Tetrahedron Letters No. 41, pp. 3893 - 3896, 1971. Pergamon Press. Printed in Great Britain.

THE CHLORINATION OF SULFONES WITH SULFURYL CHLORIDE

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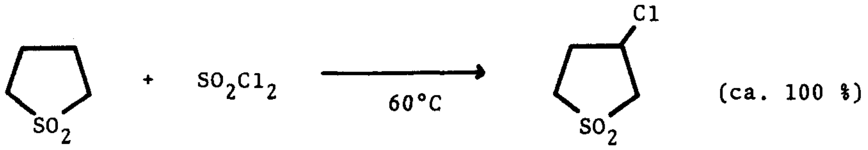
(Received in Japan 26 August 1971; received in UK for publication 15 September 1971)

The Chlorination of alkylsulfides$^{1)}$ or sulfoxides$^{2)}$ with a chlorination reagent (such as SO_2Cl_2, Cl_2, NCS, NOCl, $PhICl_2$ or t-BuOCl) is well known to occur exclusively at the α-position of the sulfur atom$^{3)}$, where the lone pair electrons on sulfur atom seem to play an important role.

Now we wish to report the exclusive or highly selective β-chlorination of diethyl sulfone and sulfolane with sulfuryl chloride. Thus, into a reaction vessel (carefully washed with fuming nitric acid) equipped with an effective condenser were added sulfolane and certain molar excess of sulfuryl chloride(freshly distilled at 69.3°C). The reaction vessel was carefully covered in order to be cut off from light.



After heating the mixture at 60°C for appropriate hours, sulfuryl chloride was evaporated and then the residue was distilled in vacuo (128°~130°/2.0~2.5 mmHg). The pasty solid distillate was recrystallized from benzene-hexane, mp. 54.2°~54.4°C. The nmr spectrum ($CDCl_3$) showed a quintet (J=5.5 Hz) at δ 4.7 (one proton), a multiplet at δ 2.9~3.8 (four protons) and a multiplet at δ 2.4~2.8 (two protons).

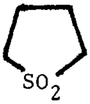
Anal. Calcd. for $C_4H_7SO_2Cl$: C, 31.07; H, 4.56; Cl, 22.94.

Found: C, 31.22; H, 4.67; Cl, 23.07.

Similarly, diethyl sulfone gave selectively β- and β,β'-chlorinated sulfones (69.2 % and 25.1 %, respectively), where only minor amount of α-chlorinated sulfone (5.7 %) was obtained. Infrared spectra showed the asym and sym stretchings of the SO_2 group at 1320 cm^{-1} (S), 1300 cm^{-1} (sh), 1135 cm^{-1} (sh) and 1120 cm^{-1} (S) for the β- and β,β'-chloroderivatives, and for the α-chloroderivative, at 1330 cm^{-1} (S), 1300 (sh), 1150 cm^{-1} (S) and 1130 cm^{-1} (S).

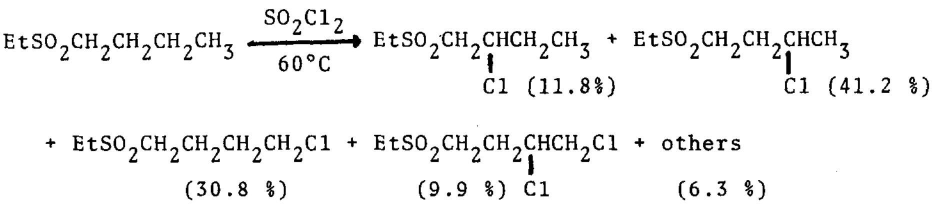
The α-chlorination was not observed in the chlorination of other sulfones Thus, di-n-propyl sulfone gave β- and γ-chlorinated products. Ethyl buthyl sulfone was chlorinated only on butyl group to give β, γ and δ chlorinated derivatives. Results are summerized in Table 1.

Table 1. Reaction Conditions and Product Distributions of Chlorination of Alkyl sulfones with Sulfuryl Chloride at 60°C.

sulfones	SO_2Cl_2 mole[a]	time (hr)	conversion (%)	product distribution (%)
	10	120	46	α 0; β 100
$CH_3CH_2SO_2CH_2CH_3$	5	120	22	α 5.7; β 69.2; β,β' 25.1
$CH_3CH_2CH_2SO_2CH_2CH_2CH_3$	5	24	41	α 0; β 43.4; γ 50.4; β,γ' 3.7; γ,γ' 2.5
	5	5^b	55	α 0; β 39.5; γ 50.0; β,γ' 6.3; γ,γ' 4.2
$\overset{\beta'}{CH_3}\overset{\alpha'}{CH_2}SO_2\overset{\alpha}{CH_2}\overset{\beta}{CH_2}\overset{\gamma}{CH_2}\overset{\delta}{CH_3}{}^c$	9	120	77	α 0; β 11.8; γ 41.2; δ 30.8; γδ 9.9

a. mole of SO_2Cl_2/mole of a sulfone. b. at 90°

c. the rest of the product, amounted to 6.3 %, was unidentified dichlorosulfones

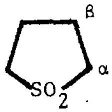


$$EtSO_2CH_2CH_2CH_2CH_3 \xrightarrow[60^\circ C]{SO_2Cl_2} EtSO_2CH_2\underset{\substack{| \\ Cl\ (11.8\%)}}{C}HCH_2CH_3 + EtSO_2CH_2CH_2\underset{\substack{| \\ Cl\ (41.2\ \%)}}{C}HCH_3$$

$$+ \underset{(30.8\ \%)}{EtSO_2CH_2CH_2CH_2CH_2Cl} + \underset{(9.9\ \%)}{EtSO_2CH_2CH_2}\underset{\substack{| \\ Cl}}{C}HCH_2Cl + \underset{(6.3\ \%)}{\text{others}}$$

With increase in the length of an alkyl group of a sulfone, the reactivity was found to increase. Therefore, considering a strong electron-withdrawing nature of a sulfonyl group, one may conclude that the present reaction proceeds via the hydride abstraction on the basis of the product distribution observed. An alternative may be the mechanism involving the hydrogen atom abstraction. Some supplementary work to elucidate the mechanism of the present chlorination is under progress but the radical mechanism may be ruled out on the basis of the following observations. a) The product distribution of the present reaction were found to be appreciably different from and more selective than the radical chlorination with sulfuryl chloride initiated by di-t-butyl peroxide (See Table 2). b) The quantitative o- and p-chlorination of toluene took place by the use of the present system (sulfolane and sulfuryl chloride at 60°C in the dark), yield 95.5 %.

Table 2. Product Distributions of Chlorination of Some Alkylsulfones with Sulfuryl chloride initiated by DTBP.

Alkylsulfones	Product Distributions (%)
	α 2.6; β 97.4
$CH_3CH_2SO_2CH_2CH_3$	α 11.3; β 82.4; β,β' 6.3
$CH_3CH_2CH_2SO_2CH_2CH_2CH_3$	α 0; β 58.0; γ 35.1; β,γ 4.0; γ,γ' 2.9

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2) Chlorination of alkyl sulfoxides; with TsCl, M. Hojo and Z. Yoshida, J. Am. Chem. Soc., 90, 4496 (1968). with NOCl, R. N. Leoppky, Tetrahedron Letters, 1968, 5415. with $PhICl_2$, M. Ciquini, Chem. Comm., 1969, 607. with t-BuOCl, S. Iriuchijima and G. Tsuchihashi, Tetrahedron Letters, 1969, 5259.

3) Only one exception was observed in the chlorination of 9-tia-bicyclo[3.3.1]nonane with sulfuryl chloride where 2-endo-chloro-9-thia-bicyclo[3.3.1]nonene was obtained. L. A. Paquette and R. W. Houser, J. Am. Chem. Soc., 91, 3870 (1969).