8H_2O$ (table 1, entries 2, 4, 6, 8, 10, 12, 14). It is noteworthy that application of the methods for deoxygenation of *para*-toluene sulfonic acid was not successful (table 1, entry 15, 16). By consideration of the minimum molar ratio requirements of $ZrCl_4$ (1 mol) and NaI (4 mol) and of $ZrOCl_2 \cdot 8H_2O$ (2 mol) and NaI (4 mol) for the completion of the reactions, we have qualitatively proposed a mechanism in which these requirements are somehow clarified (scheme 2).

Next we examined deoxygenation of sulfoxides to the related sulfides by $ZrCl_4$/NasI. For this purpose, at first the reaction of methylphenyl sulfoxide with $ZrCl_4/NaI$ in CH_3CN was

Table 1. Reductive coupling of sulfonyl chlorides to their corresponding disulfides in the presence of $ZrCl_4/NaI$ and $ZrOCl_2 \cdot 8H_2O/NaI$.[a]

Entry	Substrate	Mediator	Sub./Mediator/NaI	Time (min)	Conversion(%)	Isolated Yield%	Ref.
1	$CH_3CH_2CH_2SO_2Cl$	$ZrCl_4$	1/1/4	2	100	95	[45]
2	$CH_3CH_2CH_2SO_2Cl$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	6	100	95	[45]
3	$PhSO_2Cl$	$ZrCl_4$	1/1/4	3	100	95	[45]
4	$PhSO_2Cl$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	7	100	95	[45]
5	p-$MePhSO_2Cl$	$ZrCl_4$	1/1/4	5	100	94	[45]
6	p-$MePhSO_2Cl$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	15	95	90	[45]
7	p-$BrPhSO_2Cl$	$ZrCl_4$	1/1/4	3	100	96	[45]
8	p-$BrPhSO_2Cl$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	7	100	95	[45]
9	2-$NaphSO_2Cl$	$ZrCl_4$	1/1/4	7	100	95	[9]
10	2-$NaphSO_2Cl$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	20	100	95	[9]
11	p-O_2N-$PhSO_2Cl$	$ZrCl_4$	1/1/4	15	100	94	[9]
12	p-O_2N-$PhSO_2Cl$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	25	100	94	[9]
13	2-HO,3,5-Cl_2PhSO_2Cl	$ZrCl_4$	1/1/4	6	95	88	–[b]
14	2-HO,3,5-Cl_2PhSO_2Cl	$ZrOCl_2 \cdot 8H_2O$	1/2/4	12	95	87	–[b]
15	p-$MePhSO_3H$	$ZrCl_4$	1/1/4	24 (h)	No reaction	–	–
16	p-$MePhSO_3H$	$ZrOCl_2 \cdot 8H_2O$	1/2/4	24 (h)	No reaction	–	–

[a] The reactions were performed under reflux condition.
[b] Spectral data and elemental analysis are given in the experimental section.

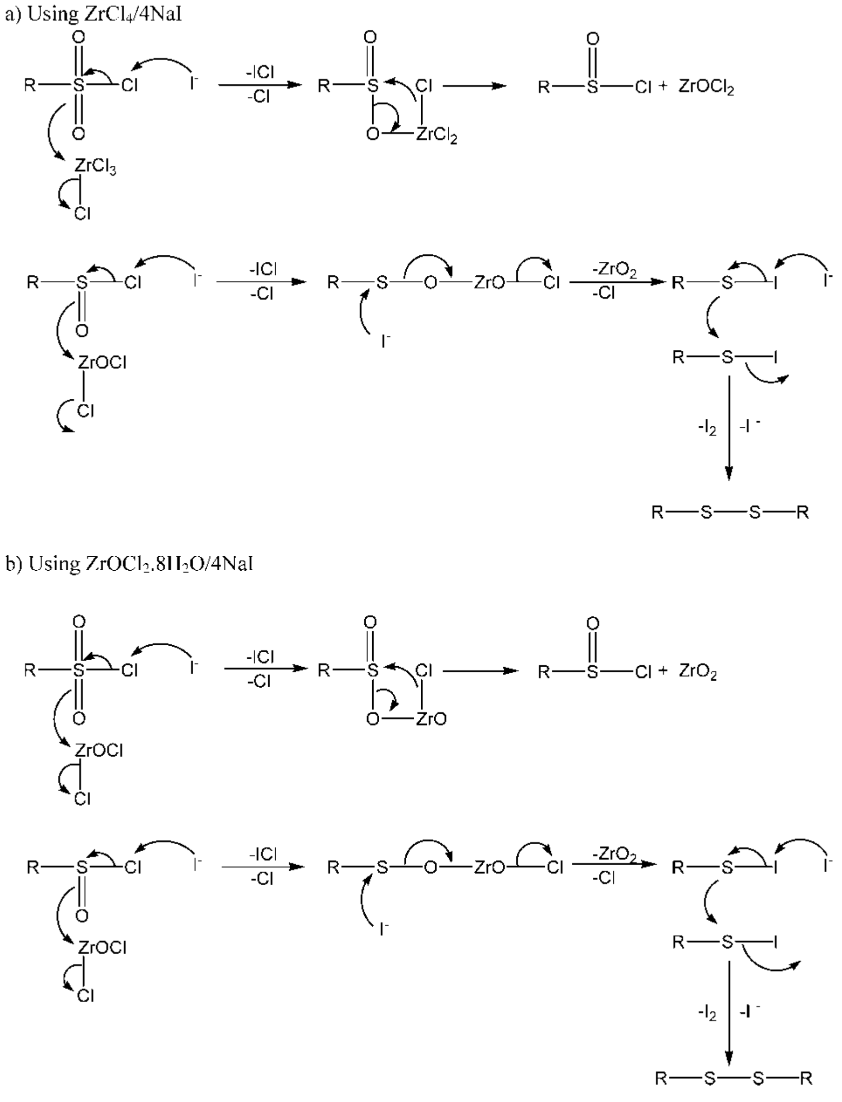
studied. We found that the optimized ratio of substrate/$ZrCl_4$/NaI was 1/0.5/2 to complete the reaction.

Then we applied similar reaction conditions for the reduction of structurally different sulfoxides. The reactions proceeded smoothly and the corresponding sulfides were obtained in good to excellent yields. As we have noticed, the rate of some of the reactions were rather slow (table 2, entries 7–14), therefore we added extra molar ratios of NaI to the reaction mixture in order to boost the rates of the reactions.

Inspection of table 2, displays the high efficiency and also the selectivity of the presented protocol. We have observed that the efficiency of reduction in this system is very dependent on the steric and electronic requirements of the substrates. Molecules with aromatic rings substituted with strong electron withdrawing groups such as $-NO_2$, $-CHO$, $-CN$ affects the rate of the reaction drastically and deoxygenation occurred in much slower rates (table 2, entries 12–14). In accord with this argument, reduction of sterically hindered and electron deficient 2,4-dinitrophenyl-4-methylphenyl sulfoxide did not occur even after 24 h (table 2, entry 15).

The novel feature of this method is its excellent chemoselectivity. Our observation well shows highly selective reduction of sulfoxides group in the presence of $-NO_2$, $-CHO$, $-CN$ functional groups in a molecule. For example, the reduction of sulfoxide gives the corresponding thioether as a sole product (scheme 3, entry 1). Inspection of the previously reported procedures such as WCl_6/NaI [9], and $NaBH_4/I_2$ [60], shows that in addition to the reduction of sulfoxide, the nitro group has been also effectively reduced to a mixture of amino and nitroso compounds. $CrCl_2$/HCl [5], and $SnCl_2$/HCl [2, 61], systems have been also used for the reduction of sulfoxide and nitro groups in different molecules. In order to show the unique selectivity of $ZrCl_4$/NaI system, we employed $CrCl_2$/HCl and $SnCl_2$/HCl for the reduction of 4-nitrophenyl 4-methylphenyl sulfoxide in our laboratory. We have observed that the sulfoxide group remained intact whereas, the nitro group was reduced to amino group in only 50% after 24 h. Therefore, $CrCl_2$/HCl and $SnCl_2$/HCl methods are not suitable for the

Proposed Mechanism:



SCHEME 2

reduction of sulfoxide group in a molecule having a nitro group. We have also shown the selectivity of our method among the structurally different sulfoxides. The effect of steric hindrance upon the selectivity of the method is also shown in scheme 3, entries 2–4.

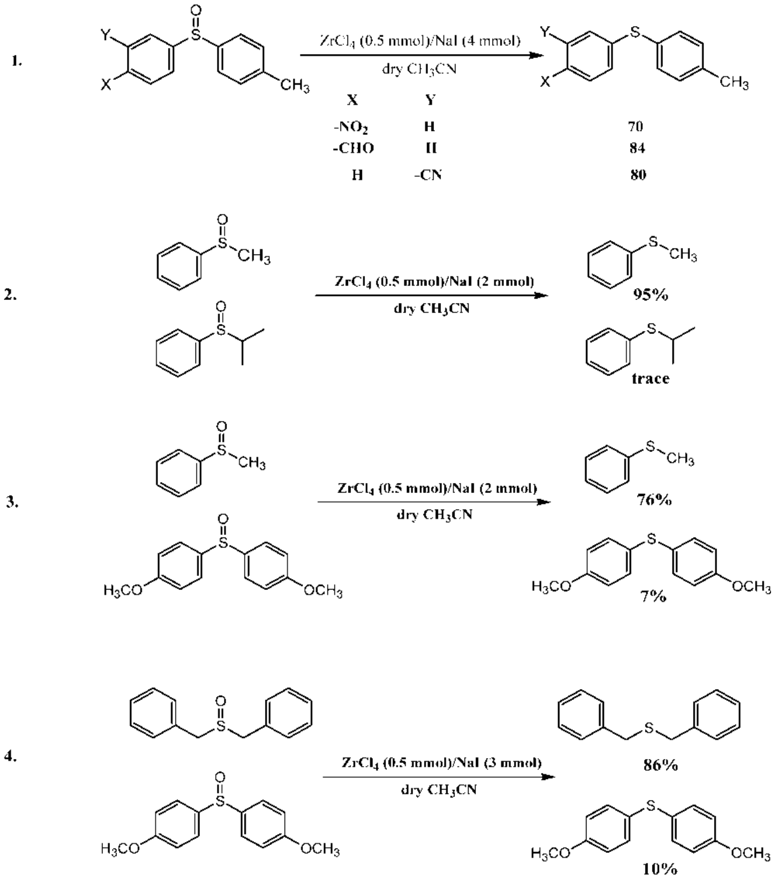
We believe reduction of sulfoxides with $ZrCl_4$ produces ZrO_2 which should be produced by the oxidation of $ZrOCl_2$. However, we studied deoxygenation of sulfoxides in the presence of commercially available $ZrOCl_2 \cdot 8H_2O$. Optimization of the reaction revealed the ratio of subst./$ZrOCl_2$/NaI to be 1/1/2. Some structurally diverse sulfoxides were smoothly reduced to their sulfides in good to high yields. Substrates substituted with nitro group such as 4-nitrophenyl 4-methylphenyl sulfoxide (table 3, entry 6) gave the corresponding sulfide in a low yield. In some sluggish reactions we had to add extra amounts of NaI in order to facile the reactions (table 3, entries 2–6).

Table 2. Deoxygenation of sulfoxides to thioethers by $ZrCl_4$/NaI system in anhydrous CH_3CN.[a]

Entry	R^1	R^2	Sub./$ZrCl_4$/NaI	Temperature (°C)	Time (min)	Conversion (%)	Isolated Yield (%)	Ref.
1	Bu	Bu	1:0.5:2	r.t	<1	100	96	[9]
2	Ph	$CH_2CH{=}CH_2$	1:0.5:2	r.t	<1	100	96	[64, 9]
3	Ph	Me	1:0.5:2	r.t	<1	100	96	[59]
4	Ph	Et	1:0.5:2	r.t	<1	100	95	[59]
5	Ph	Pr	1:0.5:2	r.t	<1	100	96	[59]
6	$PhCH_2$	Pr	1:0.5:2	r.t	<1	100	95	[59]
7	$PhCH_2$	$PhCH_2$	1:0.5:3	45	3	100	95	[59]
8	$PhCH_2$	Ph	1:0.5:4	45	15	100	95	[59]
9	Ph	$CH(CH_3)_2$	1:0.5:4	45	10	100	95	[59]
10	Ph	Ph	1:0.5:4	45	25	100	95	[59]
11	4-MeO-C_6H_4	4-$MeOC_6H_4$	1:0.5:4	45	20	100	94	–[b]
12	4-O_2N-C6H4	4-MeC_6H_4	1:0.5:4	45	60	75	70	–[b]
13	4-OHC-C_6H_4	4-MeC_6H_4	1:0.5:4	45	40	90	84	–[b]
14	3-NC-C_6H_4	4-MeC_6H_4	1:0.5:4	45	60	85	80	–[b]
15	2,4-$(NO_2)_2C_6H_4$	4-MeC_6H_4	1:0.5:4	45	24 h	trace	–	–

[a] Reaction conditions are mentioned in the text.

[b] Spectral data and elemental analysis are given in the experimental part.

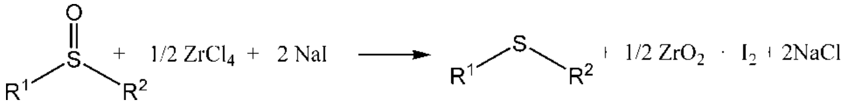


SCHEME 3

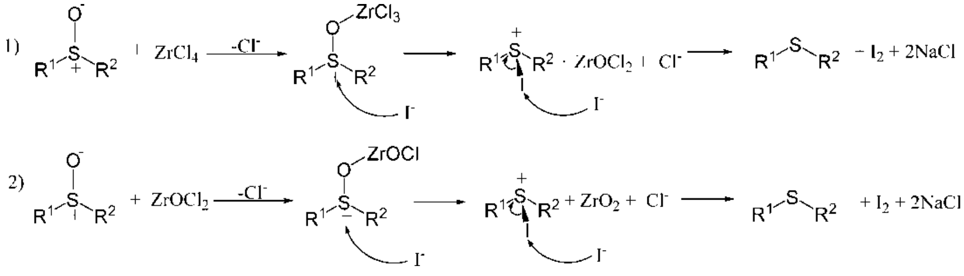
Table 3. Reduction of sulfoxides to thioethers by $ZrOCl_2$. $8H_2O$/NaI system in CH_3CN.

Entry	R^1	R^2	Sub./$ZrOCl_2$/NaI	Temperature (°C)	Time (min)	Conversion (%)	Isolated Yield (%)
1	Ph	Me	1:1:2	r.t	6	100	95
2	$PhCH_2$	$PhCH_2$	1:1:3	45	10	100	95
3	Ph	$CH(CH_3)_2$	1:1:4	45	55	90	84
4	Ph	Ph	1:1:4	45	115	80	74
5	4-$MeOC_6H_4$	4-$MeOC_6H_4$	1:1:4	45	100	90	86
6	4-O_2NC6H4	4-MeC_6H_4	1:1:4	45	120	50	44

In all experiments conducted by $ZrCl_4$ in the presence of NaI for the reduction of sulfoxides, we have observed that half a molar equivalent of $ZrCl_4$ and two molar equivalents of NaI were required to complete the reaction. We have also observed that as the reaction proceeded to completion, one molar equivalent of iodine was generated in the reaction mixture (scheme 4). The amount of the iodine in the mixture was determined by iodometric titration using a standard solution of $Na_2S_2O_3$. We have also found that similar reductions induced by $ZrOCl_2 \cdot 8H_2O$, required one molar equivalent of this mediator in the presence of two molar equivalents of NaI (table 3). On the basis of these findings, we have qualitatively proposed a mechanism in which the plausible role of Zr(IV) compounds and also the generation of iodine in the reaction mixture have been clarified (scheme 5).



SCHEME 4



SCHEME 5

We have also tried reduction of diphenyl sulfone and methylphenyl sulfone by these methods. However, even after 24 h, the starting materials were isolated intact.

In order to show the merits of $ZrCl_4$/NaI and $ZrOCl_2 \cdot 8H_2O$ systems for reductive coupling of sulfonyl chlorides and reduction of sulfoxides, we have compared the results with some of those reported in the literature (tables 4 and 5). Inspection of the results outlined in tables 4 and 5 shows the preference of $ZrCl_4$/NaI and $ZrOCl_2 \cdot 8H_2O$ systems in terms of reaction times and the yields of the products.

Table 4. Comparison of $ZrCl_4/NaI$ and $ZrOCl_2 \cdot 8H_2O/NaI$ systems with the previously reported methods for reductive coupling of sulfonyl chlorides.

	$ZrCl_4$/ NaI	$ZrOCl_2 \cdot$ $8H_2O$/NaI	Me_3SiI[47]	BI_3[45]	AlI_3[46]	$(PipH)_2WS_4$[42]	$BI_3/PhNEt_2$[44]	WCl_6/NaI[9]	WCl_6/Zn[9]
Substrate	Time (min) [Yield%][a]								
$PhSO_2Cl$	3 [97]	7 [95]	960 [100]	960 [88]	60 [94]	120 [78]	150 [92]	960 [97]	20 [89]
p-$MePhSO_2Cl$	5 [94]	15 [90]	960 [89]	960 [98]	60 [90]	120 [69]	180 [74]	1020 [94]	45 [88]
p-$BrPhSO_2Cl$	3 [96]	7 [95]	960 [86]	960 [97]	60 [93]	120 [53]	180 [94]	840 [85]	40 [25]
2-$NaphSO_2Cl$	7 [95]	20 [95]	–	–	–	–	–	960 [98]	80 [95]

[a] Isolated yields.

Table 5. Comparison of $ZrCl_4/NaI$ and $ZrOCl_2 \cdot 8H_2O/NaI$ systems with the previously reported methods for the reduction of sulfoxides.

Sulfoxide		$ZrCl_4$/ Nal	$ZrOCl_2 \cdot 8H_2O$/ Nal	3-MAP[a]/I_2[62]	$TiCl_4$/ In[12]	$SnCl_2/HCl$[2]	NaI/Org. Acid[63]	$NiCl_2$/ $NaBH_4$[8]	$MoO_2Cl_2(dmf)_2$ /$P(OPh)_3$[64]	$TiCl_4$ $LiAlH_4$[4]
R[1]	*R*[2]	Time (min) [Yield%][b]								
Bu	Bu	<1 [96]	–	25 [93]	10 [85]	120 [62]	30 [81]	60 [75]	10 [73]	–
Ph	Me	<1 [96]	6 [95]	20 [96]	10 [93]	120 [92]	360 [86]	90 [69]	20 [92]	30 [89]
Ph	*i*-Pr	10 [95]	55 [84]	240 [90]	–	–	–	–	–	120 [90]
$PhCH_2$	$PhCH_2$	3 [95]	10 [95]	90 [92]	10 [89]	120 [82]	300 [67]	120 [81]	240 [89]	120 [89]
4-O2N Ph	4-MePh	60 [70]	120 [44]	–	–	0[c]	–	–	–	–

[a] 3-Mercaptopropionic acid.

[b] Isolated yields.

[c] Our observation.

3. Conclusion

In this paper we have presented two new systems for the rapid reductive coupling of sulfonyl chlorides to their symmetric disulfides and chemoselective deoxygenation of sulfoxides to the related thioethers in the presence of NaI under mild reaction conditions. Both $ZrCl_4$ and $ZrOCl_2 \cdot 8H_2O$ are commercially available, they are cheap and safe and particularly handling of $ZrOCl_2 \cdot 8H_2O$ is easier than $ZrCl_4$. In contrast, reactions proceeded in the presence of $ZrCl_4$ were faster than $ZrOCl_2 \cdot 8H_2O$. Work-up procedures were also simple and not time-consuming.

4. Experimental

$ZrCl_4$ and $ZrOCl_2 \cdot 8H_2O$ and sulfonyl chlorides were purchased from Merck or Fluka Chemical Companies. Sulfoxides (table 2, entries 1–10, 12–15) were synthesized by oxidation of the corresponding sulfides with N_2O_4/Charcoal [65], sulfoxide (table 2, entry 11) was synthesized from the direct reaction of anisole with $SOCl_2$/TfOH [66]. Sulfides (table 2, entries 12–15) were also prepared according to the reported procedure [67]. Purity determinations of the products were accomplished by GLC on a Shimadzu model GC-14 A instrument or by TLC on silica-gel polygram SIL G/UV 254 plates. FT-IR spectra were recorded on a Shimadzu DR-8001 spectrometer. NMR spectra were recorded on a Brucker Avance DPX 250 MHz instrument. Mass spectra were recorded on a Shimadzu GC-MS-QP 1000PX.

4.1 *Typical procedure for reductive coupling of sulfonyl chlorides by $ZrCl_4$/NaI*

To a solution of phenylsulfonylchloride (0.177 g, 1 mmol), and NaI (0.6 g, 4 mmol), in dry CH_3CN (2 ml), was added $ZrCl_4$ (0.233 g, 1 mmol) in several portions. The mixture was stirred under reflux condition and the progress of the reaction was monitored by TLC. After the appropriate reaction time (table 1, 3 min), the reaction was quenched with an aqueous solution of NaOH (10%, 5 ml) and then extracted with Et_2O (2 × 10 ml). The combined ethereal extracts were washed successively with saturated solution of $Na_2S_2O_3$ (10 ml), and H_2O (10 ml) respectively. The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the almost pure product in 95% yield, 0.207 g (table 1, entry 3).

4.2 *Typical procedure for reductive coupling of sulfonyl chlorides by $ZrOCl_2 \cdot 8H_2O$/NaI*

To a solution of phenylsulfonyl chloride (0.177 g, 1 mmol), and NaI (0.6 g, 4 mmol), in CH_3CN (2 ml), was added $ZrOCl_2$ (0.644 g, 2 mmol) in several portions. The mixture was stirred under reflux condition and the progress of the reaction was monitored by TLC. After the appropriate reaction time (table 1, 7 min), the reaction was quenched with an aqueous solution of NaOH (10%, 5 mL) and then extracted with Et_2O (2 × 10 mL). The combined ethereal extracts were washed successively with saturated solution of $Na_2S_2O_3$ (10 ml), and H_2O (10 ml) respectively. The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the almost pure product in 95% yield, 0.207 g (table 1, entry 4).

4.3 *Typical procedure for deoxygenation of sulfoxides to thioethers by $ZrCl_4/NaI$*

In a typical procedure, to a solution of dibenzyl sulfoxide (0.230 g, 1 mmol) and NaI (0.45 g, 3 mmol) in dry CH_3CN (2 ml) was added $ZrCl_4$ (0.116 g, 0.5 mmol) in several portions. The mixture was stirred at 45 °C and the progress of the reaction was monitored by TLC. After the appropriate reaction time (table 2, 3 min), the reaction was quenched with an aqueous solution of NaOH (10%, 5 mL) and then extracted with Et_2O (2 × 10 ml). The combined ethereal extracts were washed successively with saturated solution of $Na_2S_2O_3$ (10 ml), and H_2O (10 ml) respectively. The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the almost pure product in 95% yield, 0.203 g (table 2, entry 7).

4.4 *Typical procedure for deoxygenation of sulfoxides to thioethers by $ZrOCl_2 \cdot 8H_2O/NaI$*

In a typical procedure, to a solution of dibenzyl sulfoxide (0.230 g, 1 mmol) and NaI (0.45 g, 3 mmol) in CH_3CN (2 ml) was added $ZrOCl_2$ (0.322 g, 1 mmol) in several portions. The mixture was stirred at 45 °C and the progress of the reaction was monitored by TLC. After the appropriate reaction time (table 3, 10 min), the reaction was quenched with an aqueous solution of NaOH (10%, 5 ml) and then extracted with Et_2O (2 × 10 ml). The combined ethereal extracts were washed successively with saturated solution of $Na_2S_2O_3$ (10 ml), and H_2O (10 ml) respectively. The organic layer was separated and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the almost pure product in 95% yield, 0.203 g (table 3, entry 2).

4.5 *Selected spectral data*

4.5.1 Entry 13, table 1: Bis(2-hydroxy-3,5-dichlorophenyl) disulfide. Yellow solid, mp = 105–108 °C, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 6.05 (2H, OH), 7.12 (s, 2H, Ar), 7.25 (s, 2H, Ar), ppm; ^{13}C NMR($CDCl_3$, TMS, 62.9 MHz): 122.7, 122.89, 127.67, 128.3, 129.26, 156.67 ppm; IR (KBr): ν 3410, 1550, 1440, 1390, 1310, 1220 cm^{-1}; MS (70 ev), m/e: 388 [M^+]. Anal. Calcd for ($C_{12}H_6Cl_4O_2S_2$): C, 37.14; H, 1.56. Found: C, 37.18; H, 1.59.

4.5.2 Entry 11, table 2: Di(p-anisol) sulfide. Cream solid, mp = 69–71 °C, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 3.71 (s, 6H, $2OCH_3$), 6.54–7.12 (m, 8H, Ar), ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 55.86, 115.09, 127.26, 137.42, 162.17, ppm; IR (KBr): ν 2810, 1255, 1180, 1105 cm^{-1}; MS (70 ev), m/e: 246 [M^+]. Anal. Calcd for ($C_{14}H_{14}O_2S$): C, 68.26; H, 5.73. Found: C, 68.34; H, 5.78.

4.5.3 Entry 12, table 2: 4-Nitrophenyl p-tolyl sulfide. Yellow solid, mp = 79–81 °C, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 2.38 (s, 3H, $1CH_3$), 7.26–8.42 (m, 8H, Ar) ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 20.3, 124.24, 128.9, 129.97, 130.89, 132.02, 136.89, 138.1, 147.2 ppm; IR (KBr): ν 1590, 1531, 1361, 1344, 1311 cm^{-1}; MS (70 ev), m/e: 245 [M^+]. Anal. Calcd for ($C_{13}H_{11}NO_2S$): C, 63.65; H, 4.52. Found: C, 63.68; H, 4.56.

4.5.4 Entry 13, table 2: 4-Formylphenyl p-tolyl sulfide. Yellow solid, mp = 56–57 °C, ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δ 2.33 (s, 3H, $1CH_3$), 7.03–7.94 (m, 8H, Ar), 9.81 (s, 1H, 1CHO), ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 20.29, 122.95, 125.09, 125.52, 126.06, 129.63, 129.84, 133.83, 134.06, 190.18 ppm; IR (KBr): ν 1662.5 (−CHO) cm^{-1}; MS (70 ev), m/e: 228[M^+]. Anal. Calcd for ($C_{14}H_{12}OS$): C, 73.65; H, 5.30. Found: C, 73.68; H, 5.42.

4.5.5 Entry 14, table 2: 3-Cyanophenyl p-tolyl sulfide. Cream solid, mp = 73–75 °C, ^1H NMR ($CDCl_3$, TMS, 250 MHz): δ 2.35 (s, 3H, CH_3), 6.87–7.53 (m, 8H, Ar), ppm; ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): 20.34, 114.3, 117.51, 129.2, 129.83, 130.7, 131.02, 132.67, 134.7, 135.45, 137.02 ppm; IR (KBr): ν 2250 (CN) cm^{-1}; MS (70ev), m/e: 225[M^+]. Anal. Calcd for ($C_{14}H_{11}NS$): C, 74.63; H, 4.92. Found: C, 74.67; H, 5.00.

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