[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, YALE UNIVERSITY, AND THE UNIVERSITY OF MAINE]

The Properties of Chloromethanesulfonyl Chloride and the Chloromethanesulfonamides

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In 1938 as a continuation of their study of the action of chlorine on various types of sulfur compounds[2] the authors had occasion to prepare chloromethanesulfonyl chloride, $ClCH_2SO_2Cl$, I. A few months later there appeared the American abstract of Kostsova's earlier discovery of this compound,[3] and more recently it has been prepared by Lee and Dougherty.[4]

It was the intention of the authors to use $ClCH_2SO_2Cl$, I, as an intermediate in the preparation of sulfonamides of possible pharmaceutical interest by replacing the chlorine atom of chloromethanesulfonamide, $ClCH_2SO_2NH_2$, II, and chloromethanesulfonanilide, $ClCH_2SO_2NHC_6H_5$, III, respectively, with various other groups. All attempts to carry out such replacements, however, met with failure, for III was recovered unchanged after boiling for three hours with aniline, or heating for twenty-four hours with sodium phenoxide, while II after heating for three hundred thirty-six hours with aniline at 100° had given up only 23% of its halogen. This result is in accord with the findings of Ziegler and Connor[5] and Ramberg and Bäcklund,[6] who have observed that a bromine atom in alpha position to a sulfone group is firmly bound. Raschig and Prahl[7] have discussed a similarly inert chlorine atom in potassium chloromethanesulfonate, $ClCH_2SO_3K$, IV. The authors' results constitute additional evidence for the generalization that the activity of an organic halogen atom in metathetical reactions is greatly diminished if it is in alpha position to a sulfone, a sulfonamide or sulfonic acid group.

Although it was found impossible to prepare derivatives of aminomethanesulfonamide from II the study yielded some unexpected results. It was early observed that II was readily hydrolyzed by boiling 5% sodium hydroxide and that not only ammonia but a chloride ion as well was liberated quantitatively. The resulting solution reduced $Ag(NH_3)_2^+$ to silver and gave a test for formaldehyde, suggesting that the hydrolysis had been accompanied by a complete decomposition according to the equation

$$ClCH_2SO_2NH_2 + 3NaOH = NaCl + NH_3 + CH_2O + Na_2SO_3 + H_2O$$

On first thought this decomposition was assumed to result from a stepwise hydrolysis which proceeded as follows

$$\begin{aligned} ClCH_2SO_2NH_2 + NaOH &= ClCH_2SO_3Na + NH_3 \\ ClCH_2SO_3Na + NaOH &= HOCH_2SO_3Na + NaCl \\ HOCH_2SO_3Na + NaOH &= CH_2O + Na_2SO_3 + H_2O \end{aligned}$$

Since the hydrolysis and decomposition was accomplished by boiling for only ten minutes with 5% sodium hydroxide and since Raschig and Prahl[7] found the chlorine of chloromethanesulfonic acid, IV, relatively inert, there seemed some doubt that the postulated mechanism was correct. Accordingly, $ClCH_2SO_2Cl$, I, was hydrolyzed in boiling distilled water, enough solid sodium hydroxide was added to make the solution 5%, and the boiling was continued for ten minutes. The solution was then analyzed and only as much chloride was found as was produced in the destructive hydrolysis of the sulfonyl chloride group. This result indicates that chloromethanesulfonic acid is stable under the conditions employed, and that the original fission of II occurs between carbon and sulfur according to the equation

$$ClCH_2SO_2NH_2 + OH^- = ClCH_2OH + (SO_2NH_2)^-$$

following which the resulting decomposition products undergo further hydrolysis.

The ease of fission between carbon and sulfur in the chloromethanesulfonamides seems to be associated with the presence of labile or ionizable hydrogens on the nitrogen atom. The chlorine was completely removed from II and to the extent of 63% from III after ten minutes of boiling in 5% aqueous sodium hydroxide. Chloromethanesulfondiethylamide, $ClCH_2SO_2N(C_2H_5)_2$, V, was boiled with the same reagent (in which it was insoluble) for thirty minutes with the removal of only 3% of the chlorine. In 5% alcoholic sodium

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[2] Johnson and Douglass, THIS JOURNAL, **60**, 1486 (1938); **61**, 2548 (1939).

[3] Kostsova, *Acta. Univ. Voronegiensis*, **8**, No. 4, 92–117 (1935); *Chem. Abs.*, **32**, 6618 (1938).

[4] Lee and Dougherty, *J. Org. Chem.*, **5**, 81 (1940).

[5] Ziegler and Connor, THIS JOURNAL, **62**, 2596 (1940). The chlorine of II failed to respond to the hydrazine hydrate test for "positive" halogen.

[6] Ramberg and Bäcklund, *Arkiv. Kemi. Mineral. Geol.*, **13A**, No. 27, 50 pp. (1940); *Chem. Abs.*, **34**, 4725 (1940).

[7] Raschig and Prahl, *Ann.*, **448**, 306–307 (1926).

hydroxide (in which it was soluble) V yielded 43% of its chlorine after one hour of boiling. The same treatment of chloromethanesulfonic acid IV changed only 20% of the chlorine to chloride ion, qualitatively suggesting that the decomposition of V had also taken place by carbon–sulfur fission rather than by preliminary amide hydrolysis. One may even conjecture, without evident means for proof, that the 20% decomposition of chloromethanesulfonic acid, IV, in alcoholic sodium hydroxide solution may also be an example of carbon–sulfur fission.

Experimental Part

The physical properties of chloromethanesulfonyl chloride and its derivatives previously reported do not agree with those determined by the authors.

Chloromethanesulfonyl Chloride, I.—Prepared by the action of chlorine on a cold water suspension of trithiane: b. p. 77° (23 mm.), $n^{20}\mathrm{D}$ 1.4868, $n^{25}\mathrm{D}$ 1.4851, $d^{0°}_{4}$ 1.6971, $d^{20°}_{4}$ 1.6672, $d^{30°}_{4}$ 1.6530 (*cf.* Kostsova,[3] Lee and Dougherty[4]).

In fractionating 150 g. of I through an efficient glass spiral-filled column a small amount of colorless solid collected in the condenser at the start of the distillation but was dissolved by the succeeding liquid. The first fraction containing most of the dissolved solid had an index of refraction $n^{20}\mathrm{D}$ 1.4945. In succeeding fractions the index of refraction reached a minimum at $n^{20}\mathrm{D}$ 1.4868. In preparations when the chlorination was incomplete a yellow product was obtained. The product from one such preparation was distilled from an ordinary Claisen flask into four fractions as follows[8]

Fraction	A	B	C	D
$n^{24}\mathrm{D}$	1.5021	1.4977	1.4945	1.5175

Chloromethanesulfonamide, II.—Colorless prisms from mixed ether–petroleum ether; needles from benzene; very soluble in water; m. p. 73–74°, b. p. 185° (20 mm.) (*cf.* Kostsova).[3] *Anal.* Calcd. for CH_4O_2NClS: N, 10.81. Found: N, 10.68.

Chloromethanesulfonanilide, III.—Colorless polygonal prisms from 50% alcohol, m. p. 81–82°. *Anal.* Calcd. for $C_7H_8O_2NClS$: N, 6.81. Found: N, 6.89.

Chloromethanesulfon-*p*-Toluide, $ClCH_2SO_2NHC_6H_4$-CH_3-*p*.—Glass-like prisms from ether–petroleum ether, m. p. 96–97°. *Anal.* Calcd. for $C_8H_{10}O_2NClS$: N, 6.38. Found: N, 6.31.

Chloromethanesulfondiethylamide, V.—Colorless plates from ether, insoluble in water, m. p. 45°. *Anal.* Calcd. for $C_5H_{12}O_2NClS$: N, 7.57. Found: N, 7.62.

Summary

1. The properties of chloromethanesulfonyl chloride and several of its derivatives are described.

2. The chlorine of the chloromethanesulfonamides is not readily removed in metathetical reactions and these compounds are not promising intermediates for the preparation of aminomethanesulfonamides.

3. The chloromethanesulfonamides are decomposed by sodium hydroxide by fission of the molecule between the carbon and sulfur atoms rather than by preliminary amide hydrolysis.

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[8] These results suggest that the chlorination of trithiane produces at least two substances in addition to I. It is the intention of the junior author to investigate further the identity of these other products to determine, if possible, the mechanism of the chlorination reaction.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Anthocyanidin-Like Pigments from α-Naphthohydroquinones

BY MARY FIESER AND LOUIS F. FIESER

In an investigation of the condensation of β-naphthohydroquinone with aldehydes under the influence of hydrogen chloride in benzene solution, it was found that two molecules of the former compound react with one of the aldehyde to give colorless substances of the type $C_{10}H_6(OH)$-$OCHArC_{10}H_5(OH)_2$.[1] The sensitive substances are cleaved easily by concentrated sulfuric acid, for example to the enolic tautomer of 4-benzyl-1,2-naphthoquinone. α-Naphthohydroquinone was observed to react with aldehydes in an apparently similar manner, but no crystalline products could be isolated. The course of the reaction evidently is highly dependent upon the conditions, for on using a mixture of acetic and hydrochloric acids in place of dry hydrogen chloride and benzene we obtained pigments of the type first described in a preliminary report by Wurgaft,[2] who stated that in acetic acid solution α-naphthohydroquinone condenses with benzaldehyde in the presence of hydrogen chloride to give a sparingly soluble, crystalline red compound of the formula ArC_{21}-

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[1] Fieser and Fieser, THIS JOURNAL, **61**, 596 (1939).

[2] Wurgaft, *J. prakt. Chem.*, **49**, 551 (1894).