SYNTHESIS OF 2-CHLOROETHYL ALKYL SULFONES BY THE OXIDATIVE CHLORINATION OF 2-HYDROXYETHYL ALKYL SULFIDES

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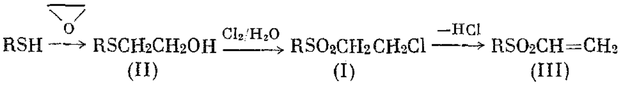
2-Chloroethyl alkyl (aryl) sulfones are key compounds in the synthesis of herbicides [1], fungicides [2], etc.

The majority of the methods of obtaining alkyl- and aryl-2-chloroethyl sulfones is based on the oxidation of 2-chloroethyl alkyl (aryl) sulfides and 2-hydroxyethyl alkyl (aryl) sulfides followed by substitution of the OH group by a chlorine when necessary [1-4]. The oxidation of these sulfides is accomplished with hydrogen peroxide [1-4], ozone, chloramine T, and sodium hypochlorite [5-7]. The oxidation with sodium hypochlorite, which is added to a suspension of the 2-hydroxyethyl aryl sulfides in HCl, is an interesting modification in the latter case; this makes it possible to obtain 2-chloroethyl aryl sulfones in one step [6, 7]. The oxidation of bis-(2-hydroxyethyl) sulfide and bis-(2-hydroxyethyl) sulfoxide with chlorine in water leads to hydroxyethyl-2-chloroethyl sulfone [8].

A study of the feasibility of also using oxidative chlorination for other aliphatic oxysulfides was of interest. The synthesis of 2-chloroethyl alkyl (phenyl) sulfones (I) with the general formula $RSO_2CH_2CH_2Cl$ (R = n-alkyl C_2—C_{10}, C_6H_5) by the oxidative chlorination of the corresponding alkyl- and phenyl ethyl sulfides (II) is described in this paper.



$$\mathrm{RSH} \longrightarrow \underset{(II)}{\mathrm{RSCH_2CH_2OH}} \xrightarrow{Cl_2/H_2O} \underset{(I)}{\mathrm{RSO_2CH_2CH_2Cl}} \xrightarrow{-HCl} \underset{(III)}{\mathrm{RSO_2CH{=}CH_2}}$$

The corresponding 2-hydroxyethyl alkyl (aryl) sulfides (II) were obtained in 90-96% yield from the aliphatic thiols by oxyethylating them with ethylene oxide in the presence of an alkali [9]. The oxidative chlorination of the former is accomplished remarkably simply: to a suspension of 2-hydroxyethyl alkyl (phenyl) sulfide in water at a mole ratio of 1 : 4 to 1 : 10 is gradually fed gaseous chlorine at such a rate that the temperature of the reaction mixture does not exceed 4-20°C until the appearance of a persistent yellowish-green color of free chlorine is obtained. After the usual treatment and crystallization of the product, the 2-chloroethyl alkyl (phenyl) sulfones (Table 1) were obtained in high yield. The oxidation of 2-hydroxyethyl alkyl (phenyl) sulfides to sulfones with the simultaneous substitution of the OH group by a chlorine is successfully accomplished by this method under mild conditions and thereby one avoids obtaining the toxic intermediate products, the 2-chloroethyl alkyl (phenyl) sulfides, the absence of which was demonstrated by GLC and TLC. Similarly the absence of the formation of 2-hydroxyl alkyl (phenyl) sulfoxides and 2-chloroethyl alkyl (phenyl) sulfoxides during the oxidative chlorination process was also determined. The formation of alkyl sulfochlorides and alkyl chlorides (1-2%) was noted however; this can be explained as due to the more extended duration of the oxidative chlorination process. The latter process becomes the principal one when tert-butyl-2-hydroxyethyl sulfide is used as the starting material. A mixture of tert-butyl chloride, 2-chloroethyl sulfochloride, tert-butyl sulfochloride, and 2-hydroxyethyl sulfochloride, which were identified by GLC by comparing them with known substances, is chiefly formed in this case as a result of the oxidative splitting that occurs. Similar extensive splitting was observed during the oxidation of dialkyl sulfides in water with gaseous chlorine [10].

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TABLE 1. 2-Chloroethyl alkyl (phenyl) Sulfones $RSO_2CH_2CH_2Cl$

R	Yield, %	m.p, °C	Found, %				Empirical formula	Calculated, %				Lit. ref.
			C	H	Cl	S		C	H	Cl	S	
C_2H_5	58	20,4—21	30,50	5,86	22,50	20,34	$C_4H_9ClO_2S$	30,67	5,79	22,64	20,47	[3]
C_3H_7	77	17,5—18,5	34,90	6,41	20,59	18,61	$C_5H_{11}ClO_2S$	35,19	6,50	20,77	18,79	—
C_4H_9	76	30,8—31,4	39,18	6,97	19,02	17,20	$C_6H_{13}ClO_2S$	39,02	7,09	19,19	17,36	—
C_5H_{11}	78	24,7—25,7	42,34	7,81	17,76	16,05	$C_7H_{15}ClO_2S$	42,31	7,61	17,84	16,19	—
C_6H_{13}	91	26	—	—	16,70	15,10	$C_8H_{17}ClO_2S$	—	—	16,66	15,07	—
C_8H_{17}*	78	37,5—38,5	50,02	8,69	14,70	13,31	$C_{10}H_{21}ClO_2S$	49,88	8,79	14,72	13,32	[1, 11]
$C_{10}H_{21}$*	76	48,5—49,5					$C_{12}H_{25}ClO_2S$					[1, 11]
C_6H_5†	70	53—54					$C_8H_9ClO_2S$					[2, 3]

* Crystallization from hexane.

†Crystallization from benzene.

The method of obtaining 2-chloroethyl alkyl (phenyl) sulfones that we developed was used to synthesize alkyl (phenyl) vinyl sulfones and in particular the herbicide alvison, the active principles of which are the alkyl vinyl sulfones (III) where R = n-alkyl C_8—C_{10} [9].

It is well known that dehydrohalogenation of similar compounds by the action of bases is easily accomplished [2-4, 6, 8, 11]. The corresponding alkyl vinyl sulfones were obtained in a yield of 90-95% (GLC data) by treating 2-chloroethyl alkyl sulfones with triethylamine in a benzene solution at 40-50°C. Alkyl vinyl sulfones were obtained in an 85-90% yield by treating the 2-chloroethyl alkyl sulfones with a 10-20% NaOH solution at 10-20°C. The oxidative chlorination of 2-hydroxyethyl alkyl sulfides followed by the dehydrohalogenation of the 2-chloroethyl alkyl sulfones (I) without preliminarily isolating them yields 84-86% of the sought-after product, calculated based on the 2-hydroxethyl alkyl sulfide. As demonstrated by GLC analysis, the product obtained in this way contains 92-96% alkyl vinyl sulfone.

EXPERIMENTAL METHOD

The GLC analysis of the reaction products was carried out on an LKhM-8MD instrument with a flame-ionization detector. The column (1500 × 3 mm) was packed with 10% E-301 silicone on Chromosorb W (60-80 mesh); 180-250°C; helium flow rate 30 ml/min. The IR spectra were run on a UR-10 spectrometer (KBr).

2-Chloroethyl Octyl Sulfone. To 28.5 g (0.15 mole) of freshly distilled 2-hydroxyethyl octyl sulfide was added 10.8 g (0.6 mole) of water and the mixture was cooled to 8-10°C. Then through a gas-feed tube with intense agitation was passed purified chlorine at a rate such that the temperature of the reaction mixture did not exceed 20°C. The appearance of a persistent yellowish-green color due to free chlorine was taken as the end of the reaction. After venting off the excess chlorine the reaction mixture was cooled to —6°C, the precipitate was isolated and washed with water until the wash waters were neutral. The product obtained (34 g) was purified by a two-fold crystallization from hexane. The pure 2-chloroethyl octyl sulfone is a white crystalline product and has an mp of 37.5-38.5°C [1, 11]; it is soluble in the majority of organic solvents and insoluble in water.

The other 2-chloroethyl alkyl sulfones were similarly obtained (Table 1). 2-Chlorodiethyl sulfone, which was isolated by extraction with benzene, is an exception. The most suitable solvent for crystallization is a hexane—ether mixture.

There are characteristic absorption bands of the sulfonyl group (1120-1140, 1310-1340 cm^{-1}), methyl and methylene groups (2930-2950, 2960-2990 cm^{-1}), and the C—Cl bond (580-590, 760-770 cm^{-1}) in the IR spectra for all the compounds.

CONCLUSIONS

1. The corresponding 2-chloroethyl alkyl(phenyl) sulfones were obtained in high yield by oxidizing the 2-hydroxyethyl alkyl(phenyl) sulfides with chlorine in water; the dehydrohalogenation of the former in the presence of bases yields the corresponding vinyl sulfones.

2. The generality of the oxidative chlorination for 2-hydroxyethyl alkyl(phenyl) sulfides, which have no branching in the α-position to the sulfur atom, was demonstrated.

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