# REARRANGEMENT OF RADICALS WITH MIGRATION OF THE CHLORINE ATOM FROM SULFUR TO CARBON DURING THE REACTION OF THIOLS WITH VINYLSULFONYL CHLORIDE

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Nearly all of the known rearrangements of radicals in solution include migration of the atom or group from carbon to carbon, or from carbon to a heteroatom, and very little is known about the possibility of rearrangement from a heteroatom to carbon [1]. Thus, in [2] it was postulated that the rearrangement can proceed with a 1,3-migration of chlorine from sulfur to carbon when sulfuryl chloride is reacted with olefins.

We studied the possibility of rearrangement on the example of the radical  $-\dot{CH}-SO_2Cl$ , which can be formed during the radical addition of thiols, like n-butanethiol and thiophenol, to vinylsulfonyl chloride. Here we expected the respective formation of  $\beta$ -chloroethyl butyl sulfide and  $\beta$ -chloroethyl phenyl sulfide by the following scheme:

$$RSH + In^* \rightarrow RS^* + InH$$
(a)

$$RS + CH_2 = CHSO_2CI \rightarrow RSCH_2CH - SO_2CI$$
(b)
$$RSCH CHSO_2CI \rightarrow RSCH_2CH - SO_2CI$$

$$BSCH CHClso* Bscu cucl + so$$

$$CH_2CHCI + RSH \rightarrow RSCH_2CH_2CI + RS(Chain)$$
 (d)

$$(\mathbf{R} = \mathbf{C}_4 \mathbf{H}_9, \mathbf{C}_6 \mathbf{H}_5) \tag{e}$$

The fragmentation (d) of such radicals, with the cleavage of  $SO_2$ , was described in [3-5].

The experiments were run at  $\sim 20^{\circ}$  in an argon atmosphere; the ratio of the reactants and the reaction time were selected in such manner that the conversion of the starting compounds was maximum (>80%). The GLC method was used to identify and quantitatively determine the amounts of  $\beta$ -chloroethyl butyl sulfide and  $\beta$ -chloroethyl phenyl sulfide in the reaction mixtures; their yield was 8-12%. In addition, it was shown qualitatively that SO<sub>2</sub> is present. The formation of these compounds indicates that the discussed rearrangement proceeds in harmony with the scheme.

Another route, which in principle could lead to the same products, is expressed by the following scheme:

	SCH.	,ĊHSO,Cl +	$RSH \rightarrow$	RSCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> Cl	+ RS'	Ċ	ĥ
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$$RSCH_2CH_2SO_2Cl + In' \rightarrow RSCH_2CH_2SO_2' + InCl$$
(g)

$$RSCH_2CH_2SO_2 \rightarrow RSCH_2CH_2 + SO_2$$
(b)

$$RSCH_2CH_2 + CH_2 = CH - SO_2CI \rightarrow RSCH_2CH_2CI + CH_2 = CH - SO_2^{\bullet}$$
(i)

$$RSCH_{2}CH_{2} + RSCH_{2}CH_{2}SO_{2}CI \rightarrow RSCH_{2}CH_{2}CI + RSCH_{2}CH_{2}SO_{2}$$
(k)

However, this route seems improbable, since the homolytic cleavage of chlorine from sulfonyl chlorides requires, as is known, high temperatures [3], or else the special addition of initiators, like peroxides [4] or copper chlorides [5].

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It should be mentioned that, besides the indicated products, HCl, water, and the corresponding disulfide RSSR (the yield of which is 60-70% when based on taken thiol) are also formed in the reaction. The formation of these products indicates that, together with the radical addition of the thiol to the double bond of the starting sulfonyl chloride, the reaction proceeds mainly in a different direction, possibly analogous to the known reaction of saturated sulfonyl chlorides with thiols [6, 7].

 $\begin{aligned} \text{RSO}_2\text{Cl} &+ 2\text{RSH} \rightarrow \text{HCl} + \text{RSO}_2\text{H} + \text{RSSR} \\ 3\text{RSO}_2\text{H} \rightarrow \text{RSO}_2\text{SR} + \text{RSO}_3\text{H} + \text{H}_2\text{O} \\ \text{RSO}_2\text{SR} + \text{RSH} \rightarrow \text{RSSR} + \text{RSO}_2\text{H} \end{aligned}$ 

#### EXPERIMENTAL METHOD

Vinylsulfonyl chloride was obtained as described in [8], while  $\beta$ -chloroethyl butyl sulfide and  $\beta$ chloroethyl phenyl sulfide were obtained as described in [9]. The structure and purity of the indicated compounds were confirmed by NMR and GLC.

The experiments were run with freshly distilled reactants by the following method. Into a flask equipped with a reflux condenser, in an argon stream, were charged 2 mmoles of vinylsulfonyl chloride and 4 mmoles of the thiol. The mixture was let stand for 2.5 h. The escaping gases were absorbed in water. The presence of SO2 and HCl in the escaping gases was shown by the decolorization of iodine water and reaction with AgNO<sub>3</sub>. In the reaction with the butanethiol, after an induction period (3-5 min), the reaction mixture warms up somewhat and becomes cloudy due to the liberated water (the cloudiness disappears on shaking with anhydrous  $Na_2SO_4$ ). With thiophenol the reaction goes without warming up; here the liberation of water is observed only in 1.5-2 h after mixing the reactants. At the end of reaction the mixture was analyzed by GLC. The C<sub>4</sub>H<sub>9</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl and C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl were identified by comparing with the authentic specimens on two phases that differed in polarity. The quantitative determinations were made by the internal standard method. The chromatographic analysis conditions were: C<sub>6</sub>H<sub>5</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl, 1a) 1 m  $\times$  3 mm steel column, 6% Silicone E-301 deposited on Chromosorb W, 135°, helium as the carrier gas (4.9 liters/h), detection by the heat conductivity, and  $\sec -C_{10}H_{21}SC_2H_5$  as the internal standard; 1b) the same column, 6% PEG-4000 deposited on Chromosorb W, 150°, and helium flow rate 6 liters/h; C4HaSCH2-CH<sub>2</sub>Cl, 2a) the same column as in 1a, helium flow rate 3.5 liters/h, 100°, and i-C<sub>3</sub>H<sub>7</sub>SC<sub>6</sub>H<sub>5</sub> as the internal standard; 2b) the same column as in 1b, 100°, and helium flow rate 2 liters/h.

Preparative experiments were run to determine the yield of the diphenyl and dibutyl disulfides.

- A. A mixture of 4.4 g of thiophenol and 2.6 g of vinylsulfonyl chloride was let stand for 2.5 h under the above described conditions, and then it was distilled. The fraction with bp 180-195° (2 mm) was collected. The yield of diphenyl disulfide was 2.6 g (60%), mp 58-59° (from alcohol). The mixed melting point with an authentic sample of diphenyl disulfide was not depressed.
- B. In a similar manner, the distillation of a reaction mixture composed of 3.6 g (40 mmoles) of n-butanethiol and 2.6 g (20 mmoles) of vinylsulfonyl chloride gave 2.4 g (66%) of dibutyl disulfide, bp 90-93° (10 mm). It was shown by GLC that the obtained compound is identical with an authentic sample of dibutyl disulfide.

# CONCLUSIONS

1. A study was made of the reaction of n-butanethiol and thiophenol with vinylsulfonyl chloride at ~20° in an argon atmosphere. The reaction products are, respectively,  $\beta$ -chloroethyl butyl sulfide and  $\beta$ -chloroethyl phenyl sulfide (8-12% yields), and SO<sub>2</sub> is liberated. The other reaction products are, respectively, the dibutyl and diphenyl disulfides (60-70% yields), HCl, and H<sub>2</sub>O.

2. Apparently, the formation of  $\beta$ -chloroethyl butyl sulfide and  $\beta$ -chloroethyl phenyl sulfide is associated with the addition of the thiyl radical to the double bond of vinylsulfonyl chloride and subsequent rearrangement of the RSCH<sub>2</sub>CHSO<sub>2</sub>Cl radicals, with the migration of chlorine from sulfur to the adjacent carbon atom.

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