Aminocyclitols. II. Stereochemical Studies of 2-Amino-1,3-cyclohexanediol

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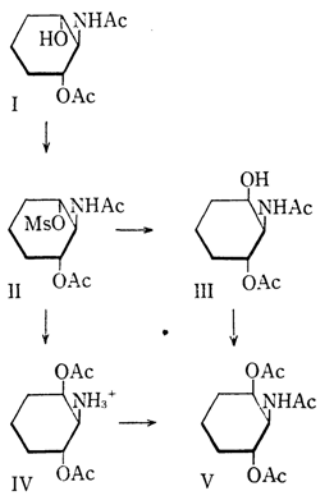
In connection with the previous studies of 2-amino-1, 3-cyclohexanediols,[1] an inversion reaction of *trans-O*-acetyl-*O*-mesyl-2-acetamido-1, 3-cyclohexanediol (II) has been studied. II is prepared by the mesylation of *trans-O*-acetyl-2-acetamido-1, 3-cyclohexanediol (I)[1] with mesyl chloride and pyridine. The displacement of the mesyloxy group of II gives DL-*O*-acetyl-2-acetamido-1, 3-cyclohexanediol (III) when the reaction is carried out with sodium acetate in aqueous 2-methoxyethanol. III is identical with an authentic sample[2] which is prepared from *trans-O*-dimesyl-2-acetamido-1, 3-cyclohexanediol. The demesylation of II takes place in boiling water without sodium acetate, and the product is identified as DL-isomer by converting it to the triacetyl derivative (V).[1,2] Moreover, V is obtained by the acetylation of III with acetic anhydride and pyridine.[2] Since there is only one mesyloxy group in II, the product III should have suffered from Walden inversion only at the place where the mesyloxy group had been linked. Thus, the previously-reported DL-configuration of III[1,2] is further confirmed by the present experiments.



Experimental*

***trans*-*O*-Acetyl-*O*-mesyl-2-acetamido-1, 3-cyclohexanediol (II).**—To a stirred solution of 1.1 g. of I in 15 ml. of pyridine, 0.8 ml. of methanesulfonyl chloride was added under ice cooling. After it had been stirred for 4 hr. at room temperature, the mixture was poured into ice and water. The solution was evaporated untile the precipitate appeared. The precipitate was collected by filtation. The second crop of the product was obtained by the further evaporation of the filtrate; the total yield was 1.05 g. (70%); m. p. 125~128°C. The product was recrystallized twice from acetone to give colorless needles; m. p. 137~139°C.

Found: C, 45.12; H, 6.61; N, 4.84; S, 10.83. Calcd. for $C_{11}H_{19}NO_6S$: C, 45.04; H, 6.53; N, 4.78; S, 10.93%.

DL-*O*-Acetyl-2-acetamido-1, 3-cyclohexanediol (III).—A mixture of 1.0 g. of II, 1.0 g. of anhydrous sodium acetate and 20 ml. of 95% 2-methoxyethanol was refluxed for 10 hr. The mixture was evaporated in vacuo to dryness, and the residue was extracted with boiling acetone. The acetone extract was evaporated, and the residue was recrystallized from ethanol-ether to give 0.28 g. (38%) of crystals (m. p. 151~152°C). The product was found identical with an authentic sample[2] on the basis of its mixed melting point and infrared spectra.

DL-Triacetyl-2-amino-1, 3-cyclohexanediol (V).—A mixture of 0.3 g. of II and 5 ml. of water was refluxed for 5 hr. The mixture was evaporated to

1) T. Suami and S. Ogawa, This Bulletin, 37, 194 (1964).
2) F. W. Lichtenthaler, *Chem. Ber.*, 96, 845 (1963).

* All melting points have been corrected.

give an acidic sirup, probably a methanesulfonate (IV), which showed a characteristic infrared absoption at 1200 cm^{-1}. The solvolysis might involve the N→O migration of the acetyl group in an acidic medium.[1] The sirup was treated with acetic anhydride and pyridine, and then evaporated in vacuo. The product was recrystallized from ether-petroleum ether to give 78 mg. (30%) of needles (m. p. 146°C). The product was found identical with an authentic sample[1,2] on the basis of its mixed melting point and infrared spectra.

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