

Anal. Calcd. for $C_{14}H_{13}N_3O_4$: N, 14.63. Found: N, 14.41, 14.70.

VI. The 2-iodo-4-amino-anisole (m. p. 74°) can be easily made directly from *p*-anisidine by heating with calcium carbonate, iodine, water and ether. It must be extracted from the reaction product as it is not volatile with steam. Under like conditions *p*-phenetidine gives the 2-iodo-4-aminophenetole.¹²

The constitution of the 2-iodo-4-nitro-anisole was further proved by diazotizing 4-nitro-*o*-anisidine. The iodine compound melted at 96° and the identity was confirmed by analysis and mixed melting point.

1-Methoxy-4-nitro-2-diphenyl-urea from the nitro-anisidine and phenyl isocyanate melted at 192° .

Anal. Calcd. for $C_{14}H_{13}N_3O_4$: N, 14.63. Found: N, 14.70.

Summary

It has been shown that the methyl cresol ethers and the nitro-anisoles can be iodinated directly at temperatures of 160 – 180° , using nitric acid as an oxidizing agent. The methoxy group has the main directing influence in the position of the iodine.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

THE CONSTITUTION OF CERTAIN CHLORO-IODO AND BROMO-IODO ANILINES AND BENZENES

BY F. B. DAINS AND A. W. MAGERS

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In the course of the study of the effect of halogens on the aromatic amines, it became necessary to prepare certain iodine substitution products of the chloro and bromo substituted anilines. The method of Wheeler was employed, wherein iodine was allowed to react with the amine in the presence of calcium carbonate and water.¹

In the paper in question² the final determination of structure of some of the derivatives was from necessity left unsettled and the present work fills in the lacunae with some additional data.

Experimental

4-Bromo-2,6-di-iodo-aniline.³—The iodination of 4-bromo-2-iodo-aniline gave a di-iodo compound (m. p. 148°). When this was diazotized in alcohol solution, the product was the known 1-bromo-3,5-di-iodobenzene (m. p. 140°).⁴

Anal. Calcd. for $C_6H_3BrI_2$: Br, 19.53; I, 62.09. Found: Br, 19.35; I, 62.01.

1-Bromo-3,4,5-tri-iodobenzene was prepared from the bromo-di-iodo-aniline

¹² Reverdin, *Ber.*, 29, 2596 (1896).

¹ Wheeler and others, *Am. Chem. J.*, 42, 441, 448 (1909); 44, 127, 500 (1910).

² Dains, Vaughan and Janney, *THIS JOURNAL*, 40, 931–936 (1918).

³ Ref. 2, p. 932.

⁴ Körner and Condardi, *Chem. Zentr.*, II, 1038 (1913); *Atti. Accad. Lincei.*, 22, 832 (1913).

(148°) by replacing the amino group by iodine. It is difficultly soluble in alcohol, non-volatile with steam and melts at 153°.

Anal. Calcd. for $C_6H_2BrI_3$: Br, 14.94; I, 71.21. Found: Br, 14.65; I, 70.91.

1-Amino-3-bromo-4-iodobenzene.³—The position of the iodine in the compound (m. p. 56°) formed by the iodination of *m*-bromo-aniline was determined as follows: on replacing the amino group by iodine, the bromo-di-*p*-iodobenzene (m. p. 68°) was formed. The same compound results when *p*-di-iodobenzene is heated with bromine and iron filings in carbon tetrachloride solution.

Anal. Calcd. for $C_6H_3BrI_2$: Br, 18.53; I, 62.09. Found: Br, 19.47; I, 61.96.

Constitution of the 1-Amino-4-chloro-2-iodobenzene³ (m. p. 46°) formed from iodine and *p*-chloro-aniline. Replacing the amino group by chlorine gave the known iodo-di-*p*-chlorobenzene (m. p. 21°), which is also formed when di-*p*-chlorobenzene is heated with iodine and nitric acid at 160°.

Structure of the *p*-Chloro-di-iodo-aniline⁵ (m. p. 129°).—This is the final product when iodine reacts with either *p*-chloro-aniline or 4-chloro-2-iodo-aniline. Elimination of the amino group gave 1-chloro-3,5-di-iodobenzene⁴ (m. p. 101°).

Anal. Calcd. for $C_6H_3ClI_2$: Cl, 9.72; I, 69.78. Found: Cl, 9.74; I, 69.86.

1-Chloro-3,4,5-tri-iodobenzene.—The chloro-di-iodo-aniline (m. p. 129°) was dissolved in concentrated sulfuric acid at 0° and treated with powdered sodium nitrate. Potassium iodide was added to the solution when the acid was poured on cracked ice. The white crystals from alcohol melted at 148°.

Anal. Calcd. for $C_6H_2ClI_3$: Cl, 7.23; I, 77.67. Found: Cl, 7.26; I, 78.00.

2-Amino-6-iodo-anisole.⁶—In the preceding paper, *o*-anisidine was found to yield with iodine a mono-iodo-*o*-anisidine (m. p. 49°). Position 6 of the iodine was determined by its transformation into 2,6-di-iodo-anisole (m. p. 35°) and into 4-nitro-2,6-di-iodo-anisole (m. p. 133–134°).⁷

Summary

The structures of some iodine derivatives of chloro- and bromo-aniline and of *o*-anisidine have been definitely determined.

LAWRENCE, KANSAS

⁵ Ref. 3, p. 933.

⁶ Ref. 3, p. 935.

⁷ Brenans, *Compt. rend.*, 134, 357 (1902); *Bull. soc. chim.*, [3] 27, 401 (1902).