Chromatographic Analysis of Purified Xanthopterin.—Paper chromatographs of the xanthopterin purified *via* the hydrochloride and by sublimation *in vacuo* were obtained by the method of Good and Johnson[7] who employed the *n*-butanol–acetic acid–water mixture of Partridge.[8] Under ultraviolet light the chromatographs showed only one fluorescent spot (Rf = 0.35–0.38) which was in agreement with the value (Rf = 0.38) reported by Good and Johnson.[7] The material was thus free of leucopterin (Rf = 0.12), dihydroxanthopterin (Rf = 0.26) and other fluorescent pterin impurities. It should be noted that some samples of synthetic xanthopterin prepared as indicated did not contain these impurities and thus required no further purification.

Absorption Spectra of Purified Xanthopterin.—Ultraviolet absorption spectra of an aqueous solution (*p*H of 11.25) of the xanthopterin purified by sublimation and *via* the hydrochloride showed absorption maxima at 255 mμ. ($E_m \times 10^{-3} = 18.2$) and 392 mμ; ($E_m \times 10^{-3} = 7.0$) in agreement with other reported spectra.[4,9]

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[7] Good and Johnson, *Nature*, **163**, 31 (1949).

[8] Partridge, *Biochem. J.*, **42**, 238 (1948).

[9] Rickes, Chaiet and Keresztesy, THIS JOURNAL, **69**, 2749 (1947).

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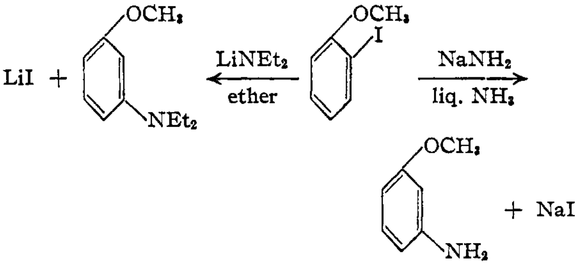
The Reaction of Sodium Amide with *o*- and *m*-Chlorotrifluoromethylbenzene

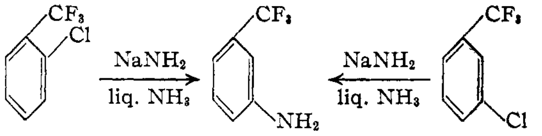
BY ROBERT A. BENKESER AND ROLAND G. SEVERSON[1]

Recently it was reported that certain aryl halides react with a liquid ammonia solution of sodium[2] or potassium amide.[3] It has also been found that ether solutions of aryl halides are attacked by lithium dialkylamides.[4] When the aryl halide has an ether, sulfide or dialkylamino group ortho to the halogen, it was observed that the amino or dialkylamino group does not take up the position which the halogen originally occupied, but rather a meta-substituted product[5,6,7] is formed



The corresponding *p*-haloethers also exhibit this tendency to undergo rearrangement when treated with lithium dialkylamides in ether, but to a somewhat lesser extent.[8]

It has now been observed that the same rearrangement occurs even when the halogen is ortho to a strong meta-directing group. Thus, *o*-chlorotrifluoromethylbenzene upon treatment with sodium amide in liquid ammonia for five hours at −33° gives a 52% yield of pure *m*-aminotrifluoromethylbenzene. Efforts to isolate any of the ortho isomer have been unsuccessful. In contrast, *m*-chlorotrifluoromethylbenzene gives the expected *m*-aminotrifluoromethylbenzene. It is noteworthy that the yield here is only 35%.



Experimental

***m*-Aminotrifluoromethylbenzene. (a) From *o*-Chlorotrifluoromethylbenzene.**—Sodium amide[9] was prepared from 16.1 g. (0.7 g. atom) of sodium and 750 ml. of liquid ammonia containing 0.4 g. of hydrated ferric nitrate. To this mixture was added 90.3 g. (0.5 mole) of *o*-chlorotrifluoromethylbenzene[10,11] (b. p. 149–150°) during a period of one hour. After stirring for an additional four hours, ammonium chloride was added and the solvent was allowed to evaporate. The residue was dissolved in ether, filtered and treated with anhydrous hydrogen chloride which precipitated 62 g. of a brown hydrochloride. From the ether filtrate 14.4 g. of *o*-chlorotrifluoromethylbenzene (b. p. 149–150°) was recovered. Crystallization of the crude hydrochloride from an ethanol–ether mixture gave 53 g. of white crystals from which the free base was obtained by adding concentrated ammonium hydroxide. After extracting the basic solution with ether, drying the ether extract over Drierite, removing the solvent, and fractionating the product through a small helices-packed column, there was obtained 35.1 g. (52% yield) of *m*-aminotrifluoromethylbenzene boiling at 86° (20 mm.), n^{20}_D 1.4801, n^{25}_D 1.4775.

The acetyl derivative[12] melted at 103–104° and the benzoyl derivative[13] at 110–111°. A mixed melting point between this acetyl derivative and that obtained from an authentic sample of *m*-aminotrifluoromethylbenzene[10] showed no depression.[14]

(b) From *m*-Chlorotrifluoromethylbenzene.—This procedure was identical with that described above. From 90.3 g. (0.5 mole) of *m*-chlorotrifluoromethylbenzene,[10] 47.8 g. of crude hydrochloride was obtained. This gave 36 g. of pure salt when crystallized from an ethanol–ether mixture and 23.9 g. (35% yield) of the free base boiling at 86° (20 mm.), n^{20}_D 1.4800. The acetyl and benzoyl derivatives melted at 103–104° and 110–111°, respectively.

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[1] Research Corporation Fellow.

[2] Gilman and Avakian, THIS JOURNAL, **67**, 349 (1945).

[3] Urner and Bergstrom, *ibid.*, **67**, 2108 (1945).

[4] Horning and Bergstrom, *ibid.*, **67**, 2110 (1945).

[5] Gilman and Nobis, *ibid.*, **67**, 1479 (1945).

[6] Gilman, *et al.*, *ibid.*, **67**, 2106 (1945).

[7] Gilman, Kyle and Benkeser, *ibid.*, **68**, 143 (1946).

[8] Gilman and Kyle, *ibid.*, **70**, 3945 (1948).

[9] Vaughn, Vogt and Nieuwland, *ibid.*, **47**, 2002 (1925).

[10] Kindly supplied by the Hooker Electrochemical Company, Niagara Falls, N. Y.

[11] For a description of numerous ortho and para derivatives of benzotrifluoride see Jones, THIS JOURNAL, **69**, 2346 (1947).

[12] Swarts, *Bull. acad. roy. Belg.*, 389 (1920); *C. A.*, **16**, 2316 (1922).

[13] *Anal.* Calcd. for $C_{14}H_{10}OF_3N$: N, 5.28. Found: N, 5.35.

[14] The literature[11,12] values for the physical constants of *o*-, *m*- and *p*-aminotrifluoromethylbenzene are

	B. p.		n_D	Acetyl deriv.	Benzoyl deriv.
	°C.	Mm.			
ortho-	72–74	21	1.4785 (25°)	94.5–95°	140–141°
meta-	74–75	10	1.481 (20°)[10]	103°	......
para-	91	19	1.4815 (25°)	152°	......

There was recovered 14.3 g. of unreacted *m*-chlorotrifluoromethylbenzene.

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Preparation of Wüstite

BY R. W. BLUE AND H. H. CLAASSEN

For X-ray diffraction studies of iron oxides it is frequently helpful to have diffraction patterns of the pure oxides for purposes of comparison. Samples of magnetite, ferric oxide and iron are readily obtained but a sample having the ferrous oxide structure is less easily prepared. Fusion of higher oxides with iron often results in samples which do not give clean diffraction patterns.

Previous work[1] indicates that the lower limit for oxygen content of this sodium chloride-type structure is 23.1% oxygen as compared with 22.27% for ferrous oxide. The name wüstite has been given to the material in the composition range, 23.1 to 25.6% oxygen, in which the sodium chloride-type of structure occurs.

A convenient way to prepare a sample of wüstite is to take advantage of the simultaneous reactions

$$\begin{array}{c} \text{Iron} + H_2O \longrightarrow \text{wüstite} + H_2 \\ \underline{\text{Magnetite} + H_2 \longrightarrow \text{wüstite} + H_2O} \\ \text{Iron} + \text{magnetite} \longrightarrow \text{wüstite} \end{array}$$

When equimolal amounts of iron and magnetite are placed in an atmosphere of water vapor in the temperature region 750 to 900°, some hydrogen is immediately formed and the water hydrogen ratio is automatically regulated for conversion of both iron and magnetite to wüstite. By keeping the iron and magnetite in separate boats one can use an excess of either reactant; the reactant not in excess is converted to material giving a clean diffraction pattern of the sodium chloride-type of structure but there is a slight difference between the diffraction patterns of the two samples which may be described as follows:

In practice magnetite obtained by burning pure iron at fusion temperatures contains 10 to 50% ferrous oxide.[2] The ferrous oxide diffraction lines obtained with these ferrous oxide–magnetite samples are doublets which become single lines when reduction occurs. When the samples are reduced in a stream of hydrogen the line in each doublet which corresponds to the smaller lattice disappears first. When reduction is carried out by the double-boat method described above, the line corresponding to the larger lattice disappears first; and when wüstite is formed from iron by the double-boat method the diffraction lines are in the mean position between the doublet positions. The latter differences correspond to only a few thousandths of an ångström but they can be clearly seen by comparing XRD patterns of samples prepared simultaneously by the double-boat method.

Oxides in the composition range 23.2 to 24.3% oxygen have been prepared under various conditions. All samples in this composition range give the same XRD pattern with the exceptions noted above depending on the source material.

In a typical experiment magnetite containing about 40% wüstite was prepared by burning Armco iron in an atmosphere of oxygen. Some of this material, after crushing and screening to 60 to 120 mesh, was reduced with hydrogen at 450° to iron. Thirty-three and one-quarter grams of the magnetite and 3.0 g. of the iron were weighed into separate alundum boats and placed in a quartz tube closed at one end and joined at the other end by a wax seal to a Pyrex tube equipped with a side tube and vacuum connection. A few cc. of water was placed in the side tube and, after the apparatus was assembled, the side tube was cooled in liquid air. The apparatus was then evacuated and the side tube was warmed to room temperature. That part of the tube containing magnetite and iron was then heated to 900°. After seventy-two hours the tube was cooled in a stream of air and the iron oxide samples were removed. (Cooling to room temperature required about five minutes.) Examination by X-ray diffraction revealed that both the wüstite from the iron and that from magnetite contained no other crystalline materials. Reduction in a stream of hydrogen at 450° showed that the wüstite from the oxide contained 23.2% oxygen.

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[1] R. W. G. Wyckoff and E. D. Crittenden, THIS JOURNAL, **47**, 2876 (1925); E. R. Jette and F. Foote, *J. Chem. Phys.*, **1**, 29 (1933); *Trans. Am. Inst. Min. and Met. Engrs., Iron and Steel Div.*, **105**, 276 (1933); L. S. Darken and R. W. Gurry, THIS JOURNAL, **67**, 1398 (1945).

[2] J. A. Almquist and E. D. Crittenden, *Ind. Eng. Chem.*, **18**, 1307 (1926).

N-(Dialkylaminoalkyl)-amides

BY R. O. CLINTON, U. J. SALVADOR AND S. C. LASKOWSKI

Since only a few simple aromatic amide derivatives have been tested as local anesthetics,[1] it seemed desirable to extend these types to include 4-aminobenzamides and related compounds. However, the initially prepared compounds proved relatively inactive in comparison with their ester analogs, and the investigation was terminated after the preparation of only a few compounds.

Attempts were also made to prepare 4-aminobenzamides derived from imino-interrupted side chains, analogous to those derived from sulfur- and oxygen-interrupted side chains.[2] Because of the complex mixtures formed, we were unable to prepare pure 4-aminobenzamides of this type.

Experimental[3]

Nitriles.—The reaction of a primary or secondary amine with acrylonitrile was carried out by the method of Whitmore, *et al.*[4]

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[1] *Cf.* Wenker, THIS JOURNAL, **60**, 1081 (1938); Blicke, Parke and Jenner, *ibid.*, **62**, 3316 (1940).

[2] Clinton, Salvador, Laskowski and Suter, *ibid.*, **70**, 950 (1948).

[3] All melting and boiling points are corrected. The authors desire to thank Mr. Morris E. Auerbach and staff for the analyses.

[4] Whitmore, *et al.*, *ibid.*, **66**, 725 (1944).