Pergamon

Tetrahedron, Vol. 52, No. 15, pp. 5607-5616, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00196-2

Ring Opening Reactions of Benzyl 2,3-Anhydro -α-D-Ribopyranoside with Nucleophiles

Pejakala K. Vasudeva and Madhavarao Nagarajan*

School of Chemistry, University of Hyderabad
Hyderabad- 500 046. India

Abstract: Nucleophilic ring opening reactions of benzyl 2,3 anhydro-α-D-ribopyranoside with different nucleophiles resulted in exclusive formation of 3-substituted-3-deoxyxylose derivatives in good yields. The regiochemical outcome of the ring opening reaction is controlled by a polar repulsive interaction between the entering nucleophile and the pyranose oxygen lone pair of electrons. Copyright © 1996 Elsevier Science Ltd

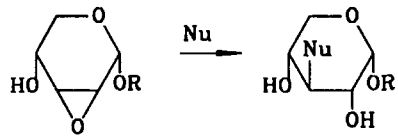
INTRODUCTION

The great interest shown in sugar epoxides stems from their value as intermediates in the synthesis of a variety of modified sugars, including deoxy, amino, thio, branched chain sugars and rarer simple sugars through nucleophilic ring opening reactions. The regiochemistry and stereochemistry of these reactions have posed problems of continuing interest.

Ring opening reactions of alkyl 2,3- anhydro-β-D-ribopyranosides have been well studied.[1] In most cases, the ring opens exclusively at C-3 to give C-3 substituted, 3-deoxyxylo derivatives.

Only three examples of nucleophilic ring opening reactions of benzyl 2,3-anhydro -α-D-ribopyranoside are reported. Thus, the reaction

of benzyl 2,3-anhydro -α-D-ribopyranoside with trimethylsilylcyanide[2] and N,N,-diethyltrimethylsilylamine[3] gave exclusively C-3 substituted xylopyranosides. (Scheme 1) The same epoxide with $Pd(PhCN)_2Cl_2$ in benzene



$R=CH_2Ph$: Nu= CN, Cl, NEt_2.
$R=CH_3$: Nu= SMe (2:1 ratio, 3:2 subs.)

Scheme 1

furnished once again the C-3 substituted xylo derivative in 15% yield.[4] On reaction with lithium bromide in presence of N,N,N',N'-tetramethylurea in refluxing toluene, 2-benzyloxy-2,5-dihydrofuran-4-carboxaldehyde was formed in 21% yield.[5] Finally, methyl 2,3- anhydro-α-D-ribopyranoside on treatment with sodium methylmercaptide gave the C-3 and C-2 substituted sugars in the ratio 2:1.[6]

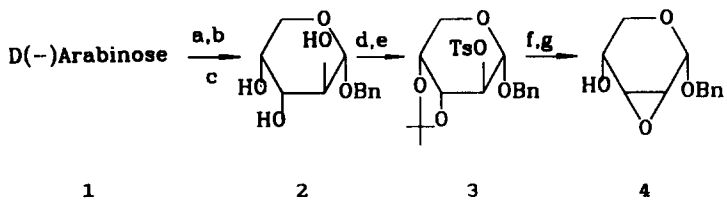
We observed that, in the ring opening reactions of 3,4-anhydroribopyranosides, the regiochemistry of ring opening is critically dependent upon the anomeric configuration.[7,8] With benzyl 3,4-anhydro-α-D-ribopyranoside, the ring opened exclusively at C-3 to give 3-substituted, 3-deoxyxylose derivatives. On the other hand, with benzyl 3,4- anhydro-β-D-ribopyranoside, ring cleavage depended upon both the nucleophile and the counter-cation employed. With magnesium as counter-cation, good C-3 selectivity was obtained. In other cases selectivity was not clear-cut and mixtures of C-3 and C-4 ring opened products were obtained.

Only a few examples were available in the literature regarding the ring opening of benzyl 2,3 anhydro -α-D-ribopyranoside. Therefore we chose to investigate ring opening reactions of this epoxide with different nucleophiles. Such a study would serve to better understand the factors governing regiochemistry of ring opening and also to substantiate the role of the pyranose oxygen in controlling the regiochemistry of ring opening. It would also be helpful in comparing the results with that of the corresponding β-anomer as well as with those of benzyl 3,4-anhydro-α and β-D-ribopyranosides.

RESULTS

Benzyl 2,3 anhydro -α-D-ribopyranoside (**4**) was prepared from

commercially available D (-)arabinose as reported (Scheme 2). Its spectral properties were in agreement with those reported in the literature.[9]



1 2 3 4

a)Ac_2O, NaOAc. b) $PhCH_2OH$, $BF_3.OEt_2$, CH_2Cl_2. c)NaOMe(cat), MeOH. d) Acetone, 2,2- dimethoxypropane, TsOH(cat.). e)TsCl, Pyridine. f)1 N H_2SO_4 acetone:water(1:10), reflux. g)NaOMe, MeOH.

Scheme 2

The NMR spectrum of **4** shows singlet anomeric signal (in $CDCl_3$) with $J_{1,2}$= 0 Hz. $J_{4,5a}$ could not be measured due to complexity in that region of the spectrum. This suggests that **4** preferentially adopts the conformer **4A** as shown in Figure 1.

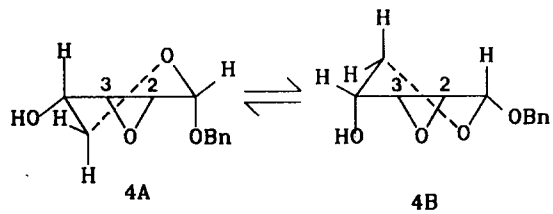
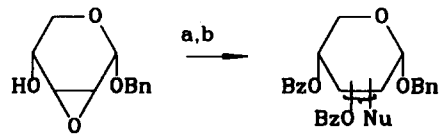


Figure 1

The free energy difference between the two conformers in the case of 2,3- and 3,4- anhydropentopyranosides is likely to be small. It can be assumed that the activation energy required for the ring opening will be much larger compared to the free energy difference between the two conformers.[10] Under these circumstances, the product ratio of the ring opening would be governed by the Curtin-Hammett principle.[11]

As shown in Table 1, nucleophilic ring opening of **4** was carried out with a variety of nucleophiles including variation of the counter-cation in order to study the effect of the nature of nucleophile and influence of the counter-cation on the course of the reaction. For the purposes of analysis and identification, the crude product was benzoylated and the dibenzoate was characterized. The regio- and stereochemistry of the ring opened products were established by ^1H COSY

Table 1. Ring opening reactions of 4 with different Nucleophiles.



a) Nucleophile. b) PhCOCl, Pyridine, rt.

Entry	Nucleophile	Metal Counter cation	Solvent	Yield(%)	Site of substitution	Product
1	Br	Mg^{2+}	THF	77	C-3	5
2	H	Li^{+}	THF	78	C-3	6
3	CN	K^{+}	DMSO	70	C-3	7
4	N_3	Na^{+}	DMF	76	C-3	8
5	SPh	Na^{+}	THF	84	C-3	9
6	OMe	Na^{+}	MeOH	83	C-3	10
7	OMe	Mg^{2+}	MeOH	85	C-3	10

experiments and analysis of the vicinal proton coupling constants, respectively. It is seen that in all cases, the yields of the ring opened products are very good and within limits of detection, only one product was obtained.

Epoxide **4** reacted with magnesium bromide in THF, giving the ring opened product **5** after benzoylation (entry 1). Reaction of **4** with LAH at room temperature in THF, after benzoylation, gave **6** (entry 2). No evidence was obtained for the formation of C-2 ring opened product. The ring opening of **4** with cyanide as nucleophile was carried out following the specific conditions of Sharpless.[12] Thus, the treatment of **4** with potassium cyanide in dry DMSO in the presence of titanium tetraisopropoxide and tetra-n-butylammonium iodide gave after benzoylation **7** (entry 3) in an overall yield of 70%.

Epoxide **4** when treated with sodium azide in DMF at 80°C yielded a product which was benzoylated to furnish **8** (entry 4). The reaction of **4** with sodium thiophenoxide in THF gave **9** after benzoylation (entry 5) in an overall yield of 83%.

Finally, when methoxide (Na^{+} counter-cation) was employed as a nucleophile, C-3 ring opened product **10** was obtained after benzoylation (entry 6). With magnesium methoxide, once again the same product **10** was obtained after usual benzoylation (entry 7). All the above products were

thoroughly characterised.

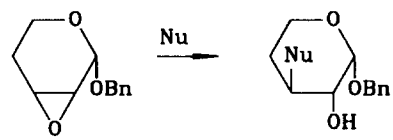
Interestingly, among the four possible 2,3- and 3,4-anhydroribopyranosides, we observed good selectivity in the α- series, Also, the α- series was more reactive compared with the corresponding β-series. The relative inertness of β- series is possibly due to the steric effect of the anomeric group towards axial attack of the nucleophile from the same side.

DISCUSSION

The regiochemistry of ring opening is governed by various factors such as the nature of nucleophile, nature of counter cation, steric, conformational and electronic effects.[1,13] In most instances, the ring opening was rationalized based on steric and conformational criteria.

Amongst the two possible conformers **4A** and **4B**, in conformer **4A** (Figure 1) there is a repulsive 1,3 interaction between the incoming nucleophile and the pyranose oxygen lone pair of electrons for attack at C-2, therefore directing it to attack at C-3. On the other hand, in conformer **4B**, there is no such repulsive interaction either at C-2 or at C-3. Here the electron withdrawing character of the anomeric carbon is likely to destabilise a developing positive charge at C-2, and attack at C-3 is anticipated to dominate.[9,14] The same effect could possibly account for the behaviour of the β- anomer as well. Thus, according to the above reasoning, the observed regioselectivity i.e. preferential attack at C-3 in **4** can be rationalized, especially when other factors of overriding importance (e.g. steric) are absent.

Recently Crotti and co-workers,[14] in their study of nucleophilic ring opening of cis- 2- benzyloxy -3,4- epoxytetrahydropyran made a similar observation, i.e. the ring opened in most cases at C-3 (Scheme 3).



Scheme 3

The attack was at C-3 in spite of the absence of hydroxyl group as is present in our case. They have suggested chelation effects of the metal cation as stabilizing one conformer over the other, leading to regioselective ring opening. A second factor mentioned by them is the electron withdrawing nature of the anomeric group, destabilizing

nucleophilic attack at C-2 vis-a-vis C-3.

In conclusion, it is clear from our present investigation and earlier reports that the regiochemistry of ring opening of benzyl 2,3 anhydroribopyranosides does not depend upon the anomeric configuration. i.e. in both α- anomer and the corresponding β- anomer the ring opening takes place at C-3. In the case of 3,4- anhydroribopyranosides the regiochemistry of the ring opening takes place depending upon the anomeric configuration. Thus, with benzyl 3,4-anhydro-α-D-ribopyranoside ring opens exclusively at C-3, whereas with benzyl 3,4- anhydro-β-D-ribopyranoside ring opens at C-3 and C-4 depending upon the nature of the nucleophile and its counter-cation.

EXPERIMENTAL

Melting points were determined by using a SUPERFIT melting point apparatus and are uncorrected. Optical rotations were measured on JASCO DIP 370 digital polarimeter at 25°. IR spectra were recorded on JASCO FT-IR 5300 instruments. Solid samples were prepared as KBr wafers and liquid samples as a film between NaCl plates. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) were obtained with a BRUKER AF 200 NMR spectrometer. All spectra were measured in chloroform-d solution with tetramethylsilane as internal standard unless otherwise stated. Spectral assignments are as follows (1) chemical shift on the δ scale(TMS = δ 0.00). (2) multiplicity, (3) number of hydrogens integrated for by the signal (4) assignment of the signal and (5) coupling constant in hertz(Hz). 2D NMR data were processed using standard software provided with the instrument. Elemental analyses were performed on a Perkin-Elmer 240 C CHN analyser.

Analytical TLC was performed on glass plates coated with 250μm and preparative TLC on glass plates coated with 0.1cm Acme silica gel GF_{254} and visualised by shining UV light and usually eluted with 2-10% ethyl acetate in hexane, unless otherwise mentioned. All moisture sensitive reactions were carried out under dry nitrogen and all solvents distilled from appropriate drying agents prior to use. After appropriate work-up, the organic extract was dried over anhydrous $MgSO_4$.

Benzyl 2,3 anhydro-α-D-ribopyranoside **(4)** was prepared in 71% overall yield from benzyl α-D-arabinopyranoside (2) according to ref 9. mp. 66-67°;$[\alpha]_D^{25}$ +137.9° (c 1.035,EtOAc) {lit[9] mp. 96-97°; $[\alpha]_D^{20}$ +134°(c 0.98,EtOAc)}. Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found. C, 64.92; H, 6.38.

General procedure for benzoylation: Benzoyl chloride (1.1 equiv.) was

slowly added to a stirred solution of alcohol (1 equiv.) in dry pyridine (5 ml) at 0^{o}. The reaction mixture was stirred for 15h at room temperature and then poured into chilled aqueous K_2CO_3(15ml). After the mixture was stirred for 1h, the product was extracted with dichloromethane(25ml x 3). The combined organic phase was washed with aqueous $NaHCO_3$, dried and evaporated. To remove the residual pyridine, toluene (5ml x 2) was added and then evaporated from the residue. The crude benzoate was then subjected to chromatographic purification.

Reaction of **4** *with Magnesium Bromide.* To a stirred mixture of anhydrous magnesium bromide (1.0 mmol) prepared from Magnesium (0.024g, 1.0 mmol) and 1,2-dibromoethane (0.090 ml, 1.0 mmol) in THF (2 ml) was added a solution of epoxy alcohol **4** (0.050g, 0.225 mmol) in THF (2 ml). The resulting mixture was refluxed for 6h. After the mixture was cooled to room temperature, saturated aqueous NH_4Cl was added and the precipitate formed was filtered and cake was washed with dichloromethane (10 ml x 2). The combined organic phase was washed with water, dried and concentrated. The residue was benzoylated and chromatographed to give 3-bromo-3-deoxy-2, 4-di-O-benzoyl-α-D-xylopyranoside (5) (0.089g, 77%). mp 156-158^{o}(ethanol) $[\alpha]_D$ +83.47^{o}(c 0.345, $CHCl_3$). IR: 1728, 1452, 1263, 1107,and 707 cm^{-1}. ^1H NMR: δ 8.13-7.16 (m, 15H, Ar); 5.42 (dt, 1H, H-4, J=10.6 and 5.8); 5.29 (dd, 1H, H-2, J=3.9 and 10.8); 5.19 (d, 1H, H-1, J=3.7); 4.79, 4.54 (dd, 2H, OCH_2Ph, J=12.4); 4.71 (t, 1H, H-3, J=10.7); 4.06 (dd, 1H, H-5, J=5.8 and 10.7); 3.82 (t, 1H, H-5′, J=10.6). ^{13}C NMR: 165.3, 165.2, 136.7, 133.4, 130.0, 129.9, 129.3, 128.4, 128.0, 127.7, 95.2, 73.5, 72.1, 69.8, 60.1,and 48.5 ppm. Anal. Calcd for $C_{26}H_{23}O_6Br$: C, 61.06; H, 4.53. Found: C, 61.12; H, 4.58.

Reaction of **4** *with LAH.* To a stirred solution of LAH (0.009g, 0.225 mmol) in THF (2 ml) was added a solution of epoxy alchohol **4** (0.05g, 0.225 mmol) in THF (2ml). The resulting mixture was stirred at room temperature for 5h and saturated aq. Na_2SO_4 was slowly added . The precipitate formed was filtered and the cake was washed with dichloromethane (2 x 5ml). The combined organic phase was dried and concentrated. The residue was benzoylated and chromatographed to give benzyl 3-deoxy-2,4-di-O-benzoyl -α-D-ribopyranoside (6) (0.076g, 78%). mp 68-70^{o}(ethanol-water). $[\alpha]_D$ +77.87^{o} (c 0.33, $CHCl_3$). IR(KBr): 1728, 1452, 1278, 1109,and 709 cm^{-1}. ^1H NMR: δ 8.04-7.25 (m, 15H, Ar); 5.23 (m, 2H, H-2, H-4); 5.09 (d, 1H, H-1, J=3.1);4.86, 4.61 (dd, 2H, OCH_2Ph, J=12.4); 3.88(m, 2H, H-5, H-5′); 2.41 (m, 2H, H-3, H-3′). ^{13}C NMR: 165.6, 165.5, 137.4, 133.1, 129.8, 129.7, 128.3, 127.7, 127.6, 94.3, 69.4, 68.6, 66.8, 60.4 and 29.6 ppm. Anal. Calcd for C H O : C, 72.21; H, 5.59. Found: C, 72.12; H, 5.49.

Reaction of **4** *with Potasium Cyanide.* To a stirred solution of epoxy alcohol **4** (0.05g, 0.225 mmol) in dry DMSO (3 ml) was added KCN (0.033g, 0.5 mmol) followed by tetra-n-butylammonium iodide (0.185g, 0.5 mmol). After 5 min, titanium tetraisopropoxide (0.179 ml, 0.60 mmol) was slowly injected and the resulting mixture was stirred at room temperature for 72h. Ether (10 ml) followed by 5% H_2SO_4 (3 ml) was added and the two phase mixture was stirred till two clear layers were formed (about 1h). The organic phase was separated, washed with water and aqueous $NaHCO_3$, dried and concentrated. The residue was benzoylated and the resulting material was chromatographed to give benzyl 3-cyano-3-deoxy-2,4-di-O-benzoyl-α-D-xylopyranoside(**7**) (0.072g, 70%). mp 142-144°(ethanol-water). $[\alpha]_D$ +94.10°(c 0.39, $CHCl_3$). IR: 2251, 1728, 1452, 1176 and 709 cm^{-1}. ^1H NMR: δ 8.15-7.16 (m, 15H, Ar); 5.35 (m, 3H, H-1, H-2, H-4); 4.79, 4.56 (dd, 2H,OCH_2Ph, J=11.9); 4.08 (dd, 1H, H-5, J=5.7 and 10.7); 3.80 (t, 1H, H-3, J=10.8); 3.73 (t, 1H, H-5′, J=10.7). ^{13}C NMR: 165.1, 164.9, 136.4, 133.7, 129.9, 128.5, 128.1, 127.7, 116.5, 92.9, 69.9, 69.1, 67.5, 59.0,and 33.8 ppm. Anal. Calcd for $C_{27}H_{23}O_6N$: C, 70.88; H, 5.06; N, 3.06. Found : C, 71.01; H, 4.78; N, 3.26.

Reaction of **4** *with Sodium Azide.* To a stirred solution of epoxy alcohol **4** (0.050g, 0.225 mmol) in DMF (3 ml) was added NaN_3(0.033g, 0.5 mmol). The resulting mixture was stirred at 80°C for 10h. It was cooled to room temperature and diluted with 1:1 acetone-ether (10 ml) and filtered. The filtrate was washed with water, dried and concentrated. The residue was benzoylated and chromatographed to give benzyl 3-azido-3-deoxy-2,4-di-O-benzoyl-α-D-xylopyranoside (**8**) (0.081g, 76%). mp 126-128°(ethanol-water). $[\alpha]_D$ +76.75° (c 0.37, $CHCl_3$). IR: 2112, 1726, 1601, 1259 and 709 cm^{-1}. ^1H NMR: δ 8.15-7.20 (m, 15H, Ar); 5.25 (d, 1H, H-1, J=3.6); 5.13 (dt, 1H, H-4, J=5.5 and 10.5); 5.00 (dd, 1H, H-2, J=3.8 and 10.1); 4.79, 4.54 (dd, 2H, OCH_2Ph, J=11.9); 4.42 (t, 1H, H-3, J=10.1); 4.05 (dd, 1H, H-5, J=5.5 and 10.8); 3.81 (t, 1H, H-5′, J=10.7). ^{13}C NMR: 165.4, 165.3, 136.7, 133.5, 129.9, 129.8, 129.2, 128.5, 128.4, 128.0, 127.7, 94.6, 72.2, 70.5, 69.9, 61.3 and 58.8 ppm. Anal. Calcd for $C_{26}H_{23}N_3O_6$: C, 65.95; H, 4.89; N, 8.87. Found : C, 66.02; H, 4.95; N, 8.92.

Reaction of **4** *with sodium thiophenoxide.* A 50% suspension of NaH (0.010g, 0.225 mmol) was placed in a three necked flask and the mineral oil was removed by washing with dry hexane. THF (2 ml) was added and a solution of thiophenol (0.023 ml, 0.225 mmol) in THF(1 ml) was added slowly. The resulting mixture was stirred for 30 min, and then a solution of **4** (0.050 g, 0.225 mmol) in THF (2 ml) was slowly added and the stirring was

continued for another 6h at room temperature. The reaction mixture was quenched with water (1 ml) and extracted with dichloromethane (2 X 10 ml). The combined organic extracts were washed with water, sodium bicarbonate, dried and concentrated. The residue was benzoylated and chromatographed to give benzyl 3-(phenylthio)-3-deoxy-2,4-di-O-benzoyl-α-D-xylopyrano -side (**9**) (0.102g, 84%). IR: 1724, 1452, 1263, 1107 and 711 cm^{-1}. ^1H NMR: δ 8.02-7.11 (m, 20H, Ar); 5.15(m, 2H, H-1, H-4); 4.97 (dd, 1H, H-2, J=3.6 and 11.0); 4.78, 4.53 (dd, 2H, OCH_2Ph, J=12.1); 4.04-3.83 (m, 3H, H-3, H-5, H-5').

Oxidation of **9** *with MCPBA.* To a stirred solution of **9** (0.102g, 0.19mmol) in dichloromethane(10 ml) at 0^oC was added a solution of MCPBA (0.093g, 0.57mmol) in dichloromethane(6ml). The resulting mixture was stirred overnight 8-9^oC. The reaction mixture was stirred at room temperature for 2h after adding 20% aqueous Na_2SO_3 (10 ml) and the separated organic phase was successively washed with aqueous $NaHCO_3$ and water , dried and concentrated. The residue was chromatographed to give 3-(phenyl-sulfonyl) -3-deoxy-2, 4-di-O-benzoyl-α-D-xylopyranoside (**9A**) (0.074g, 68%). mp 118-120^o(ethanol-water). $[\alpha]_D$ +67.10^o(c 0.38, $CHCl_3$). IR: 1726, 1452, 1309, 1259, 1147 and 706 cm^{-1}. ^1H NMR: δ 7.95-7.12 (m, 20H, Ar); 5.63 (dt, 1H, H-4, J=5.9 and 9.7); 5.43 (dd, 1H, H-2, J=3.2 and 10.6); 5.18 (d, 1H, H-1, J=3.4); 4.75, 4.49 (dd, 2H, OCH_2Ph, J=11.9); 4.33 (t, 1H, H-3, J=10.5); 4.04 (dd, 1H, H-5, J=6.0 and 10.8); 3.81 (t, 1H, H-5', J=10.6). ^{13}C NMR: 164.8, 139.2, 136.5 133.7, 133.4, 130.0, 129.9, 129.2, 128.5, 128.3, 128.0, 127.7, 93.9, 69.9, 67.6, 65.2, 63.9 and 58.8 ppm. Anal. Calcd for $C_{32}H_{28}O_8S$: C, 67.12; H, 4.92. Found : C, 67.25; H, 4.94.

Reaction of **4** *with Sodium Methoxide.* To a solution of NaOMe (0.054g, 1.0 mmol) in methanol (2 ml) was added a solution of epoxy alcohol **4** (0.050g, 0.225 mmol) in methanol (2 ml). The resulting mixture was refluxed for 12h. The reaction mixture was cooled and methanol was removed in vacuum. The residue was partitioned between water (10 ml) and chloroform (20 ml). The chloroform layer was separated and the aqueous layer was extracted with chloroform (2 x 20 ml). The combined chloroform extract was dried and concentrated. The residue was benzoylated and chromatographed to give benzyl 3-methoxy-3-deoxy-2,4-di-O-benzoyl-α-D-xylopyranoside (**10**) (0.087g, 83%). mp 108-110^o(ethanol) $[\alpha]_D$ +77.41^o(c 0.31, $CHCl_3$). IR: 1726, 1452, 1273, 1113,and 707 cm^{-1}. ^1H NMR: δ 8.11-7.18 (m, 15H, Ar); 5.21 (m, 2H, H-1, H-4); 5.09 (dd, 1H, H-2, J=3.9 and 9.6); 4.78, 4.52 (dd, 2H, OCH_2Ph, J=12.1); 4.11 (t, 1H, H-3, J=9.4); 4.01 (dd, 1H, H-5, J=5.8 and 10.7); 3.79 (t, 1H, H-5', J=10.6). ^{13}C NMR: 165.6, 165.5, 137.1, 133.2, 129.8, 129.7, 128.4, 127.8, 127.7, 95.6, 78.3, 73.2, 71.7, 69.7, 60.6 and

59.2 ppm. Anal.Calcd for $C_{27}H_{26}O_7$: C, 70.11; H, 5.66. Found: C, 70.23; H, 5.70.

Reaction of **4** *with Magnesium Methoxide.* To a stirred suspension of $Mg(OMe)_2$ (1.0 mmol) prepared from Mg (0.024g, 1.0 mmol) and methanol (2 ml) was added a solution of epoxy alcohol **4** (0.050g, 0.225 mmol) in methanol (2 ml). The resulting mixture was refluxed for 7h. The reaction mixture was cooled and concentrated. The residue was partitioned between 5% HCl(20 ml) and chloroform (20 ml) and worked up as usual. The residue was benzoylated and chromatographed to give **10** (0.089g, 85%).

ACKNOWLEDGEMENT

Financial assistance from University Grants Commission (fellowship to PKV and COSIST and SAP to the school) is gratefully acknowledged.

REFERENCES

1. Williams, N.R. *Adv. Carbohydr. Chem. Biochem.* **1970**, *25*, 109.
2. Kazmi, S. N. H.; Ahmad, Z.; Khan, A. Q.; Malik, A. *Synth. Commun.* **1988**, *18*, 151.
3. Kazmi, S. N. H.; Ahmad, Z.; Malik, A. *J. Chem. Research (S).* **1992**, 124.
4. Afza, N.; Malik, A.; Voelter, W. *Chimia.* **1983**, *37*, 422.
5. Rehnberg, N.; Magnusson, G. *J. Org.Chem.* **1990**, *55*, 5467.
6. Mukherjee, S.; Todd, A. R. *J. Chem. Soc.* **1947**, 969.
7. a) Vaman Rao, M; Nagarajan, M. *J. Org. Chem.* **1988**, *53*, 1184.
   b) Vaman Rao, M; *Ph.D Thesis*, **1987**, University of Hyderabad.
8. Vasudeva, P. K. ; Nagarajan. M. *Tetrahedron.* **1996**, *52*, 1747.
9. Inghardt, T. ; Frejd. T. ; Magnusson, G. *J. Org.Chem.* **1988**, *53*, 4542.
10. a)Chemilewski, M.; Zamojski, A. *Rocz.Chem.* **1972**, *46*, 2039.
    b)Hashimoto, H.; Araki, K.; Yoshimura, J. *Bull.Chem.Soc.Jpn.* **1981**, *54*, 3015.
11. Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111.
12. Sharpless, K. B.; Caron, M. *J. Org. Chem.* **1985**, *50*, 1557.
13. Buchanan, J. G.; Sable, H. Z. In *Selective Organic Transformations*; Thyagarajan, B.S. Ed.; Wiley Interscience: New York, **1972**. Vol.2, p 1.
14. Calvani, F.; Crotti, P.; Gardelli, C.; Pineschi, M. *Tetrahedron.* **1994**, *50*, 12999.

(*Received in UK* 21 *December* 1995; *revised* 9 *February* 1996; *accepted* 16 *February* 1996)