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A NEW FACILE OXIDATION OF SULFIDES TO SULFOXIDES*

Masaru Hojo and Ryōichi Masuda
Department of Industrial Chemistry, Faculty of Engineering,
Kobe University, Rokkodai, Kobe, 657, Japan

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Sulfuryl chloride is known to react easily with methyl phenyl sulfide to give chloromethyl phenyl sulfide in high yields[1]. We have found that, if this reaction is carried out in the presence of a small amount of wet silica gel, methyl phenyl sulfoxide is produced in an almost quantitative yield, without any formation of chloromethyl phenyl sulfide. Experiments so far revealed wide applicability of this reaction for the synthesis of various sulfoxides and we now wish to communicate the results.

$$\text{R-S-R' (or R-S-CH}_2\text{Cl)} \xrightarrow[\text{rT, in } CH_2Cl_2]{SO_2Cl_2,\ SiO_2\text{-}H_2O} \text{R-SO-R' (or R-SO-CH}_2\text{Cl)}$$

In a typical experiment a solution of sulfuryl chloride (1.08 g, 0.80 mmole) in methylene chloride (6 ml) was added dropwise at room temperature to a stirred mixture of wet silica gel (0.6 g of silicic acid, Mallinckrodt, 100 mesh and 0.6 g of water[2]) and thioanisole (0.94 g, 7.6 mmole) in methylene chloride (6 ml). Stirring was continued for two hours and the reaction mixture[3] was washed with aqueous sodium bicarbonate and water, dried with potassium carbonate and then evaporated to give 1.08 g (95 % yield) of methyl phenyl sulfoxide. This reaction proceeds quite cleanly, neither sulfones nor any chlorinated materials being detected in the raw products.

Sulfoxides prepared by this method are shown in Table I (Yields were determined by nmr before isolation). Methyl aryl sulfoxides and diaryl sulfoxides were obtained in high yields according to the procedure described above. For dialkyl and benzylic sulfides ice cold temperature was used to avoid α-chlorination and subsequent C-S bond cleavage. Allylic sulfoxides were also

Table I

Oxidation of Sulfides to Sulfoxides by SO_2Cl_2 and Wet Silica Gel

Sulfides	Yield (%) of Sulfoxides	Sulfides	Yield (%) of Sulfoxides
p-$CH_3OC_6H_4SCH_3$	85	$C_6H_5SCH_2CH{=}CH_2$	100
$C_6H_5SCH_3$	100	$C_6H_5SCH_2C(CH_3){=}CH_2$	85
p-$O_2NC_6H_4SCH_3$	87	*p*-$CH_3OC_6H_4SCH_2Cl$	100
$C_6H_5SC_6H_5$	100	$C_6H_5SCH_2Cl$	82
$C_2H_5SC_2H_5$	100	*p*-$O_2NC_6H_4SCH_2Cl$	100
$C_6H_5CH_2SCH_3$	100		

synthesized conveniently and very easily by this method (at 0°), without any chlorination at allylic position or any addition reaction to the double bond.

This reaction is also applicable to the synthesis of chloromethyl sulfoxides[4] $RSOCH_2Cl$ and seems to be particularly useful for this purpose. As for oxidation of chloromethyl sulfides, which are very susceptible to C-S bond cleavage during oxidation, ozone[5], *m*-chloroperbenzoic acid[6] and H_2O_2-V_2O_5-*t*-BuOH[7] have been reported to be specific reagents for this purpose. However, according to the present method chloromethyl sulfoxides can be obtained conveniently by oxidation, using common reagents, with simple work-up, without any by-products and in high yields.

REFERENCES AND NOTES

1. F. G. Bordwell and B. M. Pitt, J. Am. Chem. Soc., **77**, 572 (1955).
2. When commercial silica gel is used directly (without addition of any water), only chloromethyl phenyl sulfide is produced.
3. Evaporation of the reaction mixture gives practically pure compound.
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