

third ampoule provided with a break-seal and cooled with liquid nitrogen. The ampoule was sealed off, allowed to warm to -78° and then placed in an ice-bath. These precautions were taken to prevent too rapid warming of the mixture. At 0° , a white slush, presumably zinc chloride and germanium tetramethyl, was observed in the ampoule. The ampoule was removed from the ice-bath, attached to a vacuum manifold and opened. A nearly quantitative yield of germanium tetramethyl was evaporated into a receiver cooled with liquid nitrogen. Total non-condensable gases, principally methane, were measured, analyzed with the mass spectrometer, and discarded. A mass spectrometric analysis of the condensable fraction showed only a trace of germanium tetrachloride. The impurities of the combined condensable and non-condensable fractions totaled less than one mole per cent. No zinc compounds volatile at room temperature were observed.

In the second preparation a calculated 100% excess of germanium tetrachloride was used. After sealing off the reaction ampoule, it was immediately removed from the liquid nitrogen and allowed to warm directly to room temperature. Crystals of zinc chloride appeared only after 30 minutes, presumably because of the solubility in the excess germanium tetrachloride. After standing overnight at room temperature the ampoule was attached to the vacuum manifold and was opened. The excess germanium tetrachloride was almost completely removed by a single bulb-to-bulb vacuum distillation through a short column of potassium hydroxide pellets in series with the receiving bulb and attached to the manifold. This proved to be a very convenient way to remove the chloride compounds as the pellets retained sufficient water even under vacuum to hydrolyze the germanium tetrachloride. Mass spectrometric analysis of the product after removal of the chlorides indicated a purity comparable with that of the first preparation.

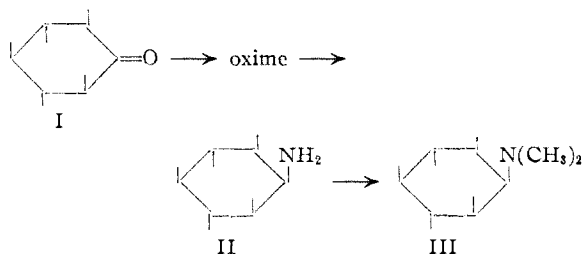
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Cyclitol Derivatives. IV. 2-Keto-*myo*-inositol Thiosemicarbazone and 2-Dimethylamino-2-desoxy-*myo*-inositol¹

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The first communication² of this series included among other N-containing cyclitols, the thiosemicarbazone of D,L-2-keto-*epi*-inositol (*rac-epi*-inosose) and an N,N-dimethylinosamine (either D,L-2-dimethylamino-2-desoxy-*epi*-inositol or D,L-4-dimethylamino-4-desoxy-*myo*-inositol) derived from this cyclose. We now wish to report two corresponding isomeric compounds which have been prepared from 2-keto-*myo*-inositol (*scyllo*-inosose) (I).



Carter, *et al.*,³ hydrogenated with Raney nickel both the oxime and the phenylhydrazone of I and obtained a mixture of inosamines. We have hydro-

(1) The nomenclature used is that proposed by H. G. Fletcher, Jr., L. Anderson and H. A. Lardy, *J. Org. Chem.*, **16**, 1238 (1951). Trivial names used previously are also given.

(2) E. L. May and E. Mosettig, *ibid.*, **14**, 1137 (1949).

(3) H. E. Carter, R. K. Clark, B. Lytle and G. E. McCasland, *J. Biol. Chem.*, **175**, 683 (1948).

genated I oxime in 50% methanol with platinum oxide and have isolated 2-amino-2-desoxy-*myo*-inositol (inosamine SA) (II).⁴

Methylation of II with formaldehyde and formic acid produced the N,N-dimethyl derivative (III). This tertiary amine, its precursor (II) and the thiosemicarbazone of I have been tested for *in vitro* activity against tuberculosis (Dubos-Davis medium H37Rv).⁵ They were not significantly active.

Experimental

Hydrogenation of 2-Keto-*myo*-inositol Oxime.—One gram of the oxime,⁶ 0.1 g. of platinum oxide, 10 ml. of water and 10 ml. of methanol absorbed two moles of hydrogen during 10 to 15 hours. Addition of water, warming to solution, filtration and evaporation of the filtrate to one-fourth volume gave 0.5 g. (55%) of 2-amino-2-desoxy-*myo*-inositol (II), m.p. 277–279.5° (cor., evac. tube).

Anal. Calcd. for C₆H₁₂N₂O₅: C, 40.2; H, 7.3. Found: C, 40.7; H, 7.3.

The hydrochloride of II (NIH 3641) melted at 230–233° (Kofler) after undergoing transition at 187–195°, while the N-acetyl derivative melted at 245–248°.^{3,4}

2-Dimethylamino-2-desoxy-*myo*-inositol (III) Hydrochloride.—Two grams of II, 2.0 ml. of 37% aqueous formaldehyde and 2.4 ml. of 98% formic acid, heated on the steam-bath for two hours, cooled, treated with a slight excess of concentrated hydrochloric acid and diluted with methanol, then ether, gave 1.7 g. (60%) of the hydrochloride of III. After three recrystallizations from methanol-ether (Norit), it melted at 218–220° (cor.).

Anal. Calcd. for C₈H₁₈ClNO₅: C, 39.4; H, 7.4. Found: C, 39.5; H, 7.3.

2-Keto-*myo*-inositol Thiosemicarbazone (NIH 3845).—One gram of I,⁶ 0.6 g. of thiosemicarbazide and 15 ml. of water were kept on the steam-bath for 10 minutes and at 5° overnight to give 0.9 g. (70%) of thiosemicarbazone. Recrystallized from water (Norit) it melted at 194.5–196° (cor., dec.).

Anal. Calcd. for C₇H₁₃N₃O₅S: C, 33.5; H, 5.2. Found: C, 33.6; H, 5.1.

Acknowledgment.—We are indebted to Dr. Laura C. Stewart of this Institute for the biochemical preparation of 2-keto-*myo*-inositol. Microanalyses are from the Institutes service analytical laboratory under the direction of Dr. William C. Alford.

(4) After our work was completed L. Anderson and H. A. Lardy, *THIS JOURNAL*, **72**, 3141 (1950), reported the preparation of inosamine SA and assigned to it the structure of II. A recent study by G. E. McCasland, *ibid.*, **73**, 2295 (1951), supports the conclusions of these authors.

(5) Testing was done at the Tuberculosis Research Laboratory, Public Health Service, Cornell University Medical College, New York, N. Y., under the direction of Dr. Bernard D. Davis.

(6) H. E. Carter, C. Belinsky, R. K. Clark, E. H. Flynn, B. Lytle, G. E. McCasland and M. Robbins, *J. Biol. Chem.*, **174**, 415 (1948).

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The Reaction of Amines with Nitroguanyl Azide

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Nitroguanyl azide (I) cyclizes rapidly with a large variety of inorganic and organic bases to form a

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