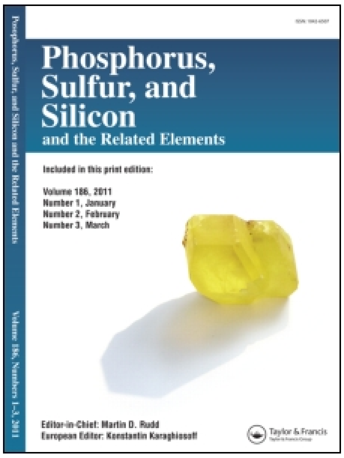

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DEOXYGENATION OF SULFOXIDES TO THIOETHERS BY MOLYBDENUM PENTACHLORIDE ($MOCL_5$) AND REDUCTIVE COUPLING OF SULFONYL CHLORIDES TO DISULFIDES

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Molybdenum pentachloride ($MoCl_5$) in the presence of NaI in dry acetonitrile or zinc powder in anhydrous THF converts sulfoxides to their thioethers in high yields. Sulfonyl chlorides can be readily reduced to their corresponding disulfides with $MoCl_5$/NaI/MeCN at room temperature or with $MoCl_5$/Zn/MeCN under reflux conditions in high yields.

Keywords: Deoxygenation; Thioethers; Reductive coupling; Sulfoxides; Sulfonyl chlorides; Disulfides

INTRODUCTION

Deoxygenation of sulfoxides to thioethers has produced an abundant literature. This reaction has gained its importance with the use of sulfoxides as intermediates in asymmetrical synthesis because the chiral sulfinyl group, after stereoselective induction, can be easily removed.[1,2] Many reagents are capable of effecting deoxygenations of various organic substrates, but only a few methods are practically useful for the rapid and mild reduction[3]. Low-valent oxophilic d-block metals have become important in deoxygenation of different types of organic substrates.[4] The successful utilization of the lower valent complexes of Ti, Mo and W in effecting the

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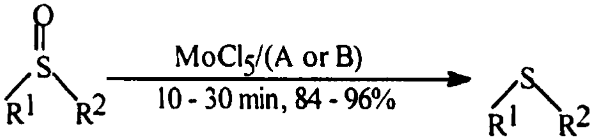
deoxygenation of certain organic molecules is the result of the usually high thermodynamic stability of Ti-, Mo-, and W- oxo bonds.[5] The examples are $TiCl_4/LiAlH_4$,[6] $TiCl_4/Zn$,[7] $TiCl_4/NaI$,[8] $MoOCl_3/Zn$[9] $TiCl_4/Sm$,[10] Cp_2TiCl_2/Sm,[11] WCl_6/NaI and WCl_6/Zn.[12] Moreover, from biological[13] and industrial[14] points of view, an important problem in organosulfur chemistry is the conversion of sulfonic and sulfinic acid derivatives to compounds with lower oxidation states. Among the low-valent oxophilic d-block metals $TiCl_4/Sm$ system[15] has been used for coupling of different kinds of sulfonic and sulfinic acid derivatives. Recently we have reported that WCl_6/NaI and WCl_6/Zn[12] are also efficient reagents for the coupling of sulfonic and sulfinic acid derivatives. Here we wish to report the use of molybdenum as $MoCl_5$ in the presence of NaI or Zn powder in CH_3CN or THF for the deoxygenation of sulfoxides and reductive coupling of sulfonyl chlorides (Scheme 1 and 2).



A =NaI 5 equiv., CH_3CN, r.t.

B =Zn 3 equiv., THF, r.t.

SCHEME 1

$$RSO_2Cl \xrightarrow[85\text{-}95\%]{MoCl_5/(A\ or\ B)} RSSR$$

R =aryl or alkyl

A =NaI 10 equiv., CH_3CN

B =Zn 3-5 equiv., CH_3CN

SCHEME 2

RESULTS AND DISCUSSION

Inspection of the data summarized in Table I reveals that dialkyl sulfoxides, alkyl aryl sulfoxides, and diaryl sulfoxides are reduced to their corresponding sulfides in yields exceeding 84%. This shows that the methods reported here are well applicable to the reduction of a variety of structurally different sulfoxides to their thioethers. Sulfonyl chlorides, a sodium sulfinate and thiosulfonate esters are reduced to their corresponding disulfides by $MoCl_5$/NaI and $MoCl_5$/Zn in acetonitrile at room temperature or under reflux conditions respectively. Applying these methods for deoxygenation of sulfonic acid, sulfonate esters, and sulfonic acid salts was not successful (Table II). Reactions conducted in THF sometimes are accompanied with the formation of a low molecular weight polymeric material that makes the reaction mixture rather viscous.

TABLE I Reduction of Sulfoxides to Thioethers

Entry	*Substrate*	*AorB/Time (min)*	*Subs./$MoCl_5$/ Reducing agent*	*m.p. or b.p. °C [lit.]/(torr)*	*Yield (%)*
1	PhSOPh	A(30)	1:0.7:5	95[96–100]/(0.1)[29a]	95
2	PhSOPh	B(15)	1:1:3	96[96–100]/(0.1)	95
3	PhSO(i-C_3H_7)	A(15)	1:0.7:5	87[89]/(14)[29b]	84
4	PhSO(i-C_3H_7)	B(10)	1:1:3	87[89]/14	85
5	$PhSOCH_2CHCH_2$	A(10)	1:0.7:5	220[223–225][29a]	85
6	$PhSOCH_2CHCH_2$	B(15)	1:1:3	220[223–225]	85
7	PhSO(n-C_4H_9)	A(12)	1:0.7:5	117[116–117]/14[29b]	92
8	PhSO(n-C_4H_9)	B(10)	1:1:3	116[116–117]/14	92
9	$PhSOCH_3$	A(10)	1:0.7:5	83[84–85]/15[29c]	92
10	$PhSOCH_3$	B(10)	1:1:3	83[84–85]/15	95
11	$PhCH_2SOCH_3$	A(10)	1:0.7:5	97[97–98]/12[29b]	94
12	$PhCH_2SOCH_3$	B(10)	1:1:3	96[97–98]/12	90
13	$PhCH_2SOCH_2Ph$	A(10)	1:0.7:5	46[44–47][29a]	95
14	$PhCH_2SOCH_2Ph$	B(10)	1:1:3	46[44–47]	90
15	$PhSOCH_2Ph$	A(20)	1:0.7:5	42[42–44][29a]	96
16	$PhSOCH_2Ph$	B(10)	1:1:3	43[42–44]	90
17	(n-C_4H_9)$_2$SO	A(10)	1:0.7:5	181[185–185.5][29d]	85
18	(n-C_4H_9)$_2$SO	B(20)	1:1:3	181[185–185.5]	89
19	DMSO	A(10)	1:0.7:5	34[37.3]/760[29d]	>98[a]
20	DMSO	B(15)	1:1:3	34[37.3]/760	>98[a]

A: $MoCl_5$/NaI/MeCN at room temperature
B: $MoCl_5$/Zn/THF at room temperature

a. G.C yield

TABLE II Reductive Coupling of Sulfonyl Chlorides to their Corresponding Disulfide

Entry	*Substrate*	*Subs./$MoCl_5$/ Reducing agent*	*AorB/Time [hr] or (min)*	*m.p. or b.p. (°C) [lit.]*	*Yield (%)*
1	$PhSO_2Cl$	1:1.2:10	A[12]	58[58–60][29a]	90
2	$PhSO_2Cl$	1:0.6:3	B(10)	57[58–60]	93
3	$p\text{-}CH_3\text{-}C_6H_4SO_2Cl$	1:1.2:10	A[15]	44[43–45][29e]	85
4	$p\text{-}CH_3\text{-}C_6H_4SO_2Cl$	1:0.8:3	B(20)	45[43–45]	92
5	$p\text{-}BrC_6H_4SO_2Cl$	1:1.2:10	A[11]	92[93.5][29e]	89
6	$p\text{-}BrC_6H_4SO_2Cl$	1:0.8:3	B(25)	92[93.5]	90
7	2-NaphthylSO_2Cl	1:1.2:10	A[10]	138[139–140][29d]	95
8	2-NaphthylSO_2Cl	1:0.8:3	B(30)	139[139–140]	95
9	CH3SO_2Cl	1:1.2:10	A[12]	106[108–110][29a]	87
10	CH3SO_2Cl	1:0.8:3	B(90)	107[108–110]	81
11	$PhSO_2Na$	1:1.2:10	A[10]	59[58–60]	92
12	$PhSO_2Na$	1:0.5:3	B(15)	59[58–60]	94
13	$PhSO_2SPh$	1:1.2:10	A[5]	57[58–60]	90
14	$PhSO_2SPh$	1:0.5:3	B(6)	58[58–60]	95
15	$p\text{-}CH_3\text{-}C_6H_4SO_3H$	1:1.2:10	A[24]	–	No reaction
16	$p\text{-}CH_3\text{-}C_6H_4SO_3H$	1:1.2:5	B(180)	–	No reaction
17	$p\text{-}CH_3\text{-}C_6H_4SO_3Na$	1:1.2:10	A[24]	–	No reaction
18	$p\text{-}CH_3\text{-}C_6H_4SO_3Na$	1:1.2:5	B(180)	–	No reaction
19	$p\text{-}CH_3\text{-}C_6H_4SO_3C_2H_5$	1:1.2:10	A[24]	–	No reaction
20	$p\text{-}CH_3\text{-}C_6H_4SO_3C_2H_5$	1:1.2:5	B(180)	–	No reaction

A: $MoCl_5$/NaI/MeCN at room temperature
B: $MoCl_5$/Zn/MeCN at reflux condition

Along this study we have also studied reductive coupling of 2-naphthylsulfonyl chloride with some electropositive metals such as Mg, Fe, Cu, Ni. Our results show that the reaction proceeded smoothly but the desired coupling product was produced in only 27–56% yields respectively. Aluminum has also been used for this purpose with failure results.

In some methods dialkyl sulfoxides remain unreacted[16] but by the methods described here, they are converted to their sulfides rapidly. The utility of $MoCl_5$ as a reducing agent is also demonstrated by the high yields of dibenzyl sulfide obtained after the reduction of the corresponding sulfoxides. Usually the sulfoxides containing a benzyl group are difficult to reduce by other reagents.[17] In order to show the utility of the presented methods with those reported in the literature we have compared the results and tabulated them in Table III and IV.

TABLE III Comparison of Different Deoxygenation Reactions of Sulfoxides to Thioethers in Literature with $MoCl_5$/NaI and $MoCl_5$/Zn Methods

Substrate	*$MoCl_5$/NaI* h(yield%)	*$MoCl_5$/Zn* h(yield%)	*NaI/Org.acid*[18] h(yield%)	*$BrSi(CH_3)_3$*[19] h(yield%)	*K_3MoCl_6*[20] h(yield%)	*$CrCl_2$/MeOH*[21] h(yield%)	*$SnCl_2$/HCl*[22] h(yield%)	*SiO_2-Cl*[23] h(yield%)	*$Fe(CO)_5$*[24] h(yield%)
PhSOPh	0.5(95)	0.25(95)	4(76)	48(mix. of products)	2(79)	-(20)	20(93)	0.5(81)	8(91)
$PhSOCH_3$	0.17(90)	0.17(90)	6(86)	–	2(90)	–	2(92)	–	–
$PhSOCH_2Ph$	0.33(96)	0.17(90)	–	–	–	–	–	–	–
$PhCH_2SOCH_2Ph$	0.17(95)	0.17(90)	5(67)	48(mix. of products)	–	-(24)	2(82)	0.17(90)	3(48)
$PhSO(CH_2)_3CH_3$	0.2(92)	0.17(92)	–	–	2(76)	–	–	–	–
$PhSOCH(CH_3)_2$	0.25(84)	0.17(85)	–	–	2(72)	–	–	–	–
$(n-C_4H_9)_2SO$	0.17(85)	0.33(89)	0.5(81)	0.5(81)	–	–	2(62)	0.17(75)	3(96)

TABLE IV Comparison of Reductive Coupling Reactions of Sulfonyl Chlorides in Literature with $MoCl_5$/NaI and $MoCl_5$/Zn Methods

Substrate	*$MoCl_5$/NaI* h(yield%)	*$MoCl_5$/Zn* h(yield%)	*WCl6/NaI*[12] h(yield%)	*WCl6/Zn*[12] h(yield%)	*$NaBH_3CN$*[25] h(yield%)	*$(PipH)_2WS_4$*[26] h(yield%)	*$TiCl_4$/Sm*[27] h(yield%)	*Sm/$NiCl_2$/KI*[28] h(yield%)
$PhSO_2Cl$	12(90)	0.17(93)	16(97)	0.33(89)	15(78)	2(78)	2(65)	3(70)
p-$MeC_6H_4SO_2Cl$	15(89)	0.33(92)	17(94)	0.75(88)	22(68)	2(69)	2(62)	3(62)
p-$BrC_6H_4SO_2Cl$	11(89)	0.42(90)	14(85)	0.66(89)	15(84)	2(53)	2(77)	3(68)
2-NaphthylSO_2Cl	10(95)	0.5(95)	16(98)	1.33(95)	6(82)	–	–	–
$PhSO_2Na$	10(92)	0.25(94)	12(95)	0.5(92)	–	–	2(83)	–

CONCLUSION

The handling of $MoCl_5$ does not need special precaution and the work-up of the reaction mixtures is not a time-consuming process. Availability of the reagent, high yields of the products, and efficiency of the reactions make this simple procedure an attractive and a practical alternative to the existing methods. The results show that reductive couplings of sulfonyl chlorides with $MoCl_5$/NaI and $MoCl_5$/Zn are less time-consuming than with WCl_6/NaI and WCl_6/Zn. Instead, for the reduction of sulfoxides to thioethers more equivalents of $MoCl_5$ and the reducing agents are required in comparison with WCl_6.

EXPERIMENTAL

General

All yields refer to isolated pure products unless otherwise stated. Most of the products were purified by column chromatography or recrystallization and were identified by comparison of their mp, bp, IR, MS, NMR, with those reported for the authentic samples. Chemicals were either prepared in our laboratories or were purchased from Fluka, Merck and Aldrich Chemical Companies. IR and UV spectra were recorded on Perkin Elmer 781 and Pye Unicam 8725 spectrometers. NMR spectra were recorded on a Bruker DPX 250. Mass spectra were recorded on Shimadzu GCMS-QP 1000EX. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on Shimadzu GC-14A instrument. All the solvents were completely dried and redistilled.

Deoxygenation of Sulfoxides to Thioethers with $MoCl_5$/NaI as a Typical Procedure

To a solution of benzyl phenyl sulfoxide (2 mmol) and NaI (10 mmol) in anhydrous MeCN (20 ml), was added $MoCl_5$ (1.4 mmol). The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After appropriate reaction time (20 min) the reaction was quenched with aq. NaOH (10%, 30 ml) and extracted with Et_2O

(2 × 50 ml). The combined ethereal extracts were washed successively with saturated $NaHSO_3$ (20 ml), brine (20 ml), and H_2O (25 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and an almost pure product was obtained. Further purification was achieved by column chromatography on silica gel using n-hexane as a solvent to give benzyl phenyl sulfide (96%, Table I).

Reductive Coupling of Sulfonyl Chlorides with $MoCl_5$/NaI as aTypical Procedure

To a suspension of benzenesulfonyl chloride (1 mmol), and NaI (10 mmol) in anhydrous MeCN, was added $MoCl_5$ (1.2 mmol). The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After the completion of the reaction (12 h) it was quenched with aq. NaOH (10%, 30 ml), and extracted with Et_2O (2 × 50 ml). The combined ethereal extracts were washed successively with saturated $NaHSO_3$(20 ml), brine (20 ml), and H_2O (25 ml). The organic layer was separated and dried over $MgSO_4$. The solvent was removed under reduced pressure and an almost pure product was gained. Further purification was achieved by column chromatography on silica gel using n-hexane as a solvent to give pure diphenyl disulfide (90%, Table II).

Doxygenation of Sulfoxides to Thioethers with $MoCl_5$/Zn as a Typical Procedure

To a solution of phenyl allyl sulfoxide (2 mmol) and Zn (3 mmol) in anhydrous THF (10 ml) was added $MoCl_5$ (2 mmol). The mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction (15 min), silica gel (1 g) was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was added on a silica gel pad (3 cm thick). and was eluded with n-hexane (200 ml). Evaporation of the solvent afforded pure phenyl allyl sulfide (85%, Table I).

Reductive Coupling of Sulfonyl Chlorides with $MoCl_5$/Zn as a Typical Procedure

In a round-bottomed flask (25 ml) equipped with a condenser and a magnetic stirrer, $MoCl_5$ (0.8 mmol) was added to a solution of 2-naphthalenesulfonyl chloride (1 mmol) and Zn powder (3 mmol) in anhydrous

MeCN (10 ml) and the resulting mixture was stirred under reflux conditions. The progress of the reaction was followed by TLC. After completion of the reaction (30 min), silica gel (1 g) was added to the mixture and the solvent was evaporated under reduced pressure. The resulting powder was added on a silica gel pad (3 cm thick) and was eluded with n-hexane (200 ml). Evaporation of the solvent afforded pure 2,2-naphthyl disulfide in 95% yield (Table II).

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