unchanged 5-bromopentanoyl chloride distilled first and then the dibromo acid chloride was collected at 138–145°, at 15 mm.; yield, 162 g., or 77%. The boiling point reported here is somewhat higher than that given by Fischer and Suzuki.[4b]

Ethyl 2,5-Dibromopentanoate.—A mixture of 430 g. of 5-bromopentanoic acid and 275 g. of thionyl chloride was allowed to react and the excess of thionyl chloride was then distilled. The residue was brominated with 420 g. of dry bromine. The crude 2,5-dibromopentanoyl chloride thus obtained was treated with 350 cc. of absolute ethyl alcohol. The ester was distilled under reduced pressure. The yield of ester, b. p. 128–135°, at 14 mm., was 400 g., or 58%. On redistillation most of the product boiled at 133–135°, at 14 mm.; d_4^{25}, 1.6289; n_D^{25}, 1.4947, M_D, calcd., 50.51. Found: 51.53.

Anal. Subs., 0.4516, 0.4182: 18.00, 16.77 cc. of 0.1737 *N* $AgNO_3$. Calcd. for $C_7H_{12}Br_2O_2$: Br, 55.6. Found: 55.4, 55.4.

6-Bromohexanoic Acid.—A mixture of 153 g. of diethyl phenoxybutylmalonate and 500 cc. of 48% hydrobromic acid was treated as described for the preparation of 5-bromopentanoic acid. The yield of product, b. p. 160–168°, at 18 mm., was 60 g., or 62%.

2,6-Dibromohexanoic Acid.—The general procedure used was that described for the bromination of 5-bromopentanoic acid. From 25 g. of 6-bromohexanoic acid, 24 g. of dry bromine and 3 cc. of phosphorus tribromide, there was obtained 28 g., or 80%, of 2,6-dibromohexanoic acid; b. p., 158–160°, at 4 mm.; n_D^{21}, 1.5245; d_4^{21}, 1.7897; M_D, calcd., 47.09; found, 46.88.

Anal. Subs., 0.1954, 0.2492: 8.23, 10.49 cc. of 0.1737 *N* $AgNO_3$. Calcd. for $C_6H_{10}O_2Br_2$: Br, 58.39. Found: 58.53, 58.50.

Summary

1. Improved methods for the preparation of 5-bromopentanoic acid and 2,5-dibromopentanoic acid and their esters and acid chlorides have been described.

2. It has been shown that the earlier description of 2,6-dibromohexanoic acid is in error and the correct description of this compound has been given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WEST VIRGINIA UNIVERSITY]

THE ALKALINE OXIDATION OF ALPHA-NITRONAPHTHALENE

BY JOHN H. GARDNER[1]

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Since it has been known for a long time that in the oxidation of α-nitronaphthalene in an acid medium, 3-nitrophthalic acid is the principal product,[2] it seemed logical to expect that the oxidation with alkaline permanganate should yield a nitrophthalonic acid, which could be converted into 3- or 6-nitrophthalaldehyde acid by procedure analogous to that used by Fuson[3] for the preparation of phthalaldehyde acid from phthalonic acid. On carrying out the oxidation, however, it was found that the nitrated ring was attacked.

[1] National Research Fellow in Chemistry.

[2] Beilstein and Kurbatow, *Ann.*, **202**, 217 (1880).

[3] Fuson, THIS JOURNAL, **48**, 1093 (1926).

α-Nitronaphthalene was oxidized by alkaline permanganate according to the same procedure that was used by Fuson for the oxidation of naphthalene. The product was condensed with aniline producing a derivative which, by melting point and analysis, was found to be identical with that obtained from phthalonic acid. This was further confirmed by its decomposition into the aniline derivative of phthalaldehyde acid and the preparation from that of phthalaldehyde acid itself.

This is not so surprising as it appears at first sight, since a similar result has been obtained in the case of other positively substituted naphthalene derivatives. For example, Graebe has shown that in the oxidation of α-naphthoylbenzoic acid and 1,2-benzanthraquinone, the ring of the naphthalene residue attached to the carbonyl groups is oxidized.[4] This reaction has been confirmed in the second case by Scholl and Schwinger, who also pointed out that in an acid medium 1,2-benzanthraquinone is oxidized to anthraquinone-1,2-dicarboxylic acid, thus showing a complete parallel with the oxidation of α-nitronaphthalene.[5]

The production of a pronounced yellow color on boiling a suspension of α-nitronaphthalene in a solution of sodium hydroxide indicates the possibility of a reaction between the two. At present, however, there is no information available to justify any conclusion as to the nature of the reaction.

Experimental Part

Oxidation of α-Nitronaphthalene.—To a boiling mixture of 43 g. of α-nitronaphthalene and 500 cc. of 0.5 *N* sodium hydroxide solution in a flask provided with a reflux condenser and an efficient mechanical stirrer, there was added in small portions a boiling solution of 212 g. of potassium permanganate in 1500 cc. of water, during a period of one and one-half hours. The mixture was maintained at the boiling temperature until half an hour after the last addition of permanganate. A little alcohol was then added to destroy any remaining permanganate, and the mixture cooled and filtered. The filtrate was acidified with 140 cc. of concd. hydrochloric acid and evaporated to 500 cc. One hundred g. of aniline was then added and the resulting solution heated on the water-bath for two hours. After cooling, the crystalline precipitate was filtered out and dried at room temperature. Drying at an elevated temperature was found to cause considerable decomposition. The yield was 67 g., or 74%.

After several recrystallizations from alcohol, using Norite the first time, the product melted at 162–164°, with decomposition.

All melting points recorded in this paper are corrected.

Fuson reports[3] for the aniline derivative of phthalonic acid, 165°. A mixed melting point of the product from α-nitronaphthalene with the aniline derivative of phthalonic acid showed no depression.

Anal. Subs., 0.3397, 0.3549: 40.60, 40.00 cc. of 0.1016 *N* HCl; 16.55, 16.10 cc. of 0.1328 *N* NaOH. Calcd. for $C_{21}H_{18}O_4N_2$: N, 7.73. Found: 7.94, 7.60.

Decomposition of the Aniline Derivative Obtained from the Oxidation Product of α-Nitronaphthalene.—Twenty-two g. of the aniline derivative was suspended in

[4] Graebe, *Ann.*, **340**, 249 (1905).

[5] Scholl and Schwinger, *Ber.*, **44**, 2992 (1911).

150 cc. of sodium-dried xylene and boiled under reflux for one and one-half hours. On cooling, there was deposited 13.2 g. of a gray powder.

On boiling the decomposition product with alcohol, 4 g. of a gray powder, softening at about 259°, remained undissolved. A similar by-product was noted in the preparation of the aniline derivative of phthalaldehyde acid by Fuson's procedure.

The alcoholic solution, after treatment with Norite, on cooling, deposited almost microscopic, colorless needles; m. p., 178°. The aniline derivative of phthalaldehyde acid melted at 176–177°. A mixed melting point showed no depression.

Anal. Subs., 0.3770, 0.3320: 30.35, 30.20 cc. of 0.1016 *N* HCl; 11.10, 12.00 cc. of 0.1328 *N* NaOH. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: 5.98, 5.94.

Preparation of Phthalaldehyde Acid.—For the preparation of phthalaldehyde acid, 44 g. of the aniline derivative of phthalonic acid, obtained from α-nitronaphthalene, was decomposed as described above. The xylene was decanted as completely as possible, and the residue boiled under reflux with 350 cc. of 10% hydrochloric acid for one and one-half hours. After cooling, the solution was filtered from a small amount of insoluble material and extracted with ether. The ether was evaporated and the residue dissolved in water. After treatment with Norite, the solution was evaporated to dryness, as the attempt to induce crystallization failed. The residue melted at 96° and showed no depression in melting point when mixed with phthalaldehyde acid. The product was free from nitrogen.

Neutral equivalent. Subs., 0.4277, 0.4177: 20.95, 20.59 cc. of 0.1328 *N* NaOH. Calcd. for $C_8H_6O_3$: neut. equiv., 150. Found: 153.7, 152.8.

Summary

It has been shown that in the oxidation of α-nitronaphthalene by potassium permanganate in an alkaline medium, the nitrated ring is attacked.

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

A SYNTHESIS OF TAURINE

BY C. S. MARVEL, C. F. BAILEY AND M. S. SPARBERG

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Taurine, 2-amino-ethylsulfonic acid, is of considerable interest to the physiological chemist since it occurs in the tissues of various lower animals and in secretions of the higher animals. In the bile it is found combined with cholic acid as taurocholic acid. The probable source of natural taurine is the amino acid, cystine. This conversion of cystine to taurine has been carried out in the laboratory by Friedmann[1] but it does not furnish a practical method of preparation.

At present the common sources for taurine are ox bile[2] and the large muscle of the abalone.[3] The first source gives a very low yield of the

[1] Friedmann, *Beitr. Phys. Path.*, **3**, 38 (1903).

[2] (a) Hammersten, *Z. physiol. Chem.*, **32**, 456 (1901); (b) Tauber, *Beitr. Phys Path.*, **4**, 324 (1904).

[3] Schmidt and Watson, *J. Biol. Chem.*, **33**, 499 (1918).