80% yield by this method. In addition, Fieser and workers[6] have shown that lead tetraacetate can act as an alkylating agent under certain conditions, but this reaction would not be expected to be of importance in this study.

Recrystallized acenaphthene, m. p. 93.6–94.1° and redistilled acenaphthenyl acetate, b. p. 167–174° at 5 mm., were used. The other reagents and solvents were of ordinary purity. The general procedure was that described by Fieser and Cason.[5] Enough benzene was used in each run to lower the boiling point of the mixture to 85 to 90°, and the reaction was carried out under reflux. If the benzene was not present in sufficient amount the temperature tended to increase quite rapidly after each addition of red lead. It was found that the reaction would not proceed in acetic anhydride as the solvent. In glacial acetic acid, the reaction became very slow after enough red lead had been consumed to convert the acenaphthene to acenaphthenol acetate. A mixture of 2 moles of acetic acid with 1 mole of acetic anhydride was adopted as giving the maximum rate of consumption of red lead throughout the reaction.

Since we were interested in either acenaphthenediol diacetate or acenaphthoquinone as products, 2 or 4 moles of red lead was used to 1 mole of acenaphthene. Two trials were made with acenaphthenyl acetate as a reactant using an equimolar amount of red lead. Most of the runs were made in 0.1 mole quantities.

When the oxidation was complete, the reaction mixture was poured into water, the benzene layer separated, and the aqueous layer extracted with a fresh portion of benzene. At times, the benzene layer was emulsified by the presence of a finely divided solid, presumably lead dioxide. The addition of glycerol eliminated this difficulty but only after a prolonged period.[7] A much more rapid scheme was the addition of small portions of a dilute solution of sodium nitrite which reacted instantly. After washing with sodium bicarbonate solution to remove acetic acid, the benzene layer was dried over sodium sulfate and the solvent removed by distillation, beginning at atmospheric pressure and finishing under vacuum.

In five out of seven runs the oily residue was distilled under vacuum, acenaphthenyl acetate being the principal product, 30–80%. In most cases, a small high boiling fraction, 180–190° at 5 mm., was also obtained. In a typical instance, a 0.1 mole run with acenaphthenyl acetate from which 0.07 mole of the reactant was recovered, 3.4 g. of this viscous yellow oily fraction yielded, when extracted with hot sodium bisulfite solution, 0.2 g. of acenaphthoquinone, identified by melting point and melting point of a mixture, 246–248°. The oil remaining, 3.2 g., yielded no alkali insoluble material upon saponification. Acidification of the solution caused the separation of only 1.5 g. of a brown solid, m. p. 292° dec. The small residues from the vacuum distillations likewise were easily saponified to give more water soluble material than acid insoluble material.

In two runs, 0.1 mole of the hydrocarbon with 0.4 mole of red lead, the oily product remaining after the removal of the benzene, was saponified with alcoholic potassium hydroxide to give a 20% yield in both cases of crude acenaphthenol. The alkaline filtrates each gave 8.7 g. of acid insoluble material of which 4.7 g. was soluble in hot sodium carbonate solution. This led to the isolation of 3.8 g. (0.018 mole) of crude naphthalic acid. The sodium carbonate insoluble residue was slightly acidic as shown by solubility in hot sodium hydroxide solution.

These results indicated that acenaphthenyl acetate was relatively stable to the action of lead tetraacetate. When forced, the reaction yielded highly acetoxylated material from which naphthalic acid could be obtained. No acenaphthenediol diacetate was obtained in any case. Small amounts of acenaphthoquinone were formed, but this substance was difficult to separate from acenaphthenyl acetate and accounted for the yellow color of the ester.

(6) Fieser and Chang, THIS JOURNAL, 64, 2043 (1942); Fieser, Clapp and Daudt, *ibid.*, 64, 2052 (1942).

(7) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 2nd ed., p. 438, 1941.

DEPARTMENT OF CHEMISTRY
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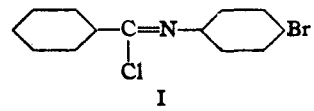
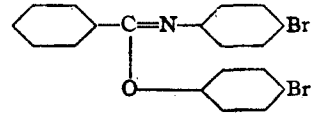
Structure of 4,4′-Dibromodiphenylamine

BY NATHAN N. CROUNSE[1] AND L. CHARLES RAIFORD[2]

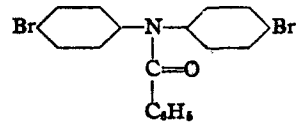
4,4′-Dibromodiphenylamine has been prepared previously by bromination of a 5% solution of diphenylamine in 20% ethanol[3] and in 5% yield by the action of hydrogen bromide on N-nitrosodiphenylamine,[4] but convincing proof of its structure was lacking. We have proved its structure by preparing the compound by a method which leaves no doubt as to the position of the bromine atoms. N-4-Bromophenylbenzimino 4-bromophenyl ether (II), prepared from N-4-bromophenylbenzimino chloride (I) and 4-bromophenol, was rearranged to the benzoyl derivative of 4,4′-dibromodiphenylamine (III), and the latter was hydrolyzed to 4,4′-dibromodiphenylamine. The rearrangement of the ether was based on similar reactions of known compounds as studied by Chapman.[5]



I



II



III

4,4′-Dibromodiphenylamine.—The supposed compound, m. p. 105.5–106°, was prepared by the method of Galatis and Megaloikonomos.[3]

Anal. Calcd. for $C_{12}H_9NBr_2$: N, 4.28. Found: N, 4.04.

N-4-Bromophenylbenzimino 4-Bromophenyl Ether (II).—A mixture of 21 g. of phosphorus pentachloride and 25 g. of 4-bromobenzanilide was heated on a water-bath, contrary to Wallach's[6] general directions, until the evolution of hydrogen chloride ceased. The phosphorus oxychloride was distilled. The intermediate imino chloride (I) was not isolated. The residue was dissolved in ether and added to a solution of 52.9 g. of 4-bromophenol as its sodium salt

(1) A portion of the thesis submitted by N. N. Crounse in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa. Present address: The Hilton-Davis Chemical Co., Cincinnati, Ohio.

(2) Deceased January 8, 1944.

(3) Galatis and Megaloikonomos, *Prakt. Akad. Athenón*, 9, 20 (1934) [*Chem. Zentr.* 105, II, 2974 (1934)].

(4) Fischer, *Ber.*, 45, 1103 (1912).

(5) Chapman, *J. Chem. Soc.*, 121, 1676 (1922); 127, 1992 (1925); 569 (1929); 2462 (1930).

(6) Wallach, *Ann.*, 184, 77 (1877).

in absolute ethanol according to the general directions of Hantzsch.[7] After twenty-four hours, the solvent was distilled. The residue after extraction with dilute alkali and acid solidified and was crystallized from methanol to give 29 g. (75%) of yellow needles, m. p. 86–87°.

Anal. Calcd. for $C_{19}H_{13}ONBr_2$: N, 3.25. Found: N, 3.27.

Rearrangement of (II).—Five grams of (II) in a Pyrex test-tube was heated to 270–280° for one hour and fifty-five minutes and then for five minutes at 285–290° according to general directions of Chapman.[5] The crude material melted at 140–142°. Crystallization from ethanol gave 4.2 g. (84%) of long white plates (III), m. p. 141.5–142°.

Anal. Calcd. for $C_{19}H_{13}ONBr_2$: N, 3.25. Found: N, 2.99.

Hydrolysis of N,N-4,4′-Dibromodiphenylbenzamide (III).—Four grams of (III) was hydrolyzed by refluxing for one-half hour with 3 g. of potassium hydroxide in 30 ml. of ethanol. After cooling, the mixture was filtered from a solid which was identified as potassium benzoate by mixed melting point after acidification. The filtrate was poured into water to yield 3 g. of tan solid, m. p. 104–106°. Crystallization from ligroin (65–70°) gave 2 g. (68%) of glistening needles, m. p. 106.5–107°. A mixed melting point with 4,4′-dibromodiphenylamine prepared above showed no depression.

Anal. Calcd. for $C_{12}H_9NBr_2$: N, 4.28. Found: N, 3.96.

Benzoylation of 4,4′-Dibromodiphenylamine.—Three grams of benzoyl chloride was added to a solution of 3.4 g. of 4,4′-dibromodiphenylamine[3] in 7 ml. of pyridine. After two hours, the resulting mixture was heated on the steam-bath for five minutes, then poured into dilute hydrochloric acid to give 4.5 g. of tan solid, m. p. 136–138°. Crystallization from ethanol gave 3.5 g. (85%) of colorless plates, m. p. 141–141.5°. A mixed melting point with (III) showed no depression.

Anal. Calcd. for $C_{19}H_{13}ONBr_2$: N, 3.25. Found: N, 2.92.

(7) Hantzsch, *Ber.*, **26**, 927 (1893).

CHEMISTRY DEPARTMENT
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The Alkaline Hydrolysis of β-Aminopropionitrile

BY JARED H. FORD

The preparation of β-alanine by the hydrolysis of β-aminopropionitrile with hydrochloric acid and subsequent removal of the acid by means of anion exchange resins has been described recently.[1] The present communication describes a more convenient method which employs alkaline hydrolysis.

β-Alanine was obtained in yields of 88–92% by boiling β-aminopropionitrile with 25–50% barium hydroxide solution for twenty to thirty minutes. Although alkaline hydrolysis was found to be less sensitive than acid hydrolysis to changes in experimental conditions, 8% barium hydroxide gave only 68% yield. Since β-aminopropionitrile[2] and bis-(cyanoethyl)-amine[3] have been reported to give β-alanine in approximately the same yields (20%) on hydrolysis with ammonium hydroxide at 180–225°, it appears that the following equilibrium is established under these conditions[4]

$$2\ NH_2CH_2CH_2CN \rightleftharpoons NH(CH_2CH_2CN)_2 + NH_3$$

This equilibrium is not established rapidly at the temperatures employed in the present investigation and prolonging the heating to two hours did not decrease the yield of β-alanine perceptibly.[5] Under the same conditions, bis-(cyanoethyl)-amine gave the monobarium salt of β,β′-iminobispropionic acid in 86% yield.

The free acid and its monoammonium salt, which are probable by-products in several of the previously reported syntheses of β-alanine, have now been characterized for the first time.[6] Although the monoammonium salt has the same elementary composition as β-alanine, its presence can be easily detected by the usual tests for ammonium salts. The addition of 10% of this compound was found to lower the melting point of β-alanine from 195–196° (dec.) to 175–180° (dec.). The free acid can be determined quantitatively in the presence of β-alanine by titration with alkali using phenol red indicator.

Experimental[7]

Hydrolysis of β-Aminopropionitrile.—Barium hydroxide octahydrate (185 g.) was fused on the steam-bath and 70 g. of β-aminopropionitrile[1] was added dropwise to the mechanically stirred solution at 90–95°. After thirty minutes, 1 liter of hot water was added and the solution was saturated with carbon dioxide. The precipitate was filtered and washed with hot water and the combined filtrates were evaporated to dryness *in vacuo*. The residue was dissolved in water and the solution, after treatment with decolorizing carbon and evaporation to a 60% concentration, was diluted with 8 volumes of methanol. After standing overnight at 5°, the β-alanine was filtered off and washed with methanol. The yield was 80.6 g. (90%); m. p. 197–8° (dec.).

Hydrolysis of Bis-(cyanoethyl)-amine.—The nitrile (44.9 g.) was added dropwise to a solution of 148 g. of barium hydroxide octahydrate in 100 ml. of water and boiled for thirty minutes. The barium was removed as before and the sirup that was obtained on concentration of the filtrates was triturated with 95% ethanol. The resulting white powder (75.2 g., 86% yield) appeared as needles under a microscope. For analysis a sample was precipitated from 20% aqueous solution with 95% ethanol and dried to constant weight *in vacuo* at 60°; m. p. 175–177°.

Anal. Calcd. for $C_{12}H_{20}N_2O_8Ba \cdot H_2O$: C, 30.30; H 4.66; Ba, 28.88; H_2O, 3.79. Found: C, 30.10; H, 4.81; Ba, 28.82, 28.70; H_2O, 3.53.[8]

β,β′-Iminobispropionic Acid.—An aqueous solution of the crude monobarium salt was treated with an equivalent

(1) Buc, Ford and Wise, THIS JOURNAL, **67**, 92 (1945).

(2) Carlson, U. S. Patent 2,336,067.

(3) Kirk, U. S. Patent 2,334,163.

(4) Experimental evidence for this equilibrium has been obtained by Dr. S. R. Buc of these Laboratories and the author. Similar equilibria may also exist for the corresponding acids and amides.

(5) This is in marked contrast with the observations reported by Abderhalden and Fodor (*Z. physiol. Chem.*, **86**, 119 (1913)), who stated that pure β-alanine evolved ammonia when warmed with dilute alkali.

(6) Heintz (*Ann.*, **156**, 40 (1870)) prepared the monolead salt and obtained the free acid as a sirup which crystallized slowly. Neither physical nor analytical data were reported.

(7) All melting points are uncorrected.

(8) Obtained by drying to constant weight at 100° in a high vacuum. The anhydrous salt reverted rapidly to the monohydrate when exposed to air.