*Anal.* Subs. 0.1025, 0.1298: $K_2SO_4$, 0.0571, 0.0721. Subs., 0.3444, 0.2476: $N_2$, 27.70, 20.20 cc. (22°, 746.5 mm.) (over 50% KOH). Subs., 03073, 0.3594: $CO_2$, 0.6963, 0.8141; $H_2O$, 0.1080, 0.1255. Calcd. for $KC_8H_6N$: K, 25.19; N, 9.03; C, 61.86; H, 3.89. Found: K, 24.97, 24.92; N, 8.95, 9.06; C, 61.79, 61.77; H, 3.90, 3.88.

**Behavior of Potassium Phenylacetonitrile.**—The crude salt is a dark yellow, crystalline substance, becoming a lighter yellow after recrystallization. It is exceedingly sensitive to traces of water and acids, which decompose the salt with the formation of hydrocyanic acid. It reacts with ethyl iodide to form α-phenylbutyronitrile, as follows

$$(C_6H_5)HC{=}C{=}NK \rightleftarrows (C_6H_5)(CN)HCK \qquad (2)$$

$$(C_6H_5)(CN)HCK + C_2H_5I \longrightarrow (C_6H_5)(CN)HC(C_2H_5) + KI \qquad (3)$$

For the preparation of α-phenylbutyronitrile by this method the salt was prepared in the usual way, the quantities of reagents being those previously specified, and was treated, without being separated from the reaction mixture, with ethyl iodide (18 g.), a 7% excess. The procedure and course of the reaction resemble that described in a previous paper[1] for the preparation of α-phenylbutyronitrile from sodium phenylacetonitrile. In the present case, however, the yield of nitrile was much better, being 10 g., or 64.4% of the theoretical yield calculated from the amount of potassium used.

## Summary

1. The preparation of potassium phenylacetonitrile is reported.

2. The identity of the salt was established by analysis and by its reactions.

3. Its decomposition by acid into hydrocyanic acid indicates a nitride structure for the salt $[(C_6H_5)HC{=}C{=}N]K$.

4. Its conversion into α-phenylbutyronitrile by treatment with ethyl iodide indicates that the salt also exists in a carbide form (tautomeric with the nitride), $[(C_6H_5)(CN)HC]K$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

## CONCENTRATION OF HYDRAZINE HYDRATE SOLUTIONS

BY CHARLES D. HURD AND C. W. BENNETT

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Usually, aqueous solutions of hydrazine contain less than 30% of available hydrazine (40–45% hydrazine hydrate), since this concentration may be realized by refluxing[1] a mixture of water (75 parts), hydrazine sulfate (200 parts) and sodium hydroxide (160 parts), and then distilling. For many purposes such a solution of hydrazine hydrate is satisfactory. When more concentrated solutions are desired, the expedient is usually adopted of starting similarly but with less water, or with a minimum volume of water and considerable alcohol.[2] Such devices are far from satisfactory owing to poor yields.

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[1] "Organic Chemical Reagents," **3,** 40 (1921), University of Illinois Bulletin, Vol. 19, No. 6, Oct. 9, 1921.

[2] Vanino, "Handbuch der Präparativen Chemie," F. Enke, Stuttgart, **1913,** Vol. I, p. 114.

In recent years, many substances have been satisfactorily dehydrated by distilling them in the presence of an immiscible liquid. It seemed not unlikely that a solution of hydrazine hydrate might be concentrated by such distillation methods and, indeed, such was found to be the case. The method is extremely simple and any degree of concentration up to about 95% of hydrazine hydrate is attainable. It is necessary merely to add a definite quantity of xylene to the dilute hydrazine hydrate solution in a distilling apparatus and heat it until the xylene has distilled away. The residue in the distilling flask, which contains most of the original hydrazine hydrate in concentrated form, may be distilled to a water-clear liquid if desired. The xylene and water which comprise the original distillate are easily separated. The aqueous portion contains varying amounts of hydrazine, which is readily recoverable; as would be expected, the xylene portion contains almost no hydrazine. Toluene may be used instead of xylene, but it is somewhat less efficient. Benzene effects but slight concentration and, therefore, is not to be recommended. Undoubtedly, other immiscible liquids with vapor pressures comparable to that of xylene would be found equally satisfactory and perhaps some would be preferable.

Some of the results may be briefly summarized. With equal parts (150 g. each) of xylene and a 41.8% solution of hydrazine hydrate, one distillation was found to effect a concentration (in 87% yields) to a hydrazine hydrate solution of about 65% strength. By taking 200 g. of xylene (with 150 g. of 41.8% hydrazine hydrate solution), one distillation brought about a change in concentration, in 64% yield, to a hydrazine hydrate solution of 82.7% strength. The latter boiled at 116–119°. The aqueous distillate which was removed by the xylene in the first experiment weighed 62.5 g. and contained 10% of hydrazine hydrate; in the second case it weighed 85 g. and contained 13% of hydrazine hydrate. Concentrations beyond 83% were effected by continued distillation with xylene, but in no case was it found possible to exceed 95–96% by this method. To obtain the latter concentration from a 33% hydrazine hydrate solution in one operation, 5 parts of the latter was distilled with 13 parts of xylene. The residual material, which represented only 12% of the original hydrazine content, boiled at 118–119° and analyzed for 95.4–95.8% of hydrazine hydrate. Although there was some loss, most of the remaining hydrazine was to be found in the aqueous layer of the distillate.

## Metathetic Methods for the Liberation of Hydrazine

To liberate hydrazine from a salt such as hydrazine hydrochloride, two modifications of the double decomposition reaction have been recorded. The more customary of these two utilizes sodium hydroxide in water solution, and the alternative procedure makes use of sodium methylate[3] in methanol solution: $NaOCH_3 + N_2H_5Cl \longrightarrow N_2H_4 + CH_3OH + NaCl$. Water and methanol, respectively, contaminate the hydrazine in these two processes. With the purpose of producing uncontaminated hydrazine by a simple procedure, the following three metathetic methods were studied.

$NaNH_2 + N_2H_5X$ into $N_2H_4 + NaX + NH_3$
$CaC_2 + 2N_2H_5X$ into $2N_2H_4 + CaX_2 + C_2H_2$
$Al_4C_3 + 12N_2H_5X$ into $12N_2H_4 + 4AlX_3 + 3CH_4$
(In these reactions X represents chloride or sulfate)

Calcium carbide and hydrazine sulfate failed to interact up to 260°, except for a slight decomposition of the sulfate into free sulfur. The dihydrochloride (of hydrazine) made an explosion, and yielded a very small amount of liquid with an acetylene odor. The only apparent reaction between the dihydrochloride and aluminum carbide was the thermal decomposition of the hydrazine salt, apparently into hydrogen chloride, ammonium chloride, nitrogen and hydrogen. The reaction of sodamide with hydrazine salts under widely varying conditions was found to proceed with explosive violence[4] if undiluted. The use of the hydrocarbons "Nujol" (mineral oil) or xylene as reaction media effectually did away with the explosions, but failed to effect anything but trivial yields of hydrazine. It is quite possible that good results would have been obtained in liquid ammonia as solvent, but we did not try this.

## Experimental Part

Solutions of hydrazine hydrate were prepared by the method given in Organic Chemical Reagents.[1] The hydrazine content of the solutions was determined by titration in acid solution (containing bromide ion) at 60° with 0.1 *N* potassium bromate solution according to the method of Kurtenacker and Wagner.[5] Three drops of a sulfuric acid solution of indigo was used as an indicator, the color changing from blue through green to yellow at the end-point.

### Distillation of Hydrazine Hydrate Solution with Benzene

A mixture of 100 cc. of hydrazine hydrate solution (24% $N_2H_5OH$) and 200 cc. of benzene was distilled in the manner later described under toluene and xylene. The temperature of the vapors was 69–71° throughout the distillation. When all the benzene had distilled, it was found that only 8 cc. of water of 1.66% hydrazine hydrate content was also in the distillate. The residue of hydrazine hydrate solution in the distilling flask was found to contain 27% of hydrazine hydrate by weight. The benzene was also analyzed but was found to contain practically no hydrazine.

### Concentration of Hydrazine Hydrate Solutions with Toluene

A mixture of 95 g. of hydrazine hydrate solution containing 24.6% of hydrazine hydrate by weight and 100 cc. of toluene was distilled using a 500-cc. flask fitted with a

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[3] De Bruyn, *Rec. trav. chim.*, **13**, 433 (1894); L. U. Spence, Master's "Dissertation," Northwestern University, 1925.

[4] Possibly due to sodium hydrazide. See Stollé, *J. prakt. Chem.*, **83**, 200 (1911); Ebler, *Ber.*, **43**, 1690 (1910).

[5] Kurtenacker and Wagner, *Z. anorg. Chem.*, **120**, 265 (1921).

cork and a Hempel column of beads. The dimensions of the column were 35 mm. diameter and 17 cm. length. From the top of this column a side arm led through a condenser into a receiver. Wherever corks were exposed to hydrazine vapors, they were protected by tin foil. In the distillation the mixture came over at 85–86°, and when all of the toluene had distilled, there was about 20 cc. of water with it. This aqueous layer contained 2.7% of hydrazine hydrate by weight, and the aqueous residue contained 30.6%. The analytical data in these typical cases are given for reference.

*Anal.* 0.4570 g. of substance consumed 10 cc. of $KBrO_3$ solution, 1 cc. of which was equivalent to 0.00125 g. of $N_2H_5OH$. Found: 2.7% of hydrazine hydrate. Subs., 0.1242; $KBrO_3$ solution, 30.4 cc. Found: hydrazine hydrate, 30.6.

The toluene was returned to the flask and the distillation repeated. Again 20 cc. of water was obtained with the same percentage of hydrazine hydrate, namely, 2.7%; the residue was nearly 40%. Again repeating this process, the residue of 25 g. analyzed for 61–61.5% of hydrazine hydrate and the aqueous distillate contained 2.8%. Again the toluene was returned and the distillation repeated. This time the mixture distilled at 89–90°. In this case, the aqueous distillate weighed 12 g., and analyzed for about 12% hydrazine hydrate content. The residue was 68% hydrazine hydrate. By returning the toluene and redistilling, it was found that the next distillation temperature of the toluene–water–hydrazine mixture was 94–95°. The distillate (aq. layer) contained 47.6% of hydrazine hydrate by weight, and the residue (5 g.) 86% of hydrazine hydrate. This residue, on fractionation, gave 2.25 g. of a clear liquid which boiled at 117–119°. Analysis before and after fractionation gave values which were almost identical.

It will be shown directly that xylene effects this concentration, and even a greater concentration much more readily, and, therefore, is to be recommended in preference to toluene.

## Concentration of Hydrazine Hydrate Solutions with Xylene

**Preparation of 65% Hydrazine Hydrate.**—A mixture of 150 g. of 41.8% hydrazine hydrate solution and 150 g. of xylene was distilled in the same apparatus as with the benzene and toluene. The distillation consumed only fifteen minutes and the vapors came over from 92–100°. All of the xylene and 62.5 g. of water came over. The watery portion of the distillate analyzed 10.5% by weight of hydrazine hydrate, whereas the residual solution in the flask, which weighed 85 g., analyzed for 65.2%. In other words, about 87% of the original hydrazine hydrate still remained in the concentrated residue.

**Preparation of 82% and of 95% Hydrazine Hydrate Solutions.**—The only difference from the preceding method was that a greater quantity of xylene was employed. These results are listed in Table I.

TABLE I

CONCENTRATION OF HYDRAZINE HYDRATE SOLUTIONS BY DISTILLING WITH XYLENE

| Xylene used, g. | Orig. hydrazine hydrate soln. | | Dist. Temp., °C. | Xylene distd., g. | Final hydrazine hydrate soln. Aqueous distillate | | Final hydrazine hydrate soln. Residue | |
|---|---|---|---|---|---|---|---|---|
| | Wt., g. | $N_2H_5OH$, % | | | Wt., g. | $N_2H_5OH$, % | Wt., g. | $N_2H_5OH$, % |
| 150 | 150 | 41.8 | 92–100 | 150 | 62.5 | 10.5 | 85 | 65.2 |
| 200 | 150 | 41.8 | 90–105 | 200 | 85 | 13 | 53[a] | 82.2 |
| 650 | 250 | 33.1 | 90–96 | 178 | 63 | 1.7 | [b] | .. |
| ... | Continued | | 96–101 | 129 | 51 | 12.8 | .. | .. |
| ... | distillation | | 101–105 | 220 | 72 | 46.1 | .. | .. |
| ... | | | 105–107.5 | 36 | 15 | 75.1 | 15[c] | 94.7 |

[a] The 53 g. of material was redistilled without xylene. The first small portion, which was oily, was discarded. Forty-eight g. of a water-clear liquid, b. p. 116–119°,

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.

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# 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).