Tetrahedron Letters No. 7, pp 617 - 618.

0040-4039/79/0208-0617$02.00/0

ALKYLATION AND PYROLYSIS OF CHLOROMETHYL PHENYL SULFOXIDE: A SIMPLE SYNTHESIS OF VINYL CHLORIDES

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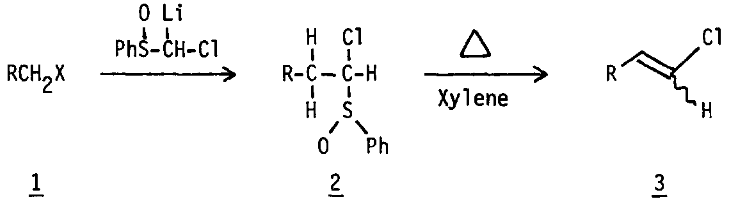
Work in our laboratory has demonstrated that chloromethyl phenyl sulfoxide is a very useful synthon in organic synthesis[1]. A recent note by More and Wemple[2] on alkylation and Pummerer rearrangement of chloromethyl phehyl sulfoxide prompts us to communicate our findings. Our results represent a novel two-step synthesis of vinyl chloride[3] with one carbon homologation from the corresponding halide (1a, b) through the reaction scheme (1).

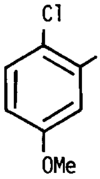
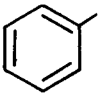


(1)

a, R = aryl; X = Br
b, R = alkyl; X = I

Lithio chloromethyl phenyl sulfoxide was generated by the addition of chloromethyl phenyl sulfoxide into the solution of lithium diisopropylamide in tetrahydrofuran (THF) at -78°C. Alkylations of benzylic bromides 1a went smoothly in THF at -78°C. However, we found that when alkyl iodides were employed, high yields of alkylated products could be obtained by adding one equivalent of hexamethylphosphoramide. The products were purified either by preparative thick layer chromatography (PLC) or by recrystallization. The pyrolysis[4], under nitrogen, of the alkylated products in xylene (160°C) in the presence of a catalytic amount of hydroquinone gave good yields of vinyl chlorides. The results are summarized in Table 1.

Table 1

Halides	Yields of 2	and 3[c]
1a, R-		
	74^a	83^d
	84^b	78^d
1b, R-		
$CH_3(CH_2)_{14}$-	96^b	87^e
$CH_3(CH_2)_{10}$-	94^b	100^e
$CH_3(CH_2)_7$-	78^b	71^e
$CH_3(CH_2)_5$-	71^b	94^e
$CH_3(CH_2)_4$-	72^b	100^e

[a] Purified by recrystallization from 1:1 water-methanol. [b] Purified by PLC; 1:4 light petroleum-chloroform. [c] Mixtures of cis and trans isomers. [d] Purified by PLC; 1:1 light petroleum-chloroform. [e] Purified by PLC; light petroleum.

The reactions shown in scheme (1) are of considerable interest because vinyl halide moeity has frequently been utilized as a latent carbonyl function in organic synthesis[5,6].

Acknowledgement We wish to thank Dr. Surachai Nimgirawath and Dr. Kosan Kusamran for their helpful discussions and their interests throughout this work.

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(Received in Japan 13 November 1978)