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An Efficient Deoxygenation of 1-Alkenyl or Alkyl Phenyl Sulfoxides to the Corresponding Sulfides Mediated by Magnesium in Alcohol

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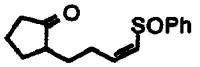
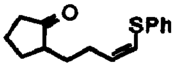
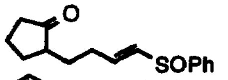
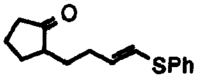
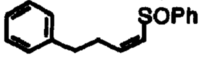
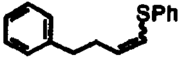
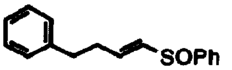
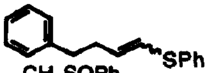
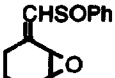
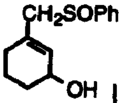
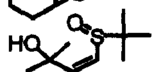
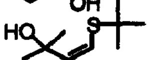
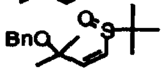
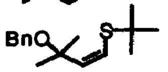
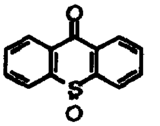
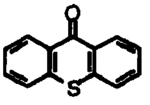
Summary: *An extremely convenient deoxygenation of 1-alkenyl, alkyl, and aryl phenyl sulfoxides with magnesium powder in absolute methanol (or ethanol) afforded the corresponding sulfides in excellent yields.*

Although numerous methods have been reported for the reduction of sulfoxides to the corresponding sulfides using various types of reagents[1] only few of these methods are practically useful for the rapid and mild reduction.[2] Various electron transferring agents such as low valent metal ions,[3] zinc in acetic acid,[4] and Grignard reagent[5] in particular have been utilized for the selective deoxygenation.

Here we report the results obtained from the reduction of various sulfoxides to the corresponding sulfides with magnesium powder in absolute methanol (or ethanol) in the presence of a catalytic amount of mercuric chloride (Table I). *E* and *Z* isomers of 1-alkenyl phenyl sulfoxides (entry 1-4) were subjected to the standard condition (Method A)[6] to give the corresponding sulfides in quantitative yields. Surprisingly, the deoxygenation reaction of keto sulfoxide (entry 1-2) proceeds without isomerization of the double bond, whereas entry 3 and 4 underwent complete isomerization to give the identical product mixture of 1 : 1 *E* and *Z* sulfides from both of the substrates. When entry 5 was subjected to the same reaction condition (Method A), hydroxy sulfoxide was obtained as a major product in 83 % yield instead of the simple deoxygenated adduct. When 1-alkenyl alkyl sulfoxides (entry 6-7) were subjected to the same reaction condition, the starting material was recovered. Even in the elevated reaction temperature (Method D) only a small amount of the corresponding sulfides was obtained with the unreacted starting materials. Sterically compressed cis-configuration of the substrates was retained in the product to provide *cis*-sulfides. In contrast, the reduction of alkyl phenyl sulfoxides (entry 8-10) was so slow at low temperature that excess amount of magnesium (6 equiv) and prolonged reaction time (5 h) were required to complete the reaction (Method C). However, the yields of the corresponding sulfides are nearly quantitative. Less reactive ethanol can also be used to facilitate the reduction of alkyl phenyl sulfoxides (entry 8-9) to the corresponding sulfides (Method E). Under this condition a small amount of ethyl (phenylsulfinyl)acetate by the transesterification was obtained as by-product from the reduction of benzyl (phenylsufinyl)acetate (entry 10) which did not take place at low temperature (Method C). In the cases of diaryl sulfoxides (entry 12-13), the corresponding sulfides were obtained in quantitative yields under the mild condition (Method B). On the other hand dialkyl sulfoxide (entry 14) was inert even after the complete consumption of magnesium. In general, alkyl sulfoxide compared to phenyl sulfoxide seems to be resistant to deoxygenation. In the case of the substrate containing protons acidic enough to react with magnesium metal, enolate formation took place first before deoxygenation. Thus in contrast to α-phenylsulfinyl ester (entry 10), the acidic proton of α-phenylsulfinyl ketone (entry 11) reacted with magnesium metal to form the corresponding enolate which was inert for further deoxygenation and was subsequently recovered after quenching with aqueous 0.5 N HCl solution.

Table I. Reduction of Sulfoxides to the Corresponding Sulfides with Magnesium Metal in Absolute Alcohol.

Entry	Sulfoxides	Products	Method[a]	Isolated Yield (%)
1			A	98
2			A	97
3			A	99 (1 : 1)[b]
4			A	99 (1 : 1)[b]
5			A	83
6			D	21
7			D	16
8	PhSOCH$_3$	PhSCH$_3$	C or E	98
9	PhSOCH$_2$Ph	PhSCH$_2$Ph	C	99
10	PhSOCH$_2$CO$_2$Bn	PhSCH$_2$CO$_2$Bn	C	99
11	PhSOCH$_2$COPh		C	no reaction
12	PhSOPh	PhSPh	B	99
13			B	98
14	t-BuSOC$_8$H$_{17}$-n		D or E	no reaction

[a]See Ref. 6. [b]Ratio in parentheses is Z/E as determined by ^{1}H NMR.

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6. (a) Method A; 3 equiv Mg/cat.HgCl$_2$, MeOH (8 mL), -43 °C, 3 h. (b) Method B; 3 equiv Mg/cat.HgCl$_2$, MeOH/THF (3/1, 8 mL), -43 °C, 3 h. (c) Method C; 6 equiv Mg/cat.HgCl$_2$, MeOH (12 mL), -43 °C, 5 h. (d) Method D; 6 equiv Mg/cat.HgCl$_2$, MeOH (12 mL), rt, 4 h. (e) Method E; 4 equiv Mg/cat.HgCl$_2$, EtOH (12 mL), rt, 3 h.

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