Tetrahedron Letters No. 44, pp 3883 - 3886, 1977. Pergamon Press. Printed in Great Britain.

AN ALTERNATIVE SYNTHETIC METHOD FOR ALDEHYDES.

REACTION OF METHYL METHYLTHIOMETHYL SULFOXIDE WITH GRIGNARD REAGENTS[1].

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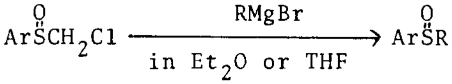
(Received in Japan 23 July 1977; received in UK for publication 19 September 1977)

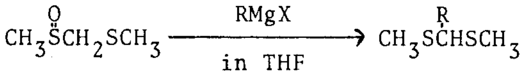
In our recent communication[2] it was reported that chloromethyl sulfoxides react easily with Grignard reagents according to equation 1 and this reaction can be utilized as an alternative synthetic method for diaryl and aryl alkyl sulfoxides.



$$\mathrm{Ar\overset{O}{S}CH_2Cl} \xrightarrow[\text{in Et}_2\text{O or THF}]{\text{RMgBr}} \mathrm{Ar\overset{O}{S}R} \qquad (1)$$

R: alkyl, aryl

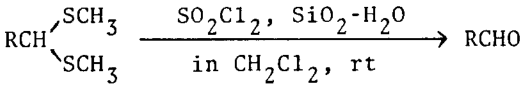
With the reasoning in mind that $-CH_2SCH_3$ group might be as good a leaving group as $-CH_2Cl$ in the above reaction, we have tried a reaction of methyl methylthiomethyl sulfoxide, which is now commercially available[3], with Grignard reagents RMgX to develop a new synthetic method for methyl sulfoxides CH_3SOR. As anticipated the reaction did proceed quite easily at room temperature using tetrahydrofuran as a solvent. However, the products actually obtained were dimethyldithioacetals of aldehydes RCHO (equation 2)[4]. Since dethioacetali-



$$\mathrm{CH_3\overset{O}{S}CH_2SCH_3} \xrightarrow[\text{in THF}]{\text{RMgX}} \mathrm{CH_3S\overset{R}{C}HSCH_3} \qquad (2)$$

R: alkyl, aryl

zation of these compounds are now readily and efficiently achieved with the use of sulfuryl chloride in the presence of a small amount of *wet* silica gel (equation 3)[5], combination of reactions (2) and (3) constitutes a new



$$\mathrm{RCH(SCH_3)_2} \xrightarrow[\text{in } \mathrm{CH_2Cl_2},\ \text{rt}]{\mathrm{SO_2Cl_2},\ \mathrm{SiO_2\text{-}H_2O}} \mathrm{RCHO} \qquad (\ 3\ )$$

R: alkyl, aryl

convenient alternative synthetic method for a variety of aldehydes. We now wish to communicate the results.

Some representative examples of the synthesis of the dimethyl dithioacetals are shown in the Table. Both alkyl- and arylmagnesium reagents afforded the

Table Reaction of Methyl Methylthiomethyl Sulfoxide with Grignard Reagents

Bromide	Product[a]	Yield(%)
p-$CH_3OC_6H_4Br$	*p*-$CH_3OC_6H_4CH(SCH_3)_2$	62,100[b]
p-$CH_3C_6H_4Br$	*p*-$CH_3C_6H_4CH(SCH_3)_2$	61.4,100[b]
PhBr	$PhCH(SCH_3)_2$	66
p-ClC_6H_4Br	*p*-$ClC_6H_4CH(SCH_3)_2$	39,56[b]
α-$C_{10}H_7Br$	α-$C_{10}H_7CH(SCH_3)_2$	58
$PhCH_2Br$	$PhCH_2CH(SCH_3)_2$	41
n-$C_6H_{13}Br$	*n*-$C_6H_{13}CH(SCH_3)_2$	54
PhCH=CHBr	$PhCH{=}CHCH(SCH_3)_2$	39,63[b]

[a] All products were checked by IR and ^{1}NMR, converted to the corresponding aldehydes[5] and confirmed by comparison with the authentic aldehydes. [b] Yields determined by ^{1}NMR ($CDCl_3$) before isolation.

dithioacetals in fair yields, which were then converted to the corresponding aldehydes in almost quantitative yields according to our method reported earlier[5].

Of these aldehydes aliphatic ones are known to be synthesized from alkyl halides by reaction with the anion of methyl methylthiomethyl sulfoxide (generated by sodium hydride) and subsequent acid-catalyzed hydrolysis.[6] In another related method[7] carbanion of 1,3-dithiane (generated by n-butyllithium) is used and the resulting dithioacetals are submitted to oxidative cleavage of the C-S bonds. In these two synthetic methods alkylation of the carbanions is involved as a key step and therefore these methods are confined only to the synthesis of aliphatic aldehydes. In this respect, the present method seems particularly useful as a convenient synthetic method for aromatic aldehydes starting with aryl halides. As is shown in the Table, the present method may also be utilized for synthesizing α,β-unsaturated aldehydes from vinyl bromides, though yields are not satisfactory at present and there still remains much to be revised in future.

Preparation of α-Naphthaldehyde: Typical Procedure. To a stirred mixture of 304 mg (12.5 mg atom) of magnesium and freshly distilled tetrahydrofuran (10 ml) was added dropwise 2.307 g (11.1 mmole) of α-bromonaphthalene. After complete dissolution of the magnesium a solution of methyl methylthiomethyl sulfoxide (606 mg, 4.89 mmole) in tetrahydrofuran (10 ml) was added dropwise and stirring was continued for 5 hr at room temperature. The reaction mixture was hydrolyzed with dilute hydrochloric acid, extracted with dichloromethane and the organic layer was washed with water, dried (Na_2SO_4), and then evaporated under reduced pressure. The resulting yellow oil (1.806 g) was submitted to column chromatography on silica gel, by which 660 mg (yield 57.6 %) of dimethyl dithioacetal of α-naphthaldehyde was eluted with n-hexane-benzene (9:1-4:1) as oily material. IR and ^{1}H-NMR spectra of this substance agreed well with those of the authentic specimen.

To a mixture of the dithioacetal (444 mg, 1.90 mmole) and *wet* silica gel (500 mg of silicic acid, Mallinckrodt, 100 mesh and 500 mg of water) was added dropwise a solution of sulfuryl chloride (400 mg, 2.96 mmole) in dichloromethane (5 ml) and stirring was continued for 2 hr at room temperature. A small amount of anhydrous potassium carbonate was added and the mixture was filtered. The filtrate was washed with water, dried (Na_2SO_4) and the solvent was removed under reduced pressure to give 472 mg of brown oil. Purification by column chromatography on silica gel (eluted with benzene) gave 275 mg of α-naphthaldehyde: m.p. 0-2°[8], yield 92.8 % (based on the dithioacetal).

REFERENCES AND NOTES

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