refrigerating twenty-four hours, and filtering off the precipitates. This final filtrate was then concentrated to one-fifth its original volume *in vacuo*. Six additional hydrolyses were carried to this stage and the concentrated filtrates combined. The resulting solution was again covered with *p*-xylene, shaken and refrigerated for twenty-four hour each, filtered, and the filtrate concentrated to a thin sirup *in vacuo*. In order to remove any lower saccharides and lithium chloride the amyloheptaose was precipitated by adding four volumes of absolute ethanol. The sirupy precipitate was taken up in a small amount of water and reprecipitated in like manner five times. Finally the precipitate was dehydrated with absolute ethanol to which a small amount of absolute butanol was added, filtered, and washed with dry butanol.[12] The material was finally dried to constant weight in the vacuum oven at 70°, $[\alpha]_D + 175.5°$ (c = 2, water); another preparation, +176.5°; theoretical, +179.6°.[9,10] Molecular weight by alkaline ferricyanide,[10] 1200; by the Kline and Acree hypoiodite method,[13] 1206; theoretical, 1152.

Potassium Amyloheptaonate.—The method of Levine, Foster and Hixon[10] for the preparation of dextrinic acids was applied to 0.5 g. of amyloheptaose. After the final grinding and acetone extraction, the potassium salt was dried to constant weight and a weighed sample ashed with ammonium sulfate. The molecular weight was calculated from the potassium content: observed, K 3.34%, m. wt. 1167; calcd., m. wt. 1206.

Amyloheptaose Phenylhydrazone.—The phenylhydrazone was prepared by a modification of the method of Bergmann and Machemer[14] previously described.[10] Nitrogen was determined by the micro-Dumas method and the molecular weight of the derivative calculated assuming two atoms of nitrogen per molecule: observed, N 2.19%, 2.27%, m. wt. 1275, 1235; calcd., m. wt. 1242.

Chromatographic Test for Lower Saccharides.—A 20 mg. sample of the sugar was dissolved in 0.3 ml. of water and 4.8 ml. of absolute ethanol added. The resulting mixture was placed on a chromatographic column consisting of 12 g. of a 3:1 mixture of Florex XXX and Celite 535 as described by Lew, Wolfrom and Goepp.[15] The sugars were eluted with 90% ethanol and the concentration of sugar in the eluate determined colorimetrically by the diphenylamine method.[16] The rate of flow of the individual sugars was found to be sufficiently characteristic and the diphenylamine test sufficiently sensitive that an amount of glucose, maltose or trisaccharide as low as 0.01 mg./ml. could be readily detected.

On testing 20 mg. of amyloheptaose in this manner, there was no evidence whatsoever for contamination by glucose, maltose or trisaccharide. The column was then extruded, cut into 2-cm. portions and the individual portions extracted and tested for carbohydrate. The top 2-cm. portion was carbohydrate free, the next two 2-cm. portions contained carbohydrate, and the remainder of the column was carbohydrate free.

A cycloheptaamylose sample which was hydrolyzed for *ca.* 7000 minutes (k_2t = 0.35) was similarly chromatographed, and glucose, maltose and trisaccharide were found to be present in sizable amounts (109 mg., 81 mg. and 62 mg.).

Summary

Amyloheptaose has been prepared by controlled acid hydrolysis of cycloheptaamylose. The analytical constants of amyloheptaose, its potassium aldonate and its phenylhydrazone agree with those calculated for a heptasaccharide.

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[12] The butanol was used to prevent condensation of water and consequent gumming of the amyloheptaose due to the evaporation of the ethanol during the filtration and drying.

[13] Kline and Acree, *Ind. Eng. Chem. Anal. Ed.*, **2**, 413 (1930).

[14] Bergmann and Machemer, *Ber.*, **63**, 322 (1930).

[15] Lew, Wolfrom and Goepp, This Journal, **68**, 1449 (1946).

[16] See Oppel, *Biochem. Z.*, **229**, 85 (1930), and Davidson, Kermack Mowat and Stewart, *Biochem. Z.*, **30**, 433 (1936), for two modifications of the quantitative diphenylamine method.

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[Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute]

The Reaction of Diethanolamine with Nitriles and Potassium Cyanide

By William H. Rauscher, Irving S. Goldstein and Maxwell Breslau

Since ethanolamines have been used as agents for the reduction of organic compounds,[1] especially nitro compounds, it was though possible they might convert nitriles to amines. However, benzonitrile and benzyl cyanide, when refluxed with substantially dry diethanolamine, undergo hydrolysis rather than reduction to yield benzoic and phenylacetic acid, respectively, with concomitant evolution of ammonia. Maximum yields are obtained with a nitrile to diethanolamine ratio of 1:5 and a reflux period of forty-eight hours.

From larger scale runs, conducted in an attempt to isolate intermediate products, it was possible to obtain substantial quantities of water and piperazino-1,4-bis-(β-ethanol). It appears therefore that diethanolamine undergoes cyclization to the piperazine and water which effects hydrolysis of the nitrile. No other details of the mechanism have been established.

Under similar conditions, potassium cyanide yields ammonia and a mixture of potassium formate and succinate. The latter salt, the formation of which was unexpected, was always obtained in much larger amount than the formate. It was established that only a small amount of ammonia is evolved by refluxing diethanolamine alone and that the presence of a small amount of potassium cyanide in refluxing diethanolamine does not catalyze the evolution of ammonia from the amine or cause its cyclic dehydration to the piperazine. Potassium succinate was not formed by refluxing potassium formate with diethanolamine. The mechanism of the conversion of potassium cyanide to potassium succinate has not been determined.

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[1] (a) M. Meltsner, C. Wohlberg and M. J. Kleiner, This Journal, **57**, 2554 (1935); (b) C. B. Kremer, *ibid.*, **59**, 1681 (1937); (c) M. Meltsner, L. Greenstein, G. Gross and M. Cohen, *ibid.*, **59**, 2660 (1937); (d) C. B. Kremer and B. Kress, *ibid.*, **60**, 1031 (1938); (e) C. B. Kremer and A. Bendich, *ibid.*, **62**, 1279 (1940).

Experimental

Materials.—Diethanolamine was the Carbide and Carbon Chemicals Corporation product purified by redistillation at 3 mm. Benzonitrile and benzyl cyanide were redistilled Eastman Kodak Co. products. Potassium cyanide was the C. P. grade. All melting points are corrected. Typical runs are described.

Benzoic Acid from Benzonitrile.—Five grams (0.05 mole) of benzonitrile and 27.5 g. (0.25 mole) of diethanolamine were refluxed for forty-eight hours in an apparatus employing standard taper joints. The condenser was water cooled. Evolved ammonia was swept out through the condenser into a measured quantity of standard acid by a gentle stream of purified air. At the end of forty-eight hours the reaction mixture was cooled and diluted with 100 ml. of water, complete solution taking place. The solid which appeared immediately on acidification with concentrated hydrochloric acid was removed by filtration and recrystallized from water. The filtrate was warmed for several hours on the steam-bath and cooled, but no additional solid was obtained; weight recrystallized acid 3.1 g. or a 52.4% yield; m. p. 121–122°; neut. equiv. 120.5; m. p. of *p*-nitrobenzyl ester 88–89°. The values for benzoic acid are: m. p. 121.4; neut. equiv. 122.1; m. p. *p*-nitrobenzyl ester 89°. During the reflux period ammonia evolved corresponded to 61% of the nitrogen of benzonitrile.

Phenylacetic Acid from Benzyl Cyanide.—Five grams (0.05 mole) of benzyl cyanide and 28 g. (0.25 mole) of diethanolamine were refluxed similarly for forty-eight hours. On adding 100 ml. of water complete solution took place. The solution was made acid with hydrochloric acid and warmed on the steam-bath for one hour. After cooling it was extracted three times with 50-ml. portions of ether. The solid recovered from the ether solution was recrystallized from petroleum ether; weight recrystallized acid 4.5 g. or a 77.4% yield; m. p. 76.5–77°; neut. equiv., 135; m. p. of *p*-nitrobenzyl ester 64.5–65°. The values for phenylacetic acid are: m. p. 76.7°; neut. equiv., 136.2; m. p. of *p*-nitrobenzyl ester 65°. During the reflux period evolved ammonia corresponded to 71% of the nitrogen of benzyl cyanide.

Piperazino-1,4-bis-(β-ethanol).—One-half mole (58.5 g.) of benzyl cyanide and 2.5 moles (260 g.) of diethanolamine were refluxed in a 3-necked, 500-ml. flask provided with a water cooled condenser and thermometers placed in the liquid and the vapor, standard taper joints being used. After several hours refluxing the liquid temperature fell to 145° and the vapor temperature to 101°, both temperatures remaining quite constant to the end of reflux. After forty-eight hours 36.5 g. of water were removed through a short Vigreux column at atmospheric pressure. On further distillation at 3 mm. considerable decomposition resulted and very little material could be distilled. On cooling overnight the remaining reaction mixture became a pasty solid. Pyridine was added with warming until it constituted about one third of the homogeneous solution resulting. On cooling the solution in the refrigerator a yellowish crystalline solid was obtained. It was removed and washed with pyridine and acetone. The dried product weighed 45 g. After several recrystallizations from acetone a colorless crystalline solid melting at 134.6–135.2° was obtained. As the identity of the material was not suspected at this time it was extensively investigated and the following data collected. *Anal.* C, 55.22, 55.10; H, 10.44, 10.23; N, 15.99, 16.1; neut. equiv. (using methyl red) 175.6, 175.0; weight of base combining with 1 mole of hydrochloric acid (gravimetric) 86.86, 86.88; per cent. chlorine in hydrochloride 28.67, 28.66; m. p. *p*-nitrobenzoate 158–160°. Piperazino-1,4-bis-(β-ethanol) has the following values. *Anal.* C, 55.14; H, 10.41; N, 16.08; m. p. 135–135.5°; mol wt. 174.2; weight combined with 1 mole hydrochloric acid 87.12; chlorine in dihydrochloride, 28.67; m. p. *p*-nitrobenzoate 158–158.5°.[2]

Potassium Formate and Potassium Succinate from Potassium Cyanide.—Thirty-three grams (0.5 mole) of potassium cyanide and 260 g. (2.5 moles) of diethanolamine were refluxed for forty-eight hours as in the 0.5 mole benzyl cyanide run described above. Evolved ammonia corresponded to 74.4% of the nitrogen of potassium cyanide. Soon after reflux began the liquid temperature was 238° but gradually fell to 156°, where it remained fairly constant. On cooling the reaction mixture became very viscous and crystals appeared. Sufficient absolute alcohol was added to permit the solid to be removed by filtration. This solid (A) was washed with absolute alcohol and dried in a vacuum desiccator to give 19.4 g. of product. The alcohol in the filtrate from (A) was removed by distillation and chloroform added as long as its addition gave evidence of the precipitation of a solid (B). Solid (B) was collected on a filter, washed with chloroform and dried in a vacuum desiccator to give 3 g. of material.

Solid (A) was shown to be potassium succinate from the following data: Solid (A) yielded an acid of m. p. 187–188°; neut. equiv., 60.1; mixed m. p. with authentic succinic acid 186–187°; *p*-bromophenacyl ester m. p. 212–213°; *p*-nitrobenzyl ester m. p. 86–87°. For succinic acid the values are: m. p. 188°; neut. equiv. 59.05; m. p. *p*-bromophenacyl ester 211°; m. p. *p*-nitrobenzyl ester 88°. The equivalent weight of solid (A) by the sulfate method was found to be 93.0, 92.5. The equivalent weight of potassium succinate is 97.1.

Solid (B) was shown to be potassium formate from the following data: m. p. 166–167°; m. p. of *p*-bromophenacyl ester 138–139°; equiv. wt. by sulfate method 86.0, 89.0. For potassium formate the values are: m. p. 167.5°; m. p. *p*-bromophenacyl ester 140°; equiv. wt., 84.

Summary

By refluxing with substantially dry diethanolamine, benzonitrile and benzyl cyanide are hydrolyzed to the corresponding acids. Water required for the hydrolysis is apparently supplied by a cyclic dehydration of diethanolamine to piperazino-1,4-bis-(β-ethanol). In the case of potassium cyanide a substantial yield of potassium succinate and a small yield of potassium formate result. No mechanism is suggested for the formation of the succinate.

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(2) D. E. Adelson, L. G. MacDowell and C. B. Pollard, THIS JOURNAL, 57, 1988 (1935).