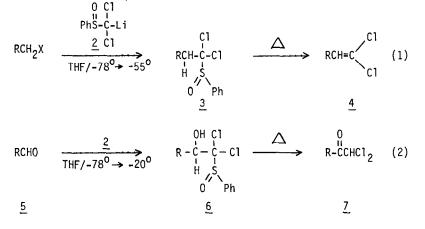
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<u>ABSTRACT</u>: Lithio dichloromethyl phenylsulfoxide reacts with aldehydes and alkyl halides to give the corresponding addition and alkylated products respectively. Pyrolysis of these compounds result in the formation of dichloroketones and terminal vinyl dichlorides.

The chemistry of $\underline{\alpha}$ -halosulfinyl carbanions has been investigated and it has been shown that these species have considerable potential in organic synthesis¹. However, the properties and chemistry of $\underline{\alpha}$ -dichlorosulfinyl carbanion $\underline{2}$ is still unknown². In this communication, we wish to report some chemistry of compound 2 demonstrating its potential applications in organic synthesis.

The lithic $\underline{\alpha}$ -dichloromethyl phenyl sulfoxide $\underline{2}$ is best generated at -78° C by the reaction of $\underline{\alpha}$ -dichloromethyl phenylsulfoxide³ with lithium diisopropylamide (LDA) using tetrahydrofuran as a solvent. The sulfinyl carbanion $\underline{2}$ appears to be stable in the range of -78° to -20° C. The alkylation and addition reactions of the anion $\underline{2}$ with alkyl halides and carbonyl compounds gave the corresponding alkylated products and $\underline{\beta}$ -hydroxy- $\underline{\alpha}$ -dichlorosulfoxides. The products with hydrogen beta to the sulfinyl group undergo the loss of benzene sulphenic acid upon pyrolysis. The processes are shown in equations (1) and (2).



The following procedure is representative: lithio dichloromethyl phenyl sulfoxide was generated by the reaction of LDA in THF at -78° C. Halides or aldehydes were added at this temperature and the mixture was stirred either at -78° to -55° C (over a period of $1\frac{1}{2}$ hr for halides) or at 78° to -20° C (over a period of 1 hr aldehydes). The reaction was quenched with

saturated ammonium chloride and the product was isolated with chloroform. The results are summarized in <u>Tables I and II</u>.

L, Halides	<u>3</u> , Products %	<u>4</u> , Products %
H ₃ (CH ₂) ₆ CH ₂ I	97	67
СН ₃ (СН ₂) ₈ СН ₂ I	94	80
CH ₃ (CH ₂) ₁₀ CH ₂ I	98	83
OMe	66	76

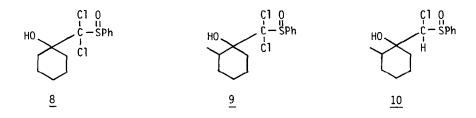
Pyrolysis, under nitrogen, of compound $\underline{3}$ in the presence of a catalytic amount of hydroquinone^{1b} in xylene gave the vinyl dichlorides⁴ in excellent yields.

5, Aldehydes	<u>6</u> , Products %	<u>7</u> , Products %
с2н5сно	74	-
с ₂ н ₅ сно с ₇ н ₁₅ сно	64	-
	94	80
CHO	83	98
	94	87

Table II

The neat pyrolysis of compound $\underline{6}$ was carried out at 150° C for 5 minutes under reduced pressure (1.0 mm/Hg). In the cases of octanaldehyde and propanaldehyde, no corresponding dichloroketones⁵ could be isolated upon pyrolysis of product 6.

The carbanion 2 also added to ketones; its reaction with cyclohexanone gave the expected hydroxy compound 8 in 57% yield. No adduct 9 could be isolated in the case of the reaction of compound 2 with 2-methylcyclohexanone. Apparently the second chlorine atom on the carbon alpha to



the sulfinyl group provides considerable steric hindrance in the reaction. The reaction of $\underline{\alpha}$ lithic chloromethyl phenyl sulfoxide with 2-methylcyclohexanone gave compound 10 in 26% yield.

The products, $\underline{\beta}$ -hydroxy- $\underline{\alpha}$ -dichlorosulfoxides $\underline{3}$, are quite sensitive to basic conditions. When compounds $\underline{6}$ (R = C₆H₃-) and $\underline{8}$ were separately treated with base (5% KOH-CH₃OH), the reaction gave complex mixtures, from which a small quantity of $\underline{\alpha}$ -dichloromethyl phenyl sulfoxide could be isolated but no corresponding epoxide could be detected.⁶ This property of <u>6</u> and <u>8</u> is quite in contrast to that of <u> β </u>-hydroxy- $\underline{\alpha}$ -chlorosulfoxide^{1a}, whose epoxide could be isolated in high yields.

Our results provide a highly convenient method for the preparations of terminal dichlorovinyl compounds and dichloromethylketones. Further exploratory work is in progress.

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