

trast with the case of acetylmesitylene where these forms are almost completely eliminated. This inductance is not apparent for the mesityl ketone, acid chloride or ester, probably because the size of these groups does not allow the complete coplanarity necessary to take full advantage of these effects.

Both the dipole moment and Raman data are consistent in showing values for acetyldurene, acetylmesitylene, 2,4,6-trimethylbenzoyl chloride and nitromesitylene, that are intermediate between the values for the corresponding aromatic and aliphatic compounds.

Summary

It has been shown that the steric effects of ortho methyl groups in nitromesitylene and mesitylenic carbonyl derivatives may be detected readily in the Raman spectra of these compounds. The frequencies of the carbonyl and nitro groups in the above compounds approach the values found for unconjugated derivatives. This indicates that resonance between the ring and carbonyl or nitro group is greatly reduced. These conclusions are consistent with those drawn from dipole moment data for the same compounds.

CHICAGO, ILLINOIS

RECEIVED AUGUST 23, 1941

[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES, NORTHEASTERN UNIVERSITY]

Ammonium Salts of Aliphatic Carboxylic Acids

BY SAVERIO ZUFFANTI

A review of the literature indicates that very few of the ammonium salts of aliphatic carboxylic acids have been prepared in the anhydrous state. Ammonium formate (m. p. 116–117°) has been prepared by Groschuff,¹ and also by Kendall and Adler.² Davidson and McAllister³ prepared ammonium acetate (m. p. 113–114°) by introducing dry ammonia gas into a desiccator containing anhydrous acetic acid in a small evaporating dish placed over soda-lime. The ammonia in the salts thus prepared was always found to check the theoretical value to within a few tenths of one per cent.

Ammonium propionate has been prepared but no constants are reported. Reik⁴ states that, on vacuum distillation, this salt melts with brisk evolution of ammonia and leaves a residue of propionic acid. No information is available on any of the other ammonium salts of aliphatic carboxylic acids.

These salts are very hygroscopic, *i. e.*, anhydrous ammonium propionate (reported in this paper) has a melting point of 107°, but short contact with the atmosphere caused it to gain water resulting in a product that melts at 45°.

The purpose of this paper is to describe a method of preparing the anhydrous salts and also obtaining their melting points without the necessity of transferring the products and allow-

ing contact with atmospheric moisture. Keeping the salts in an atmosphere of ammonia, during the melting point determination, also decreases the tendency of the salts to decompose into mixtures of salt and free acid which would have varying melting points.⁵

Experimental

Materials.—Formic and acetic acids were made anhydrous by the methods of Kendall and Gross.⁵ All the other acids used were purchased from Eastman Kodak Co. and were made anhydrous by fractional crystallization and distillation under anhydrous conditions until the proper freezing points were obtained.⁶

Apparatus.—The apparatus consists of three 10-cm. U-tubes connected in series. The center U-tube is used as the reaction chamber, while the other two U-tubes are filled with barium oxide and serve as drying tubes. The end U-tube is connected to a bubbler, containing a few cubic centimeters of concentrated ammonium hydroxide, which serves to indicate the rate of flow of the ammonia gas. The center U-tube is immersed in a glycerol-bath to obtain uniform heating. Two thermometers are used to obtain the temperature inside (*t*¹) and outside (*t*²) of the reaction chamber.

Preparation of the Anhydrous Ammonium Salts.—Ammonia gas is allowed to sweep out the system for approximately fifteen minutes. A small amount (about 0.5 cc.) of the anhydrous carboxylic acid is sprayed down the wall of the center U-tube using a medicine dropper with a restricted opening. A thin layer of white crystals of the ammonium salt immediately forms on the wall of the U-tube. The flow of gas is continued at the rate of approximately one bubble per second for a half hour or until the reaction appears to be complete, before starting the melting

(1) Groschuff, *Ber.*, **36**, 1783 (1903).

(2) Kendall and Adler, *THIS JOURNAL*, **43**, 1473 (1921).

(3) Davidson and McAllister, *ibid.*, **52**, 507 (1930).

(4) Reik, *Monatsh.*, **23**, 1053 (1902).

(5) Kendall and Gross, *THIS JOURNAL*, **43**, 1431 (1921).

(6) Belcher, *ibid.*, **60**, 2744 (1938).

point determination. Check runs, with longer reaction periods, were made to check the completeness of the reaction. It is apparent from the analyses that, under the conditions used in this work, there is no tendency for the salts to form crystalline amines with the excess ammonia gas present.

Procedure.—The melting point of the salts is obtained by raising the temperature of the glycerol-bath rapidly to within 15–20° of the melting point of the salt. The difference between t^1 and t^2 is about 8° at this point. Retarding the rate of heating reduced this difference to within 2° in a few minutes. At this point the temperature of the system is slowly raised until the white salt melts.⁷ The flow of ammonia gas is continued throughout the melting point determinations.

The hygroscopicity was estimated by placing a few crystals of the salt on very dry days on a watch glass and observing the rate at which it absorbed moisture and liquefied.

The results obtained with the twelve acids used in these experiments appear in Table I. The melting points are uncorrected.

The accuracy of these results is established by the exact agreement of the observed melting points of ammonium formate and ammonium acetate with the previously reported values.^{1,2,3} Duplicate measurements agreed to within $\pm 1^\circ$. In general the hygroscopicity decreases with increase in molecular weight.

(7) The melting points reported were all taken at atmospheric pressure. When taken at a pressure of 1.5 mm. they were about 7–8° lower and inconsistent. No immediate brisk evolution of ammonia was observed, but on heating considerably above the m. p. decomposition can be seen to take place readily.

TABLE I

Ammonium salt of acid	M. p., °C.	Hygroscopic	Analyses, % NH	
			Calcd.	Found
Formic	116	Very	26.98	26.63
Acetic	114	Very	22.07	21.81
Propionic	107	Extremely	18.68	18.19
<i>n</i> -Butyric	108	Very	16.18	15.72
Isobutyric	118	Slightly	16.18	15.69
<i>n</i> -Valeric	108	Very	14.27	13.93
Isovaleric	91	Extremely	14.27	13.77
<i>n</i> -Caproic	108	Moderately	12.77	12.48
Isocaproic	102	Moderately	12.77	12.52
<i>n</i> -Heptylic	112	Slightly	11.56	11.31
<i>n</i> -Caprylic	114	Slightly	10.56	10.17
<i>n</i> -Pelargonic	115	Slightly	9.72	9.46

The salts of lower molecular weight show a greater tendency to sublime than do those of higher molecular weight. Although no accurate solubility determinations were made, it was obvious from washing out the tubes that the solubility of the salts in water decreases rapidly with increase in molecular weight.

Summary

1. An apparatus for preparing the anhydrous ammonium salts of aliphatic carboxylic acids and determining their melting points is described.

2. The melting points of the anhydrous ammonium salts of twelve of the lower aliphatic acids are reported.

BOSTON, MASSACHUSETTS

RECEIVED JUNE 12, 1941

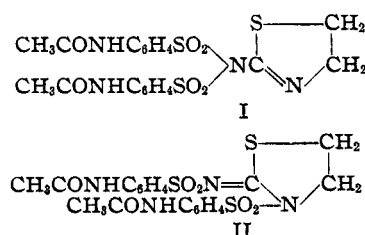
[CONTRIBUTION FROM THE DERMATOLOGICAL RESEARCH LABORATORIES, DIVISION OF ABBOTT LABORATORIES]

2-Sulfanilyl-aminothiazoline

BY GEORGE W. RAIZISS AND LEROY W. CLEMENCE

In a series of N^1 -heterocyclic sulfanilamide derivatives¹ which we prepared and are investigating biologically one of the compounds, 2-sulfanilyl-aminothiazoline, proved to be of particular interest, both chemically and therapeutically. It was prepared by the condensation of *p*-acetylsulfanilyl chloride with 2-aminothiazoline. This reaction produced a bisacetylsulfanilyl derivative,² regardless whether one or two moles of the sulfonyl chloride was used. 2-(Di-acetylsulfanilyl)-aminothiazoline (I) and 2-acetylsulfanilylimino-3-

acetylsulfanilylthiazolidene (II) are the possible structures of the products formed in this reaction.



After hydrolysis of the diacetyl compound with boiling 10% hydrochloric acid, we obtained on cooling a small amount of insoluble material which was shown to be sulfanilic acid. The acid soluble material, precipitated by neutralization, showed

(1) Raiziss, Clemence and Freifelder, *THIS JOURNAL* **63**, 2739 (1941).

(2) Sprague and Kissinger in a recent paper, *ibid.*, **63**, 578 (1941), published while this paper was being written, also observed the formation of a di-substituted derivative and hydrolysis to 2-sulfanilylaminothiazoline.