

gave 4 g. of crude starting material. Next the column was eluted with nine 100-ml. portions of 50% benzene-50% petroleum ether. Evaporation of these fractions gave 1.6 g. of white crystals which after recrystallization from ether melted at 183–184° (0.48 g.).

Anal. Calcd. for  $C_{24}H_{16}$ : C, 94.70; H, 5.30; mol. wt., 304. Found: C, 95.08; H, 5.63; mol. wt., 298.

**Triphenylene.** Santowax (crude 1,2-diphenylbenzene), 23 g., was dissolved in 78 g. of thiophene-free benzene and this solution was then passed over 10 ml. of chromia on alumina catalyst at 625° during the course of 215 min. The catalyst activity as indicated by the rate of hydrogen evolution was almost constant during the course of the run. The benzene was evaporated from the condensate and the white solid remaining was crystallized from 320 ml. of ethanol. Crude triphenylene (2.6 g.) m. p. 182–193° was obtained. This material was again crystallized from ethanol to give 2 g. of pure triphenylene m.p. 197–198°. No melting point depression was observed when a mixed melting point was made with triphenylene as prepared above and an authentic sample.

A number of variations of the above procedure were tried in attempts to improve the yield. Temperatures of 500 to 650° at various space velocities were investigated without success, however.

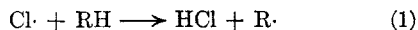
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### Chlorosulfonation of Ethyl Chloride

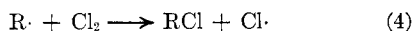
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The photochemical reaction of hydrocarbons with sulfur dioxide and chlorine to yield alkanesulfonyl chlorides (the Reed reaction)<sup>1</sup> has received much technical investigation as a step in the preparation of synthetic detergents and in the modification of polyethylene. It is considered<sup>2,3</sup> to be a radical chain process involving the propagating steps



in which (2) competes with chlorination,



and, in fact, alkyl chlorides are often obtained as by-products.

The sulfochlorination of small molecules has received relatively little study, although Asinger and co-workers have studied the reaction of propane,<sup>4</sup> butane,<sup>5</sup> and isobutane,<sup>6</sup> and Helberger, Manecke

(1) C. F. Reed, U. S. Pat. 2,174,492 (September 26, 1939).

(2) M. S. Kharasch, T. H. Chao, and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 2393 (1940).

(3) J. Stauff, *Z. Elektrochem.*, **49**, 550 (1942).

(4) F. Asinger, W. Schmidt, and F. Ebeneder, *Ber.*, **75**, 34 (1942).

(5) F. Asinger, F. Ebeneder, and E. Böck, *Ber.*, **75**, 42 (1942).

(6) F. Asinger and F. Ebeneder, *Ber.*, **75**, 344 (1942).

and Fischer<sup>7</sup> have investigated the reaction of propyl and higher chlorides.

The reaction attracted our attention as a possible route to derivatives of 2-substituted ethanesulfonic acids, and we find in fact that 2-chloroethanesulfonyl chloride can be prepared in reasonable yield by this route.

Trials of various experimental conditions indicated that the best yields are obtained under strong illumination by the slow introduction of chlorine into a mixture of sulfur dioxide and ethyl chloride, allowed to reflux under a Dry Ice-condenser. Typical results appear in Table I, and it is evident that various additives had a deleterious effect on the process, as did attempts to generate chlorine and sulfur dioxide *in situ* from  $SO_2Cl_2$  and pyridine.<sup>2,8</sup>

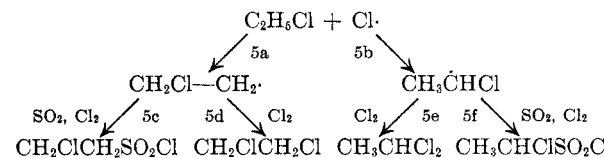
TABLE I  
SULFOCHLORINATION OF ETHYL CHLORIDE

Reactants (Moles)			Time of $Cl_2$ Addn. (hr.)	Yield (% <sup>a</sup> )	
EtCl	$SO_2$	$Cl_2$		$C_2H_5SO_2Cl$	$C_2H_4Cl_2$
1.0	2.34	1.31	3.5	26.6	18.2
4.0	9.37	4.0	11	31.8	28.3
6.0	14.0	6.0	8	35.0	25.5
7.5	14.0	6.0	4	12.0	—
2.12 <sup>b</sup>	4.7 <sup>b</sup>	2.0 <sup>b</sup>	1.5	13	17
2.5 <sup>c</sup>	4.7 <sup>c</sup>	2.0 <sup>c</sup>	1.5	Trace	56
7.5 <sup>d</sup>	13.0 <sup>d</sup>	6.0 <sup>d</sup>	4	2	7.7
1.0 <sup>e</sup>	0.5 ( $SO_2Cl_2$ ) <sup>e</sup>	—	—	5.2	35.9

<sup>a</sup> Based on  $Cl_2$  added. <sup>b</sup> 10 cc. water added. <sup>c</sup> 0.5 cc.  $C_2H_5SH$  added. <sup>d</sup> 1 cc. pyridine added. <sup>e</sup> 0.5 cc. pyridine added.

The sulfonyl chloride obtained was identified as the 2-chloro isomer by its physical constants, and by conversion to known derivatives by reaction with aniline and with thiourea, and none of the lower-boiling 1-chloro isomer was detected on fractional distillation. The best yield was 35%, based on  $Cl_2$ , or 58% based on organic products isolated. The difference probably represents  $SO_2Cl_2$  formed by reaction between  $SO_2$  and chlorine, and considerable quantities were actually detected during product work-up. The dichloroethane produced was chiefly 1,1-dichloroethane, containing a small amount (<7%) of 1,2-dichloroethane.

Aside from any possible synthetic utility, the sulfochlorination of ethyl chloride has some interesting features, since the products arise from a rather complicated set of competitive radical reactions shown in Equation 5.



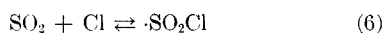
(7) J. H. Helberger, G. Manecke, and H. M. Fischer, *Ann.*, **562**, 23 (1949).

(8) M. S. Kharasch and A. T. Read, *J. Am. Chem. Soc.*, **61**, 3089 (1939).

Evidently, under our conditions (5a-5c) and (5b-5e) are the only important paths, the 2-chloroethyl radical picking up SO<sub>2</sub>, while the 1-chloroethyl radical reacts preferentially with chlorine. This rather striking difference in selectivity has some parallel in the behavior of SO<sub>2</sub>-olefin copolymerization reactions. Hydrocarbonradical attack on SO<sub>2</sub> is a highly reversible process, the reversibility increasing (as evidenced by lower ceiling temperatures) with increasing substitution,<sup>9</sup> and the reaction is also repressed by electron-withdrawing groups on the hydrocarbon radical.<sup>10</sup> Thus, vinyl chloride, which grows through a 1-chloroalkyl radical analogous to the product of (5b) is one of the few olefins giving a copolymer containing several monomer units per SO<sub>2</sub> residue.<sup>11</sup>

If we attempt to reconcile our yields with chlorination data, the results are more puzzling. The photochlorination of ethyl chloride gives approximately 80% 1,1-dichloroethane,<sup>12</sup> indicating that step (5b) occurs 4 times as rapidly as (5a), and since we are dealing with a chain process, this should set an upper limit of 20% on the possible yield of 2-chlorosubstituted products. In contrast, our data indicate yields of at least 35-60% of 2-chloroethanesulfonyl chloride.

At present we can offer no unequivocal resolution of this discrepancy, but it may be due to the high SO<sub>2</sub> media in which our reactions have been carried out. Recently Russell and Brown have noted significant differences in selectivity for different C-H bonds in chlorinations employing Cl<sub>2</sub> and SO<sub>2</sub>Cl<sub>2</sub>, and has suggested that the latter involve the ·SO<sub>2</sub>Cl radical.<sup>13</sup> In our system it is certainly possible that the equilibrium



lies well to the right so that ·SO<sub>2</sub>Cl is the actual attacking species in (5a) and (5b). Alternatively, SO<sub>2</sub> may act as a "complexing" solvent for chlorine atoms analogous to aromatic solvents<sup>14,15</sup> and alter their reactivity without forming an actual covalently bonded radical. Admittedly these two alternatives would be extremely difficult to differentiate

(9) R. D. Snow and F. E. Frey, *Ind. Eng. Chem.*, **30**, 176 (1938).

(10) For a more detailed discussion see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 223-8.

(11) C. S. Marvel and L. H. Dunlap, *J. Am. Chem. Soc.*, **61**, 2709 (1939).

(12) Gas phase chlorination at about 200° gives 80% 1,1-dichloroethane, W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **6**, 479 (1941), and J. D'Ans and J. Kautzsch, *J. Prakt. Chem.*, **2**, 305 (1909) report at least 70% in the liquid phase at the boiling point. A recent measurement by M. F. Mayahi at Columbia indicates 81.5% 1,1- and 18.5% 1,2-dichloroethane at 0° in CCl<sub>4</sub>.

(13) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4031 (1955).

(14) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957).

(15) C. Walling and B. Miller, *J. Am. Chem. Soc.*, **79**, 4181 (1957).

by experiment, and the latter could be an explanation of Russell and Brown's SO<sub>2</sub>Cl<sub>2</sub> results.<sup>13</sup>

#### EXPERIMENTAL

*Materials* were ordinary commercial reagents. The ethyl chloride had a slight mercaptan odor, so in some experiments it was treated with cold, concentrated sulfuric acid before use, but without significant change in results.

*Sulfochlorinations* were carried out in all-glass equipment, using a round-bottomed flask fitted with a gas inlet tube and a Dry Ice-cooled condenser. During reaction the system was illuminated by one or two Westinghouse RS 275-watt sunlamps at a distance of about 6 in.

*Product isolation and identification.* Reaction mixtures were first separated by atmospheric pressure distillation from a water bath. The amount of dichloroethanes in the low-boiling fraction was determined by adding a 20-g. aliquot to 125 g. of 20% NaOH solution frozen at -70° and warming slowly to 0°. This procedure removed HCl, SO<sub>2</sub>, and SO<sub>2</sub>Cl<sub>2</sub>. The solution was next neutralized with HCl and the dichloroethanes separated by steam distillation into a calibrated trap.

1,1-Dichloroethane boils at 57°, and 1,2-dichloroethane boils at 83°. Fractional distillation of the dichlorides from one run showed that most of the material boiled below 65°. Analysis of the higher-boiling fractions by index of refraction indicated a total of 6-7% 1,2-dichloroethane.

2-Chloroethanesulfonyl chloride was obtained from the residue of the first separation by vacuum distillation as a water-white lachrymatory liquid, b.p. 84°/12 mm.,  $d_4^{20}$  1.560,  $n_D^{20}$  1.4934, lit.,<sup>16</sup>  $d_4^{20}$  1.550,  $n_D^{20}$  1.4920, and containing 44.95% Cl. The 1-chloro isomer is reported<sup>17</sup> to boil at 70-1°/13 mm., but no significant lower boiling fraction was detected. On reaction with excess aniline in ether, the sulfonyl chloride gives a chlorine-free product, m.p. 69.6-70.2° on recrystallization from CCl<sub>4</sub>, apparently identical with that reported by Kohler<sup>18</sup> who gives m.p. 69-70°. Kohler considered this product to have a cyclic structure, but its infrared spectrum is consistent with the expected ethylenesulfonanilide, CH<sub>2</sub>=CHSO<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub>, reported m.p. 69°. Although isolation of the ethylenesulfonanilide was not quantitative due to losses during recrystallization, during the reaction in ether aniline hydrochloride, 1.82 moles, precipitated out and was separated by filtration and identified by neutralization equivalent (129.8, calc., 129.6). The analogous reaction of 1-chloroethanesulfonyl chloride has not been described, but it is reported to react with ammonia to give 1-chloroethanesulfonamide<sup>17</sup> and should accordingly liberate only one mole of aniline hydrochloride. A better proof of structure was obtained by hydrolyzing the sulfonyl chloride by boiling with water, neutralizing with bicarbonate, and converting to 2-S-thiuronium ethanesulfonate. The product, obtained in 42.6% yield, had an x-ray powder diagram identical with authentic material,<sup>20</sup> and also the proper iodine titration on hydrolysis to 2-mercaptoethanesulfonate ion.

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(16) E. F. Landau, *J. Am. Chem. Soc.*, **69**, 1219 (1947).

(17) E. Müller and H. Raudenbusch, *Ber.*, **64B**, 94 (1931).

(18) E. P. Kohler, *Am. Chem. J.*, **19**, 744 (1897).

(19) P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, 121 (1922).

(20) C. H. Schramm, H. Lemaire, and R. H. Karlson, *J. Am. Chem. Soc.*, **77**, 6231 (1955).