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Stereochemistry of the Ring Opening of 2,3-Iminobutane by Acetic Acid[1,2]

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Isomeric forms of 2,3-iminobutane (2,3-dimethylaziridine) react with acetic acid to give products that are converted by acetic anhydride to 2-acetoxy-3-acetamidobutanes in essentially quantitative yields. The product from *cis*-2,3-iminobutane is DL-*threo*-2-acetoxy-3-acetamidobutane and the one from L(−)-2,3-iminobutane is L(−)-*erythro*-2-acetoxy-3-acetamidobutane. In each case a Walden inversion accompanies the reaction and leads to a *trans*-opening of the imine ring.

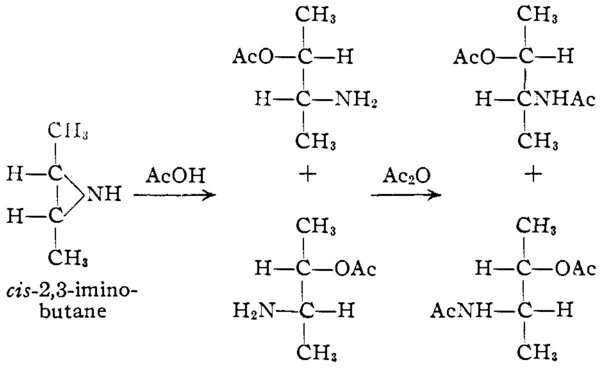
In the reactions of *cis*- and L(−)-2,3-iminobutanes with ammonia and water, *trans*-openings of the imine ring have been established.[4] In the present work it has been found that the stereochemistry of the ring openings with acetic acid is similar. This has been established by converting the first formed 2-acetoxy-3-aminobutane, without isolating it, to 2-acetoxy-3-acetamidobutane. The products were identified by comparing their properties with those of the known diacetyl derivatives of the isomeric 3-amino-2-butanols.[4]

The product from the *cis*-imine is optically inactive and that from the active *trans*-imine is active. The physical data are shown in Table I along with the data of inactive and active derivatives of the 3-amino-2-butanols. It is seen that the two products are, respectively, the diacetyl derivatives of DL-threo- and L(−)-*erythro*-3-amino-2-butanol. Mixed melting points with authentic compounds gave no depression when paired on the basis of the physical data, and depression of > 25 degrees when paired oppositely.

TABLE I

ROTATIONS AND MELTING POINTS OF 2-ACETOXY-3-ACETAMIDOBUTANES

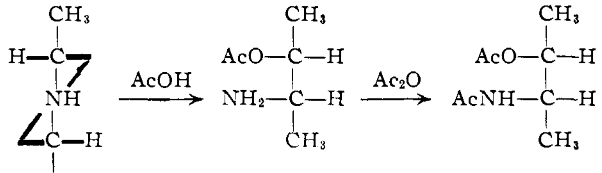
		$\alpha^{22}D$ °	Melting point, °C. Original[4]	Pure compd.	Mixture
1	DL-*erythro*	0	51.0–52.4	51.5–52.8	1 and 5, softens, 25
2	DL-*threo*	0	73.4–74.4	73.3–74.4	2 and 5, 73.4–74.5
3	L(−)-*erythro*	−33.0	62.3–63.3	62.5–63.2	3 and 6, 62.6–64.3
4	L(−)-*threo*	−35.0	59.3–59.6	59.6–60.7	4 and 6, <29–37
5	Product from *cis*-imine	0		74.3–74.7	
6	Product from L(−)-imine	−30.6		63.3–63.9	



cis-2,3-imino-butane

DL-*threo*-2-acetoxy-3-aminobutane

DL-*threo*-2-acetoxy-3-acetamidobutane



L(−)-*trans*-2,3-iminobutane

L-*erythro*-2-acetoxy 3-aminobutane

L(−)-*erythro*-2-acetoxy-3-acetamidobutane

Experimental

Reaction of *cis*-2,3-Iminobutane.—To 60 g. (1.0 mole) of glacial acetic acid, cooled in a water-bath was added with stirring, 7.1 g. (0.10 mole) of *cis*-2,3-iminobutane over 30 minutes. The temperature was not allowed to rise above 30°. After standing two days, there was added with stirring 20.4 g. (0.20 mole) of acetic anhydride (redistilled) over a period of 40 minutes. The temperature was kept below 25°. After standing another two days, the apparatus was equipped for fractionation, and the excess acetic acid and acetic anhydride distilled at 12 mm. through an 8-inch column of raschig rings, until the pot temperature reached 60°. It was then subjected to a pressure of 1 mm. for 2 hours, with the temperature kept at 60°.

After cooling, the viscous material was placed in a vacuum desiccator over potassium hydroxide and sulfuric acid (1 mm. pressure). After 3 days a small amount was solidified in Dry Ice, and used to seed the large portion. All quickly solidified to give 16.9 g. (98% yield) of very light-colored material; m.p. 71.5–73.5°.

Recrystallization from dry diisopropyl ether gave 13.1 g. (76%) of white prisms, m.p. 74.3–74.7° (cor.).

Reaction of L(−)-*threo*-2,3-Iminobutane.—The reaction was carried out as for the inactive imine, but on a smaller scale (0.05 mole of imine). The diacetate solidified readily without being seeded, even before being placed in a desiccator. A yield of 8.5 g. (98%) resulted. Recrystallization from dry diisopropyl ether gave 7.4 g. (85%) of pure product, m.p. 63.3–63.9° (cor.).

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[4] F. H. Dickey, W. Fickett and H. J. Lucas, THIS JOURNAL, **74**, 944 (1952).