was obtained. Its hydrazine hydrate content was 82.7%. This concentrated solution represents about two-thirds of the original hydrazine content. Although there is some loss, much of the remaining third is readily recoverable from the first aqueous distillate.

[b] Values not determined because the distillation was uninterrupted until a temperature of 107.5° was reached.

[c] The 15 g. of 94.7% concentration was redistilled without xylene to obtain 10.5 g. of a fraction which boiled at 118–119°, and which analyzed for nearly 96% of hydrazine hydrate (95.4 and 95.4% in two determinations). The yield of 10.5 g. of this high concentration represents about 12% of the quantity of hydrazine hydrate that was in the original dilute solution. Although there is some loss by retention in the column of beads, and some actual loss, much of the remaining hydrazine is to be found in the "aqueous distillate."

Other attempts to obtain higher than 95–96% hydrazine hydrate by this method were not successful.

## Summary

Dilute hydrazine hydrate solutions may be readily concentrated to solutions of 65% strength by distilling them with an equal weight of xylene until all the hydrocarbon is removed. By beginning with more xylene and distilling similarly, concentrations up to 95–96%, but apparently not higher, may be effected in a single operation. Toluene is considerably less efficient than xylene, and benzene is quite unsatisfactory for this purpose.

A few experiments are described wherein hydrazine salts are treated in turn with sodamide, calcium carbide and aluminum carbide. The latter two substances fail to react but sodamide reacts violently if undiluted. Hydrocarbons are unsatisfactory diluents for the purpose of preparing anhydrous hydrazine by this method.

Evanston, Illinois

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[Contribution from the Chemical Laboratory of Stanford University]

# BENZOIN-ANIL-ANILIDE AND BENZOIN-PARA-TOLYL PARA-TOLUIDE AS AMMONO BENZOIN ACETALS

By Harold H. Strain

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## Introduction

Upon carrying out a series of reactions to support the view that the Schiff's bases are aldehyde-acetals of an ammonia system of compounds, the writer found[1] that both benzylidene-aniline and benzylidene-*p*-toluidine undergo the benzoin condensation reaction, forming benzoin-anil-anilide and benzoin-*p*-tolyl-toluide, ammono compounds which are analogous to benzoin.[2]

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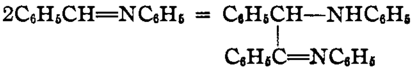
[1] Strain, This Journal, **50**, 2218 (1928).

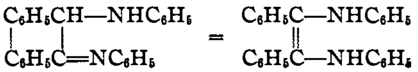
[2] For an explanation of the ammonia system of compounds *cf.* Franklin, *Am. Chem. J.*, **47**, 285 (1912); This Journal, **46**, 2137 (1924).

This reaction, as well as the probable structure of these ammono benzoins, is illustrated by the following equation.



$$2C_6H_5CH{=}NC_6H_5 = \begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad\;\;\; | \\ C_6H_5C{=}NC_6H_5 \end{array}$$

In addition to being analogous to the aquo benzoins, the ammono benzoins are also analogous to the aquo esters or acetals in that they have organic radicals attached to the nitrogen atoms. In this respect they resemble the ammono aldehyde acetals from which they are prepared and may therefore be regarded as ammono benzoin acetals. Furthermore, the ammono benzoin acetals may also be considered as substituted ammono glycolic aldehydes and should therefore exhibit the familiar enediol tautomerism characteristic of aquo glycolic aldehyde and other $\alpha$-hydroxy aldehydes, as shown herewith.



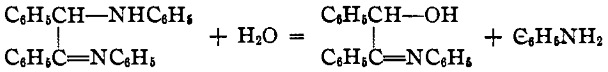
$$\begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad\;\;\; | \\ C_6H_5C{=}NC_6H_5 \end{array} = \begin{array}{l} C_6H_5C{-}NHC_6H_5 \\ \quad\;\;\; \| \\ C_6H_5C{-}NHC_6H_5 \end{array}$$

(keto form) (enediol form)

If the above analogies are real, then the ammono benzoins should undergo all of the reactions characteristic of aquo benzoin and aquo acetals. Upon hydrolysis they should form aquo benzoin and ammono alcohols, while upon ammonolysis they should form ammono benzoin and ammono alcohols. Nitridizing agents should convert them into ammono compounds analogous to the oxidation product of benzoin, that is, benzil. The ammono benzils thus formed should in turn be hydrolyzed to aquo benzil. The ammono benzoins should also be easily converted into indole derivatives, since they represent the intermediate compounds assumed to be formed when indole derivatives are prepared by the action of aniline hydrochloride on benzoin-anilide.[3]

As a matter of fact, all the foregoing predictions have been justified by the experimental work described in this paper.

Upon treatment with water, the ammono benzoins are partially hydrolyzed, forming aquo ammono benzoins and ammono alcohols. Thus benzoin-anil-anilide gives rise to benzoin-anilide and aniline



$$\begin{array}{l} C_6H_5CH{-}NHC_6H_5 \\ \quad\;\;\; | \\ C_6H_5C{=}NC_6H_5 \end{array} + H_2O = \begin{array}{l} C_6H_5CH{-}OH \\ \quad\;\;\; | \\ C_6H_5C{=}NC_6H_5 \end{array} + C_6H_5NH_2$$

while benzoin-*p*-tolyl-*p*-toluide forms benzoin-*p*-toluide and *p*-toluidine.[4]

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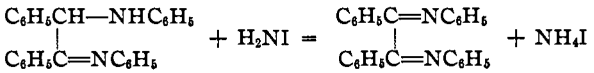
[3] Bischler and Fireman, *Ber.*, **26**, 1336 (1893).

[4] According to Voigt [(a) *J. prakt. Chem.*, (2) **31**, 544 (1885), and (b) (2) **34**, 2 (1886)] and (c) Japp and Murray [*Ber.*, **26**, 2638 (1893)] the structure of benzoin-anilide should be represented by Formula I, below. (d) Lachowicz [*Monatsh.*, **15**, 402

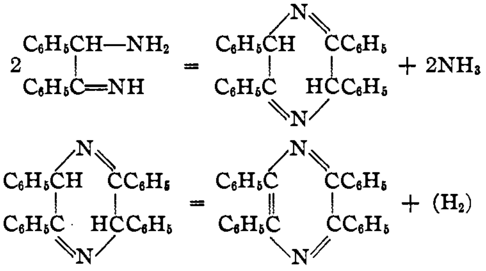
Nitridizing agents convert benzoin-anil-anilide into the corresponding ammono benzil, benzil-dianil, as illustrated by the following equation



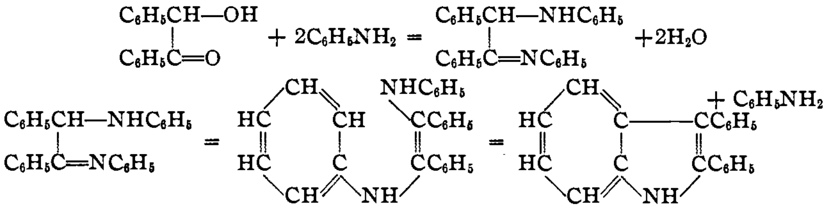
$$\begin{array}{l}C_6H_5CH{-}NHC_6H_5\\ \quad|\\ C_6H_5C{=}NC_6H_5\end{array} + H_2NI = \begin{array}{l}C_6H_5C{=}NC_6H_5\\ \quad|\\ C_6H_5C{=}NC_6H_5\end{array} + NH_4I$$

while benzoin *p*-tolyl-*p*-toluide is nitridized to benzil-di-*p*-tolyl.

When ammonolyzed, the ammono benzoin acetals form tetraphenylpyrazine in rather poor yields. This reaction probably takes the course illustrated by the following equations, although no free hydrogen has been observed as a reaction product.



In studying the action of aniline upon benzoin at 200°, Lachowicz[4d] found that, in the presence of hydrogen chloride, benzoin and aniline reacted to form 2,3-diphenylindole.[3,4c,5] In order to explain the reaction Bischler and Fireman proposed the following mechanism, although they were unable to isolate the benzoin-anil-anilide as an intermediate product.



This mechanism has been verified by the writer by the conversion of the

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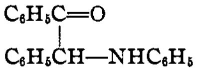
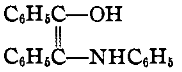
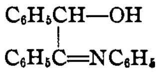
(1894)], on the other hand, thinks that this compound has the structure represented by Formula III.



I



II



III

As a matter of fact, Formulas I and III are related to each other in a manner which may be shown by writing the transition compound, Formula II. Any one of the three formulas written above is derived from the other by the shift of a hydrogen atom analogous to that which takes place in the keto-enol isomerism of acetoacetic ester. However, no evidence is at hand to show that the stable form of the compound may be represented by any particular one of the above formulas.

[5] Japp and Murray, *J. Chem. Soc.*, **65**, 892 (1894).

ammono benzoins into the corresponding substituted indoles, as illustrated by the last reaction written above.

## Experimental

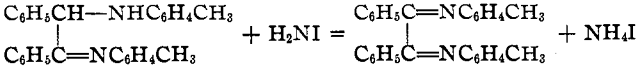
**Hydrolysis of the Ammono Benzoins.**—Benzoin-anil-anilide was hydrolyzed to the aquo ammono benzoin, benzoin-anilide, when boiled with 80% alcohol containing some hydrochloric acid. The benzoin-anilide obtained by this reaction melts at 99°. It was identical with benzoin-anilide prepared by the writer by the action of aniline on benzoin as described by Voigt,[4b] both compounds having the same crystalline form and the same solubility in alcohol, water and acids. A mixture of the two compounds melted at 99°.

Benzoin-*p*-tolyl-*p*-toluide was hydrolyzed by alcoholic hydrochloric acid to benzoin-*p*-toluide and *p*-toluidine. The mixed aquo ammono benzoin was found to be identical with that prepared by Voigt, both in melting point and solubility in acids and alcohol.[6]

**Nitridation of the Ammono Benzoins.**—Three-tenths g. of the ammono benzoin was dropped into a solution of 0.6 g. of iodine in liquid ammonia contained in a Faraday tube, which was then sealed and placed in an ice-bath until all of the iodine color had disappeared (about eight hours). At the end of this time, the deep yellow crystals of the benzoin-anil-anilide had completely dissolved, while light yellow crystals were found covering the walls of the tube. These crystals were washed several times and dried in a vacuum. They melted at 144°. The melting point given for benzil-dianil, prepared from benzil and aniline, by Lachowicz[7] is 142° and that by Siegfeld[8] is 141–142°. This difference in melting point must have been due to impurities contained in the previous preparations because both compounds had the same solubility in alcohol, water, ether and benzene. The writer repeated the work of Lachowicz and Siegfeld and found that it was impossible to obtain a compound which looked as pure as that obtained by the nitridation reaction. The melting point of the crystals thus prepared was 142°, but it was not changed when mixed with the crystals melting at 144°. Both compounds were hydrolyzed to benzoin and aniline as described by Lachowicz.

The writer also nitrized (oxidized) benzoin-anil-anilide to the ammono benzil by passing a current of air through a solution of the former in toluene or benzene. However, if the air is saturated with water vapor, a small quantity of benzanilide is formed, proving that the carbon to carbon bond is broken, a reaction which indicates that benzoin-anil-anilide may exist in the enediol form discussed above.

Benzoin-*p*-tolyl-*p*-toluide is only slowly nitridized by ammono hypo-iodous acid, due possibly to the slight solubility of this ammono benzoin in liquid ammonia. On the other hand, the reaction takes place very readily when carried out in benzene solution using air as the de-electronizing agent.



$$\begin{array}{l} C_6H_5CH{-}NHC_6H_4CH_3 \\ \quad | \\ C_6H_5C{=}NC_6H_4CH_3 \end{array} + H_2NI = \begin{array}{l} C_6H_5C{=}NC_6H_4CH_3 \\ \quad | \\ C_6H_5C{=}NC_6H_4CH_3 \end{array} + NH_4I$$

The benzil-di-*p*-tolyl obtained by the above reaction melted at 162° and was identical in every respect with that prepared by Lachowicz.[9]

**Ammonolysis of the Ammono Benzoins.**—Upon heating benzoin-anil-anilide or benzoin-*p*-tolyl-*p*-toluide with liquid ammonia in a sealed tube at 130° for ten hours, the ammono benzoins were found to dissolve while a few colorless, needle-shaped crys-

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[6] Voigt, ref. 4 b, p. 15.

[7] Lachowicz, *Monatsh.*, **14**, 283 (1893).

[8] Siegfeld, *Ber.*, **25**, 2601 (1892).

[9] Lachowicz, ref. 7, p. 289.

tals were formed. These crystals proved to be tetraphenylpyrazine. They dissolve in concentrated sulfuric acid, forming a deep red solution from which the pyrazine compound could be recrystallized upon dilution with water.

The melting point of the tetraphenylpyrazine obtained from the ammono benzoins was 252°, while that given by earlier investigators,[10] who used other methods of preparation, is 245–246°. The writer then repeated the work of Japp and Wilson and found that it was possible to prepare tetraphenylpyrazine by the action of ammonium acetate on benzoin, which melted at 252°. The crystals thus obtained showed no depression in melting point when mixed with those obtained by the ammonolysis reaction.

The liquid ammonia decanted from the crystals of tetraphenylpyrazine contained free aniline, or *p*-toluidine. No other pure compounds could be separated although the yield of tetraphenylpyrazine amounted to only a few per cent. of the weight of the ammono benzoins used in the reaction.

**Formation of Substituted Indoles.**—Benzoin-anil-anilide does not break down when heated to its boiling point. However, if it is dissolved in benzene or toluene which is saturated with dry hydrogen chloride and the resulting solution heated in a sealed tube for two hours at 180–200°, the reaction products are found to be 2,3-diphenylindole and aniline hydrochloride. The latter is insoluble in the hydrogen chloride solution while the former is very soluble so that the two are easily separated. The yield is almost quantitative.

Benzoin-*p*-tolyl-*p*-toluide is converted into 2,3-diphenyl-5-methylindole and *p*-toluidine hydrochloride when heated with benzene and hydrogen chloride. One-half g. of the ammono benzoin formed 0.3 g. of the indole derivative and 0.13 g. of *p*-toluidine hydrochloride. The 2,3-diphenyl-5-methylindole melted at the recorded temperature and formed a chocolate brown picrate melting at 154°, as described by Bischler and Fireman.[11]

The experiments described in this paper were carried out under the direction of Dr. E. C. Franklin, to whom the writer is greatly indebted for the many helpful suggestions received during the course of the work.

## Summary

Benzoin-anil-anilide and benzoin-*p*-tolyl-*p*-toluide are ammono benzoin acetals. As ammono acetals they can be ammonolyzed and hydrolyzed. As ammono benzoins they can be nitridized to ammono benzils.

The ammono benzoins are converted into indole derivatives by hydrogen chloride.

The structure of benzoin-anilide and the ammono benzoins has been discussed.

STANFORD UNIVERSITY, CALIFORNIA

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[10] Leuckart, *J. prakt. Chem.*, [2] **41**, 333 (1890); Japp and Wilson, *J. Chem. Soc.*, **49**, 826 (1886).

[11] Bischler and Fireman, ref. 3, p. 1342.