polymorphism in high molecular weight normal aliphatic hydrocarbons,[2] alcohols,[2] esters,[3] acids[4] and nitriles[5] are reported in the literature. Polymorphism in triglycerides is well known.

The solubility curves for the amine acetates in anhydrous benzene (Fig. 4) were in the same order as the curves for these salts in 95% ethanol. No indication of polymorphism of octadecylamine acetate and hexadecylamine acetate was found with benzene as the solvent.

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(2) Carey and Smith, *J. Chem. Soc.*, 635, 1348 (1933).

(3) Bellinghen, *Bull. soc. chim. Belg.*, **47**, 640 (1938).

(4) Dupré la Tour. *Ann. phys.*, **18**, 199 (1932).

(5) Levene and Taylor, *J. Biol. Chem.*, **59**, 905 (1924).

## Summary

The solubilities of a series of high molecular weight aliphatic primary amine hydrochlorides in 95% ethanol and of a series of high molecular weight aliphatic primary amine acetates in 95% ethanol and in anhydrous benzene have been determined.

Polymorphic modifications of octadecylamine acetate and hexadecylamine acetate are reported.

CHICAGO, ILLINOIS RECEIVED MAY 2, 1941

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

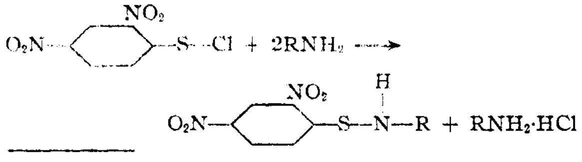
# The Formation of Solid Derivatives of Amines. II

BY JOHN H. BILLMAN,[1] JOSEPH GARRISON, R. ANDERSON AND BERNARD WOLNAK

It has been shown[2] that *o*-nitrobenzenesulfenyl chloride can be used advantageously for the identification of amines since the derivatives form readily, are usually solid, and can be decomposed quickly to give nearly quantitative yields of the amine hydrochlorides. However, some low-melting amines give oily or low-melting derivatives and it therefore appeared of interest to test the feasibility of using 2,4-dinitrobenzenesulfenyl chloride for the identification of amines.

2,4-Dinitrobenzenesulfenyl chloride was prepared as a yellow solid (m. p. 94–96°) from 2,2′,4,4′-tetranitrodiphenyl disulfide and chlorine by a method analogous to the one described for the preparation of *o*-nitrobenzenesulfenyl chloride.[3] When removing the nitrobenzene which is used as a solvent for the reaction, care must be taken to keep the temperature below 135°. Vigorous decomposition is likely to occur above this temperature.

The amides (Table I) were prepared readily by the addition of an ethereal solution of the 2,4-dinitrobenzenesulfenyl chloride to an ethereal solution of the amine at room temperature. The reverse procedure worked equally well with aromatic amines.



In the case of an aqueous solution of an amine, enough ether was added to make the mixture homogeneous before reaction. Addition of the reagent was continued until no further precipitation was noticed. The amine hydrochloride was filtered off and washed with ether; the filtrates were combined and evaporated until all of the ether was removed. The resulting material was dissolved in hot 95% alcohol and recrystallized two or three times from this solvent. The addition of pyridine to the ethereal solution of the amine before the addition of the reagent did not in any way aid the reaction. A solution containing 10% alkali failed to dissolve any of the primary amine derivatives.

TABLE I

PROPERTIES OF THE AMINE DERIVATIVES

| Amines | M. p.[a] of amides, °C. | Anal. of amides, % N Calcd. | Found |
|---|---|---|---|
| Aniline | 142.5–143 | 14.43 | 14.33 |
| *p*-Anisidine | 158 –159 | 13.09 | 13.06 |
| *p*-Bromoaniline | 180.5–181 | 11.36 | 11.17 |
| *n*-Butylamine | 88.5– 89 | 15.50 | 15.40 |
| *p*-Chloroaniline | 164 –164.5 | 12.91 | 13.11 |
| Cyclohexylamine | 109.5–110 | 14.14 | 14.06 |
| Ethylamine | 66 – 66.5 | 17.28 | 17.17 |
| Methylamine | 99 – 99.5 | 18.34 | 18.23 |
| N-Methylcyclohexylamine | 95.5– 96 | 13.46 | 13.32 |
| α-Naphthylamine | 188.5–189 | 12.32 | 12.29 |
| β-Naphthylamine | 167 –168 | 12.32 | 12.27 |
| *n*-Propylamine | 94 – 94.5 | 16.34 | 16.33 |
| *o*-Toluidine | 155 –156 | 13.77 | 13.73 |
| *p*-Toluidine | 161 –161.5 | 18.77 | 18.63 |

[a] Melting points are uncorrected.

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(1) Present address: Indiana University, Bloomington, Indiana.

(2) Billman and O'Mahony, THIS JOURNAL, **61**, 2340 (1939).

(3) "Organic Syntheses," Vol. XV, 1935, p. 45.

The melting points of all of the 2,4-dinitro amides, except that derived from *β*-naphthylamine, were approximately 20 to 70° higher than the corresponding mononitro amides. All of the amines tested yielded satisfactory solids except *n*-amylamine, which formed an oil.

The 2,4-dinitrobenzenesulfenyl chloride was found to react more rapidly with amines than with water, and it could be used in testing for amines in aqueous solution having a concentration of 30% of the amine.

To study the effect of acid upon the amides, hydrogen chloride was passed for three minutes through ethereal solutions of the amides formed from aniline, *p*-anisidine, ethylamine, *n*-butylamine and N-methylcyclohexylamine. The hydrochlorides were then filtered off, dried and weighed. All were found to have been decomposed by this treatment to yield 90–92% of the original amine hydrochlorides.

The authors wish to thank The Sharples Solvents Corporation and Commercial Solvents Corporation for some of the amines used in this work.

## Summary

1. 2,4-Dinitrobenzenesulfenyl chloride has been found to form desirable solid derivatives of both aliphatic and aromatic amines.

2. The reaction was instantaneous and practically quantitative, one-half of the amine going to form amine hydrochloride, the other half to produce the sulfenamide derivative.

3. Aqueous as well as anhydrous amines may be used.

4. The amide derivatives were readily cleaved with hydrogen chloride to the corresponding amine hydrochloride.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# Hydrogen Fluoride as a Condensing Agent. XV. The Preparation of Esters and Ethers[1]

BY J. H. SIMONS AND A. C. MEUNIER

In this series of papers the use of hydrogen fluoride to promote a number of organic chemical reactions has been described. It has now been found that esters and ethers can be made by the action of this catalytic agent. Secondary olefins reacted with acetic and normal butyric acids to give good yields of esters, whereas the tertiary olefin, trimethylethylene, gave no detectable quantity of amyl acetate when treated with acetic acid, polymerization of the olefin overshadowing any reaction with the acid. It was found that hydrogen fluoride also promoted the esterification of glacial acetic acid with ethyl alcohol, as well as the reverse hydrolysis reaction. All these experiments were performed at atmospheric pressure and approximately 0°.

In a previous paper[2] it was reported that anisole was formed by the action of hydrogen fluoride upon a mixture of phenol and methanol. It has now been found that dicyclohexyl ether can be obtained by the action of cyclohexene on a mixture of cyclohexanol and hydrogen fluoride at 0°. In other attempted preparations of ethers, either there was no appreciable reaction at this temperature or excessive amounts of polymers were formed.

## Experimental

**Reactions of Acids with Olefins.**—The technique was essentially the same as that hitherto employed with hydrogen fluoride in these laboratories.[3]

Molar quantities were used. The olefin was added dropwise to a solution of the acid or alcohol in the catalyst held in an ice-bath. A ratio of at least five moles of catalyst per mole of acid or alcohol was used, due to the reduction of the catalytic activity caused by both the reacting acid or alcohol and the water produced. Esterification was effected with a few hours stirring at 0°. In some cases, redistillation was necessary to obtain a pure product. Acetic acid reacted with cyclohexene to form cyclohexyl acetate, b. p. 173.5° at 735, $n^{19.5}\text{D}$ 1.4405, $d^{20}$ 0.9732, in a yield of approximately 70%, and with no tar formation. Normal butyric acid reacted with the same olefin to give cyclohexyl *n*-butyrate, b. p. 207.6° at 735, $n^{20}\text{D}$ 1.4423, $d^{20}$ 0.9431, in the same yield. Acetic acid reacted with a mixture of octenes 1 and 2 to give octyl acetate, b. p. 192° at 721, $n^{20}\text{D}$ 1.4146, $d^{20}$ 0.8628, in approximately 29% yield and *n*-

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(1) For the previous paper of this series see Simons and Bassler, THIS JOURNAL, **63**, 880 (1941).

(2) Simons and Passino, *ibid.*, **62**, 1624 (1940).

(3) Simons and Archer, *ibid.*, **60**, 2952 (1938).