

the mixture. The following values were used in this computation, $\Lambda_{Ca}^{\circ} = 59.48$, $\Lambda_{Cl}^{\circ} = 76.32$ and $\Lambda_{H}^{\circ} = 349.72$.¹⁴ The formulas which have been used in this computation are limiting laws, strictly valid only at very low concentrations. As suggested in the introduction values computed for an ionic strength of 0.15 can consequently indicate little more than the order of magnitude of the effect.

The following comparison of the results presented in this paper with those for mixtures of hydrogen chloride and potassium chloride⁹ may possibly be significant. For the latter mixtures, also at a total concentration of 0.1 normal, the observed decrease of the equivalent conductance of the hydrogen ion constituent in passing from a solution of hydrogen chloride to one of potassium chloride is $\Delta\Lambda_{H}^{H-K}$ (obsd.) = 10.96 and the corresponding computed value is $\Delta\Lambda_{H}^{H-K}$ (calcd.) = 24.79, giving 0.442 as the ratio of the observed to the computed value. The value of the corresponding ratio for the mixtures of hydrogen chloride and calcium chloride is 0.441. The agreement between these two ratios may indicate that the same phenomena which produce devia-

tions from the limiting equations are operative in the two cases.

I am glad to acknowledge my indebtedness to Dr. D. A. MacInnes for constructive criticism and to Dr. Theodore Shedlovsky for placing the conductivity bridge at my disposal during the course of the measurements.

Summary

The transference numbers of the hydrogen ion constituent in aqueous mixtures of hydrogen chloride and calcium chloride at a constant total concentration of 0.1 normal have been measured at 25°. The conductances of the same mixtures have also been determined and from a combination of these data with the transference numbers the mobility of the hydrogen ion constituent in each of the mixtures has been computed. The observed decrease in the mobility of this constituent in passing from the solution of pure hydrogen chloride to one of pure calcium chloride has been compared with the value computed from the interionic attraction theory of electrolytic conductance and also with a similar effect that was observed in mixtures of hydrogen chloride and potassium chloride.

(14) MacInnes, Shedlovsky and Longworth, *ibid.*, **54**, 2758 (1932).

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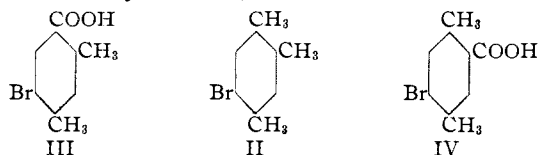
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Xylic Acids Obtained in the Oxidation of 5-Bromo and 5-Nitropseudocumene

BY C. HAROLD FISHER AND CHEVES T. WALLING

It has been reported¹ that the compound (I, m. p. 172–173°) produced in the oxidation of 5-bromopseudocumene (II) is 5-bromo-2,4-xylic acid (III). This oxidation has been repeated, and it was shown by direct comparison that the product (I) is not 5-bromo-2,4-xylic acid.²

A further study of this oxidation has indicated that the melting point of the oxidation acid (I) may be raised to 173–174° by prolonged purification, and that this substance is a sharply-melting mixture of 5-bromo-2,4-xylic acid (III) and 4-bromo-2,5-xylic acid (IV).



Separation of the oxidation product (I) into its components (III and IV) could not be effected by numerous crystallizations, and an identical substance was prepared by crystallizing a mixture of equal amounts of III and IV.

Both bromoxylic acids (III and IV) were synthesized for comparison by methods that leave no doubt as to their structures. At the beginning of this work it was expected that I would be identical with 4-bromo-2,5-xylic acid, since the methyl group para to the bromine atom is attacked preponderantly in the oxidation³ of 4-bromo-*o*-xylene.

The oxidation of 5-nitropseudocumene has been claimed⁴ to give 5-nitro-2,4-xylic acid, but no proof of structure was offered. The oxidation of a compound having ortho, meta and para

(1) Sussenguth, *Ann.*, **215**, 244 (1882).

(2) Fisher and Grant, *THIS JOURNAL*, **57**, 718 (1935).

(3) Keuning and Evenhuis, *Rec. trav. chim.*, **54**, 73 (1935).

(4) Schaper, *Chem. Centr.*, **39**, 837 (1868).

methyl groups influenced by a nitro group was considered interesting, and therefore the oxidation of 5-nitropseudocumene was repeated.

Treatment more drastic than that used for 5-bromopseudocumene was necessary to oxidize the corresponding nitropseudocumene. In confirmation of previous reports^{4,5} it was found that the methyl group affected was the one meta to the nitro group. The product was identical with the acid obtained by the nitration and subsequent oxidation of 2,4-dimethylacetophenone; only 5-nitro-2,4-xylic acid could be formed, barring unusual rearrangements, from both 5-nitropseudocumene and 2,4-dimethylacetophenone as described above.

An isomeric compound, 4-nitro-2,5-xylic acid, was prepared for comparison from 4-nitro-2,5-xylonitrile, but this acid (m. p. 165.5–166.5°) was found to have properties clearly different from those of the acid (m. p. 197–198°) obtained by oxidizing 5-nitropseudocumene.

In connection with the oxidation of pseudocumene derivatives having substituents in the 5-position, it is interesting to note that 2-acetyl-amino-4,5-xylic acid is formed in the oxidation of 5-acetylaminopseudocumene.⁶

Experimental

5-Bromopseudocumene.—This compound may be prepared conveniently from technical pseudocumene (Eastman Kodak Company) by treatment with bromine in the presence of acetic acid and iron filings. After distillation at ordinary pressure, and crystallization of the higher fractions from methyl alcohol, the product melted at 71–72° alone, or when mixed with 5-bromopseudocumene prepared by diazotization from pseudocumidine.

Oxidation of 5-Bromopseudocumene.—The sharply-melting mixture of 5-bromo-2,4-xylic acid and 4-bromo-2,5-xylic acid was prepared by oxidation of bromopseudocumene as previously described.² Treatment with thionyl chloride and then with ammonia gave a mixture of amides. This mixture was crystallized several times (m. p. 191.5–192.5°; somewhat elevated when mixed with 5-bromo-2,4-xylamide,² m. p. 197.5–198.5°, or 4-bromo-2,5-xylamide, m. p. 209–210°), and hydrolyzed. The resulting product was crystallized many times from dilute alcohol and from ligroin. It then melted at 173–174°, and was identical with the homogeneous substance obtained by crystallizing a mixture of equal parts of pure 5-bromo-2,4-xylic acid and 4-bromo-2,5-xylic acid.

The mixture of amides (0.6 g., m. p. 191.5–192.5°) mentioned above was heated for one-fourth hour with a solution of 3 cc. of sulfuric acid and 2 cc. of water. The portion not hydrolyzed (about 50%) was crystallized fifteen times from about 20% alcohol. The product thus obtained was

shown to be 4-bromo-2,5-xylamide by the mixed melting point method. No effort was made to isolate the isomeric amide from the mother liquors.

4-Bromo-2,5-xylonitrile.—By diazotization, and subsequent treatment with cuprous cyanide, the nitrile was prepared from 4-bromo-2,5-dimethylaniline.⁷ The melting point was 103–104°.

Anal. Calcd. for C₉H₉NBr: C, 51.43; H, 3.84. Found: C, 51.60; H, 4.01.

4-Bromo-2,5-xylic Acid (IV).—The nitrile (3 g.) was heated for one hour with 15 cc. of sulfuric acid and 10 cc. of water. After crystallization from dilute alcohol and from ligroin the melting point of the product was 171.5–172.5°.

Anal. Calcd. for C₉H₉O₂Br: C, 47.16; H, 3.96. Found: C, 47.34; H, 4.03.

4-Bromo-2,5-xylamide.—Prepared by treating the acid with thionyl chloride, and then adding ammonia, the amide melted at 209–210° (crystallized from dilute methanol).

Anal. Calcd. for C₉H₁₀ONBr: C, 47.36; H, 4.42. Found: C, 47.55; H, 4.53.

5-Nitropseudocumene.—Technical pseudocumene was purified as directed by Smith and Cass,⁸ and nitrated by the method of Schultz.⁹ A yield much lower than the one claimed (92%) was obtained. The melting point was 67–68°, after crystallization from methanol.

Oxidation of 5-Nitropseudocumene.—Two grams of the nitro compound was heated on a steam-bath with 4 cc. of concd. nitric acid and 7 cc. of water for fifty-five hours. More nitric acid (5 cc.) was added, and heating was continued for thirty-nine hours. The acidic portion of the product was crystallized several times from dilute alcohol, and many times from benzene and ligroin. The m. p. was 197–198°; a mixed m. p. with 5-nitro-2,4-xylic acid was not lowered. The melting point previously reported⁴ for this acid, as obtained by oxidation, is 195°.

The neutral portion of the product obtained in the above-described oxidation was heated for eighty hours with 10 cc. of concd. nitric acid and 7 cc. of water to get more of the nitroxylic acid. There was recovered 0.5 g. of 5-nitropseudocumene melting at 68–69°.

4-Nitro-2,5-dimethylaniline.—Nitration of 2,5-dimethylacetanilide as previously directed¹⁰ gave principally the dinitro derivative which, after hydrolysis and crystallization from benzene and from acetic acid, was obtained as 2,4-dinitro-3,6-dimethylaniline,¹¹ yellow needles melting at 203–204.5°. Sonn¹¹ also obtained the dinitro derivative by using fuming nitric acid.

The desired amine was finally prepared by adding slowly (temperature below 20°) 7.5 cc. of concd. nitric acid to 8 g. of 2,5-dimethylacetanilide in 15 cc. of sulfuric acid. After standing for about one-fourth hour the mixture was added to water. Hydrolysis and steam distillation (to remove the volatile 2-nitro-3,6-dimethylaniline) left nearly pure 4-nitro-2,5-dimethylaniline. After crystallization from alcohol the product melted at 144–145°.

(7) Wheeler and Constable, *ibid.*, **45**, 1999 (1923).

(8) Smith and Cass, *ibid.*, **54**, 1607 (1932).

(9) Schultz, *Ber.*, **42**, 3605 (1909).

(10) Noeltig, Witt and Forel, *ibid.*, **18**, 2665 (1885).

(11) Sonn, *ibid.*, **49**, 622 (1916).

(5) Ahrens, *Ann.*, **271**, 19 (1892).

(6) Bogert and Bender, *THIS JOURNAL*, **36**, 570 (1914).

The acetyl derivative, 4-nitro-2,5-dimethylacetanilide, was prepared by nitration of 2,5-dimethylacetanilide (numerous crystallizations were required to remove the 2-nitro isomer), and by acetylation of 4-nitro-2,5-dimethyl-aniline; the m. p. was 168–169°.

4-Nitro-2,5-xylonitrile.—The method of Bogert and Hand¹² was used to convert the amine into the nitrile. After crystallization from alcohol the m. p. was 160–161°. The nitrile may be purified also by sublimation.

Anal. Calcd. for C₉H₉O₂N₂: C, 61.36; H, 4.58. Found: C, 61.18; H, 4.63.

4-Nitro-2,5-xylic Acid.—The cyanide was hydrolyzed with sulfuric acid, and the product was crystallized from alcohol and from ligroin; the m. p. was 165.5–166.5°.

Anal. Calcd. for C₉H₉O₄N: C, 55.38; H, 4.65. Found: C, 55.48; H, 4.71.

5-Nitro-2,4-xylic Acid.—Ten grams of 2,4-dimethylacetophenone was nitrated by a method purported to yield mainly 5-nitro-2,4-dimethylacetophenone.¹³ The crude

product thus obtained was agitated with sodium hypobromite (11 cc. of bromine in 300 cc. of 10% sodium hydroxide) during four hours. The product was crystallized from alcohol and from benzene and ligroin; the m. p. was 197.5–198.5°. The melting point previously reported⁵ for this acid, prepared from 5-nitro-2,4-xylonitrile, is 196–197°.

Summary

The oxidation product of 5-bromopseudocumene, previously claimed to be 5-bromo-2,4-xylic acid, is a sharply-melting mixture of this acid and an isomeric compound, 4-bromo-2,5-xylic acid.

In the oxidation of 5-nitropseudocumene the methyl group meta to the nitro group is attacked chiefly, yielding 5-nitro-2,4-xylic acid.

Some new substituted xylic acids and related compounds are described.

CAMBRIDGE, MASS.

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(12) Bogert and Hand, *THIS JOURNAL*, **24**, 1035 (1902).

(13) Claus, *J. prakt. Chem.*, [2] **41**, 495 (1890).

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

The Photochlorination of Pentane

BY T. D. STEWART AND BERNARDT WEIDENBAUM

In connection with other work we had occasion to measure the quantum efficiency of the photochlorination of *n*-pentane in the liquid phase, and with the rigid exclusion of oxygen. Great care was taken in purification and handling of the reagents. The consistency of the results together with the apparent absence of an induction period point to the absence of disturbing factors in this measurement.

Purification of Chemicals.—The pentane was obtained from a commercial source. It was first treated with alkaline potassium permanganate with constant agitation until no more reaction was obtained, then treated with chlorosulfonic acid to remove isomers other than normal pentane¹ and finally fractionated very carefully in a 6.1-meter packed fractionating column which Dr. R. E. Cornish kindly placed at our disposal. The temperature of distillation (uncorrected) was 36.0°, and no drop in temperature was observed if the distillation continued for so long as ten hours with total reflux. The pentane was dried and deoxygenated by allowing it to stand over sodium-potassium alloy for at least three months,

(1) Shepard and Henne, *Ind. Eng. Chem.*, **22**, 356 (1930).

and then distilled, as needed, from an all-glass distilling apparatus into a large bulb in the line.

The chlorine was from a commercial cylinder of liquid chlorine and was known to be free of hydrochloric acid. It was dried by passing over calcium chloride and magnesium perchlorate, and then was frozen in a liquid air trap. A first portion was distilled away; the bulk of the chlorine was then distilled into a liter bulb which was thereafter used as the source of supply for these experiments.

The nitrogen was from a commercial cylinder. To remove oxygen it was bubbled through an alkaline solution of pyrogallol and then through a solution of ammonium carbonate in which copper wire was suspended; it was then scrubbed with concentrated sulfuric acid, dried with phosphorus pentoxide, and stored in two one-liter bulbs at about 100 cm. pressure. The nitrogen was used to force the pentane into the reaction flask when the chlorine solution was being made. It was also used to force the solution from the reaction flask into the quenching solution of potassium iodide at the conclusion of the experiment, as well as being used to flush the line prior to its evacuation.