

Stereoselective synthesis and Characterization of Oxiranes from Trans-4-amino cyclohexanol

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Abstract

Oxiranes (epoxides) are three membered cyclic ethers .Because of their highly polarized oxygen-carbon bonds and strained ring, epoxides are quiet reactive with nucleophiles. A series of novel oxiranes (3a-e) have been synthesized.Trans-4-aminocyclohexanol(1) on reaction with chloroacetyl chloride gave N(4'hydroxycyclohexane) chloroacetamide (2)which were then condensed with different aromatic aldehydes to give substituted oxiranes. The products formed were analysed by IR and NMR.

Key Words: Trans-4-aminocyclohexanol, Chloroacetyl chloride, Oxiranes

Introduction

In view of their practical and theoretical ⁽¹⁻²⁾ applications oxiranes represent one of the class of three membered heterocycles. Oxiranes are ethers with the oxygen in a saturated three membered ring. The most important and simplest epoxide is ethylene oxide. It is an important feed stock in manufacturing of ethylene glycol, which is used as antifreeze, liquid coolant, solvent and also used in the production of polyester and polyethylene terephthalate. Ethylene Oxide is used in medical applications as a sterilizing agent for surgical instruments.The interior bond angles of epoxides are about 60° which is in contrast with the ideal bond angle of 109.5° for tetrahedral carbon. Due to the strained bond angles oxiranes have bent bonds (banana bonds) . The strain of the three membered ring makes an epoxide much more reactive than a typical acyclic ether. Oxiranes have marked industrial⁽³⁾and physiological⁽⁴⁻¹⁰⁾ importance due to which epoxidation⁽¹¹⁻¹²⁾ was carried out starting from trans -4-aminocyclohexanol.

We report herein the synthesis of novel Oxiranes 3a-e(scheme-1)from trans -4-aminocyclohexanol(1)which on reaction with chloroacetyl chloride gave N(4'hydroxycyclohexane) chloroacetamide (2).This was then condensed with different aromatic aldehydes in the presence of sodium hydroxide to give substituted oxiranes.PMR spectral studies revealed that the structure was in accordance with their spectral data . Two distinct doublets in the region of δ 3.40-4.40(J=2 Hz of vicinal coupling) corresponds to one proton .This value of the coupling constant is consistent with a trans isomer as reported.

Experimental

Materials Used

All the chemicals used were of analytical Reagents (AR) grade. Melting points were taken on a Thomas-Hoover melting point apparatus. IR spectra were recorded on a Perkin -Elmer

spectrophotometer model 599 using KBr discs, ^1H NMR on a Perkin -Elmer R-32(90 MHz)instrument using TMS as an internal standard. The purity of the compounds were checked on silica coated Al Plates (Merck).

Synthesis of Trans-4-aminocyclohexanol(1).

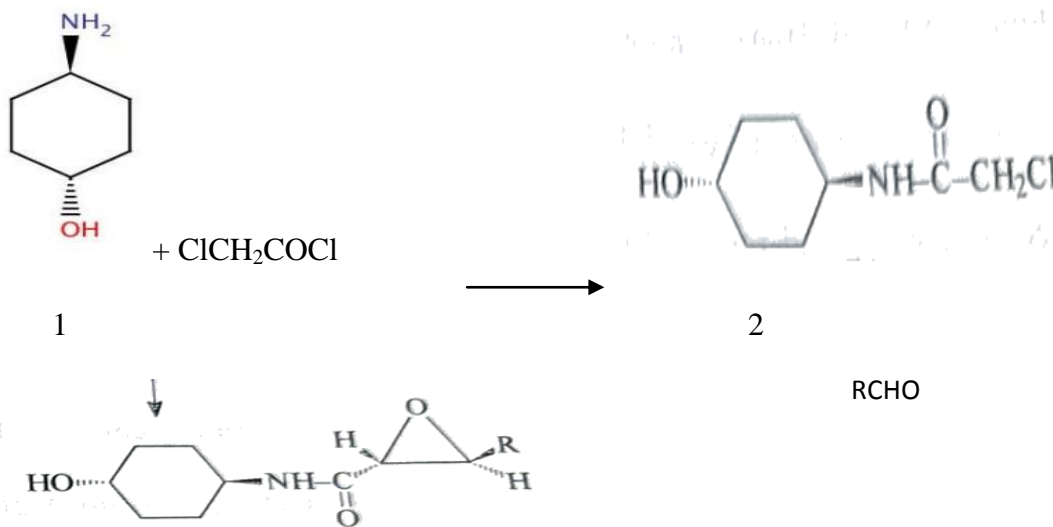
It was prepared according to the literature method⁽¹³⁾.

Synthesis of N(4'-hydroxycyclohexane)Chloroacetamide (2).

Chloroacetyl chloride (0.02 mol)was added with stirring to a cooled solution of Trans-4-aminocyclohexanol (0.01mol) in methanol. The reaction mixture was refluxed for 3hrs. The progress of the reaction was checked by TLC. After the completion of the reaction the solid separated was filtered washed with water and recrystallised from methanol to give the product.

Synthesis of N(4'-hydroxycyclohexane)-3-(substituted-2,3-epoxy-propanamide).

N(4'-hydroxycyclohexane) chloroacetamide(0.05 mol),substituted aldehyde (0. 05 mol),sodium hydroxide were taken in 20 ml methanol. The reaction mixture was stirred at room stirred at room temperature for 5-6 hrs. The progress of the reaction was checked by TLC. After completion of the reaction, the reaction mixture was filtered. The clear filtrate obtained under reduced pressure is precipitated with water and separated which was recrystallised from ethanol to give the product. The physical and spectral data of the compounds (3a-e) are given in table 1.



Scheme-1

Table-1 :Physical& Spectral Data of Compounds

Compo und no.	Yield %	M.P. °C	IR(ν_{\max} cm^{-1})	$^1\text{H NMR}(\text{CDCl}_3)$ δ ppm
2	70	227	1655(C=O),3240(NH),3400(OH)	0.90-2.20 (complex m, 8H C_6H_8) 2.45-2.85(m,1H,CHOH), 3.30(m,1H CHNH),4.2(s,2H,-COCH ₂),5.00(br., 1H,OH),10.30(br,1H,NH)
3a	70	88	1655(C=O),3240(NH),3400(OH)	0.90-2.20 (complex m, 8H C_6H_8), 2.45-2.70 (m,1H,CHOH), 2.9-3.1 (m,1H, CHN) ,3.45 (d,1H,1-CH J=1.9 Hz), 3.70 (d,1H,2-CH J=1.9 Hz), 5.00 (br , 1H, OH), 7.0-7.8 (m, 5H,Ar-H),10.30(br,1H,NH)
3b	68	130	1660(C=O),3250(NH),3410(OH)	0.80-2.20 (complex m, 8H C_6H_8), 2.45-2.60 (m,1H,CHOH), 2.8-3.0 (m,1H, CHN) ,3.45 (d,1H,1-CH J=1.9 Hz), 3.70 (d,1H,2-CH J=1.9 Hz), 5.00 (br , 1H, OH), 7.0-7.7(m, 5H,Ar-H),10.20(br,1H,NH)
3c	72	89	1660(C=O),3245(NH),3400(OH)	0.90-2.10 (complex m, 8H C_6H_8), 2.4-2.6 (m,1H,CHOH), 2.8-2.95 (m,1H, CHN) ,3.40 (d,1H,1-CH J=1.9 Hz), 3.70 (d,1H,2-CH J=1.9 Hz), 4.8 (br , 1H, OH), 6.6 (s, 6H,N(CH ₃)),7.0-7.8 (m, 4H,Ar-H),10.20(br,1H,NH)
3d	70	68	1655(C=O),3240(NH),3410(OH)	0.90-2.20 (complex m, 8H C_6H_8), 2.45-2.70 (m,1H,CHOH), 2.8-2.90 (m,1H, CHN) ,3.40 (d,1H,1-CH J=1.9 Hz), 3.70 (d,1H,2-CH J=1.9 Hz), 4.8 (br , 1H, OH), 6.6 (s, 1H,OH),7.0-7.7 (m, 4H,Ar-H),10.30(br,1H,NH).
3e	67	75	1660(C=O),3245(NH),3400(OH)	0.8-2.2 (complex m, 8H C_6H_8), 2.3-2.50 (m,1H,CHOH), 2.7-2.90 (m,1H, CHN) ,3.40 (d,1H,1-CH J=1.9 Hz), 3.70 (d,1H,2-CH J=1.9 Hz), 4.8 (br , 1H, OH), 7.1-7.7 (m, 4H,Ar-H),10.40(br,1H,NH)

Result and Discussion

PMR spectral studies revealed that the structure was in accordance with their spectral data . Two distinct doublets in the region of δ 3.40-4.40($J=2$ Hz of vicinal coupling) corresponds to one proton .This value of the coupling constant is consistent with atrans isomer as reported.

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