[Contribution from the Chemical Laboratory of Stanford University]

AMMONO FURALDEHYDES

By Harold H. Strain

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Introduction

Because extensive investigations have shown that furaldehyde very closely resembles the common aromatic aldehydes in its chemical properties, a study of the reaction of furaldehyde with ammonia was undertaken with the hope of obtaining a series of compounds analogous to those obtained by the reaction of benzaldehyde with ammonia. Thus furaldehyde and ammonia should form hydrofuramide

$$3C_4H_3OCH{=}O + 2NH_3 = (C_4H_3OCH{=})_3N_2 + 3H_2O$$

just as benzaldehyde has been found to react with ammonia to form hydrobenzamide.[1] The hydrofuramide should then react with liquid ammonia to form furylidene-imine which is analogous to benzylidene-imine.[1]

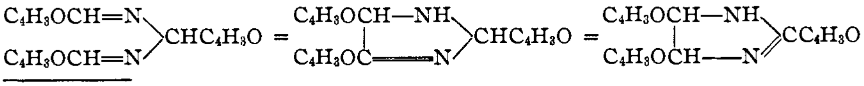
$$(C_4H_3OCH{=})_3N_2 + NH_3 = 3C_4H_3OCH{=}NH$$

Hydrofuramide and furylidene-imine may also be regarded as aldehydes of an ammonia system of compounds as postulated by Franklin and his co-workers.[1,2] These ammono furaldehydes should therefore undergo the reactions characteristic of the ammono aldehydes such as condensation, nitridation, etc.

As a matter of fact several of the reactions mentioned above were demonstrated. However, the ammono furaldehydes proved to be much more reactive and much less stable than the corresponding ammono benzaldehydes. This reactivity, marked by ease of condensation, prevented the formation of furylidene-imine from hydrofuramide, as will be described later. As a result, only the reactions of hydrofuramide could be studied.

The formation of hydrofuramide from furaldehyde and aqueous ammonia has long been known.[3]

When hydrofuramide is treated with liquid ammonia under conditions which should ammonate it to furylidene-imine, a condensation takes place which results in the formation of furine, trifuryldihydro-imidazole. This reaction is similar to the condensation of hydrobenzamide to amarine which workers in this Laboratory consider to be analogous to the benzoin condensation followed by a Cannizzaro reaction.[4]



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[1] Strain, This Journal, **49**, 1558 (1927).

[2] Franklin, *Am. Chem. J.*, **47**, 285 (1912); This Journal, **46**, 2137 (1924).

[3] Fownes, *Ann.*, **54**, 55 (1844); Schiff, *Ber.*, **10**, 1188 (1877).

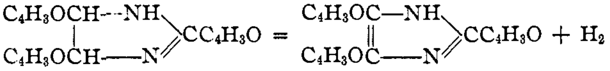
[4] Strain, Ref. 1, p. 1565.

The formation of furine from hydrofuramide has also been accomplished by heating hydrofuramide with aqueous alkali.[3] The same reaction takes place quantitatively in liquid ammonia, so that very pure furine may be obtained by simply dissolving hydrofuramide in liquid ammonia and then evaporating or concentrating the solvent until crystallization occurs.

Attempts to nitridize furine with a solution of iodine in ammonia[5] to compounds analogous to those formed by the nitridation of hydrobenzamide such as lophine, cyaphenine, benzonitrile and benzamidine,[1] resulted in the formation of tar.

Similarly, attempts to convert furine into an iso-furine, just as amarine is converted into an iso-amarine, likewise met with failure.

When furine is treated with an excess of potassium amide in liquid ammonia, hydrogen is liberated. However, the quantity of hydrogen is much less than that required by the reaction


I II

In addition it was impossible to isolate the furyl compound corresponding to lophine (Formula II).[6]

Experimental

Preparation of Hydrofuramide.—Freshly distilled furaldehyde was permitted to stand for several days with an excess of concentrated aqueous ammonia, when the crystals of hydrofuramide which had formed were filtered off and recrystallized from alcohol.

Preparation of Furine.—Hydrofuramide, which is only slightly soluble in liquid ammonia at room temperature, dissolves in the course of an hour or so forming furine which is very soluble. The speed of this reaction is greatly increased by the addition of very small quantities of potassium amide. Long thin crystals of the furine thus pre-

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[5] Although we are wont to explain the reactions of a solution of iodine in liquid ammonia on the basis of the formation of ammono hypoiodous acid, there is no direct evidence that such an acid exists. Bergstrom, THIS JOURNAL, **48,** 2319 (1926).

[6] The writer has found that amarine, triphenyldihydro-imidazole, reacts with a solution of potassium amide in liquid ammonia to form hydrogen and lophine, triphenylimidazole. The analogous oxidation of many organic compounds by fused alkalies with the simultaneous evolution of hydrogen has long been known. More recently, Fry, Schulze and Weitkamp [*ibid.*, **46,** 2268 (1924)] have proposed that the reaction is caused by sodium hydroxide which has undergone acidic dissociation.

$$NaOH = NaO^- + H^+$$

The analogous dissociation of potassium amide is illustrated by the following reactions.

$$KNH_2 = KNH^- + H^+$$
$$KNH^- = KN^{=} + H^+$$

Whether such a dissociation takes place in liquid ammonia solution or not is problematical. Solutions of hydrogen chloride in liquid ammonia do not cause the evolution of hydrogen from the hydramides.

pared are obtained by cooling the concentrated solution to −35°. These crystals melt at 117° and when mixed with crystals of furine prepared by boiling hydrofuramide with aqueous potassium hydroxide the mixture melts at 117°. The completeness of the reaction just described is attested by the fact that the residue does not give rise to the red color characteristic of furaldehyde and hydrofuramide when treated with aniline acetate.

Attempts to Ammonate Hydrofuramide to Furylidene-imine.—A suspension of hydrofuramide in liquid ammonia was treated with an excess of ammonium chloride (or ammonium bromide) while the temperature was maintained at −35° for several hours when it was found that the hydrofuramide failed to dissolve at an appreciable rate. By carrying out the reaction at 0° or at room temperature the hydrofuramide dissolved very slowly, indicating its conversion into furylidene-imine or furine. In spite of the fact that large quantities of furine were isolated from the reaction mixture, some furylidene-imine must also have been formed, as evidenced by the formation of furaldehyde when the reaction mixture was treated with aqueous acid. It was impossible to separate the furylidene-imine by crystallization from liquid ammonia.

Attempts to Nitridize Furine and Hydrofuramide.—A suspension of hydrofuramide or a solution of furine in liquid ammonia was cooled to −35° and treated with an excess of iodine. The ammonia was then allowed to boil very slowly at −33° until all the iodine had dissolved. In every experiment brown decomposition products which could not be crystallized were obtained. In many nitridations a few crystals separated from the solution. From 12 g. of furine less than 0.09 g. of crystals were obtained. They were recrystallized from glacial acetic acid and found to melt at 239° uncorr. but could not be identified.

Reaction of Furine and Potassium Amide.—The furine was treated with an excess of potassium amide (more than 1 mole) in liquid ammonia solution, when a very vigorous reaction took place accompanied by the evolution of heat and gas and by the production of red and brown colors. The gas which was collected over water in an eudiometer tube proved to be hydrogen.[7] No pure compounds could be isolated from the reaction mixture. The results of several experiments are tabulated below (Table I).[8]

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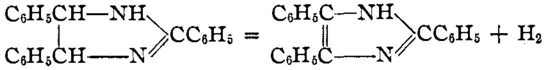
[7] For method of collecting gas see Bergstrom, THIS JOURNAL, **47**, 2320 (1925).

[8] In reporting the reaction of an excess of potassium amide and amarine the writer failed to include any of the experimental results [Strain, *ibid.*, **49**, 1564 (1927)]. They are included here because they illustrate the difference in reactivity of the corresponding benzylidene and furylidene compounds. The experimental procedure was the same as that described above for furine.

Expt.	Amarine, g.	Vol. of H (N. T. P.), cc.	Calcd.	% of calcd.
I	0.40	29.2	30.1	97.0
II	.30	21.4	22.6	94.7

In Expt. II 0.27 g. of lophine was recovered, indicating that the following reaction takes place almost quantitatively.



Salicylhydramide was found to react with potassium amide with the evolution of hydrogen. To effect this reaction a very large excess of potassium amide was necessary (4.5 moles). At the same time a deep blue color was produced. Although two-thirds of the hydrogen was liberated at the end of the first hour, five hours were required for its complete evolution. Two experiments using 1.5-g. portions of salicylhydramide each of which should have liberated 97.1 cc. of hydrogen (N. T. P.) resulted in the production of 89.8 and 72.5 cc. of hydrogen.

TABLE I

EXPERIMENTAL RESULTS

Expt.	Furine, g.	Vol. of H (N. T. P.), cc.	Calcd.	% of calcd.
I	0.268	13	22.4	58
II	0.500	26	41.8	62
III	1.070	43	89.4	48

Furine Nitrate.—Transparent crystals of furine nitrate prepared for the purpose of identifying furine were found to melt at 94° instead of at 154° as previously recorded.[9] After standing for two years, the crystals which had become opaque no longer melted at 94° but decomposed at 180–182°. That the change in appearance which had already been noted[10] was not due to oxidation or to the loss of water of crystallization was proved by analysis. It was then found possible to recrystallize the nitrate, when crystals melting at 94° were obtained. As these crystals were heated above their melting point they became solid again and finally decomposed at 182°. Crystals obtained from an alcohol-ether solution on the other hand decomposed at 182° without previous melting. Whether these two modifications represent dimers or whether they are the result of some more profound change in the molecule such as occurs in amarine was not determined.

The writer wishes to express publicly his appreciation of the many helpful suggestions received from Dr. E. C. Franklin.

Summary

A study of the reaction of furaldehyde and ammonia has shown that furaldehydes of the ammonia system of compounds are formed. These ammono furaldehydes are much less stable than the corresponding ammono benzaldehydes, although they do undergo many reactions characteristic of the latter.

Furine nitrate has been shown to exist in two crystalline modifications.

The reaction of potassium amide and some aromatic ammono aldehydes dissolved in liquid ammonia has been described.

CARNEGIE INSTITUTION OF WASHINGTON
LABORATORY FOR PLANT BIOLOGY
STANFORD UNIVERSITY, CALIFORNIA

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[9] Delépine, *Bull. soc. chim.*, [3] **19**, 175 (1888).

[10] Stenhouse, *Ann.*, **74**, 283 (1850).