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.

PHILLIPS PETROLEUM COMPANY
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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).

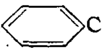
[2] Clinton, Salvador, Laskowski and Suter, *ibid.*, **70**, 950 (1948).

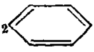
[3] All melting and boiling points are corrected. The authors desire to thank Mr. Morris E. Auerbach and staff for the analyses.

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

TABLE I

4-SUBSTITUTED BENZAMIDES

4-Nitrobenzamides, NO_2$CONH—X—NR_2$

X	R_2	Derivative	M. p., °C.	Formula	Nitrogen analyses, % Calcd.	Found
$-(CH_2)_3-$	$(C_2H_5)_2$	Picrate	147.5–148.5	$C_{20}H_{24}N_6O_{10}$	16.53	16.30
$-(CH_2)_3-$	C_5H_{10}[a]	Base	50.5–51.0	$C_{15}H_{21}N_3O_3$	14.42	14.34
$-(CH_2)_3-$	C_5H_{10}[a]	Picrate	206.0–206.5	$C_{21}H_{24}N_6O_{10}$	16.15	16.27
$-(CH_2)_3-$	C_6H_{12}[b]	Base	71.5–72.5	$C_{16}H_{23}N_3O_3$	13.81	14.15
$-(CH_2)_3-$	C_6H_{12}[b]	Picrate	174.0–175.0	$C_{22}H_{26}N_6O_{10}$	15.76	16.14
$-(CH_2)_3-$	C_7H_{14}[c]	Picrate	190.0–191.0	$C_{23}H_{28}N_6O_{10}$	10.22[d]	10.43[d]
$-(CH_2)_3NH(CH_2)_3-$	$(C_2H_5)_2$	Dipicrate	161.0–162.0	$C_{29}H_{34}N_{10}O_{17}$	17.63	17.42
$-(CH_2)_3NH(CH_2)_3-$	C_5H_{10}[a]	Dipicrate	170.0–171.0	$C_{30}H_{34}N_{10}O_{17}$	17.37	17.00
$-(CH_2)_3NH(CH_2)_3-$	C_6H_{12}[b]	Picrate	165.0–166.0	$C_{25}H_{33}N_7O_{10}$	9.46[d]	9.50[d]
4-Aminobenzamides, NH_2$CONH—X—NR_2$						
$-(CH_2)_3-$	$(C_2H_5)_2$	Dipicrate	149.0–150.5	$C_{26}H_{29}N_9O_{15}$	11.88[d]	11.62[d]
$-(CH_2)_3-$	$(C_2H_5)_2$	Dihydriodide[e]	202.0–203.5	$C_{14}H_{25}I_2N_3O$	8.31	8.05
$-(CH_2)_3-$	C_5H_{10}[a]	Base[f]	168.3–169.5	$C_{15}H_{23}N_3O$	16.14	15.96
$-(CH_2)_3-$	C_5H_{10}[a]	Dipicrate	120.5–122.0	$C_{27}H_{29}N_9O_{15}$	11.68[d]	11.90[d]
$-(CH_2)_3-$	C_6H_{12}[b]	Base[g]	121.0–122.8	$C_{16}H_{25}N_3O$	15.26	15.24

[a] 1-Piperidyl. [b] 2-Methyl-1-piperidyl. [c] 2,6-Dimethyl-1-piperidyl. [d] Nitro nitrogen by titration with titanous chloride. [e] Calcd.: HI, 50.65. Found: HI, 50.13. [f] Calcd.: C, 69.19; H, 8.90. Found: C, 69.15; H, 8.73. [g] Calcd. C, 69.78; H, 9.15. Found: C, 70.01; H, 9.17.

3-(2-Methyl-1-piperidyl)-propionitrile, 87% yield, b. p. 126.4° at 18.0 mm., n^{25}_{D} 1.4689.

Anal. Calcd. for $C_9H_{16}N_2$: N, 18.41. Found: N, 18.31.

The picrate had m. p. 132.5–133.5°.

Anal. Calcd. for $C_{15}H_{19}N_5O_7$: N, 18.37. Found: N, 18.56.

A compound believed to be 3-(2,6-dimethyl-1-piperidyl)-propionitrile (*vide infra*) was obtained in 30% crude yield, b. p. 137–149° at 14 mm. The condensation required prolonged heating; the low yield was probably due to steric effects.[4] The crude compound could not be obtained sufficiently pure for analysis, nor did it yield a crystalline derivative.

3-(3-[1-Piperidyl]-propylamino)-propionitrile, 67% yield, b. p. 116.0° at 0.45 mm., n^{25}_{D} 1.4790.

Anal. Calcd. for $C_{11}H_{21}N_3$: N, 21.52. Found: N, 21.28.

The dipicrate had m. p. 177.0–178.3°.

Anal. Calcd. for $C_{23}H_{27}N_9O_{14}$: N, 19.28. Found: N, 19.22.

3-(3-[2-Methyl-1-piperidyl]-propylamino)-propionitrile, 86% yield, b. p. 110.0° at 0.15 mm., n^{25}_{D} 1.4794.

Anal. Calcd. for $C_{12}H_{23}N_3$: N, 20.08. Found: N, 20.01.

The dipicrate had m. p. 163.5–165.0°.

Anal. Calcd. for $C_{24}H_{29}N_9O_{14}$: N, 18.89. Found: N, 19.18.

Amines.—The propionitriles were reduced in methanolic ammonia at 100° and 1200 lb. pressure, using Raney nickel catalyst.[4]

3-(2-Methyl-1-piperidyl)-propylamine, 62% yield, b. p. 77.0° at 0.42 mm., n^{25}_{D} 1.4742.

Anal. Calcd. for $C_9H_{20}N_2$: N, 17.93. Found: N, 18.20.

The dipicrate had m. p. 216.5–218.0°.

Anal. Calcd. for $C_{21}H_{26}N_8O_{14}$: N,[5] 4.56. Found: N,[5] 4.54.

The cinnamamide hydrochloride had m. p. 181.0–183.2°.

Anal. Calcd. for $C_{18}H_{27}ClN_2O$: N, 8.67; Cl, 10.98. Found: N, 8.50; Cl, 10.89.

3-(2,6-Dimethyl-1-piperidyl)-propylamine, 58% yield, b. p. 66.3° at 0.20 mm., n^{25}_{D} 1.4714.

Anal. Calcd. for $C_{10}H_{22}N_2$: N, 16.46. Found: N, 16.84. A crystalline derivative could not be obtained.

3-(3-[1-Piperidyl]-propylamino)-propylamine, 83% yield, b. p. 111.0° at 0.44 mm., n^{25}_{D} 1.4844.

Anal. Calcd. for $C_{11}H_{25}N_3$: N, 21.08. Found: N, 21.15.

The tripicrate had m. p. 208.0–209.0°.

Anal. Calcd. for $C_{29}H_{34}N_{12}O_{21}$: N, 18.96. Found: N, 18.84.

3-(3-[2-Methyl-1-piperidyl]-propylamino)-propylamine, 91% yield, b. p. 104.5° at 0.25 mm., n^{25}_{D} 1.4843.

Anal. Calcd. for $C_{12}H_{27}N_3$: N, 19.69. Found: N, 19.57.

The tripicrate melted at 184.5–186.0°.

Anal. Calcd. for $C_{30}H_{36}N_{12}O_{21}$: N,[6] 13.99. Found: N,[6] 13.82.

4-Nitrobenzamides and 4-Aminobenzamides.—The 4-nitrobenzamides were prepared from 4-nitrobenzoyl chloride and the amine by the sodium bicarbonate–chloroform–water procedure.[2] The yields were good, but the compounds derived from the tribasic amines proved extremely difficult to purify. The 4-aminobenzamides were obtained by reduction with ferrous sulfate and ammonia. Purification proved difficult in most cases, and with the more complex imino-interrupted side-chain compounds a pure base or characteristic derivative could not be obtained. The 4-nitro- and 4-aminobenzamides are listed in Table I.

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(5) Basic amino nitrogen by titration with perchloric acid in glacial acetic acid solution.

(6) Nitro nitrogen by titration with titanous chloride.