



Fig. 2.

mining the loss of weight of the salt after heating at a pressure of 9 mm Hg to 100°C (Fig. 2). The calculated loss of weight is 55.5 %, that found 54.6 %.

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1. Walden, P. *Z. anorg. Chem.* **25** (1900) 214.
2. Gutmann, V. *Z. anorg. Chem.* **266** (1951) 22.
3. Gutmann, V., and Lindqvist, I. *Z. phys. Chem. (In press)*.
4. Tovborg Jensen, A. *Krystalliniske Salt-hydrater*, Kjöbenhavn 1948.

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On the Synthesis of Methoxinine

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Methoxinine, the oxygen analog of methionine, has been prepared by Roblin¹ by alkylating ethyl phthalimidomalonate with β -methoxyethyl bromide, followed by

hydrolysis and decarboxylation of the resultant ethyl (β -methoxyethyl)phthalimidomalonate.

In an attempt to repeat this synthesis, using ethyl acetamidomalonate and either β -methoxyethyl chloride or β -methoxyethyl *p*-toluenesulfonate it was found difficult to obtain the intermediate ethyl β -methoxyethyl acetamidomalonate in a pure state. The substance was therefore prepared by the method of Barry and Hartung² using γ -methoxy- α -oximino butyric acid as an intermediate. Hydrogenation of this oximino acid in aqueous ammonia gave methoxinine in a pure state.

Experimental. (Micro analyses are made by Mr. P. Hansen. All melting and boiling points are uncorrected.)

Ethyl- β -methoxyethylmalonate was prepared in conventional manner³ from ethyl malonate, sodium ethoxide and β -methoxyethyl chloride in 69 % yield. B.p. 124—5°/10 mm; n_D^{25} 1.4228; $C_{10}H_{16}O_5$ (218.2): Calc. C 55.0; H 8.3. Found C 54.9; H 8.0.

γ -Methoxy- α -oximinobutyric acid was prepared according to the directions of Barry and Hartung² in 80 % yield. M.p. 112—3° (from ethyl acetate). $C_5H_9NO_4$ (147.1): Calc. C 40.8; H 6.2; N 9.5. Found C 41.0; H 6.1; N 9.2; Acid eqv. 147.

Methoxinine: A solution of 36 g of γ -methoxy- α -oximino butyric acid in 360 ml of 10% aqueous ammonia was treated with hydrogen at 50° and 100 atm for 6 hours using 10 g of Raney-nickel as a catalyst. The catalyst was filtered off and the solution concentrated to 100 ml in vacuum, treated with hydrogen sulfide to remove some dissolved nickel salts, filtered, and the solution concentrated to approx. 50 g, 150 ml of 99 % ethanol added, and the solution left in the ice box for 15 hours. Filtration gave 18 g (55 %) of colorless leaves, decomposing at 220—250° without melting (Roblin² gives m.p. 253° (dec. with effervescence)). $C_5H_{11}NO_3$ (133.1). Calc. C 45.1; H 8.3; N 10.5. Found C 44.9; H 8.0; N 10.5; Formol titr. 134.

1. Roblin, R. O., Jr., Lampen, J. O., English, J. P., Cole, Q. P., and Vaughan, H. R., Jr. *J. Am. Chem. Soc.* **67** (1945) 290.
2. Barry, R. H., and Hartung, W. H. *J. Org. Chem.* **12** (1947) 460.
3. *Org. Syntheses Coll. Vol. 1* (1946) 250.

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