should give the corresponding ketones. Actually, its distillation has led to a solid product which was insoluble in water but soluble in alcohol. Under the microscope it was seen to consist of leaflets. The substance (not quite pure) melted at 74°. The pure ketones, stearone, palmitone and myristone, have the melting points of 87.8, 82.8 and 75°, respectively. However, taking into consideration the mode of preparation of the substance, and the inability to purify it for lack of material and, furthermore, that a mixture of compounds not infrequently melts below the constituent having the lowest melting point, it seems reasonable to regard it as a mixture of the ketones mentioned.

Summary

Of the solid products formed by *Bacterium pruni* in skim milk, tyrosine, leucine and the higher fatty acids (a mixture of myristic, palmitic and stearic) have been identified. The latter have been shown to be present partly as such, and partly in the form of a calcium salt.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

HYDROBENZAMIDE AND BENZYLIDENE IMINE AS AMMONO ALDEHYDES

BY HAROLD H. STRAIN

RECEIVED FEBRUARY 24, 1927 PUBLISHED JUNE 7, 1927

Working upon the hypothesis that ammonia is analogous to water, Franklin[1] has shown that it is possible to prepare a number of acids, bases and salts which are related to ammonia as the familiar oxygen acids, bases and salts are related to water. Most of the compounds discussed by Franklin were inorganic substances. In a recent article,[2] however, he has indicated that organic substances containing trivalent negative nitrogen should be considered as ammonia derivatives and he has briefly shown the relation of some of these ammono compounds to the corresponding aquo compounds.

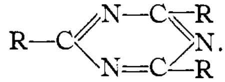
Expatiating the analogies outlined above, one would expect a number of compounds which are related to ammonia as the alcohols, ethers, aldehydes, acetals, ketones, carboxylic acids, etc., to be related to water. As a matter of fact, many such substances have been prepared. Their relationship to the aquo compounds, which is quite evident after a little study, is slightly complicated because of the trivalence of nitrogen which makes possible a greater number of combinations than is possible in the case of oxygen. Thus, corresponding to the alcohols one finds the primary

---

[1] (a) Franklin, *Am. Chem. J.*, **47**, 285 (1912); (b) *Proc. Eighth Int. Cong. Appl. Chem.*, **6**, 119 (1912).

[2] Franklin, THIS JOURNAL, **46**, 2137 (1924).

and secondary amines, while the tertiary amines correspond to the ethers. At this point attention should be called to the fact that the terms primary, secondary and tertiary as commonly applied to the amines bear no relation to the ammono alcohols, for a primary amine may be a primary, secondary or tertiary ammono alcohol, while a secondary amine may be a primary, secondary, tertiary ammono alcohol or a mixed alcohol such as primary-secondary, secondary-tertiary, etc. It follows then that triphenylmethylamine, a primary amine, corresponds to a tertiary ammono alcohol; that diethylamine, a secondary amine, represents a primary ammono alcohol; that propyl*iso*propylamine, a secondary amine, is a primary-secondary ammono alcohol.

The acid amidines, $RC(NH)NH_2$, known in this Laboratory as carbazylic acids, are the ammonia analogs of the carboxylic acids. Upon the loss of ammonia the carbazylic acids are converted into nitriles, which are the acid anammonides corresponding to the acid anhydrides of the water system of compounds; $R—C(NH)NH_2 = R—C\equiv N + NH_3$. Some of these acid anammonides, contrary to the analogous acid anhydrides, can be induced to polymerize to compounds of the type .

Cornell,[3] working in this Laboratory, has shown that the nitriles react with metallic amides, the ammono bases, to form salts of the amidines, the ammono acids, just as the acid anhydrides react with aquo bases to form aquo salts. He has found that the metallic salts of the amidines decompose upon heating, forming a hydrocarbon and cyanamide, a reaction entirely analogous to the formation of a hydrocarbon and carbon dioxide by the pyrogenetic decomposition of the sodium salts of the carboxylic acids.

From a theoretical point of view one might expect to obtain the ammono aldehydes by substituting the NH= group for the oxygen atom in the aldehyde molecule. However, the compounds thus obtained contain a hydrogen atom attached to nitrogen, in which respect they resemble the ammono acids and the ammono alcohols; $CH_3CH=O + NH_3 = CH_3$-$CH=NH + H_2O$. These aldimines, therefore, should exhibit acidic or alcoholic as well as aldehydic properties.

Alkyl and aryl derivatives of the amines, better known as Schiff's bases, must be regarded as ammono acetals as well as ammono aldehydes. A large number of such substances have been prepared and are noted for their conspicuous aldehydic properties.

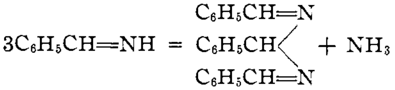
Just as some of the aquo aldehydes, chloral for example, add water to form the dihydroxy compounds, so certain ammono aldehydes might be expected to add ammonia, forming the diamino compounds. Although

---

[3] Cornell, *Thesis*, Stanford University, 1926.

the diamino derivatives, like many of the corresponding dihydroxy compounds, are unknown, their alkyl and aryl derivatives have been prepared and are entirely analogous to the acetals.

Upon the loss of ammonia the imines are converted into hydramides.



$$3C_6H_5CH{=}NH = \begin{matrix} C_6H_5CH{=}N \\ C_6H_5CH\langle \\ C_6H_5CH{=}N \end{matrix} + NH_3$$

These hydramides contain two true ammono aldehyde groups and one other group which is very similar to the acetals in that two valences of the central carbon atom are satisfied by two nitrogen atoms rather than by the same nitrogen atom.[4]

If the imines and hydramides are analogous to the aquo aldehydes as postulated above, then they should undergo a number of reactions analogous to those which the last-mentioned substances are known to undergo; that is to say, they should give all the characteristic aldehyde reactions, such as the aldol or benzoin condensation, the Cannizzaro reaction, the formation of addition compounds with the acid sulfites and with hydrocyanic acid, the formation of polymers, the formation of oximes and phenylhydrazones with hydroxylamine and phenylhydrazine, the formation of acetals with ammono alcohols. These ammono aldehydes should be reduced to primary ammono alcohols, nitridized to ammono acids, and hydrolyzed to aquo aldehydes.

In order to substantiate the analogy between the corresponding aquo and ammono aldehydes the following experimental evidence is presented, using hydrobenzamide and benzylidene imine as representative aromatic ammono aldehydes.

Ammonolysis of Benzaldehyde.—Laurent[5] observed that benzaldehyde is readily converted into hydrobenzamide when allowed to stand in contact with aqueous ammonia; $2NH_3 + 3C_6H_5CH{=}O = (C_6H_5CH)_3N_2 + 3H_2O$. This reaction must be interpreted as consisting in the ammonolysis of an aquo aldehyde to the corresponding ammono aldehyde, while the inverse reaction, as represented by reading the equation from right to left, consists in the hydrolysis of an ammono aldehyde to an aquo aldehyde.

Hydrolysis of Hydrobenzamide.—When hydrobenzamide is boiled with water or treated with dilute acid it is completely hydrolyzed to benzaldehyde and ammonia.

---

[4] Because of the trivalence of nitrogen it is impossible to formulate an ammono aldehyde which is exactly analogous to the aquo aldehydes. The ammono aldehydes must be mixed aldehyde acids or aldehyde alcohols, as represented by the aldimines, or mixed aldehyde acetals as represented by the Schiff bases and the hydramides. Of course, the hydramides may also be considered as deammonation products of the imines, being related to the latter as the ethers are related to the alcohols and as the acid anhydrides are related to the acids.

[5] Laurent, *Ann.*, **21**, 130 (1837).

Busch[6] found that a similar reaction takes place when hydrobenzamide is treated with alcohol in the presence of hydrogen chloride. In this case alcohol, a substituted water, is the hydrolyzing agent while the products of the hydrolysis are benzylidene imine hydrochloride, an ammono aldehyde, and benzylidene diethyl ether, an aquo acetal. Although Busch made many attempts to separate free benzylidene imine he always met with failure. The explanation of this, however, will be evident when the properties of the substance are considered.

Ammonation of Hydrobenzamide to Benzylidene Imine.—Just as certain aquo aldehydes are hydrated to the dihydroxy compounds, so it is to be expected that hydrobenzamide might be ammonated to benzylidene imine, another ammono aldehyde.[7] That this is true is shown by the following experiments.

When hydrobenzamide is placed in liquid ammonia at room temperature, it is found to be only slightly soluble. Upon warming the solution to about 60° for a few minutes the solubility of the hydrobenzamide is increased to such an extent that the compound may be recrystallized. The recrystallized material melted at 101° and upon analysis it proved to be unchanged hydrobenzamide.

After standing in contact with liquid ammonia for 30 to 40 hours, hydrobenzamide slowly dissolves. By concentrating and cooling the resulting solution, an oil separates which is slow to crystallize. If enough hydrobenzamide (1–2 g.) is used, so that the solution (14–20 cc.) becomes saturated with the oil formed in the reaction, large, transparent crystals of this material are obtained. It also happens that the reaction proceeds much more rapidly if an acid such as ammonium chloride is present; hence, in preparing the following samples, a small amount of acid was generally used. The analyses are given in Table I.

PREPARATION I.—Hydrobenzamide was allowed to stand in liquid ammonia containing ammonium azide. The crystals which formed were washed free of ammonium azide, dried in a vacuum at 25°, and analyzed for nitrogen by the method of Kjeldahl.

PREPARATION II.—The crystals were prepared by ammonating hydrobenzamide with ammonium chloride in liquid ammonia solution.

PREPARATION III.—The material was prepared by ammonating hydrobenzamide in the presence of ammonium bromide.

TABLE I

ANALYSES

Calcd. for $C_6H_5CHN=H$: C, 80.0; H, 6.7; N, 13.3

Preparation	Subs., g.	Base, g.	CO_2, g.	H_2O, g.	Found, %		
					N	C	H
I	0.1226	0.01624			13.2		
II	.2200	.02894			13.2		
III	.1736		0.5072	0.1035		79.7	6.6
IV	.1118		.3252	.0679		79.3	6.8
V	.1132		.3313	.0650		79.8	6.4

---

[6] Busch, *Ber.*, **29**, 2137, 2143 (1896).

[7] This reaction may be looked upon as the ammonation of one aldehyde to another, as has been done, or as the ammonolysis of an ammono acetal to an ammono aldehyde. In the latter case an alcohol and an aldehyde should be formed if the reaction is to be analogous to the hydrolysis of an acetal. However, benzylidene imine is in itself an ammono alcohol as well as an ammono aldehyde; hence, it is found as the sole product of the reaction.

Preparation IV.—A sample was prepared for analysis by dissolving benzylidene imine hydrochloride, obtained by the action of alcohol on hydrobenzamide in the presence of hydrogen chloride, in liquid ammonia and separating the product from the ammonium chloride by crystallization.

Preparation V.—This specimen was prepared by the ammonation of hydrobenzamide without an acid.

Molecular Weight of Benzylidine Imine.—Since aldehydes often polymerize, forming the trimolecular compounds, it was thought that benzylidene imine might exist as the trimer. Attempts were made, therefore, to determine its molecular weight in benzene solution. Upon dissolving in benzene or any solvent other than ammonia, benzylidene imine loses ammonia, forming hydrobenzamide; hence, its molecular weight could not be determined. However, in view of the fact that this compound loses ammonia so easily, it seems reasonable to assume that it actually exists in the monomolecular form.

Deammonation of Benzylidine Imine.—Crystals of benzylidene imine become opaque when allowed to stand in dry air or in a vacuum, due to the loss of ammonia and the simultaneous formation of hydrobenzamide. Similarly, when benzylidene imine is heated very slowly in a capillary tube, the melting point observed is that of hydrobenzamide. The following reaction, then, must take place: $3_6CH_5CH{=}NH = (C_6H_5\text{-}CH)_3N_2 + NH_3$.

In order to ascertain whether or not this reaction is quantitative, some benzylidene imine was heated in a test-tube provided with a two-hole rubber stopper, so that the ammonia evolved could be swept into a standard acid solution by means of a current of air while the sample was heated at 160° for about ten minutes. The ammonia liberated agreed closely with that calculated on the basis of the above reaction.

Anal. Subs., 0.2680. Calcd.: NH_3, 0.01447. Found: 0.01448.

The residue, recrystallized from alcohol, melted at 98–100°, and when mixed with an equal quantity of hydrobenzamide melting at 101°, the mixture melted at 101°.

Reduction of Benzylidene Imine.—Since an aquo aldehyde is reduced to a primary alcohol, it is to be expected that an ammono aldehyde would be reduced to a primary ammono alcohol. That this is true is shown by the following experiment.

One g. of sodium was added to a solution of 0.5 g. of benzylidene imine and 2 g. of alcohol in liquid ammonia. When all of the sodium had reacted, as shown by the disappearance of the blue color, the ammonia was evaporated and the residue was extracted with ether. The ether was then evaporated, the residue dissolved in water and acidified with oxalic acid. A small amount of benzylamine oxalate, m. p. 176°, was obtained. When this material was mixed with pure benzylamine oxalate, m. p. 176°, its melting point was not changed. A small amount of a hydrocarbon, probably toluene, was also formed by the reducing action of the sodium solution.

Similar results were obtained by O. Fischer,[8] who reduced hydrobenzamide in alcoholic solution with sodium amalgam. Besides benzylamine

---

[8] Fischer, *Ber.*, **19**, 748 (1886); *Ann.*, **241**, 328 (1887).

and toluene, Fischer also obtained dibenzylamine, a primary ammono alcohol.

Metallic Salts of Benzylidene Imine.—Because of the negative character of the benzylidene group, benzylidene imine should be regarded as a weak ammono acid and as such it should form metallic salts. As a matter of fact, it reacts with sodium and potassium amides, forming salts which are extremely soluble in ammonia. Benzylidene imine does not dissolve calcium or lithium amides.

SODIUM BENZYLIDENE IMINE.—A solution of benzylidene imine in liquid ammonia dissolves sodium amide, forming a salt which is so soluble that it cannot be made to crystallize from a concentrated solution at —80°. The solution of this salt is very deep red in color.

Two preparations of the sodium salt were made. The first was prepared by allowing benzylidene imine to react with an equivalent quantity of sodium amide. The resulting deep red-colored solution was evaporated to dryness, and the residue analyzed for sodium and nitrogen. The values obtained varied widely from the calculated figures. The second preparation was made in a similar manner except that in this case a large excess of sodium amide was used, the colored solution of the salt being decanted from the excess of sodium amide before it was evaporated. The percentages of sodium and nitrogen in this sample approximated the calculated values.

Since the sodium salt could not be crystallized, concordant analyses could hardly be expected. The analyses also indicated that the salt was partly ammonolyzed, because in each preparation the relative percentage of nitrogen was much too high.

POTASSIUM BENZYLIDENE IMINE.—One-half g. of benzylidene imine was allowed to react with a solution of potassium amide in liquid ammonia. The potassium salt thus formed was crystallized from a concentrated solution at the temperature of a carbon dioxide-ether bath and washed with a small quantity of solvent. The crystals were dissolved, recrystallized, dried in a vacuum at 60° and analyzed. One fifth of the sample was used for each analysis.

Anal. Subs., 0.3940: K_2SO_4, 0.0491; N, 0.00842. Calcd. for $C_6H_5CH{=}NK$: K, 27.3; N, 9.8. Found: K, 28.0; N, 10.7.

When benzylidene imine is treated with an ammono base, a deep red color is always produced. In fact, the potassium salt seems to be colored.

Cannizzaro Reaction.—Benzylidene imine, when heated with potassium amide in ammonia solution, undergoes intermolecular oxidation and reduction just as benzaldehyde does when treated with aqueous potassium hydroxide. In the case of the ammono aldehyde, an ammono alcohol and an ammono acid are the products of the reaction; in the case of the aquo aldehyde, the aquo acid and alcohol are the end products. The analogy between these two examples of the Cannizzaro reaction is shown by the equations $2C_6H_5CH{=}O + KOH = C_6H_5COOK + C_6H_5CH_2OH$; $2C_6H_5CH{=}NH + KNH_2 = C_6H_5C(NK)NH_2 + C_6H_5CH_2NH_2$.

One g. of benzylidene imine, 20 cc. of liquid ammonia, and an excess of potassium amide were sealed up in a bomb tube. Apparently no reaction other than the production of a red color took place after the tube had stood 24 hours. The tube was then heated at 210° for 24 hours in the bomb tubes described by Blair.[9] After cooling,

---

[9] Blair, THIS JOURNAL, **48**, 87 (1926).

the tube was found to contain a considerable quantity of flake-like crystals, which appeared to be identical with those of potassium benzamidine (potassium ammonobenzoate). Since the crystals could not be purified they were not analyzed. The mother liquor was drained from them and evaporated to dryness. The crystals of potassium ammonobenzoate were dried, dissolved in a little alcohol and water, and acidified with hydrochloric and picric acids. Long, needle-shaped crystals of an insoluble picrate soon separated. This picrate, after recrystallization from alcohol, melted at 233°. According to Krafft,[10] the melting point of benzamidine picrate is 233°. When mixed with pure benzamidine picrate the crystals again melted at 233°. The yield of benzamidine was about 20%.

The residue obtained by evaporating the solution decanted from the crystals of potassium benzamidine, was extracted with ether. Upon evaporation of the ether on the water-bath, a liquid was obtained which solidified upon standing in contact with the air. This solidification was due to the absorption of carbon dioxide, which was given off when the compound was treated with acid. An aqueous solution of the ethereal extract formed an oxalate which melted at 176°. When mixed with an equal quantity of benzylamine oxalate melting at 176°, the mixture again melted at 176°.

The residue from the ether extraction melted at 274° when recrystallized from alcohol. It also showed luminescence when treated in the dark with alcoholic potassium hydroxide, thereby proving that it was lophine.

The lophine accounted for about 60% of the benzylidene imine used. Its formation is readily explained, since benzylidene imine in ammonia solution is slowly converted into amarine which, in the presence of the excess of potassium amide, loses hydrogen to form lophine.

Nitridation of Benzylidene Imine.—Upon oxidizing an aldehyde one obtains a carboxylic acid. However, to convert an ammono aldehyde into a carboxylic acid, oxygen and oxygen compounds must be avoided because of the fact that the oxygen may displace the nitrogen, giving rise to an aquo compound. The de-electronizing agent should, therefore, be a nitridizing agent, such as hydrazoic acid, ammono nitric acid,[11] or a solution of iodine in liquid ammonia. These two reagents have been found to give a number of reactions which are analogous to the oxidation reactions of nitric and hypo-iodous acids.[12]

The following experiments show that benzylidene imine is easily nitridized to benzamidine by the action of iodine in liquid ammonia solution.

An excess of iodine was added to a solution of benzylidene imine in liquid ammonia at —39°. The iodine color slowly disappeared without any nitrogen being evolved. All the while a white precipitate separated, which was slightly soluble. When the iodine color had disappeared, the precipitate was washed and dried. It was only slightly soluble in alcohol, ether, benzene and chloroform, and insoluble in water. Recrystallized from alcohol it melted at 231°. The melting point of cyaphenin is 231°.

The washings from the cyaphenin were evaporated to dryness, extracted with a little water and treated with a picric acid solution. A picrate, crystallizing in long needles, soon separated. These crystals melted at 232° after recrystallization from alcohol. Mixed with pure benzamidine picrate they melted at 232.5°.

---

[10] Krafft, *Ber.*, **22**, 1760 (1889).

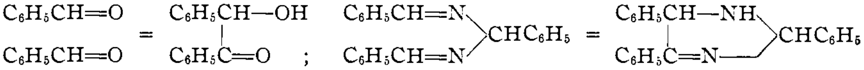
[11] In explanation of the oxidizing (nitridizing) properties of hydrazoic acid, compare Turrentine, THIS JOURNAL, **34**, 385 (1912). Thiele, *Ber.*, **44**, 2522 (1911). Ref. 1b.

[12] Chuck, *Thesis*, Stanford University, **1925**.

The cyaphenin accounted for about 20% of the benzylidine imine used, while the benzamidine accounted for about 40%. A small portion of the benzylidine imine was not nitridized. Some benzonitrile was probably formed, as evidenced by its characteristic odor, but it could not be detected by chemical means.

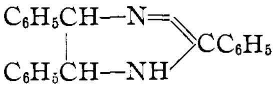
Although benzamidine was the only nitridation product of benzylidene imine which the writer expected to find, the presence of benzonitrile and cyaphenin is easily explained. Upon nitridation, benzylidene imine should form benzamidine, ammonobenzoic acid; $C_6H_5CH{=}NH + INH_2 = C_6H_5C(NH)NH_2 + HI$. The benzamidine then loses ammonia, forming benzonitrile, benzoic anammonide; $C_6H_5C(NH)NH_2 = C_6H_5C{\equiv}N + NH_3$; this then polymerizes to cyaphenin, a polymerized, acid anammonide;[13] $3C_6H_5C{\equiv}N = (C_6H_5C{\equiv}N)_3$.

Benzoin Condensation.—It has long been known that hydrobenzamide is transformed into an isomeric compound when heated.[14] The formation of this isomer, known as amarine, is entirely analogous to the formation of benzoin from benzaldehyde, as the following parallel equations indicate.



The above reactions consist in the nitridation of one aldehyde group to a ketone group and the reduction of the other to a secondary alcohol group.

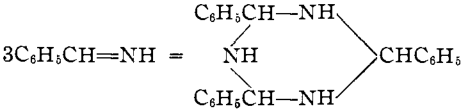
Amarine has been found to exist in the *d*, *l*, racemic, and *meso* forms and, in order to explain this isomerism, Japp and Moir[15] have shown that the structural formula must be



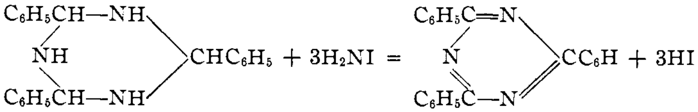
The transformation of the formula obtained by the benzoin condensation into the one just given is another example of the Cannizzaro reaction, in that an ammono ketone has been reduced to a secondary alcohol, while an aldehyde

---

[13] Another feasible explanation of the formation of cyaphenin upon the nitridation of benzylidene imine can be arrived at if we assume benzylidene imine to exist in solution in the monomolecular and the trimolecular forms.



This trimer, which is analogous to the polymerized aldehydes such as paraldehyde, should give cyaphenin upon nitridation.



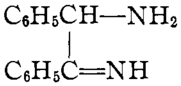
[14] Laurent, *Ann.*, **52**, 359 (1844). Fownes, *Ann.*, **54**, 364 (1845). Bertagnini, *Ann.*, **88**, 127 (1853).

[15] Japp and Moir, *J. Chem. Soc.*, **77**, 608 (1900).

has been oxidized to an acid. Amarine is, therefore, to be regarded as an ammono acid, and an ammono ester.

The formation of amarine from hydrobenzamide takes place almost instantly if a little potassium amide or other ammono base be added to a suspension of hydrobenzamide in liquid ammonia. The amarine thus formed is extremely soluble, remaining as a thick, viscous mass when the solvent is evaporated. Amarine has been obtained in large cubical crystals by very slow evaporation of the ammonia.

Benzylidene imine, when allowed to stand in ammonia for several months, is slowly converted into amarine. As noted previously, the presence of a base does not cause benzylidene imine to change into amarine or lophine except when heated to a comparatively high temperature. The formation of amarine from benzylidene imine may be explained in one of two ways. First, benzylidene imine may lose ammonia, forming hydrobenzamide which then forms amarine by undergoing the benzoin condensation. Second, two molecules of benzylidene imine may undergo the benzoin condensation giving an ammono benzoin,



$$\begin{array}{l} C_6H_5CH\text{—}NH_2 \\ \;\;| \\ C_6H_5C{=}NH \end{array}$$

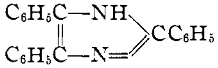
which then loses ammonia with a third molecule of benzylidene imine, thereby forming amarine.

Nitridation of Amarine.—Fischer,[16] in attempting to determine the structure of amarine, found that this substance was easily oxidized to lophine and reported that the reaction seemed analogous to the oxidation of benzoin to benzil. In order to keep within the ammonia system it was deemed interesting to attempt the nitridation of amarine to lophine. This reaction takes place readily when iodine is used as the nitridizing agent, but fails when hydrazoic acid is used.

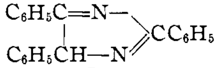
Three-tenths g. of amarine was treated with an excess of iodine in liquid ammonia at —39°. The iodine color slowly disappeared while lophine separated from the solution in characteristic fiber-like crystals. When the iodine had completely reacted, the crystals were washed several times, dried and recrystallized from alcohol. One-fourth g. of lophine was obtained; m. p., 274°.

An attempt to nitridize amarine with hydrazoic acid failed. Upon heating amarine, ammonia and ammonium azide to 150° for eight hours, a precipitate formed which was only slightly soluble in ammonia and which melted at 198°. A second preparation was made using ammonium chloride instead of ammonium azide when the same insoluble substance was formed. This compound proved to be iso-amarine.

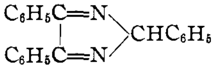
Structure of Lophine.—The structure of lophine has been discussed by many workers, but no one has presented facts which would prove conclusively the structure of this compound. Of the three possible formulas,



I



II



III

---

[16] Fischer, *Ann.*, **211**, 217 (1882).

Japp and Robinson[17] believe Formula I to be correct while Radziszewski,[18] on the other hand, prefers Formula III because benzil, ammonia and benzaldehyde react to form lophine. Kulisch[19] attempted to prepare lophine having a formula corresponding to Formula II by treating benzoin with benzamidine. The lophine which was obtained, however, was identical with that which had been prepared by previous investigators from other substances.

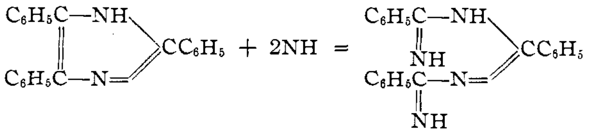
Another argument in favor of Formula I was propounded by Japp,[20] who found that lophine could be oxidized to an equimolecular mixture of benzamide and dibenzamide. The breaking of the union between the two carbon atoms would indicate that they were held by a double bond.

If we regard lophine as an ammono compound, then the conversion of Formula III into Formula II is an example of the Cannizzaro reaction in that an ammono aldehyde has been nitridized to an ammono acid, while an ammono ketone has been simultaneously reduced to an ammono alcohol. Formulas I and II, however, are tautomeric, the former being related to the latter as the enol form of aceto-acetic ester is related to the keto form. This tautomerism should prevent the formation of the optical isomers which one might expect from a casual observation of Formula II. As a matter of fact, no observations of the separation of lophine into optical isomers are on record, while attempts made by the writer to effect a separation, using *d*-tartaric acid, failed because lophine does not form a salt with this acid in alcoholic solution.

In view of this evidence, it appears that Formula I or II probably represents the true structure of lophine, which must then be regarded as an acid ammono ester, or an ammono ketone ester.

To demonstrate the fact that lophine actually possesses acid properties, the author [21] has recently prepared a number of metallic salts of this compound and has shown that lophine in liquid ammonia solution dissolves metallic magnesium.

Nitridation of Lophine.—Since lophine may be oxidized at the double bond to benzamide and dibenzamide, both of which are mixed aquo ammono acids, it is to be expected that lophine might be nitridized to an analogous ammono acid as follows.



---

[17] Japp and Robinson, *Ber.*, **15,** 1268 (1882).

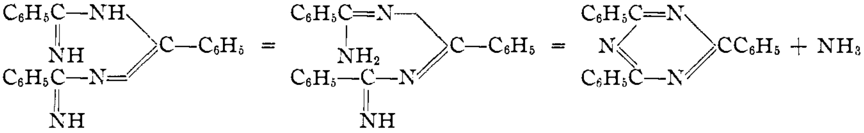
[18] Radziszewski, *Ber.*, **15,** 1493 (1882).

[19] Kulisch, *Monatsh.*, **17,** 300 (1896).

[20] Japp, *Ber.*, **15,** 2416 (1882).

[21] Strain, forthcoming publication

Upon nitridizing lophine with iodine in ammonia, the main product of the reaction was found to be cyaphenin. The formation of this substance from the hypothetical compound given above is easily explained as follows.



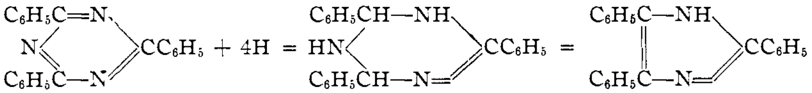
The cyaphenin thus formed is the trimer of the anammonide of a carbazylic acid.

The nitridation of lophine was carried out in the following manner.

An excess of iodine was added to a suspension of 0.25 g. of lophine in liquid ammonia. The solution was then boiled gently to keep the lophine stirred. After five hours the iodine color had completely disappeared while the lophine had been converted into long, silky crystals which did not settle well. These crystals were washed and dried, then washed with water, and finally with boiling alcohol. One-fifth g. of material was obtained; m. p., 230–231°. When mixed with pure cyaphenin melting at 231° the crystals melted at 231°.

The washings from the cyaphenin gave no test for benzamidine when treated with picric acid.

Reduction of Cyaphenin.—By the use of sodium amalgam and alcohol Radziszewski[18] has found it possible to reduce cyaphenin to lophine. This reaction is the reverse of the nitridation reaction described above and may be formulated as taking the following steps.



The formation of a double bond by the loss of a molecule of ammonia is a reaction analogous to the formation of a double bond by the dehydration of alcohols. In the case of the ammono compound, however, the double bond is formed between two carbon atoms which were not attached to each other.

A reaction resembling that just discussed takes place when dibenzylamine, an ammono alcohol, is distilled,[22] ammonia and stilbene being the products of the reaction. Another similar reaction takes place when thiobenzamide, a mixed ammono thio acid, is reduced with zinc dust and hydrochloric acid.[23] In this case the products of the reaction are stilbene, ammonia and hydrogen sulfide.

Addition of Hydrocyanic Acid to Benzylidene Imine.—In developing the ammonia system of compounds, Franklin has shown that hydrocyanic acid possesses aldehydic properties,[24] and that its addition to aquo alde-

---

[22] Brunner, *Ann.*, **151**, 133 (1869).

[23] Bamberger and Lodter, *Ber.*, **21**, 55 (1888).

[24] Franklin, *J. Phys. Chem.*, **27**, 167 (1923).

hydes is to be regarded as an example of the aldol condensation between an aquo and an ammono aldehyde. Now, if hydrocyanic acid should combine with benzylidene imine we should have an example of the aldol condensation between two ammono aldehydes. The following experiment shows that this reaction does take place, the condensation product being a cyanamine analogous to the cyanhydrines: $HC{\equiv}N + C_6H_5CH{=}NH = C_6H_5CH(NH_2)C{\equiv}N$.

One g. of benzylidene imine in solution in liquid ammonia was allowed to stand for several days with an excess of ammonium cyanide, formed by treating sodium cyanide with a slight excess of ammonium chloride in liquid ammonia solution. The solution, which was light yellow in color, was evaporated to dryness and the residue extracted with ether. Upon evaporation of the ether, flaky crystals were obtained; m. p., 55°. According to Minovici,[25] the melting point of benzylidene cyanamine is 55°. The crystals were very hygroscopic and soon decomposed, forming a dark brown mass.

Addition of Hydrocyanic Acid to Hydrobenzamide.—Upon combining hydrocyanic acid and hydrobenzamide, Plöchl[26] found that a compound is formed which contains two molecules of hydrocyanic acid. This di-iminodinitrile still contains an ammono acetal group so that it is easily hydrolyzed to benzaldehyde and benzylidene cyanamine.

In order further to substantiate the analogy between benzylidene imine and benzaldehyde, the reactions of the former with a number of characteristic aldehyde reagents were carried out. In every case the reactions in liquid ammonia showed a great similarity to those of benzaldehyde.

Formation of Benzylidene Phenylhydrazone.—Benzylidene imine reacts readily with phenylhydrazine in ammonia solution, forming benzylidene phenylhydrazone which is very soluble; $C_6H_5CH{=}NH + C_6H_5NH{-}NH_2 = C_6H_5CH{=}N{-}NHC_6H_5 + NH_3$. The benzylidene phenylhydrazone formed by this reaction melted at 155° and when placed in the sunlight showed the color change characteristic of this compound.

Formation of Benzylidene Oxime.—Benzylidene imine reacts with hydroxylamine, forming benzylidene oxime, which is moderately soluble in ammonia. The reaction may be represented by the equation $C_6H_5{-}CH{=}NH + H_2NOH = C_6H_5CH{=}NOH + NH_3$. The benzylidene oxime obtained by the above reaction melted at 36°, and when mixed with benzylidene oxime prepared from benzaldehyde it melted at 35.5°.

Reaction of Benzylidene Imine with Aniline.—Benzylidene imine reacts with aniline, forming benzylidene aniline just as benzaldehyde reacts with aniline to form the same compound; thus, $C_6H_5CH{=}NH + C_6H_5NH_2 = C_6H_5CH{=}NC_6H_5 + NH_3$. The benzylidene aniline thus obtained melted at 54° and showed no depression of the melting point

---

[25] Minovici, *Ber.*, **29**, 2103 (1896).

[26] Plöchl, *Ber.*, **13**, 2118 (1880); **14**, 1139 (1881).

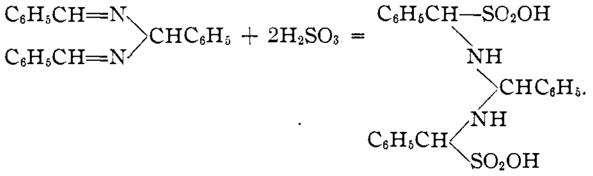
when mixed with some benzylidene aniline prepared by the action of aniline on benzaldehyde.

Reaction of Hydrobenzamide with Aniline.—Hydrobenzamide has been found to react with aniline to form benzylidene aniline and ammonia.[27] This reaction represents the ammonation of an ammono aldehyde by a substituted ammonia to an ammono aldehyde-acetal. The mechanism of this reaction, in all probability, is shown by the equations $(C_6H_5CH)_3N_2 + C_6H_5NH_2 = 2C_6H_5CH{=}NH + C_6H_5CH{=}NC_6H_5$; $2C_6H_5CH{=}NH + 2C_6H_5NH_2 = 2C_6H_5CH{=}NC_6H_5 + 2NH_3$. This reaction is entirely analogous to the formation of benzylidene imine and benzylidene diethyl ether by the action of alcohol on hydrobenzamide.

Addition of Sulfurous Acid to Hydrobenzamide.—Otto[28] has reported that sulfurous acid forms an addition product with hydrobenzamide in absolute alcohol, which has the empirical formula $C_7H_9O_3NS$. This compound is undoubtedly the sulfurous acid addition product of benzylidene imine. Its formation must then take the course shown by the equations $(C_6H_5CH)_3N_2 + 2SO_2 + 4H_2O = 2C_6H_5CH(NH_2)SO_2OH + C_6H_5CH(OH)_2$; $C_6H_5CH(OH)_2 + 2C_2H_5OH = C_6H_5CH(OC_2H_5)_2 + 2H_2O$.

According to Otto, the above reaction took place in absolute alcohol, which was prevented from coming into contact with damp air. In repeating the experimental work van de Griendt[29] has shown that hydrobenzamide will not combine with dry sulfur dioxide in absolute alcohol. Upon the addition of the requisite amount of water, the sulfite addition product described by Otto rapidly crystallizes from the solution.

Since hydrocyanic acid combines with hydrobenzamide to form a di-iminodinitrile, one would expect that sulfurous acid might form an addition compound with this ammono aldehyde. This compound has been prepared by van de Griendt by adding the necessary quantity of water to a solution of hydrobenzamide and sulfur dioxide in benzene. The formation of this substance is shown by the following equation.



$$\left.\begin{array}{l}C_6H_5CH{=}N\\ C_6H_5CH{=}N\end{array}\right\rangle CHC_6H_5 + 2H_2SO_3 = \begin{array}{l}C_6H_5CH{-}SO_2OH\\ \quad\quad NH\\ \quad\quad\quad \rangle CHC_6H_5.\\ \quad\quad NH\\ C_6H_5CH\langle SO_2OH\end{array}$$

If a slight excess of water is added, the hydrobenzamide addition compound hydrolyzes, forming the benzylidene imine addition compound reported by Otto, and benzaldehyde.

In the case of the aquo aldehydes the sulfurous acid addition products

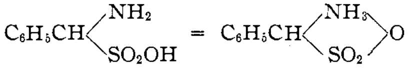
---

[27] Lachowicz, *Monatsh.*, **9**, 695 (1888).

[28] Otto, *Ann.*, **112**, 305 (1859).

[29] van de Griendt, *Thesis*, Stanford University, **1926**.

all exist as salts. Attempts to liberate the free acid have always resulted in the hydrolysis of the compound. The sulfurous acid addition products of hydrobenzamide and benzylidene imine represent combinations unknown in the water system of compounds. Their existence may be explained by assuming the acid and amino groups to form an inner salt, as shown below for the benzylidene imine addition compound.



$$C_6H_5CH\begin{matrix}\diagup NH_2\\ \diagdown SO_2OH\end{matrix} = C_6H_5CH\begin{matrix}\diagup NH_3\diagdown\\ \diagdown SO_2\diagup\end{matrix}O$$

The writer wishes to take this opportunity to express his thanks to Dr. E. C. Franklin for his amiable guidance in the experimental work and for his suggestive criticisms of this paper.

Summary

Benzylidene imine, although found to decompose easily, has been prepared in the free state.

Hydrobenzamide and benzylidene imine are aldehydes of the ammonia system of compounds, as evidenced by their reactions, such as their reduction to ammono alcohols, their nitridation to ammono acids, and their formation by ammonolysis of the corresponding aquo compounds.

Hydrobenzamide has been found to undergo the benzoin condensation, benzylidene imine gives the Cannizzaro reaction, while both compounds form addition products with hydrocyanic and sulfurous acids.

Benzylidene imine reacts with aniline, phenylhydrazine and hydroxylamine, forming benzylidene aniline, benzylidene oxime, and benzylidene phenylhydrazone.

Benzylidene imine is a weak ammono acid, as evidenced by the formation of the sodium and potassium salts.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

NEW DERIVATIVES OF VANILLIN AND SOME OF THEIR REACTIONS[1]

BY L. CHAS. RAIFORD AND G. CARROLL HILMAN

RECEIVED MARCH 18, 1927 PUBLISHED JUNE 7, 1927

The simplest derivatives of vanillin on record are the monohalogenated and mononitro substitution products. Carles[2] obtained a mono-iodovanillin as early as 1872, but did not prove its structure. Hann[3] assumes that iodine occupies Position 5 (CHO = 1) in that product. Tiemann

---

[1] Adapted from a portion of the thesis submitted to the Graduate College of the State University of Iowa, August, 1925, by G. Carroll Hilman, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Carles, *Bull. soc. chim.*, **17**, 14 (1872).

[3] Hann, THIS JOURNAL, **47**, 2000 (1925).