

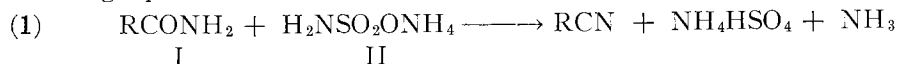
# SYNTHESIS OF NITRILES BY FUSION OF AMIDES WITH AMMONIUM SULPHAMATE<sup>1</sup>

BY JEAN L. BOIVIN

## Abstract

It has been found that a good yield of nitriles can be obtained by fusing amides with ammonium sulphamate. The method has been applied successfully to simple aliphatic and aromatic amides. There is evidence that the mechanism of this transformation involves reaction between amides and ammonium sulphamate, giving rise to ammonium N-alkoyl or N-aroysulphamates which rearrange into ammonium bisulphate and nitriles.

During the course of a study carried out in this laboratory on nitriles, it was found that these substances could be prepared by the fusion of amides (I) with either ammonium sulphamate (II) or a mixture of sulphamic acid and ammonium carbonate at 180–210°C. The reaction takes place with the liberation of ammonia and the formation of ammonium bisulphate according to the following equation:—



The above reaction was carried out, using various amides as starting materials. Liquid nitriles were distilled over, whereas solid nitriles were extracted with a suitable solvent.

The ease of this preparation and the good yields obtained (see Table I) compare favorably with the usual methods of preparing nitriles. The main disadvantage lies in the high cost of the ammonium sulphamate. This was minimized, however, by preparing it *in situ* by heating equivalent amounts of ammonium carbonate and sulphamic acid which is now manufactured from urea and fuming sulphuric acid (4, 7). The yields reported in Table I were obtained by fusing equimolar quantities of reagents. However, nearly quantitative yields were obtained on employing a small excess of ammonium sulphamate.

The transformation of amides into nitriles is known to take place through dehydration of the amide (6). It was of interest to know what role ammonium sulphamate played in this dehydration.

Since according to Equation (1) one mole of ammonium bisulphate is formed from one mole of ammonium sulphamate, it could be thought that the essential dehydration step comprises the reaction:—



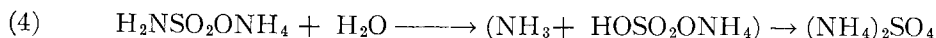
At high temperatures the escape of ammonia would be promoted, thus preventing further reaction to ammonium sulphate according to the following equation:—



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On this basis, it would be expected that in aqueous solution, ammonium sulphamate would readily add water in accordance with the following scheme:—



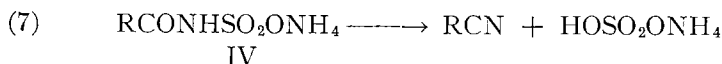
Actually, such addition of water to ammonium sulphamate does not take place at all readily. After refluxing for 15 hr. in aqueous solution, ammonium sulphamate was recovered almost intact and only traces of sulphate could be detected. Again, whereas glycerol yields acrolein when heated in the presence of a dehydrating agent, the fusion of ammonium sulphamate with glycerol at 200°C. gave no acrolein and only traces of sulphate.

From the above data, it is evident that ammonium sulphamate does not behave simply as a normal dehydrating agent, and an alternative reaction mechanism must be sought.

Berglund (2) reported that the fusion of sulphamic acid alone yields sulphur dioxide, sulphuric acid, nitrogen, and water. He also stated that ammonium sulphamate (m.p. 131°C.) when heated at about 170–180°C. is transformed into ammonium imidodisulphonate (III) and ammonia (Equation (5)).



By analogy it appeared possible that a mechanism involving an initial condensation with elimination of ammonia, followed by internal rearrangement and splitting, would account for nitrile formation.

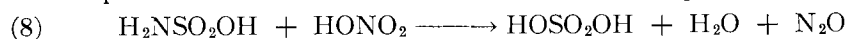


In order to prove this mechanism of formation of nitriles by the action of sulphamates on amides, the following experiments were made. Firstly, the stoichiometric quantities illustrated in Equation (1) were verified by analysis. When equimolar amounts of acetamide and ammonium sulphamate were fused, nearly one mole of ammonia was evolved while acetonitrile was isolated in 90% yield.

The total sulphate present in the residue was found to be equal to 1.01 moles. However, the ammonia formation in this reaction (Equation (6)) is not entirely conclusive, since the sulphamate fused alone gives half a mole of ammonia (Equation (5)).

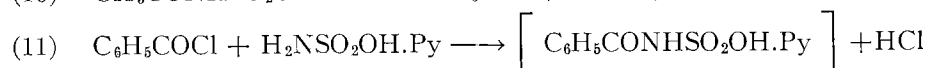
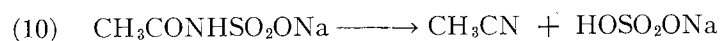
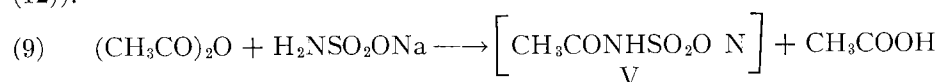
Ammonium N-benzoylsulphamate (IV, R: C<sub>6</sub>H<sub>5</sub>) was synthesized unequivocally by reacting benzamide with a solution of sulphuric acid in acetic anhydride. The benzamide salt of N-benzoylsulphamic acid was converted by means of ammonia into compound IV. This salt, which is not described in the literature, had a melting point of 190–191°C. A cold aqueous solution of this N-substituted sulphamate showed no precipitation with barium ion, but, at the boiling point, barium sulphate was formed. Moreover, cold dilute nitric

acid oxidized IV to a sulphate; it is known from the work of Baumgarten (1) that sulphamic acid or its salts could be oxidized to sulphuric acid.



When ammonium N-benzoylsulphamate was heated above its melting point, benzonitrile and ammonium bisulphate were isolated in quantitative yield, no ammonia being produced during the fusion (Equation (7)).

The same reactions were carried out, although not as clearly, owing to difficulties of purification of intermediate products, when sodium sulphamate was treated with acetic anhydride to give rise to the expected sodium N-acetylsulphamate (V). The residue, after evaporating the reaction mixture to dryness, was heated in the usual way, whereupon acetonitrile distilled over and sulphates were formed (Equations (9) and (10)). Similarly, the action of benzoyl chloride on sulphamic acid in a pyridine solution gave a product from which benzonitrile was obtained on heating the residue (Equations (11) and (12)).



From this study it is concluded that the transformation of amides into nitriles by means of ammonium sulphamate is not a simple dehydration. It involves deamination and condensation between the amides and ammonium sulphamate, giving rise to ammonium N-alkoyl or N-aroysulphamates which rearrange into nitriles.

## Experimental

### *Preparation of Nitriles*

#### *(a) Liquid Nitriles*

In a distilling flask equipped with a short column were placed finely powdered sulphamic acid (9.7 gm., 0.10 mole), ammonium carbonate (9.6 gm., 0.05 mole), and an amide (0.10 mole). The mixture was heated in a metal bath at 100–120°C. whereupon the formation of ammonium sulphamate took place with evolution of carbon dioxide. Then the temperature was raised to 150–160°C. whereupon ammonia was evolved and the ammonium N-alkoyl or N-aroysulphamate was formed. At 190–200°C., the nitrile was produced and distilled over. The results are shown in Table I.

#### *(b) Solid Nitriles*

The proportions used were the same as in the above preparation and the heating was effected in the same way. When reaction was complete, the mix-

ture was cooled and boiled with water to dissolve the ammonium salt. The water insoluble material was filtered, washed with water, and crystallized from a suitable solvent. The results are summarized in Table I.

TABLE I  
PREPARATION OF NITRILES, RCN

R	B.p., °C.	M.p. °C.*	$n_D^{20}$	% Yield†
CH <sub>3</sub>	81-82	—	1.3460 <sup>20</sup>	90
C <sub>2</sub> H <sub>5</sub>	96-97	—	1.3689 <sup>15</sup>	91
C <sub>3</sub> H <sub>7</sub>	117-118	—	1.3816 <sup>25</sup>	90
C <sub>6</sub> H <sub>5</sub>	190-191	—	1.5290 <sup>20</sup>	85
<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	—	146-147	—	92

\* All melting points are uncorrected.

† Yields obtained from equimolar amounts of amides and ammonium sulphamate.

An excess of 0.2 mole of ammonium sulphamate gave a nearly quantitative yield.

#### *Ammonia and Sulphates Formed in the Reaction*

In a distilling flask, a mixture of ammonium sulphamate, m.p. 131°C. (11.4 gm., 0.10 mole) and acetamide (5.9 gm., 0.10 mole) was fused in the manner described above. The ammonia eliminated during the reaction was swept from the flask by a stream of nitrogen and absorbed in an acid solution. The amount of ammonia titrated was equal to 1.62 gm., which is equivalent to 0.095 mole. The residue, after the acetonitrile had been distilled over, was analyzed as it was. Calc. for SO<sub>4</sub>HNH<sub>4</sub>: SO<sub>4</sub>, 83.5%; NH<sub>3</sub>, 14.8%. Found: SO<sub>4</sub>, 84.3%; NH<sub>3</sub>, 15.1%. Since nitric acid readily oxidized sulphamic acid, the precipitation of barium sulphate was made in dilute hydrochloric acid.

#### *Heating of Ammonium Sulphamate with Water and Glycerol*

Ammonium sulphamate, fused alone at 180°C. and then at 300°C., gave a good yield of ammonium imidodisulphonate (5). When ammonium sulphamate was boiled under reflux for 15 hr., no ammonia was evolved and the starting material was recovered unchanged. A mixture of ammonium sulphamate and glycerol heated at 200-220°C. did not yield acrolein.

#### *Ammonium N-Benzoylsulphamate (IV, R: C<sub>6</sub>H<sub>5</sub>)*

To a cold mixture of acetic anhydride (70 gm.) and concentrated sulphuric acid (9.6 gm., 0.098 mole) was added benzamide (24.2 gm., 0.2 mole). The mixture was stirred at room temperature. When all the benzamide was dissolved, a new crystalline solid separated out. The mixture was allowed to stand in the refrigerator overnight. The solid was filtered, washed with acetic anhydride, and finally several times with anhydrous ether. This benzamide salt of N-benzoylsulphamic acid melted at 150-151°C., instead of 145-146°C. as reported by Bühner (3). Yield, 30.5 gm. (94%). This sulphate-free substance was dissolved in cold ammonium hydroxide (10%, 200 ml.). Benzamide, which

separated out, was filtered, while the aqueous layer was extracted several times with ether to remove any dissolved benzamide. Then the aqueous solution which was free from sulphate was evaporated *in vacuo*. If evaporation was done at 50–60°C., some sulphate was formed. The crystalline compound obtained melted at 190–191°C. with decomposition. Yield, 20.3 gm. (93% from benzamide). Calc. for  $C_7H_{10}O_4N_2S$ : S, 14.6%. Found: S, 14.7%. The sulphur content was determined by boiling the sample in a dilute solution of nitric acid and adding barium chloride.

*Benzonitrile from Ammonium N-Benzoylsulphamate*

Ammonium N-benzoylsulphamate (2.18 gm., 0.01 mole) was fused at 200°C. for one hour. No ammonia was formed. Benzonitrile distilled over, b.p. 190–191°C. Yield, 0.8 gm. By washing the apparatus and extracting the residue with ether, an additional quantity of benzonitrile was obtained amounting to 0.2 gm. The total yield amounted to 1.0 gm. (97%). By treating the residue with barium ion in dilute hydrochloric acid, 2.35 gm. (0.0101 mole) of barium sulphate was formed.

*Action of Acetic Anhydride on Sulphamates*

A mixture of acetic anhydride (50 ml.), sulphamic acid (9.7 gm., 0.1 mole), and sodium carbonate (5.3 gm., 0.05 mole) was refluxed for five hours. The mixture was evaporated to dryness under reduced pressure. The residue was heated at 200–220°C. whereupon acetonitrile distilled over, b.p. 82°C., without any formation of ammonia. Yield, 3.0 gm. (73%). The residue, which contained a large amount of sulphates, was not analyzed.

*Action of Benzoyl Chloride on Sulphamate*

A mixture of benzoyl chloride (14.0 gm., 0.10 mole) and finely divided sulphamic acid (9.7 gm., 0.10 mole) in pyridine (50 ml.) was refluxed for five hours. After the mixture was evaporated to dryness, the residue was heated at 200–220°C., whereupon benzonitrile distilled over, b.p. 190–191°C. Yield, 8.2 gm. (80%). No ammonia was evolved during the distillation. The residue contained a large amount of sulphates.

### Acknowledgment

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### References

1. BAUMGARTEN, P. Ber. 71: 80. 1938.
2. BERGLUND, E. Bull. soc. chim. France, 29 (2): 422. 1878.
3. BÜHNER, A. Ann. 333: 283. 1904.
4. CUPERY, M. E. Ind. Eng. Chem. 30: 627. 1938.
5. FERNELIUS, W. C. Inorganic syntheses. Vol. 2, 1st ed. McGraw-Hill Book Company, Inc., New York. 1943.
6. GATTERMANN, L. Laboratory methods of organic chemistry. 24th ed. MacMillan and Co. Ltd., London, 1943.
7. GORDON, W. E. and CUPERY, M. E. Ind. Eng. Chem. 31: 1237. 1939.