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STEREOCHEMISTRY OF THE RING CLOSURE REACTION OF OPTICALLY ACTIVE 1-AMINO-2-PROPANOL

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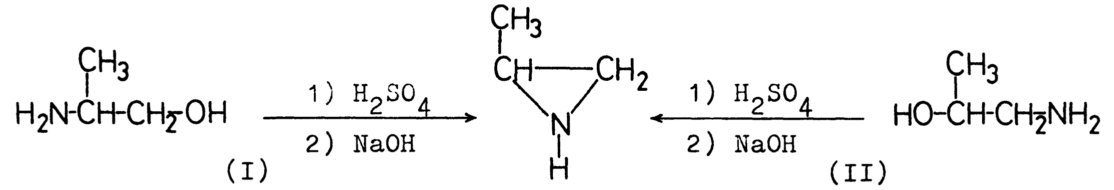
Optically active 2-methylethylenimine has been prepared via ring closure reaction of (R)- or (S)- 1-amino-2-propanol. The reaction is explained by an intramolecular S_N2 mechanism.

Optically active 2-alkylethylenimines such as (S)-2-methylethylenimine¹⁾, (R)-2-ethylethylenimine²⁾ and (S)-2-isobutylethylenimine³⁾ have been prepared from the sulfates of the corresponding optically active 2-amino-1-alkanols. Minoura et al¹⁾ obtained an optically active 2-methylethylenimine from the (R)- or (S)-2-amino-1-propanol. Hirai and Furuta prepared optically inactive 2-methylethylenimine from racemic 1-amino-2-propanol.⁴⁾



The reaction (I) is floating as a conventional process for the preparation of (S)-2-methylethylenimine.¹⁾ The configuration of the product is the same to that of the starting material. On the other hand, 2-methylethylenimine is obtained easily according to the process (II). Since this reaction, however, proceeds with the elimination of OH group attached to the asymmetric carbon atom of the aminoalcohol, it is ambiguous that 2-methylethylenimine produced shows optical activity or not, when an optically active aminoalcohol was employed.

The resolution of racemic 1-amino-2-propanol was carried out according to Sullivan's procedure.⁵⁾ The acid tartrate of the racemic 1-amino-2-propanol was prepared by mixing an aqueous solution of the aminoalcohol to that of (2R,3R)-tartaric acid. The precipitate produced was filtrated, washed and recrystallized five times from water. The product was obtained as tabular crystals; mp 68-69°, $[\alpha]_D$=+30.2° (c=2.54, H_2O). Further, acicular crystals were obtained by reworking the mother liquors; mp 57-58°, $[\alpha]_D$=+1.98° (c=2.32, H_2O). The crystals were dissolved in an aqueous solution of calcium hydroxide. The pH of the solution was set to 10.6. Then the optically active aminoalcohol was liberated after evaporation under reduced pressure, the pure optically active aminoalcohol, (S)-1-amino-2-propanol, was obtained in 58 % yield $[\alpha]_D$=+25.81° (c=1.73, C_2H_5OH).(R)-1-amino-2-propanol was liberated also by means of the same manner from the acicular crystals.

Optically active 2-methylethylenimine was prepared from (R)- or (S)- 1-amino-

2-propanol. A mixture of (S)-1-amino-2-propanol and an excess of 50 % aqueous sulfuric acid was evaporated under reduced pressure. A white solid mass was obtained. After addition of 40 % aqueous solution of sodium hydroxide to the solid, the mixture was distilled. The distillate was saturated with potassium hydroxide and the organic layer separated was dried with potassium hydroxide and finally with sodium metal. The product was recognized to be (R)-2-methylethylenimine; bp 66-67°, yield 72 %; $[\alpha]_D$=+12.58° (c=1.43, C_2H_5OH), n_D^{29}=1.4152. Anal. Calcd for C_3H_7N; C,63.15; H,12.27; N,24.56 %. Found: C,62.99; H,12.35; N,24.41 %. (S)-2-Methylethylenimine was prepared from (R)-1-amino-2-propanol in a same manner; bp 66-67°, yield 67 %, $[\alpha]_D$=-12.48° (c=1.10, C_2H_5OH), n_D^{29}=1.4150. The characteristic infrared absorption of imine ring was observed in 3050 cm^{-1}. The results are summarized in the Table.

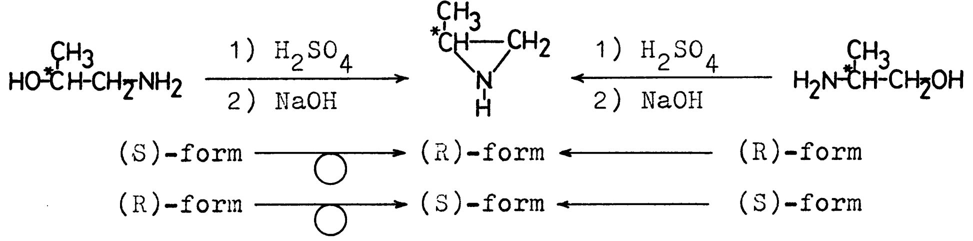
Table. Ring closure reaction of optically active 1-amino-2-propanol

1-Amino-2-propanol			2-Methylethylenimine		
$[\alpha]_D$	O.Y.(%)[a]	Conf.	$[\alpha]_D$	O.Y.(%)[b]	Conf.[c]
+25.81°	100	S	+12.58°	98.3	R
-26.11°	100	R	-12.48°	100	S

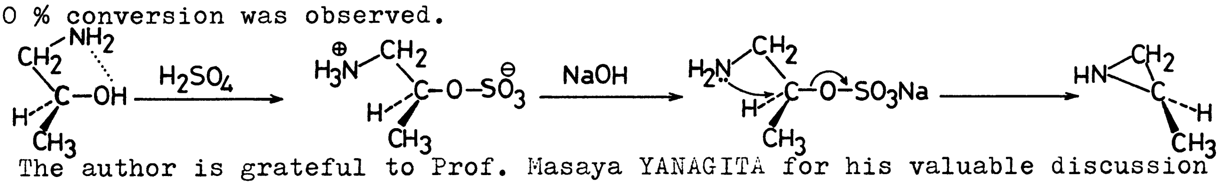
a) Optical yield was calculated from the specific rotation of the product and that of optically pure 1-amino-2-propanol ((S)-1-amino-2-propanol $[\alpha]_D$=+25.8° in C_2H_5OH).

b) Optical yield was calculated from the specific rotation of the product and that of optically pure 2-methylethylenimine ((S)-form $[\alpha]_D^{25}$=-12.4°(c=2.58, C_2H_5OH), (R)-form $[\alpha]_D^{25}$=+12.8°(c=2.27, C_2H_5OH).

c) Configuration of predominant isomer.



The reaction can be explained by an intramolecular S_N2 mechanism, and nearly 100 % conversion was observed.



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