Methoxyamine Hydrochloride. An Improved Preparative Method

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Methoxyamine hydrochloride is a commonly used reagent for converting oxo-compounds into isomer free O-methyloximes.

The compound has been prepared by numerous procedures involving the formation and subsequent cleavage of O-methylethers of benzaldoxime,[1] benzophenone oxime,[2,3] ethylhydroxamic acid,[4,5] monochloramine,[6] and hydroxyurethane.[7,8]

Methylation of the above named compounds usually leads to a mixture of the O- and N-ethers, whereas a satisfactory yield of the pure methoxyamine is obtained by a fairly complicated procedure proposed by Traube, Ohlendorf and Zander,[9,10] consisting in methylation of sodium hydroxylaminedisulfonate, followed by hydrolysis. A simplified one-step modification of that method is presented.

Procedure. In a 2-litre beaker fitted with a stirrer and a thermometer and surrounded by an ice and salt bath 40.0 g (0.58 mole) of sodium nitrite is dissolved in 100 ml of water. A solution of 90.0 g (0.47 mole) of sodium pyrosulphite in 200 ml of water is added while stirring over a period of 2 min. To this solution 150 g of ice followed by 30 ml (0.5 mole) of glacial acetic acid are introduced[a] and the stirring is continued until the conversion of the sodium hydrogensulphite in the course of 30–60 min [b] is complete.[c] The beaker is removed from the ice and salt bath and a solution of 60 g (*ca.* 1.5 moles) of sodium hydroxide in 100 ml of water cooled to room temperature is added.[d] From a dropping funnel 138 g (1.1 moles) of dimethyl sulphate [e] is admitted over a period of 30 min with stirring, which is continued until the dimethyl sulphate is converted and the solution has become homogeneous, yellowish and the temperature has raised to about 40°.

A mixture of 100 g (55 ml, 1 mole) of concentrated sulphuric acid in 100 ml of water is added, and the solution is boiled under reflux for 2–3 h.[f] The reaction mixture is cooled to room temperature, is made alkaline by slow addition of a solution of 140 g (*ca.* 3.5 moles) of sodium hydroxide in 200 ml of water and is steam distilled. About 500 ml of distillate is collected in a mixture of 50 ml (*ca.* 0.5 mole) of concentrated hydrochloric acid and 150 ml of water. The acid solution is evaporated to complete dryness, and the solid residue (25–27 g) is dissolved in 125 ml of absolute ethanol. The solution is concentrated on a steam bath to beginning crystallization, and after cooling on ice the crystals are collected on a Büchner funnel, are washed twice with 30-ml portions of ether and are dried in a vacuum desiccator. The yield of product, melting at 148–149° [g], is 20–22 g (51–56 %).

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[a] The amounts of sodium nitrite, sodium pyrosulphite and glacial acetic acid are critical, and the salts must be pure qualities.

[b] The temperature of the solution should be kept in the range −5 to 0°. Higher temperatures lead to the formation of too much nitrido trisulphonate, and at lower temperatures the rate of reduction is very slow and will last more than 60 min.

[c] No hydrogen sulphite remains when 1 ml of the solution and 1 ml of a 1 % starch solution causes a persistant blue colour after addition of 1 drop of 0.001 N iodine.

[d] An alkaline reaction during the methylation is necessary because one of the sulphonic acid groups in the hydroxylamine disulphonate is very easily hydrolyzed in acid medium, which results in a lower yield.

[e] The excess stated of dimethyl sulphate is necessary in order to complete the methylation of the disulphonate, otherwise the final product will be contaminated with hydroxylamine hydrochloride and it will reduce Fehlings solution.

[f] When a mixture of 2 ml of the solution, 2 ml of 4 N hydrochloric acid, and excess of barium chloride, after centrifuging does not give a precipitate upon addition of 1 ml of 0.1 N sodium nitrite the hydrolysis is complete and the sulphonic acid groups in the hydroxylamine disulphonic acid have been removed.

[g] If the product reduces Fehlings solution it must be recrystallized from absolute ethanol.

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A Single Crystal X-Ray Diffraction Study of $Mn(OH)_2$

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Earlier X-ray studies [1-3] have shown $Mn(OH)_2$ to have the cadmium iodide structure. There is, however, a discrepancy between the Mn—O distance (2.19 Å) obtained by Aminoff,[2] who studied the mineral pyrochroite by Laue techniques, and that of Natta [3] (2.28 Å) from a powder pattern of synthetic $Mn(OH)_2$. It was therefore decided to redetermine the Mn—O distance in stoichiometric $Mn(OH)_2$ by a three-dimensional single-crystal X-ray analysis.

Crystals of $Mn(OH)_2$ were formed by treating 75 ml of a 1.3 m solution of manganese chloride with 100 ml of a 3.7 m solution of lithium hydroxide in a 220 ml pressure bomb lined with pure silver. The balanced pressure technique was used. The average temperature of the pressure bomb was 300°C. The pressure was measured as 650 atm. Thin crystal flakes were formed within 65 h. The pressure bomb was filled and emptied under oxygen free nitrogen, and the crystals of $Mn(OH)_2$ were washed, dried and stored in an atmosphere of oxygen free nitrogen. The crystals were white and remained so for 6 months.

Table 1. X-Ray diffraction data for $Mn(OH)_2$.

$a = 3.322 \pm 0.002$ Å, $c = 4.734 \pm 0.002$ Å

d obs	*d* calc	*h*	*k*	*l*	*j*
4.750	4.734	0	0	1	50
2.885	2.877	1	0	0	50
2.461	2.458	1	0	1	100
1.828	1.828	1	0	2	25
1.661	1.661	1	1	0	50
1.568	1.567	1	1	1	20
1.375	1.376	2	0	1	20

A plate-shaped crystal of dimensions 0.25 mm × 0.25 mm × 0.01 mm was investigated by precession methods. Integrated precession photographs were taken using Zr-filtered Al-screened Mo$K\alpha$-radiation of (*hk*0), (*hk*1), (*hk*2) and (0*kl*). 60 independent reflections were measured photometrically. No absorption correction was applied. The unit cell dimensions were determined using a Guinier focussing camera with Cu$K\alpha_1$ radiation and germanium as internal standard. Optical densities of the lines were measured by means of a recording doublebeam microdensitometer. Table 1 gives the indexing of the powder pattern.

The crystal data obtained are: Crystal system: trigonal; using hexagonal setting, the axes are: $a = 3.322 \pm 0.002$ Å, $c = 4.734 \pm 0.002$ Å; space group: No. 164, *P*3*m*. Absorption coefficient $\mu = 74$ cm^{-1} for Mo$K\alpha$-radiation. The crystals are tabular on (001).

$Mn(OH)_2$ is isostructural with $Ca(OH)_2$.[1] In $Ca(OH)_2$ [4] the metal ions are at the centre of symmetry (0,0,0) and the oxygen atoms are in special positions ± (1/3, 2/3, 0.2341). These coordinates were used when the refinement was started. Coordinates and temperature factors were refined by the method of Bhuiya and Stanley.[5] The atomic scattering factors used were from Vol. III of *International Tables for X-ray Crystallography*. The interpolation formula of Bassi [6] was applied. The refinement gave

Table 2. Atomic coordinates and temperature factors.

Atom	*x*	*y*	*z*	σz	*B* (Å^2)	σB (Å^2)
Mn	0.0	0.0	0.0		0.48	0.05
O	0.33333	0.66667	0.231	0.003	1.2	0.2