

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

**BENZYLIDENE ANILINE AND BENZYLIDENE PARA-TOLUIDINE
AS AMMONO ALDEHYDE-ACETALS**

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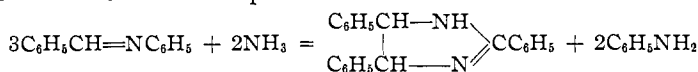
Introduction

According to the views of Franklin and his co-workers, the Schiff's bases are aldehyde-acetals of an ammonia system of compounds.¹ Moreover benzylidene aniline and benzylidene *p*-toluidine, typical aromatic Schiff's bases, are known to form addition compounds with hydrocyanic acid² and with Grignard reagents³ which are analogous to the familiar addition products formed from aquo aldehydes and these same reagents. Benzylidene aniline is also reduced by nascent hydrogen to a secondary amine⁴ which is a primary ammono alcohol.

As ammono aldehyde-acetals the aromatic Schiff's bases should be expected to undergo the Cannizzaro reaction and the benzoin condensation. These ammono compounds should also be nitrized to ammono acids and ammonolyzed to ammono aldehydes and ammono alcohols.

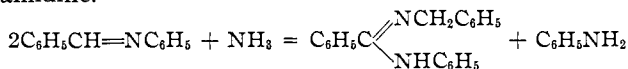
The reactions outlined in the previous paragraph have all been found to take place. In addition, a reaction resulting in the formation of a possible polymerized ammono aldehyde-acetal has been observed.

Ammonolysis.—When benzylidene aniline is ammonolyzed, amarine and aniline are the reaction products.



The benzylidene imine which one should expect to find as a product of the reaction must condense to form amarine, a reaction known to take place.⁵ Benzylidene *p*-toluidine is ammonolyzed to amarine and *p*-toluidine.

Cannizzaro Reaction.—The Cannizzaro reaction of the ammono aldehyde-acetals takes place readily when these compounds are treated with an excess of an ammono base. In this reaction, however, the ammono acids and the ammono alcohols which are formed are found in the form of ammono esters; namely, benzylphenylbenzamidine and benzyl-*p*-tolylbenzamidine.⁶



¹ Franklin, *Am. Chem. J.*, **47**, 285 (1912); *Proc. Eighth Int. Cong. Appl. Chem.*, **6**, 119 (1912); *THIS JOURNAL*, **46**, 2137 (1924); Strain, *ibid.*, **49**, 1559 (1927).

² Cech, *Ber.*, **11**, 246 (1878).

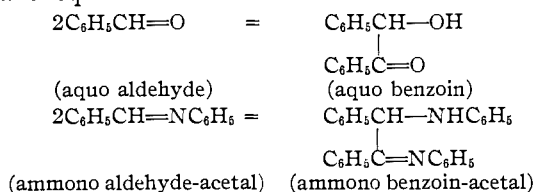
³ Busch and Rinck, *Ber.*, **38**, 1764 (1905).

⁴ Schiff, *Ann. Suppl.*, **3**, 354 (1864).

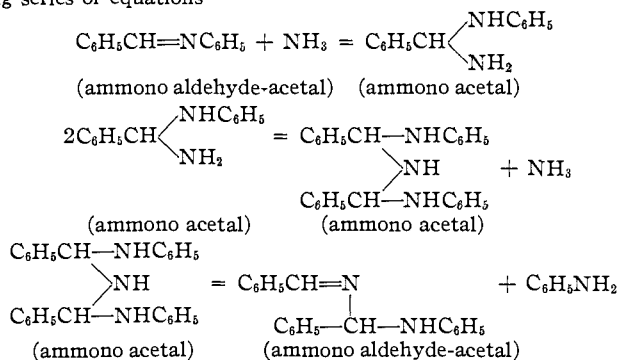
⁵ Strain, *THIS JOURNAL*, **49**, 1566 (1927).

⁶ The formation of benzylphenylbenzamidine can perhaps be best explained by

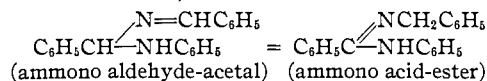
Benzoin Condensation.—When treated with an alkaline cyanide in liquid ammonia the ammono aldehyde-acetals undergo the benzoin condensation forming ammono benzoin-acetals; namely, benzoin-anililide and benzoin-*p*-tolyl-*p*-toluide.⁷ This reaction, which is analogous to the benzoin condensation of aquo aldehydes, is illustrated by the following parallel equations



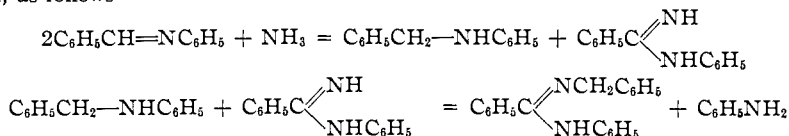
the following series of equations



The ammono aldehyde-acetal last written may undergo intramolecular oxidation and reduction, the aldehyde group being reduced to an ammono alcohol, the acetal group being nitridized (oxidized) to an ammono acid. This reaction, obviously an example of the Cannizzaro reaction, is shown herewith.



The formation of benzylphenylbenzamidine from benzylidene aniline can also be explained by assuming the Cannizzaro reaction to take place before the ester formation, as follows



It is interesting to note that these reactions take place in accordance with the theories proposed by Lachman [THIS JOURNAL, 45, 2356 (1923)] who observed the aquo ester benzylbenzoate as an intermediate product when benzaldehyde undergoes intermolecular oxidation and reduction.

⁷ Evidence will be presented in a following paper to show that these compounds undergo a number of reactions which substantiate the view that they are related to ammonia as the familiar benzoin and acetals are related to water.

Nitridation.—Benzylidene aniline is nitridized with difficulty with the result that tar-like decomposition products are formed along with small quantities of benzonitrile (benzoic anammonide).

Polymerization.—When treated with small quantities of alkali in liquid ammonia the ammono aldehyde-acetals form polymerized compounds whose structure has not been definitely established. The proposed formulas will therefore be described in the experimental part.

Experimental

Ammonolysis.—The ammonolysis reaction was carried out by allowing the ammono aldehyde-acetals to stand in liquid ammonia solution for thirty to thirty-five days. The ammonia was then evaporated and the residue extracted with alcohol which was then diluted with water, whereupon an oil separated. The clear liquid was then decanted from the oily layer, the latter was dissolved in a little concentrated hydrochloric acid, the solution diluted with an equal volume of water and cooled. When crystals ceased to form, the mixture was filtered and the crystals removed to a flask, where they were boiled with alcoholic ammonium hydroxide until a clear solution was obtained. Upon cooling and diluting this solution with water, large crystals of amarine were obtained. The identity of the crystals was established by a mixed melting point. The yields varied from 60 to 91% of the theoretical. The aniline and *p*-toluidine were identified in the respective filtrates.

It was also found that the ammonolysis reaction could be completed in ten to fourteen hours by heating the ammono aldehyde-acetals with liquid ammonia in the presence of ammonium chloride to a temperature of 120–150°.⁸

Cannizzaro Reaction.—Benzylidene aniline, or benzylidene *p*-toluidine, was treated with two or more molecular equivalents of potassium amide in liquid ammonia solution at room temperature. A considerable quantity of heat was evolved, indicated by the vigorous boiling of the solution, and a deep blue color was produced. This color disappeared upon the addition of more of the respective ammono aldehyde-acetal and reappeared upon the further addition of potassium amide. The reaction products could not be induced to crystallize from this dark blue solution even when the latter was concentrated and cooled to –35°. The ammonia was, therefore, allowed to escape, when a flaky blue residue was obtained. This material was dissolved in hot 95% alcohol (the blue color immediately disappeared) and the alcoholic solution then diluted with water until a slight turbidity appeared. Upon cooling, the solution was found to deposit beautiful, colorless, needle-shaped crystals of benzylphenylbenzamidine, or benzyl-*p*-tolylbenzamidine. A considerable quantity of aniline or *p*-toluidine was always found in the mother liquor. The yield of the ammono acid esters usually amounted to 60% of the weight of the ammono aldehyde-acetals used in the reaction.

The benzylphenylbenzamidine melted at 99–100° and when mixed with benzylphenylbenzamidine prepared by the action of phosphorus pentachloride and aniline on benzanilide⁹ the mixture melted at 99–100°.

The crystals were analyzed and their molecular weight was determined in benzene solution by the cryoscopic method.

Anal. Calcd. for C₂₀H₁₈N₂: C, 83.9; H, 6.3; N, 9.8. Found: C, 83.8, 83.6; H, 6.7, 6.6; N, 9.8, 9.7. *Mol. wt.* Calcd. for C₂₀H₁₈N₂: 286. Found: 271, 282.

⁸ For method of heating, see Blair, *THIS JOURNAL*, **48**, 87 (1926).

⁹ (a) Beckmann and Fellrath, *Ann.*, **273**, 9 (1893); (b) Pechmann and Heinze, *Ber.*, **30**, 1787 (1897).

In order to make more certain of the structure of the benzylphenylbenzamidine, the benzenesulfonyl derivative was prepared by treating some finely pulverized crystals with benzenesulfonylchloride and alkali. The white, crystalline derivative thus obtained was insoluble in alkalies and melted at 148°. It was analyzed by the method of Carius.

Anal. Calcd. for $C_{26}H_{22}O_2N_2S$: S, 7.5. Found: S, 7.1.

The benzyl-*p*-tolylbenzamidine prepared from benzylidene *p*-toluidine melted at 127–127.5°. The molecular weight in benzene solution was determined by the cryoscopic method.

Mol. wt. Calcd. for $C_{21}H_{20}N_2$: 300. Found: 294, 289. *Anal.* Calcd. for $C_{21}H_{20}N_2$: C, 84.0; H, 6.7; N, 9.3. Found: C, 83.9, 84.1; H, 7.0, 6.9; N, 9.1, 8.9.

Since benzyl-*p*-tolylbenzamidine was not known it seemed advisable to prepare this compound in order to compare it with the material obtained by the Cannizzaro reaction. The synthesis was accomplished by heating benz-*p*-toluide with phosphorus pentachloride and benzylamine. The crystals thus obtained melted at 127° and when mixed with those obtained from benzylidene *p*-toluidine, the mixture melted at 127°. The two preparations appeared to be identical in crystalline form and solubility, being insoluble in water, moderately soluble in alcohol and acetone, and readily soluble in ether and benzene.

Benzoïn Condensation.—From 3 to 5 g. of ammono aldehyde-acetal and 0.5 to 1.0 g. of freshly pulverized potassium cyanide were dissolved in about 20 cc. of liquid ammonia and the clear solution was allowed to stand at room temperature. After several hours a heavy, viscous liquid separated from the solution. Twenty-four hours later a few crystals had formed in this liquid, but due to its high viscosity the growth of the crystals was retarded to such an extent that it seemed best to repeat the experiment, using the crystals first formed to seed the reaction product before any large quantity of the viscous material could be formed. Accordingly, the crystals were drained of the mother liquor and uncrystallized oil, dried and transferred to a freshly prepared solution of the aldehyde-acetal and potassium cyanide in liquid ammonia. After standing for several hours the solution was found to be filled with crystals.

The crystals formed from benzylidene aniline were hexagonal yellow prisms having a greenish fluorescence. These crystals were washed, dried and analyzed.¹⁰

Anal. Calcd. for $C_{20}H_{22}N_2$: C, 86.2; H, 6.1; N, 7.7. Found: C, 85.9, 85.9; H, 6.2, 6.2; N, 7.5. *Mol. wt.* (Benzene). Calcd. for $C_{20}H_{22}N_2$: 362. Found: 321, 331.

The yellow crystals of benzoïn-anil-anilide are insoluble in water, moderately soluble in boiling alcohol and very soluble in hot benzene and toluene, from which they may be recrystallized. When heated these crystals begin to soften at 185° but do not melt completely until a temperature of 200° is reached. At a higher temperature the benzoïn-anil-anilide distills with only slight decomposition.

The ammono benzoïn obtained from benzylidene *p*-toluidine is slightly soluble in liquid ammonia, separating as a clear, colorless, viscous liquid or as colorless crystals. It is moderately soluble in hot alcohol and crystallizes from a concentrated solution in

¹⁰ It is interesting to note at this time that Schiff reported a compound having the empirical formula $C_{26}H_{22}N_2$ which he obtained by heating benzylidene aniline in a sealed tube [*Ann. Suppl.*, **3**, 354 (1864); *Ann.*, **148**, 336 (1868)]. However, Voigt, [*J. prakt. Chem.*, [2] **31**, 544 (1885); [2] **34**, 2 (1886)] and v. Miller and Plöchl [*Ber.*, **25**, 2020 (1892)], and the writer were unable to duplicate Schiff's results. In attempting to prepare benzoïn-anil-anilide by the action of aniline on benzoïn, Lachowicz [*Monatsh.*, **15**, 402 (1894)], found that benzoïn-anil was the sole product of the reaction, the ammonolysis failing to go to completion.

beautiful colorless prisms. After recrystallization this compound was found to melt at 122° .¹¹

Anal. Calcd. for $C_{23}H_{25}N_2$: C, 86.2; H, 6.7. Found: C, 86.2, 86.3; H, 6.8, 6.8.

Nitridation.—Benzylidene aniline (1 g.) in solution in liquid ammonia was treated with an excess of iodine and the temperature of the solution maintained at 0° until the iodine color had completely disappeared (eight hours). During this time a considerable quantity of nitrogen was evolved while the solution became quite dark in color. Upon evaporation of the ammonia, a dark, tarry mass was obtained which smelled strongly of phenylisocyanide. Neither benzamidine or phenylbenzamidine could be detected in the aqueous and dilute acid extracts of the residue. From the ether extract a few drops of an oily liquid which smelled strongly of benzonitrile were obtained; boiling point of benzonitrile, 191° ; found, 180° .

Polymer from Benzylidene Aniline.—After standing in a solution of potassium amide in liquid ammonia containing less than one molecular equivalent of potassium amide, benzylidene aniline is converted into a very soluble material which is best obtained by evaporating the ammonia and recrystallizing the residue from alcohol. The time necessary for this reaction varies from five to fifteen days. The yields vary between 10 and 60% of the weight of benzylidene aniline used.

The crystals obtained from alcohol grow very slowly and take the form of prisms. They melt at 132 – 134° . After digestion with dilute alcoholic potassium hydroxide, the crystals melt at 136° , but upon recrystallization from alcohol they melt again at 132 – 134° .

This new substance is insoluble in acids, alkalies and water, but is moderately soluble in benzene and toluene. It is only slowly attacked by aqueous hydrochloric acid at the boiling temperature, a blue-green coloring matter being produced. Ammonio hypiodous acid failed to nitridize the material in liquid ammonia solution.

When treated with an excess of potassium amide, 0.4 g. of the unknown crystals produced 0.3 g. of phenylbenzylbenzamidine and when heated with a solution of ammonium chloride in liquid ammonia the crystals gave rise to another compound which melted at 168° and which has not as yet been identified.

The composition and the molecular weight of the crystals melting at 132 – 134° were determined, the latter in benzene solution by the cryoscopic method.

Anal. Calcd. for $C_{33}H_{29}N_3$: C, 84.8; H, 6.2; N, 9.0. Found: C, 85.1, 85.0, 85.1; H, 6.5, 6.2, 6.5; N, 8.6, 8.6. *Mol. wt.* Calcd. for $C_{33}H_{29}N_3$: 467. Found: 418, 438.

When this compound obtained by the action of potassium amide on benzylidene aniline is treated with alcoholic hydrochloric acid, it forms a soluble hydrochloride which separates as a white, finely crystalline mass when the solution is diluted with water. Upon heating this hydrochloride with ammonium hydroxide, the original base is regenerated. Two preparations of the hydrochloride were made.

Anal. Calcd. for $C_{33}H_{29}N_3 \cdot HCl$: Cl, 7.1. Found: Cl, 6.9, 7.4.

Polymerization of three molecules of benzylidene aniline to a six membered heterocyclic ring with the subsequent elimination of one molecule of aniline by ammonolysis would yield a compound whose hydrochloride would have the formula $C_{33}H_{29}N_3 \cdot HCl$.

Polymer from Benzylidene *p*-Toluidine.—When treated with potassium amide,

¹¹ Schiff [*Ann.*, **140**, 96 (1866)] reported a compound having the formula $C_{23}H_{25}N_2$ and melting at 120 – 125° , which he obtained by heating benzylidene *p*-toluidine in a sealed tube at 180° for twenty-four hours. However, v. Miller and Plöchl [*Ber.*, **25**, 2020 (1892)] and, more recently, the writer were unable to duplicate Schiff's results. Nevertheless, the melting point of Schiff's compound agrees fairly well with that of the ammonio benzoin obtained as a result of the benzoin condensation in liquid ammonia.

as just described above for benzylidene aniline, benzylidene *p*-toluidine forms a compound which melts at 136–137° when recrystallized from alcohol. The crystals thus obtained are much more difficult to purify than those obtained from benzylidene aniline. Furthermore, they are very easily converted into benzyl *p*-tolylbenzamidine, this reaction taking place when less than one molecular equivalent of potassium amide is present in the ammonia solution.

Anal. Calcd. for $C_{35}H_{33}N_3$: C, 84.8; H, 6.7. Found: C, 84.6, 84.3; H, 6.7, 6.3.
Mol. wt. Calcd. for $C_{35}H_{33}N_3$: 495. Found: 399, 401.

It is with the greatest pleasure that the writer takes this opportunity to express his thanks to Dr. E. C. Franklin for the care which he exercised in directing the experimental work and in reading this manuscript.

Summary

Experimental evidence has been presented to show that the aromatic Schiff's bases, benzylidene aniline and benzylidene *p*-toluidine, are aldehyde-acetals of the ammonia system of compounds.

The ammonolysis of ammono aldehyde-acetals has been accomplished. Benzylphenylbenzamidine and benzyl-*p*-tolylbenzamidine have been prepared by the Cannizzaro reaction.

Benzoin-anil-anilide and benzoin-*p*-tolyl-*p*-toluide have been prepared by the benzoin condensation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN ORGANOMAGNESIUM HALIDES AND ALKYL SULFONATES

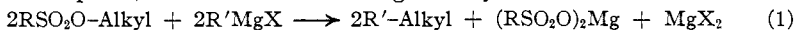
BY HENRY GILMAN AND LLOYD L. HECK

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Introduction

Alkyl esters of sulfonic acids differ from aryl esters of sulfonic acids in their reaction with organomagnesium halides. With alkyl esters, alkylation takes place, and this reaction has generally been formulated as follows¹



With aryl esters, sulfones and phenols are formed, as follows



When molecular equivalents of alkyl sulfonate and Grignard reagent are used, according to Reaction 1, the yield of alkylation product does not generally exceed 50%.² This prompted a further investigation of the

¹ Gilman, Robinson and Beaber, *THIS JOURNAL*, **48**, 2715 (1926). References to earlier studies are contained in this paper.

² Gilman and Beaber, *ibid.*, **47**, 518 (1925). The only exception to the 18 alkylation reactions reported by them was in the reaction between benzyl *p*-toluenesulfonate and benzylmagnesium chloride. In this case a 55% yield of dibenzyl was obtained, but it is quite probable that part of this high yield is due to some dibenzyl that is generally