

TABLE II

Diethylamido- sulfonate	<i>d</i> <sub>4</sub> <sup>25</sup>	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*-diethylamidodisulfonates are pleasant smelling liquids, only slightly soluble in water but quite soluble in the common organic solvents.

The methyl esters of the *N,N*-dialkylamidodisulfonic 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*-dialkylamidodisulfonates 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- amidodisulfonic acid	135	16.46	16.4
<i>N,N</i> -Di- <i>n</i> -butyl- amidodisulfonic 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*-dialkylamidodisulfonic acids. Some of the properties of these compounds have been studied and reported.

LAFAYETTE, INDIANA

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

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

BY BARTLETT T. DEWEY AND ROBERT B. SPERRY

Donleavy,<sup>1</sup> Chambers and Scherer,<sup>2</sup> and Veibel and Lillelund<sup>3</sup> 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 Donleavy<sup>1</sup> and by Veibel and Lillelund<sup>3</sup> 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).

By observing the following precautions, hydrolytic decompositions have been prevented: avoid excess base; keep solutions cool during mixing; avoid long contact of salt with mother liquor; recrystallize from dioxane.

The melting points of twenty-two of the salts prepared lie between 140 and 170°. There is not sufficient diversity to make these salts satisfactory derivatives of general application. Mixtures of salts with identical or nearly identical melting points produce depressions of 5 to 9°. They do offer advantages over S-benzylthiuronium salts in making certain distinctions; formate from butyrate, for example.

Analyses of the salts by the Kjeldahl method show good agreement with the calculated values.

#### I. ALIPHATIC SALTS

	M. p. cor., °C.		M. p. cor., °C.
Acetate	140	Oxalate	194
Butyrate	139	Palmitate	146
Caproate	143	Propionate	143
Formate	148	Succinate	167
Monochloroacetate	158	Trichloroacetate	148
Oleate	131	Valerate	142

#### II. AROMATIC SALTS

Benzene sulfonate	184	<i>m</i> -Iodobenzoate	154
Benzoate	155	<i>p</i> -Iodobenzoate	177
<i>o</i> -Bromobenzoate	165	Phthalate	166
<i>m</i> -Bromobenzoate	161	Salicylate	162
<i>p</i> -Bromobenzoate	172	Sulfosalicylate	181
<i>o</i> -Chlorobenzoate	159	<i>o</i> -Toluate	150
<i>m</i> -Chlorobenzoate	157	<i>m</i> -Toluate	151
<i>p</i> -Chlorobenzoate	173	<i>p</i> -Toluate	161
Cinnamate	167	<i>p</i> -Toluenesulfonate	193
<i>o</i> -Iodobenzoate	162		

#### Summary

*p*-Chlorobenzyl pseudothiuronium chloride has been prepared and used as the reagent in the preparation of *p*-chlorobenzyl pseudothiuronium salts of organic acids.

The melting points of the salts of thirty-one organic acids have been recorded.

Dioxane has been found to be a satisfactory solvent for the recrystallization of these salts.

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## Infrared Absorption Studies. IX. Bonding of Hydrogen in Nitrogen Compounds

BY A. M. BUSWELL, J. R. DOWNING AND W. H. RODEBUSH

The behavior of hydroxyl hydrogen has been treated at length in previous publications by ourselves and by other authors. In organic molecules the hydrogen of hydroxyl is usually sufficiently active to show bonding (association, chelation or perturbation) with oxygen, hydroxyl or other basic groups. The hydroxyl group is active in the infrared, showing a strong absorption usually in the neighborhood of 2.75  $\mu$ . When association or chelation takes place, this absorption is increased markedly and shifted to the neighborhood of 3.0  $\mu$ , the extent of the shift and the breadth of the resulting band depending to a considerable extent upon the particular molecules involved. Enolization, for example, is nearly always the result, rather than the cause, of such bonding. With a few exceptions, therefore, the behavior of hydroxyl hydrogen is easily followed by the infrared absorption and definite statements can be made as to whether the hydrogen is bonded or not.

As a matter of fact, little doubt need usually be felt as to the exceptions mentioned above. Certain alcohols show a somewhat lower hydroxyl

frequency (longer wave length) than is customary. Examples are given in Figs. 1 and 2. The hydroxyl in benzoin shows an absorption at 2.87  $\mu$  under circumstances where there seems to be no question of association or chelation. This displacement must be due to the phenyl group but other factors may be involved.

One peculiar case has been discussed elsewhere. Wulf<sup>1</sup> and his collaborators investigated the *cis* monoxime of benzil and found the second harmonic present contrary to the predictions from the assigned structure. So far as the infrared is concerned the two compounds might be identical and both molecules show evidence of association with increasing concentration. As might have been expected, we have verified the results of Wulf that no chelation occurs.

In a previous publication<sup>2</sup> we have presented results of our investigation of association in the acid amides and oximes. Those compounds in which the hydrogen attached to nitrogen is acidic,

(1) G. E. Hilbert, O. R. Wulf, S. B. Hendricks and U. Liddell, *THIS JOURNAL*, **58**, 548 (1936).

(2) A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2444 (1938).