on various kinds of membranes, their permeabilities and properties. Brown[1] has shown that membranes allowing dialysis in almost any sort of solvent, even such as alcohol, acetone, glacial acetic acid, toluene, benzene, etc., can be made. This indicates that pervaporation and ultrafiltration are by no means limited to aqueous solutions.

Summary.

A new form of ultra-filter has been described which depends on pervaporating both the dialysate and the diffusate solutions during dialysis.

Its usefulness in biological and synthetic organic chemistry for the removal of humus, coloring matter and colloids in general, has been pointed out and illustrated.

The apparatus makes it possible now, for the first time, to dialyze quantitatively.

ALBANY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

GLACIAL ACETIC ACID AS A SOLVENT FOR PRUSSIC ACID. BENZALHYDRAZINOPHENYLACETONITRILE AND SOME DERIVATIVES.

BY J. R. BAILEY AND R. H. PRITCHETT.

Received May 17, 1918.

Introduction.

Bailey and co-workers have recently reported investigations[2] of the use of cyanic acid in glacial acetic acid, and this work very naturally suggested the use of prussic acid in the same solvent. Work in this direction had been under way for some time, when in *Chemical Abstracts* there appeared a reference to an article by R. von Walther and R. Hübner entitled "Conversion of Aldehydes and Ketones into α-Amino Nitriles and Derivatives of the Latter." The very efficient method of preparation used here is to dissolve an aldehyde or ketone together with a suitable amine in glacial acetic acid and add potassium cyanide, *e. g.*, phenylaminophenylacetonitrile, $C_6H_5NHCH(CN)C_6H_5$, is conveniently made by allowing benzaldehyde, aniline, and potassium cyanide to react in glacial acetic acid "to which a little water is added." As Walther and Hübner have undoubted priority in this work, and it is their announced intention to continue the investigation on the use of prussic acid in glacial acetic acid, we have no desire to interfere with their problem, and will simply announce the results obtained by us in this direction. The article of Walther and Hübner referred to above appeared[3] in 1916, but,

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[1] *Loc. cit.*

[2] THIS JOURNAL, 37, 940, 1884 (1915); 39, 279 (1917).

[3] *J. prakt. Chem.*, 93, 119 (1916).

owing to war conditions, was not abstracted by the American Chemical Society until June, 1917.[1]

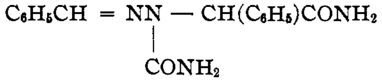
In the present paper it is shown that benzalazine,

$$C_6H_5CH = N - N = CHC_6H_5,$$

dissolved in glacial acetic acid, readily takes up one molecule of hydrocyanic acid upon stirring in solid potassium cyanide. The product here formed, benzalhydrazinophenylacetonitrile, has the constitution

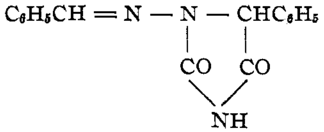
$$C_6H_5CH = NNHCH(C_6H_5)CN.$$

The same substance was obtained by Darapsky and Adamczewski,[2] by the action of hydrazine monochloride, and potassium cyanide on benzaldehyde in aqueous or methyl alcoholic solution. These investigators prepared the substance under different experimental conditions, but always obtained a colored product, *e. g.*, the sample used for analysis consisted of "yellow leaflets." In our method of preparation, the nitrile is obtained colorless. However, the product, especially when impure, readily colors and it then appears impossible to remove the color. In order to confirm the constitution of the reaction product of prussic acid on benzalazine in glacial acetic acid as benzalhydrazinophenylacetonitrile, a few derivatives were made from the substance prepared by this new method. As was to be expected, benzalhydrazinophenylacetonitrile, or better benzalhydrazinophenylacetamide, reacts with cyanic acid in glacial acetic acid[3] forming an α-carbamyl derivative, the structure of which may be exemplified by the amide derivative

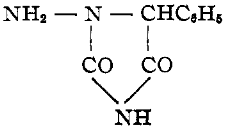


$$C_6H_5CH = N\underset{\displaystyle CONH_2}{\underset{|}{N}} - CH(C_6H_5)CONH_2$$

The latter substance under the influence of alkalies yields benzalaminophenylhydantoin,



This hydrazone in dil. sulfuric acid solution splits off benzaldehyde, giving in poor yield aminophenylhydantoin,



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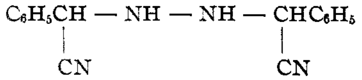
[1] *C. A.*, 11, 1629 (1917).

[2] Dissertation (Heidelberg), 1911. So far as our observation goes, this work has not appeared in journal form.

[3] Cf. THIS JOURNAL, 38, 1784 (1916).

All attempts to add two mols. of hydrocyanic acid to one mol. of benzalazine, and thus arrive at hydrazophenylacetonitrile,



$$\underset{\displaystyle CN}{\underset{|}{C_6H_5CH}} - NH - NH - \underset{\displaystyle CN}{\underset{|}{CHC_6H_5}}$$

were fruitless, although it is well known that the ketazine

$$(CH_3)_2C = N - N = C(CH_3)_2$$

and the aldazine

$$CH_3CH = N - N = CHCH_3$$

by hydrocyanic acid addition give hydrazoisobutyronitrile and hydrazopropionitrile, respectively.

Experimental Part.

Benzalhydrazinophenylacetonitrile, $C_6H_5CH = NNHCH(C_6H_5)CN$.—To 10 g. of benzalazine, $C_6H_5CH = N - N = CHC_6H_5$, in 100 cc. of glacial acetic acid are added 15 g. of finely powdered potassium cyanide in 3 g. portions. After each addition of the cyanide the mixture, which it is convenient to have in a liter flask, is well shaken to effect solution, while toward the end of the reaction it is necessary to warm the mixture cautiously to dissolve the cyanide completely. The flask is now allowed to stand in ice-water for one-half hour, at the end of which time the benzalhydrazinophenylacetonitrile is precipitated by the addition of 750 cc. of water. Adamczewski describes the nitrile as "very readily soluble in warm alcohol, readily soluble in benzene, and difficultly soluble in ether and ligroin." The product obtained by us conforms to these solubilities. The pure white product obtained in the improved process of making benzalhydrazinophenylacetonitrile melts at 114°, whereas Adamczewski reports 111–112°. The low melting point found by him was probably due to failure to obtain a pure product, since he describes the substance as possessing a yellow color. We find that the compound, even after careful recrystallization from alcohol and thorough drying, readily colors on standing. However, the product may be kept colorless by covering it with a little alcohol. The best yields were obtained by Adamczewski by preparing the benzalhydrazinophenylacetonitrile from benzalhydrazine and mandelic acid nitrile, in which reaction he reports a 75% yield. The process employed by us gives a practically quantitative yield and, besides furnishing a pure product, is much simpler than that of the German investigator.

Calc. for $C_{15}H_{13}N_3$: C, 76.60; H, 5.53; N, 17.87. Found: C, 76.24; H, 5.56; N, 18.19.

Doubtless this method of preparing benzalhydrazinophenylacetonitrile opens up a convenient source of hydrazinophenylacetic acid, for Adamczewski states that "benzalhydrazinophenylacetonitrile on standing with conc. hydrochloric acid in the cold readily takes up a molecule of water, passing to the corresponding amide. The latter, on boiling, with normal hydrochloric acid in slight excess, splits off the benzal rest quantitatively, yielding the hydrochloride of hydrazinophenylacetamide, and this is quickly saponified by boiling with alkalis, preferably barium hydroxide, to hydrazinophenylacetic acid."

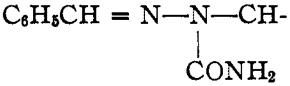
Another convenient method of preparation of hydrazinophenylacetic acid, where the materials are available, is to treat phenylbromo- or -chloroacetic acid with hydrazine hydrate in alcoholic solution.[1]

On standing with conc. hydrochloric acid, as stated above, benzalhydrazinophenylacetonitrile passes to the corresponding amide,

$$C_6H_5CH = NNHCH(C_6H_5)CONH_2.$$

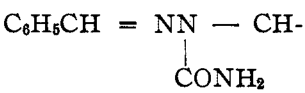
According to Adamczewski, this, on heating, contracts at 164°, and melts between 165–167° with decomposition. This derivative, made by us, was found to melt at 171° to a yellow liquid, indicating only a slight decomposition.

Calc. for $C_{15}H_{15}ON_3$: C, 71.12; H, 5.92; N, 16.63. Found: C, 71.06; H, 5.97; N, 16.62.



Benzalcarbamylhydrazinophenylacetonitrile, $C_6H_5CH = N-\underset{\displaystyle CONH_2}{N}-CH(C_6H_5)CN$.—10 g. of benzalhydrazinophenylacetonitrile is dissolved in 100 cc. of glacial acetic acid, and then 15 g. of finely ground potassium cyanate is added in one g. portions during the course of an hour. After each addition of cyanate the mixture is well stirred and finally, to complete the reaction, after all the cyanate has dissolved, the solution is kept at 80° for one hour. To isolate the reaction product, the acetic acid is distilled off *in vacuo*, and the smeary residue washed with 250 cc. of water to remove potassium acetate and any soluble impurities. The product is next well washed with petrolic ether, taken up in absolute alcohol, and the alcoholic solution poured into a crystallizing dish. As the alcohol evaporates the benzalcarbamylhydrazinophenylacetonitrile separates in a crystalline form. For further purification, it is washed with a little alcohol and then recrystallized from this solvent in the form of rectangular plates, which melt with decomposition at 228°. It is soluble in the common organic solvents with the exception of petrolic ether, but insoluble in water. The yield obtained in the above method of preparation was about 63% of the theoretical.

Calc. for $C_{16}H_{14}ON_4$: C, 69.06; H, 5.04; N, 20.19. Found: C, 69.18; H, 5.44; N, 20.44.



Benzalcarbamylhydrazinophenylacetamide, $C_6H_5CH = N\underset{\displaystyle CONH_2}{N} - CH-$

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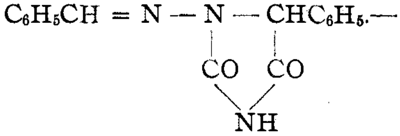
[1] Darapsky, *Z. angew. Chem.*, 1910, 2320; *Chem. Ztg.*, 34, 1280 (1910).

$(C_6H_5)CONH_2$.—This carbamyl derivative may be prepared from benzalhydrazinophenylacetamide similarly to the foregoing substance with an yield of about 80%. On recrystallization from absolute alcohol, it is obtained in the form of short prisms with dome-shaped end faces. On heating it begins to contract at about 150°, melting to a brown liquid at 183°, and finally decomposing at 193° with gas evolution. The solubilities are similar to those of the corresponding nitrile.

Calc. for $C_{16}H_{16}O_2N$: C, 64.84; H, 5.40; N, 18.93. Found: C, 64.61; H, 5.52; N, 18.88.

1-Benzalamino-5-phenylhydantoin,



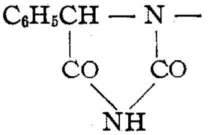
$$C_6H_5CH = N - \begin{array}{c} N - CHC_6H_5. \\ | \qquad\quad | \\ CO \quad CO \\ \diagdown \;\; \diagup \\ NH \end{array}—$$

To 30 cc. of 10% potassium hydroxide is added 5 g. of benzalcarbamylhydrazinophenylacetamide, and the mixture boiled until after complete solution all ammonia is expelled. With vigorous stirring it is made acid with acetic acid, cooled, and filtered. Purification is effected by recrystallization from glacial acetic acid with subsequent washing with water, or by recrystallization from 70% alcohol. The hydantoin can also be prepared directly from benzalhydrazinophenylacetonitrile as follows:

The carbamyl derivative is prepared according to directions given under benzalcarbamylhydrazinophenylacetonitrile, and the crude product, after removal of acetic acid, allowed to stand with 10 times its weight of conc. hydrochloric acid for 12 hours. The acid solution is now diluted to 10 times its volume, whereupon the hydantoin separates in 50% yield. On heating it softens at about 245°, turning yellow, this color changing to a deep brown at 250°.

Calc. for $C_{16}H_{13}ON_3$: C, 68.82; H, 4.66; N, 15.05. Found: C, 68.42, 68.82; H, 4.84; N, 14.93, 15.16.

1-Amino-5-phenylhydantoin,



$$\begin{array}{c} C_6H_5CH - N - NH_2. \\ | \qquad\quad | \\ CO \quad CO \\ \diagdown \;\; \diagup \\ NH \end{array}$$

—If benzalaminophenylhydantoin, dissolved in sulfuric acid diluted with an equal volume of water, is steam distilled, benzaldehyde splits off readily. The resulting aminophenylhydantoin is obtained by neutralizing the sulfuric acid and then purified by first washing with dilute alcohol and finally by dissolving in glacial acetic acid and precipitating with water. The yield in this reaction is very poor, and we have not succeeded in obtaining a colorless product. The sample analyzed was of a light yellow color, readily soluble in glacial acetic acid, and only sparingly soluble in the other common solvents. On heating it begins to contract at about 215°, turning yellow on further heating, and at 232° decomposes with partial sublimation, leaving a small amount of a black residue.

Calc. for $C_6H_9O_2N_3$: N, 22.00%. Found: N, 21.87.

AUSTIN, TEXAS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

2,4-DIHYDROXYBENZOYLTETRACHLORO-*o*-BENZOIC ACID AND 2,3,4-TRICHLORO-6-HYDROXYXANTHONE-1-CARBOXYLIC ACID AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND W. A. ADAMSON.

Received May 23, 1918.

Historical.

Dihydroxybenzoylbenzoic acid was first prepared by Baeyer[1] in connection with his investigation of fluorescein. It was made by evaporating fluorescein in sodium hydroxide solution, containing 3 times its weight of sodium hydroxide, until the color becomes brownish yellow, dissolving in water and precipitating with acid. The substance was purified by dissolving in dilute sodium hydroxide solution, neutralizing with hydrochloric acid, heating to boiling, adding alcohol until the fluid became clear and allowing to crystallize. This product was found to have a melting point of about 200°, and to contain one molecule of water of crystallization. To this compound, which Baeyer called "*monoresorcinphthalein,*" he assigned the formula $C_6H_3(OH)_2.CO.C_6H_4.COOH$. He found that monoresorcinphthalein, when fused with resorcinol, or even when heated alone above its melting point, gave fluorescein. In the latter case the reaction seemed to proceed according to the following equation:

$$\underset{\text{Monoresorcin-phthalein.}}{2C_{14}H_{10}O_5} = \underset{\text{Fluores-cein.}}{C_{20}H_{12}O_5} + \underset{\text{Phthalic anhydride.}}{C_8H_4O_3} + 2H_2O$$

Dihydroxybenzoylbenzoic acid was also made by Liebig[2] in his investigation of resorcinbenzein and fluorescein. His method of preparation was the same as that of Baeyer, while his method of purification differed somewhat. His purified acid contained one and a half molecules of water of crystallization, and melted at 210–211°. He also prepared a diacetyl derivative, having a melting point of 136°. According to Liebig,[3] when fluorescein is made by fusing dihydroxybenzoylbenzoic acid, two modifications are obtained, one red and the other yellow.

R. Meyer and Conzetti[4] obtained dihydroxybenzoylbenzoic acid, along with other products, by the fusion of fluorescein chloride with sodium hydroxide. They give its melting point as about 200°.

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[1] *Ann.*, **183**, 23 (1876).

[2] *J. prakt. Chem.*, **85**, 261 (1912).

[3] *Ibid.*, **85**, 113 (1912).

[4] *Ber.*, **30**, 970 (1897).