[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Naphthalenearsonic Acids. The Application of the Béchamp Reaction to α-Naphthylamine

BY HAROLD P. BROWN[1] AND CLIFF S. HAMILTON

p-Aminobenzenearsonic acid has been prepared by heating aniline with arsenic acid, the reaction being known as the Béchamp reaction.[2] In 1908, O. and R. Adler[3] applied the reaction to α-naphthylamine, and obtained an aminonaphthalenearsonic acid, "Adler acid,"[4] m. p. 173–175°,[5] which they designated as 4-amino-1-naphthalenearsonic acid. In 1932, 4-amino-1-naphthalenearsonic acid, m. p. 210° (d) was prepared from 4-nitro-1-naphthylamine[6] by coupling the diazo derivative of the latter with sodium arsenite, and reducing the resultant nitro compound.

The present investigation explains the discrepancy between these two melting points recorded in the literature for 4-amino-1-naphthalenearsonic acid, by identifying Adler acid as 1-amino-2-naphthalenearsonic acid.

1-Amino-2-naphthalenearsonic acid, m. p. 177° (dec.) has been prepared from 1-nitro-2-naphthylamine by the Bart reaction.[6] The near coincidence of the melting point of this acid with that of Adler acid (173–175°)[5] led Saunders[7] to suggest that 4-amino-1-naphthalenearsonic acid rearranges to 1-amino-2 acid under the conditions of the Béchamp reaction in a manner comparable to the rearrangement of 4-amino-1-naphthalenesulfonic acid.[8] No proof of such rearrangement was advanced, but it was suggested that if the rearrangement of the 4-amino-1 acid to 1-amino-2 acid in boiling naphthalene could be demonstrated, the difference in the melting point of the product obtained when the 4-amino-1 acid was prepared by means of the Bart reaction instead of the Béchamp reaction would be explained. Attempts to effect rearrangement of 4-amino-1 acid or of the sodium salt of the acid by suspension in naphthalene at various temperatures proved unsuccessful, as did the heating of the dry sodium salt. The Béchamp reaction as it has been applied to α-naphthylamine employs an excess of the amine, and hence if rearrangement of the 4-amino-1 acid occurs during the reaction it must take place in an α-naphthylamine medium. Samples of 4-amino-1 acid heated with α-naphthylamine until solution of the arsonic acid occurred were converted into an aminonaphthalenearsonic acid, m. p. 173–175° (d), which when mixed with an equal portion of either Adler acid, or 1-amino-2 acid gave no depression of the melting point of the acid. The acetyl derivative of the product melted with decomposition at 247–248°, which agrees with the melting point of acetylated Adler acid (244–246° (d)), and that of 1-acetylamino-2-naphthalenearsonic acid (240–245° (dec.)),[6] and mixed melting points indicated that the product was identical with both of these arsonic acids. Therefore, Adler acid was obtained from 4-amino-1-naphthalenearsonic acid by heating the latter in α-naphthylamine.

4-Amino-1-naphthalenearsonic acid prepared by the method of Saunders[7] was structurally identified by converting the acetyl derivative into 4-acetylamino-1-chloronaphthalene by the action of phosphorus pentachloride. Adler acid was identified as 1-amino-2-naphthalenearsonic acid by the preparation of an acetyl derivative, m. p. 244–246° (d.), which when mixed with an equal quantity of 1-acetylamino-2-naphthalenearsonic acid melted simultaneously with a sample of the pure derivative, and the conversion of acetylated Adler acid into 1-acetylamino-2-chloronaphthalene.

Experimental

Preparation of Adler Acid. (a) From α-Naphthylamine Hydrogen Arsenate and α-Naphthylamine. (b) By Fusion of α-Naphthylamine Hydrogen Arsenate. (c) From α-Naphthylamine and Arsenic Acid.—(a) (A modification of the procedure employed by O. and R. Adler.)[3] To 10 g. of molten α-naphthylamine, in a 250-cc. casserole heated by an oil-bath, was added 22.5 g. of α-naphthylamine hydrogen arsenate.[9] The mixture was heated rapidly, with constant stirring, to 195° and kept at that temperature for ten minutes. The resultant purple tarry mass was allowed to cool to approximately 100°, extracted by

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[1] Parke, Davis and Co. Fellow.

[2] Ehrlich and Bertheim, *Ber.*, **40**, 3292–3297 (1907).

[3] O. and R. Adler, *Ber.*, **41**, 931–934 (1908).

[4] The term "Adler acid," will be used throughout this article to designate the arsonic acid obtained from α-naphthylamine by the Béchamp reaction.

[5] Benda and Kahn, *Ber.*, **41**, 1672–1678 (1908).

[6] Saunders and Hamilton, THIS JOURNAL, **54**, 636 (1932).

[7] Thesis, University of Nebraska, 1930, p. 13.

[8] Cain, "The Manufacture of Intermediate Products for Dyes," The Macmillan Company, New York, 1918, p. 181; German Patent 72,833 (1892); Erdmann, *Ann.*, **275**, 225–230 (1893); Landshoff and Meyer, German Patent 56,563 (1890).

[9] Boon and Ogilvie, *Pharm. J.*, **101**, 129–130 (1918).

boiling with 200 cc. of 0.5 *N* sodium hydroxide, filtered through a thin charcoal pad, and the filtrate acidified to Congo red paper with 6 *N* hydrochloric acid. The white or slightly pink precipitate of aminonaphthalenearsonic acid was reprecipitated from 0.5 *N* sodium carbonate; maximum yield 5% based on arsenic acid used; m. p. 175–176° (d) (O. and R. Adler,[3] and Benda and Kahn[5] reported 173–175°).

(b) In a 50-cc. beaker suspended in an oil-bath, 5 g. of α-naphthylamine hydrogen arsenate was heated with constant stirring at 180–190° until fusion had occurred, the tarry mass extracted by boiling with 100 cc. of 1 *N* sodium hydroxide, cooled and filtered through a thin charcoal pad, and the filtrate acidified to Congo red paper with 6 *N* hydrochloric acid, precipitating an aminonaphthalenearsonic acid; maximum yield, 6%; m. p. 175° (d). (Similar fusion by heating at 170–177° until fusion just started, gave a product melting at 194° (d), which mixed melting points indicated was 4-amino-1-naphthalenearsonic acid, and which was not identical with the product melting at 175° (d).)

(c) (Modification of method of Andreev[10]) ten grams of solid arsenic acid, dried for three hours at 110°, was slowly stirred into 50 g. of molten α-naphthylamine (previously heated to 150° for ten minutes and then allowed to cool to 75–90°), contained in a 250-cc. casserole suspended in an oil-bath. The mixture was heated rapidly to 170° and then for fifteen minutes at 165–175° with constant stirring, allowed to cool to about 100°, poured into 250 cc. of 0.5 *N* sodium hydroxide, and heated to boiling. The extract was allowed to cool with occasional stirring until the tar had solidified, filtered through a thin charcoal pad, and the filtrate acidified to Congo red paper with 6 *N* hydrochloric acid. The white precipitate of arsonic acid was purified by dissolving in 0.5 *N* sodium carbonate, filtering through charcoal, and reprecipitating with hydrochloric acid. Dried in the oven at 110° the arsonic acid turned slightly pink on the surface; maximum yield 5.6 g. or 30% based on arsenic acid used, average yield 20%, m. p. 175–176° (d).

That Adler acid was identical with 1-amino-2-naphthalenearsonic acid, and was not identical with the 4-amino-1 acid, was indicated by the following simultaneously determined pure and mixed melting points: Adler acid, 175–176° (d); 4-amino-1 acid, 210–211° (d); 1-amino-2 acid, 176–177° (d); 4-amino-1 and 1-amino-2 acids, 166–168° (d); 4-amino-1 and Adler acids, 169–170° (d); 1-amino-2 and Adler acids, 175–177° (d).

Rearrangement of 4-Amino-1-naphthalenearsonic Acid.—Rearrangement was effected by adding 5 g. of boiling α-naphthylamine to 1 g. of 4-amino-1 acid in a test-tube, heating until the resultant solution *just started* to turn purple, cooled to about 100°, poured into 50 cc. of 1 *N* sodium hydroxide, heated to boiling, filtered through a thin charcoal pad, and the filtrate acidified to Congo red paper with 6 *N* hydrochloric acid, which precipitated an aminonaphthalenearsonic acid, m. p. 174–175° (d); maximum yield, 0.5 g. (50%); average yield, 0.38 g. (38%). The following simultaneously determined pure and mixed melting points indicated that the product was identical with Adler acid and 1-amino-2 acid, but was not identical with 4-amino-1 acid: Adler acid and above product, 172–174° (d); 1-amino-2 acid and above product, 172–173° (d); 4-amino-1 acid and above product, 168–172° (d); above product, 174–175° (d).

The acetyl derivative of rearranged 4-amino-1-naphthalenearsonic acid was prepared by a method similar to that used by Saunders[7] to prepare 1-acetylamino-2-naphthalenearsonic acid. The following simultaneously determined pure and mixed melting points indicated that the white solid obtained was identical with acetylated Adler acid and acetylated 1-amino-2 acid, and was not identical with acetylated 4-amino-1 acid: above product, 247–248° (d); above product and 4-acetylamino-1 acid, 235–240° (d); above product and 1-acetylamino-2 acid, 243–245° (d); above product and acetylated Adler acid, 247–248° (d).

Acetylated Adler acid was prepared by a modification of Saunders'[7] method for the preparation of 1-acetylamino-2-naphthalenearsonic acid. The product was a white solid, m. p. 245–246° (d), yield 77%. The following simultaneously determined pure and mixed melting points indicated that acetylated Adler acid was identical with 1-acetylamino-2 acid, and was not identical with 4-acetylamino-1 acid: 4-acetylamino-1 acid, 269–271° (d); 1-acetylamino-2 acid, 246–247° (d); 4-acetylamino-1 and 1-acetylamino-2 acids, 235–238° (d); acetylated Adler acid, 242–243° (d); Adler acid and 4-acetylamino-1 acid 230–237° (d); Adler acid and 1-acetylamino-2 acid, 240–243° (d).

Preparation of 4-Acetylamino-1-chloronaphthalene from 4-Acetylamino-1-naphthalenearsonic Acid.—Five grams of 4-acetylamino-1 acid was ground to a paste with 15 cc. of carbon tetrachloride in a 50-cc. beaker. Ten grams of phosphorus pentachloride in 15 cc. of carbon tetrachloride was then added to the arsonic acid at room temperature with constant stirring, a vigorous reaction occurring after about twenty seconds. When reaction at room temperature had ceased, it was completed by evaporating the mixture almost to dryness on a water-bath. The residue was dissolved in 35 cc. of ethyl alcohol, filtered through a thin charcoal pad, the filtrate diluted to 125 cc. with cold water, placed in the refrigerator for two hours, filtered, redissolved in ethyl alcohol, charcoaled and precipitated with cold water. Filtration gave a white solid, m. p. 186–187°, weight 0.3 g., giving a negative test for the arsonic acid group[11] and a positive Beilstein cupric oxide test for halogen. (Reverdin and Crépieux[12] gave 186.5° as the melting point of 4-acetylamino-1-chloronaphthalene.)

Preparation of 1-Acetylamino-2-chloronaphthalene from Acetylated Adler Acid.—This was prepared by the preceding method. (The crude product obtained was refluxed for thirty minutes with 50 cc. of 6 *N* hydrochloric acid, reprecipitated from ethyl alcohol, and refluxed for two hours with 50 cc. of 0.5 *N* sodium carbonate to remove unreacted and deacetylated material which was present.) The yield was 0.2 g. from 2 g. of Adler acid, m. p. 190–191°, negative test for arsonic acid group[11] and positive Beilstein cupric oxide test for halogen. (Charrier and Ferreri[13] have reported that 1-acetylamino-2-chloronaphthalene

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(10) Andreev, *J. Russ. Phys. Chem. Soc.*, **45**, 343 (1913).

(11) Scott and Hamilton, This Journal, **52**, 4127 (1930).

(12) Reverdin and Crépieux, *Ber.*, **33**, 682 (1900).

(13) Charrier and Ferreri, *Gazz. chim. ital.*, **41**, I, 726 (1912).

melts at 191°.) The following simultaneously determined pure and mixed melting points indicated that the product was not identical with that obtained from 4-acetylamino-1 acid: derivative from 4-acetylamino-1 acid, 186–187°; derivative from acetylated Adler acid, 190–191°; mixture of the two derivatives, 173–178°.

Preparation of 1-Acetylamino-2-chloronaphthalene from 1-Acetylamino-2-naphthalenearsonic Acid.—Employing the method of the preceding procedure, 0.45 g. of 1-acetylamino-2 acid was converted into a white solid, m. p. 190–192°, which gave a negative test for the arsonic acid group[11] and a positive Beilstein cupric oxide test for halogen. (Charrier and Ferreri[13] have reported that 1-acetylamino-2-chloronaphthalene melts at 191°.) The following simultaneously determined melting points demonstrated that acetylated Adler acid and 1-acetylamino-2 acid are identical: derivative from 1-acetylamino-2 acid, 191–192°; derivative from acetylated Adler acid, 189–191°; mixture of these two derivatives, 190–192°.

Summary

1. The aminonaphthalenearsonic acid obtained by the direct arsonation of α-naphthylamine by means of the Béchamp reaction has been identified structurally as 1-amino-2-naphthalenearsonic acid by a series of mixed melting points, the preparation of an acetyl derivative, and the preparation of 1-acetylamino-2-chloronaphthalene from this acetyl derivative.

2. The assignment of this structure instead of that of 4-amino-1-naphthalenearsonic acid as reported in the literature involves a correction of the structure of all naphthalene arsenicals dependent on the Béchamp reaction as a part of their method of preparation, including certain substituted naphthalenearsonic acids, the only known hydroxynaphthalenearsonic acid, and the product at present assigned the structure of the naphthalene analog of arsphenamine.

3. 1-Amino-2-naphthalenearsonic acid was obtained from 4-amino-1-naphthalenearsonic acid by heating the latter in α-naphthylamine, thus demonstrating that in a medium of α-naphthylamine at temperatures above 175°, the former isomer is more stable than the latter.

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The Synthesis of Pyrazine by the Catalytic Dehydrogenation of Ethanolamine

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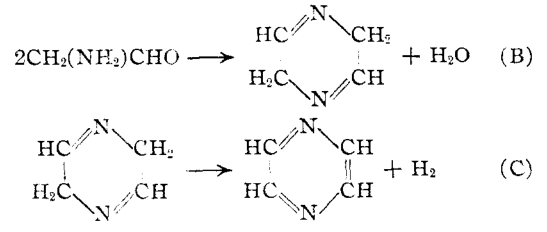
A study of the dehydrogenation of the vapor of ethanolamine has been made using catalysts at temperatures varying from 230 to 300°. The catalysts used were copper, copper and zinc oxide, zinc oxide and sodium carbonate. In each case pyrazine is formed directly, the reactions involved presumably being

$$CH_2(NH_2)CH_2OH \longrightarrow CH_2(NH_2)CHO + H_2 \qquad (A)$$



One mole of ethanolamine should thus yield one-half mole of pyrazine and one and one-half moles of hydrogen. The best yields were obtained at 300° using a copper catalyst. The yield was then 5.6% of pyrazine isolated as the mercuric chloride double salt although the hydrogen obtained was 0.54 mole per mole of ethanolamine. It thus appears that most of the amino acetaldehyde disappeared by side reactions producing resins. These resins eventually rendered the catalyst inactive.

Experimental

For each run one mole of redistilled ethanolamine (b. p. 168–170°) was used. This was kindly furnished by the Carbide and Carbon Chemical Corporation.

The catalysts used were A, finely divided copper; B, an equimolecular mixture of finely divided copper and zinc oxides; C, zinc oxide with 4.5% by weight of sodium carbonate. The first two were prepared by the method used by Frolich, Fenske and Quiggle,[1] except that the mixed hydroxides were pasted while wet on rolled copper gauze, and slid into the tube. The catalyst was then dried, heated to 300° to convert to oxides, and reduced in a current of hydrogen, diluted with nitrogen, at about 200°. The third was made by mixing sodium carbonate (4.5% by weight) with zinc oxide which had been prepared from zinc nitrate solution by precipitation with ammonium hydroxide and drying overnight at 120°. It was supported on moistened tile.

The catalyst tube was about 2 cm. inside diameter and 75 cm. long with a small inside tube running from end to end for a thermocouple. It was wrapped with an electrical heater, and surrounded by an air jacket consisting

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[1] Frolich, Fenske and Quiggle, *Ind. Eng. Chem.*, **20**, 694 (1928).