MIGRATION OF AN EPISULFIDE BRIDGE IN A NUMBER OF ESTERS OF 2,3-EPOXY-4,5-EPITHIOVALERIC ACIDS

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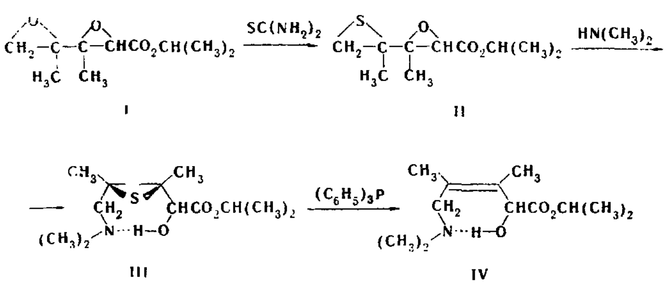
UDC 547.478.279

A configurationally homogeneous isopropyl 3,4-dimethyl-2,3-epoxy-4,5-epithiovalerate (II) was obtained by reaction of a mixture of diastereomers of isopropyl 3,4-dimethyl-2,3,4,5-diepoxyvalerate (I) [1] with thiourea. Opening of the thiirane ring in II with dimethylamine proceeds with migration of the episulfide bridge to give isopropyl 5-dimethylamino-2-hydroxy-3,4-dimethyl-3,4-epithiovalerate (III). The position of the thiirane ring in III was established by desulfuration with thriphenylphosphine to isopropyl 5-dimethylamino-2-hydroxy-3,4-dimethyl-3-pentenoate (IV). The presence of an intramolecular hydrogen bond (IHB) between the hydroxyl group and the nitrogen atom, as indicated by the unchanged position of the absorption band at 3200-3300 cm^{-1} in the IR spectra of III and IV on dilution of solutions in CCl_4 to 10^{-3} M, is associated with the cis configuration of the thiirane ring in ester III and the double bond in IV.



I II III IV

EXPERIMENTAL

A mixture of 0.25 mole of I and 0.30 mole of thiourea in 300 ml of methanol was held at 50° for 3h, after which it was diluted with water and extracted with ether. The ether was removed, and the residue was vacuum distilled to give II (44%) with bp 98° (2 mm), d_4^{20} 1.0853, and n_D^{20} 1.4770. Found: S 14.6%; MR_D 56.3. $C_{10}H_{16}O_3S$. Calculated: S 14.8%; MR_D 56.0. PMR spectrum in CCl_4: 1.27 (d, J = 7 Hz, two CH_3); 1.48 and 1.68 (S, 3- and 4-CH_3); 2.08 and 2.46 (s, CH_2); 3.24 (s, 2-H); 5.02 ppm (quintet, J = 7 Hz, CH).

A solution of 0.20 mole of II and 0.25 mole of dimethylamine in 50 ml of 2-propanol was allowed to stand for 10 days, after which the alcohol was removed by distillation, the residue was dissolved in 300 ml of ether, and HCl was bubbled through the solution. The hydrochloride of ester III was separated and crystallized from acetone-2-propanol (1 : 1) to give 63% of a product with mp 183°. Found: Cl 12.2%. $C_{12}H_{23}NO_3S \cdot HCl$. Calculated: Cl 11.9%. The base had mp 61°. Found: N 5.2; S 12.4%. $C_{12}H_{23}NO_3S$. Calculated: N 5.4; S 12.2%. IR spectrum: 3520-3540 (IHB between the OH group and the S atom or COOR group), 3200-3300 (IHB between the OH group and the N atom), 1740 cm^{-1} (CO). PMR spectrum: 1.33 (d, J = 7 Hz, two CH_3); 1.38 and 1.68 (s, 3- and 4-CH_3); 2.22 [s, $N(CH_3)_2$]; 2.48 and 2.63 (two d, J = 13 Hz, CH_2); 3.40 and 4.00 (s, OH and 2-H); 5.08 ppm (quintet, J = 7 Hz, CH).

A 0.05-mole sample of III and 0.10 mole of triphenylphosphine were refluxed in 50 ml of tetrahydrofuran for 10 h, after which the solvent was removed by distillation, the residue was diluted with petroleum

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ether, the precipitated triphenylphosphine sulfide was separated, and HCl was bubbled through the filtrate. The precipitated hydrochloride of ester IV was crystallized from acetone to give a product with mp 156° in 65% yield. Found: Cl 13.6%. $C_{12}H_{23}NO_3 \cdot HCl$. Calculated: Cl 13.4%. The base had bp 78° (1 mm), d_4^{20} 0.9817, and n_D^{20} 1.4635. Found: N 6.1%; MR_D 64.4. $C_{12}H_{23}NO_3$. Calculated: N 6.1%; MR_D 64.5. IR spectrum: 3560-3580 (IHB between the OH group and the COOR group), 3300 (IHB between the OH group and the N atom), and 1750 cm^{-1} (C=O). PMR spectrum: 1.18 and 1.27 (d, J = 7 Hz, two CH_3), 1.53 and 1.83 (two quartets, J = 1.4 Hz, 3- and 4-CH_3); 2.12 [s, $N(CH_3)_2$]; 2.76 and 2.90 (2 d, CH_2); 3.04 (s, OH); 4.91 (s, 2-H), 5.00 ppm (quintet, J = 7 Hz, CH).

LITERATURE CITED

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