

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, PURDUE UNIVERSITY]

Organic Syntheses with Sulfuryl Chloride¹

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The present investigation is a study of sulfuryl chloride in condensation reactions with the lower aliphatic alcohols and the lower dialkylamines.

Esters of Chlorosulfonic Acid.—Since there is some disagreement in the values of the physical constants of the esters of chlorosulfonic acid, we have prepared these substances again and have purified them by careful rectification.²

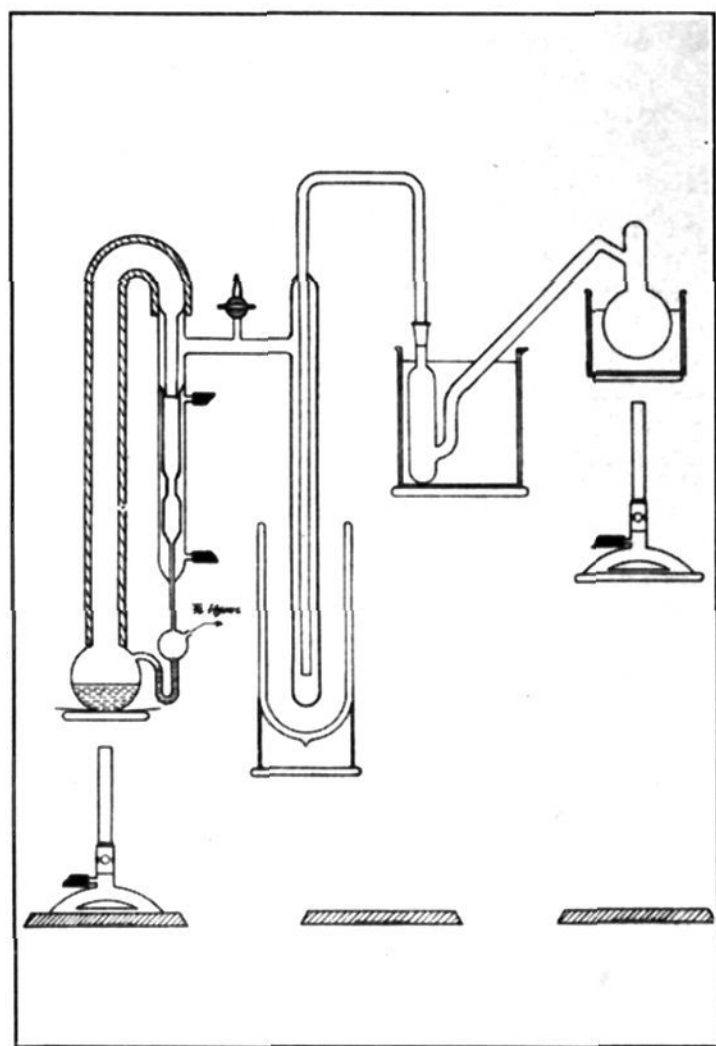


Fig. 1.

Dialkylaminesulfuryl Chlorides.—The lower dialkylaminesulfuryl chlorides may be prepared by the action of sulfuryl chloride on the amine hydrochlorides. However, these chlorides may be obtained in better yields by the careful addition of the amine to a large excess of sulfuryl chloride, followed by gentle refluxing for twenty-four hours.

(1) Abstracted from a portion of a thesis submitted by W. W. Binkley in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1939.

(2) Binkley and Degering, *THIS JOURNAL*, **60**, 2810 (1938).

Experimental

Sulfuryl chloride (one-third mole) was placed in a three-necked distilling flask equipped with a mechanical stirrer, a reflux condenser, and a small dropping funnel. The flask was surrounded with an ice-bath, and the amine (one-third mole) was added very slowly to the sulfuryl chloride during vigorous agitation. The reaction mixture was warmed and poured into a flask which was connected to a reflux condenser by means of a ground-glass joint. Gentle refluxing was held for twenty-four hours. The dialkylaminesulfuryl chlorides were extracted from the reaction mixture by means of anhydrous ethyl ether and the dimethyl and diethyl compounds purified by rectification under diminished pressure. However, the di-*n*-propyl and di-*n*-butylaminesulfuryl chlorides will not withstand long heating and are better purified by repeated distillations under diminished pressure in the apparatus shown in Fig. 1. The characteristic physical constants and analyses are collected in Table I.

TABLE I

-Aminesulfuryl chloride	d_{25}^4	Ref. index 20°	B. p., °C.	Chlorine, %	
				Calcd.	Found
Dimethyl	1.337	1.4526	66.0/10	24.74	24.7
Diethyl	1.221	1.4564	69.0/5	20.70	20.8
Di- <i>n</i> -propyl	1.195	1.4615	83.5/4	17.79	17.9
Di- <i>n</i> -butyl	1.142	1.4648	95-6/3	15.60	15.5

All the lower dialkylaminesulfuryl chlorides have an irritating effect on the skin, and the dimethylaminesulfuryl chloride is also a lachrymator. They are colorless liquids insoluble in water but dissolve in the common organic solvents. They react slowly with aqueous solutions of acids and are not attacked readily by aqueous alkali.

Esters of N,N-Dialkylamidodisulfonic Acids.

—These esters were obtained from the metathesis of diethylaminesulfuryl chloride and the proper sodium alkoxide, and in small yields by the action of the appropriate ester of chlorosulfonic acid on diethylamine.

Experimental

Sodium (0.1 mole), dissolved in 50 ml. of the proper alcohol, was placed in a flask equipped with a mechanical stirrer and a dropping funnel. The dialkylaminesulfuryl chloride (0.1 mole), dissolved in an equal volume of anhydrous ethyl ether, was added dropwise into the sodium alkoxide-alcohol solution during vigorous agitation. After twelve hours of stirring, the insoluble solids were separated with a centrifuge, and the esters purified by rectification under diminished pressure. The average yield was about 6 g. The characteristic physical constants and sulfur contents of only the ethyl, *n*-propyl and *n*-butyl esters are listed in Table II since the methyl ester was not obtained by this procedure.

TABLE II

Diethylamido- sulfonate	<i>d</i> ₄ ²⁵	Ref. in- dex 20°	B. p.		Sulfur, %	
			°C.	Mm.	Calcd.	Found
Ethyl	1.076	1.4307	86	5	17.68	17.8
<i>n</i> -Propyl	1.068	1.4331	80.5	3	16.41	16.3
<i>n</i> -Butyl	1.046	1.4352	73.5	2.25	15.31	15.3

The alkyl *N,N*-diethylamidosulfonates are pleasant smelling liquids, only slightly soluble in water but quite soluble in the common organic solvents.

The methyl esters of the *N,N*-dialkylamidosulfonic acids were prepared by the action of methyl chlorosulfonate on the dialkylamine hydrochlorides and by the alcoholysis of the dialkylaminesulfuryl chlorides with methyl alcohol.

The dialkylamine hydrochloride (0.1 mole) was added in small quantities to methyl chlorosulfonate (0.2 mole) in a small flask. After heating this mixture for one hour on a steam cone, the excess methyl chlorosulfonate was removed with a water pump, and the heating continued for twenty-four hours. The product was purified with methyl alcohol. Yields were 4-6 g.

The dialkylaminesulfuryl chloride (0.1 mole) and 50 ml. of anhydrous methyl alcohol were allowed to reflux for forty-eight hours. The solid ester was crystallized from

the reaction mixture and purified further with methyl alcohol. Yields were 2-4 g.

Analytical data and melting points of the methyl *N,N*-dialkylamidosulfonates are recorded in Table III.

TABLE III

Methyl ester of	M. p., °C.	Sulfur, %	
		Calcd.	Found
<i>N,N</i> -Diethylamido- sulfonic acid	80	19.16	19.3
<i>N,N</i> -Di- <i>n</i> -propyl- amidosulfonic acid	135	16.46	16.4
<i>N,N</i> -Di- <i>n</i> -butyl- amidosulfonic acid	117	14.25	14.2

Summary

Sulfuryl chloride has been condensed with lower aliphatic alcohols and/or lower dialkylamines to yield (1) esters of chlorosulfonic acid, (2) dialkylaminesulfuryl chlorides, and (3) *N,N*-dialkylamidosulfonic acids. Some of the properties of these compounds have been studied and reported.

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RECEIVED JULY 31, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTH PACIFIC COLLEGE OF OREGON]

The Identification of Organic Acids by the Use of *p*-Chlorobenzyl Pseudothiuronium Chloride

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Donleavy,¹ Chambers and Scherer,² and Veibel and Lillelund³ have suggested the use of *S*-benzylthiuronium chloride as a reagent for the identification of organic acids. The method has the advantages of cheapness and ease of preparation of the reagent, rapidity of the reaction, ease of recovery of the salts, and well-defined crystalline structure of the products. Some of the salts, however, are readily hydrolyzed with subsequent decomposition of the free base into products which have very unpleasant odors, and the salts do not show a satisfactory distribution of melting points.

Thirty-one salts of *p*-chlorobenzyl pseudothiouria have been prepared and their melting points determined in an attempt to find a reagent which retains the desirable features of the above method with a diminution of the undesirable ones.

Experimental.—The reagent was prepared by refluxing a mixture of 161 g. of *p*-chlorobenzyl chloride and 76 g. of thiourea in 200 cc. of ethanol for thirty minutes. The

reaction mixture was cooled and the ethanol removed on a suction filter. The *p*-chlorobenzyl pseudothiuronium chloride was recrystallized from a mixture of equal parts of concentrated hydrochloric acid and water. The melting point was 197°. No evidence of polymorphism was observed similar to that recorded by Donleavy¹ and by Veibel and Lillelund³ for *S*-benzylthiuronium chloride. Analysis showed 11.68% N; calculated 11.84%.

In the preparation of the salts of organic acids, the acid was carefully neutralized to phenolphthalein with sodium or potassium hydroxide. Care must be exercised that no excess of base is present, for basic solutions cause the formation of the unstable *p*-chlorobenzyl pseudothiuronium hydroxide. To the aqueous solution of the sodium or potassium salt of the acid an equivalent quantity of a cold 10% alcoholic solution of *p*-chlorobenzyl pseudothiuronium chloride was added. If the salt did not precipitate immediately, some of the solvent was removed under diminished pressure and the remaining solution was cooled in ice water. The precipitated salt was removed by filtration.

The precipitated salt was obtained in the pure state in most cases. Ethanol, ether, benzene, ligroin, carbon tetrachloride, and dioxane were tried as solvents when recrystallization was necessary. Some decomposition took place in hot alcoholic solutions. The solubility of the salts in ether, benzene, ligroin, and carbon tetrachloride was too small to make these practicable solvents. The solubility of the salts in dioxane was satisfactory. No decomposition was apparent when the solution was boiled for one hour.

(1) J. J. Donleavy, *THIS JOURNAL*, **58**, 1004 (1936).

(2) R. F. Chambers and P. C. Scherer, *Ind. Eng. Chem.*, **16**, 1272 (1924).

(3) S. Veibel and H. Lillelund, *Bull. soc. chim.*, (5) **5**, 1153 (1938).