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# New Optically Pure Sugar Hydroperoxides. Synthesis and Use For Enantioselective Oxygen Transfer

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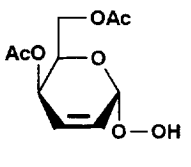
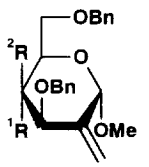
***Abstract***: 2-Deoxy-2-*C*-methylene methyl glycosides undergo oxidation with hydrogen peroxide in the presence of molybdenum trioxide as catalyst to afford the corresponding anomeric hydroperoxides. These hydroperoxides were used as chiral oxidants of allylic alcohols and prochiral sulfides to offer moderate enantioselectivities which were, however, higher than those reported before for oxidation with optically active peroxyacids. Copyright © 1996 Elsevier Science Ltd

Enantioselective epoxidation of prochiral allylic alcohols with optically pure 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl hydroperoxide (**1**)[1] in the presence of $Ti(Oi\text{-}Pr)_4$ affords chiral epoxy alcohols.[2] The moderate enantiomeric excess observed in these reactions could be ascribed to little differentiation of the neighbourhood of the hydroperoxide group.[2]

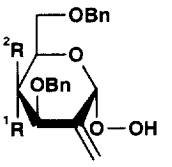
Balasubramanian et al.[3,4] have recently reported on the synthesis of 2-deoxy-2-*C*-methylene methyl glycosides **2** and **3**. Oxidation of compounds **2** and **3** with hydrogen peroxide in the presence of molybdenum trioxide as catalyst should provide anomeric hydroperoxide **4** and **5**, which are of potential value as chiral oxidants.



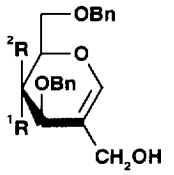

1




2: $R^1$=OBn, $R^2$= H
3: $R^1$= H, $R^2$ = OBn




4: $R^1$= OBn, $R^2$ = H
5: $R^1$ = H, $R^2$ = OBn




6: $R^1$ = OBn, $R^2$ =H
7: $R^1$= H, $R^2$ = OBn

## Results and Discussion

### *Formation of hydroperoxides*

Anomeric oxidation of **2** and **3** was performed as described before for compound **1**, but due to the lypophilic character of these compounds, the oxidation required a higher concentration of hydrogen peroxide (50-60%). After chromatographic purification hydroperoxides **4** and **5** were obtained in 65 and 75% yield, respectively. Hydroperoxides **4** and **5** could also be obtained by oxidation under the same conditions of hydroxymethyl-glycals **6** and **7** [3,4] but the yield was lower (30-40%).

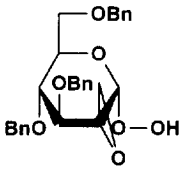
The α-configuration of **4** was proven by x-ray crystallography (cf. Experimental). Compound **5** did not produce crystals suitable for diffractometric measurements and its configuration was assigned by the similarity of $^1$H NMR and $^{13}$C NMR ($J_{C1,H1}$) spectral data of both hydroperoxides **4** and **5.**

Enantioselective epoxidation of olefins by hydroperoxides **4** and **5** containing the double bond raises the question of self-oxidation. It was of interest to investigate the post-reaction mixture obtained after the anomeric oxidation of unsaturated glycosides, with the aim of finding any side products that could accompany the formation of hydroperoxides. It was also of interest to investigate the self-oxidation of the double bond of hydroperoxides **4** and **5** in the presence of Ti(O-i-Pr)$_4$. For these studies the glycoside **2** and the hydroperoxide **4** obtained by anomeric oxidation of **2** were selected.

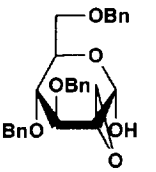
Careful examination of the post-reaction mixture obtained after the anomeric oxidation of **2** led to the isolation of two epoxides **8** (6%) and **9** (2.5%) which accompanied the main product **4** (60%). The structure and configuration of **8** and **9** were assigned by $^1$H NMR and $^{13}$C NMR spectroscopy. NOE experiments in both cases showed spin interaction between one of the methylene protons from the epoxide group and the anomeric proton. In the case of **8** irradiation of the signal due to H-1 (δ 4.87) was found to enhance the intensity of the signal due to one of the methylene protons (δ 2.75) by 5%. Conversely, the signal due to H-1 was enhanced by 9.6% when the corresponding signal due to the methylene group was irradiated. The corresponding values found for epoxide **9** amounted to 3% and 10%. In both cases the NOE interactions between H-3 and epoxide methylene protons were not observed. The NOE-based assignments were confirmed by x-ray crystallography of **8** (cf. Experimental).

The $^{13}C$ spectrum of hydroperoxide **8** showed *ca* 10 ppm downfield shift of the anomeric carbon atom in comparison with hemiacetal **9**. This observation was in agreement with our previous findings noticed for 2,3-unsaturated hydroperoxides[1] and their corresponding hemiacetals.[5] The hydroperoxide group also enhances the $J_{C1,H1}$ coupling constant in comparison with that found for the hydroxyl counterparts. In the case of **8** it amounts to 178.5 Hz versus 170.6 Hz found for **9**.

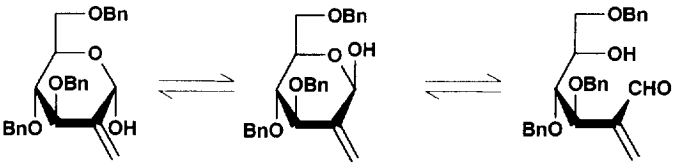
In the presence of $Ti(O\text{-}i\text{-}Pr)_4$ hydroperoxide **4** underwent self-oxidation to afford epoxide **9** and hemiacetal **10** in a ratio of about 1:2. The hemiacetal **10** exists in $CDCl_3$ as a tautomeric mixture of the α-anomer **10a**, the β-anomer **10b** and the open chain hydroxyaldehyde **10c** as was determined by $^1H$ NMR (cf.Experimental).




**8**

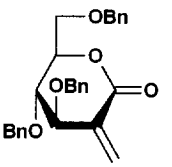



**9**

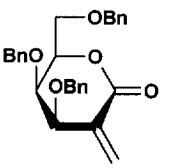



**10a** **10b** **10c**

Treatment of hydroperoxides **4** and **5** with acetic anhydride-pyridine mixture according to the known procedure [1] afforded unsaturated lactones **11** and **12**, respectively. Lactones **11** and **12** have been obtained by an alternative method [6] and have served as acceptors of glycosyl radicals in the synthesis of methylene bridged *C*-disaccharides[7].



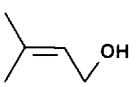

**11**



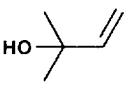

**12**

***Enantioselective oxidation***

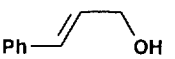
Allylic alcohols **13, 14** and **15** were epoxidized by **4** and **5** in the presence of $Ti(O\text{-}i\text{-}Pr)_4$ in $CH_2Cl_2$.




**13**




**14**




**15**

After complete conversion of the hydroperoxide the enantiomeric excess of the epoxy alcohol formed was estimated in the reaction mixture by gas chromatography on cyclodextrin chiral stationary phases.[2,8] The results obtained for three allylic alcohols **13-15** are summarised in Table 1.

Table1.Enantioselective Epoxidation of AllylicAlcohols(**13-15**) with Optically Active Hydroperoxides( **4**and **5** )

| Oxidant | Allylic alcohol | T°C | Epoxyalcohol | |
|---|---|---|---|---|
| | | | e.e. ( % )[a] | abs.confign. |
| **4** | **13** | -20 | 28 | (+) - (R) |
| **4** | **14** | RT | 4 | (-)-(S) |
| **4** | **15** | -20 | 10 | (2R,3S) |
| **5** | **13** | -20 | 44 | (+)-(R) |
| **5** | **14** | RT | 11 | (-)-(S) |
| **5** | **15** | -20 | 18 | ( 2R,3S ) |

[a)] Determined by GLC on cyclodextrin phases.[2,8]

We found lower optical inductions for α-D-arabino-**4** than for α-D-lyxo-hydroperoxide **5**. In both cases the best results were obtained with the allylic alcohol **13**. The e.e. in the oxidation of **13** with **5** is particularly noteworthy because it is, so far, the best outcome obtained when a chiral hydroperoxide was used as the epoxidation reagent. The values of e.e. obtained by us are higher than those reported before in asymmetric epoxidation with optically active peroxyacids. It is remarkable that it is also possible to epoxidize a tertiary alcohol such as **14**, because attempts to prepare the corresponding epoxy alcohol by the Sharpless epoxidation failed.[9]

Asymmetric oxidation of methylphenyl sulfide **16** and methylp-tolyl sulfide **17** by **4** and **5** gave the corresponding sulfoxides with about 25% e.e. (Table 2). This value of e.e. is in the range of the best results obtained when hydroperoxides derived from thiazolidine derivatives were examined in the oxidation of prochiral sulfides.[10]

Table 2. Asymmetric Oxidation of Prochiral Sulfides with Optically Active Hydroperoxides

| Oxidant | Sulfide | T°C | Sulfoxide | |
|---|---|---|---|---|
| | | | e.e. ( % )[a] | abs.cofign. |
| **4** | **16** | -20 | 25 | (-)-(S) |
| **4** | **17** | -20 | 24 | (-)-(S) |
| **5** | **16** | -20 | 26 | (-)-(S) |
| **5** | **17** | -20 | 24 | (-)-(S) |

[a)] Determined by HPLC on CHIRALCEL OD or CHIRALCEL.[11]

## Experimental

All $^1H$ and $^{13}C$ NMR spectra were recorded with Varian Gemini 200 and Bruker AM 500 spectrometers. IR spectra were taken with a Perkin-Elmer FT-IR-1600 spectrophotometer. Optical rotations were measured with a JASCO Dip-360 digital polarimeter and the temperature of the measurement was 20°C. Mass spectra were recorded with a AMD 604 mass spectrometer. Column chromatography was performed on Merck Kieselgel (230-400 mesh).

**General procedure for oxidation of unsaturated glycosides with $H_2O_2$.**

The suspension of unsaturated glycoside (**2** or **3**, 8.0 mmol) and molybdenum trioxide (0.12 g) in aqueous 60% hydrogen peroxide (50 mL) was stirred at room temperature until disappearance of the substrate (6 or more days); the progress of reaction was monitored by TLC. Subsequently water (100 mL) was added and the mixture was extracted with dichloromethane (3x60 mL). The combined extracts were washed four times with water, then with brine, dried over $MgSO_4$ and evaporated at room temperature. The residue was purified on silica gel by flash chromatography using hexane/ethyl acetate 7.5:2.5 v/v as an eluent to afford hydroperoxide **4** or **5.**

**3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-arabinohexopyranosyl-hydroperoxide (4),** 60%; m.p. 91-93°C ; $[\alpha]_D$ +47.3 °( *c* 1.4 , $CH_2Cl_2$ ) ; IR (film): 3315 $cm^{-1}$ ; $^1H$ NMR ($CDCl_3$) : 3.47 (dd , 1H, *J* 8.4, 9.8 Hz, H-4), 3.65 (dd, 1H, *J* 5.7, 10.4 Hz, H-6), 3.76 (dd, 1 H, *J* 1.9, 10.4 Hz, H-6`), 4.06 (ddd, 1H, *J* 1.9, 5.7, 9.8 Hz, H-5), 4.22 (dt, 1H, *J* 1.8, 2.0, 8.4 Hz, H-3), 4.48, 4.83 (2d, 2H, *J* 11.1 Hz, Bn), 4.56 (s, 2H, Bn), 4.64, 4.72 (2d, 2H, *J* 11.4 Hz, Bn), 5.34 (m,1H, =C**H**$_A$CH$_B$), 5.44 (dd, 1H, *J* 1.0, 2.0 Hz, = CH$_A$C**H**$_B$), 5.62 (s, 1H, H-1), 7.12-7.38 (m ,15H, 3xPh), 9.17 (bs, 1H, -OOH); $^{13}$C NMR ($CDCl_3$): sugar and benzyl carbon atoms, absorption of C-2 is not visible: 69.52, 71.99, 73.24, 73.58, 74.69, 79.63, 80.89, 105.00 (C-1, $J_{C1,H1}$178.0), 114.65; MS (LSIMS) m/z : 485 $(M+Na)^+$.

**3,4,6-Tri-*O*-benzyl-2-*C*:2-*O*-methylidene-α-D-glucohexopyranosyl-hydroperoxide (8) and 3,4,6-tri-*O*-benzyl-2-*C*:2-*O*-methylidene-α-D-glucohexopyranose (9).**

The postreaction mixture obtained after oxidation of glycoside **2** was separated on a silica gel column using hexane /t-butyl methyl ether 7.5:2.5 v/v as an eluent. In addition to **4** (60%) two side products were isolated **(8),** less polar, 6%, m.p.87-88°C; $[\alpha]_D$ + 62.8 ° ( *c* 1.1, $CH_2Cl_2$ ); IR (KBr): 3483,3281 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) : 2.74 (d, 1H, *J* 5.4 Hz, >C**H**$_A$CH$_B$), 3.24 (d,1H, *J* 5.4 Hz, >CH$_A$C**H**$_B$), 3.52 (dd, 1H, *J* 9.1, 10.0 Hz, H-4), 3.67 (dd, 1H, *J* 6.0, 10.4 Hz, H-6), 3.80 (dd,1H, *J* 1.8, 10.4 Hz, H-6`), 4.07 (d, 1H, *J* 9.1 Hz, H-3), 4.15 (ddd, 1H, *J* 1.8, 6.0 ,10.0 Hz, H-5), 4.48, 4.82 (2d, 2H, *J* 10.9 Hz, Bn), 4.56, 4.70 (2d, 2H, *J* 11.0 Hz, Bn), 4.56 (s, 2H, Bn), 4.87 (s, 1H, H-1); $^{13}$C NMR ($CDCl_3$):sugar and benzyl carbon atoms: 48.12, 58.57, 69.85, 71.59, 73.68, 75.12, 75.36, 76.95, 77.91, 104.79 (C-1, $J_{C1,H1}$ 178.5 Hz), MS (LSIMS) m/z: 477 $(M-H)^-$, 501$(M+Na)^-$. **(9),** more polar, 2.5%, m.p.97-98°C; $[\alpha]_D$+ 17.3 ° ( *c* 1.4, $CH_2Cl_2$ ); IR ( KBr ): 3416 $cm^{-1}$; $^1H$ NMR ( $CDCl_3$ ): 2.67 (d,1H, *J* 5.2 Hz, >C**H**$_A$CH$_B$), 3.18 (d,1H, *J* 5.2 Hz,>CH$_A$C**H**$_B$), 3.22 (d, 1H, *J* 3.5 Hz, OH), 3.55 (dd ,1H, *J* 9.1, 9.9 Hz, H-4), 3.61 (dd, 1H, *J* 2.3, 10.5 Hz, H-6) , 3.64 (dd, 1H, *J* 4.5, 10.5 Hz, H-6`), 4.14 (ddd, 1H, *J* 2.3, 4.5, 9.9 Hz,H-5), 4.21 (d,1H, *J* 9.1 Hz, H-3), 4.41, 4.75 (2d, 2H, *J* 11.0 Hz, Bn), 4.44, 4.52 (2d,2H, *J* 12.2 Hz, Bn), 4.54,4.66 (2d, 2H, *J* 11.0 Hz, Bn), 4.73 (d,1H, *J* 3.5 Hz, H-1); $^{13}$C NMR ($CDCl_3$), sugar and benzyl carbon atoms : 48.67, 60.23, 68.84, 70.97, 73.52, 74.99, 75.33, 76.80, 76.21, 95.11 (C1, $J_{C1,H1}$ 170.6 Hz); MS (LSIMS) m/z : 461 $(M-H)^+$, 485 $(M+Na)^+$.

**3,4,6-Tri-*O*-benzyl-2-deoxy-2-*C*-methylene-α-D-lyxohexopyranosyl-hydroperoxide (5),** 75%, m.p. 58-60°C; $[\alpha]_D$ +31.0° (*c* 1.7, $CH_2Cl_2$); IR(film): 3448,3508 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) :3.42 (dd, 1H, *J* 5.2, 9.7 Hz, H-6), 3.64 (dd, 1H, *J* 6.9, 9.7 Hz, H-6`), 3.86 (bd,1H, *J* 2.0 Hz, H-4), 4.14 (bt,1H, *J* 5.2, 6.9 Hz, H-5), 4.19 (q,1H, *J* 2.0, 2.2, 2.3 Hz, H-3), 4.40, 4.49 (2d, 2H, *J* 11.8 Hz,Bn),4.57, 4.67 (2d, 2H, *J* 12.1 Hz, Bn), 4.61, 4.88 (2d, 2H, *J* 11.9 Hz, Bn), 5.42 (bs,1H, = C**H**$_A$CH$_B$), 5.57 (dd, 1H, *J* 1.1, 2.2 Hz, =CH$_A$C**H**$_B$), 5.64 (s 1H, H-1), 7.22-7.39 (m, 15 H, 3xPh), 9.70 (bd, 1H, *J* 1.6Hz, OOH); $^{13}$C NMR; sugar and benzyl carbon atoms:

70.07, 71.65, 71.75, 73.67, 73.95, 74.90, 78.02, 105.58 (C-1, $J_{C1,H1}$ 178.4 Hz), 115.61, 120.30; MS (LSIMS) m/z: 463 $(M+H)^+$, 485 $(M+Na)^+$.

***X-Ray stuctural determination of compounds 5 and 8.***

Crystals suitable for x-ray structure determination have been grown from ethyl acetate/hexane mixture. Experiment has been performed on the four-circle Enraf-Nonius diffractometer MACH3 using express mode. Unit cell parameters and details of data collection and structure refinement are shown in Table 3.

X-ray analysis of the compounds **5** and **8** confirmed the presence of a hydroperoxide unit located in the α-position at the anomeric carbon atom. Both compounds cocrystallize with one molecule of water. As it is shown on Fig.1, the molecule **5** contains one disordered benzyl residue. Further refinement of this group in anisotropic mode showed tendency for further splitting of atomic positions. Due to this not well defined disorder of the benzyl group and probable presence in the crystal of another diffused water molecule, precision of the structure determination is low. Fig. 2 shows three-dimensional structure of the molecule of compound **8**. The oxygen atom from epoxy unit belonging to carbon atom *C2* is located at α -side of the sugar ring.

Table 3. Crystal Data and Structure Refinement for Compounds **5** and **8**.

| Identification code | **5** | **8** |
|---|---|---|
| Empirical formula | $C_{28}H_{30}O_6$ | $C_{28}H_{30}O_7$ |
| Formula weight | 462.5 | 478.5 |
| Temperature (K) | 293(2) | 293(2) |
| Wavelength (Å) | 1.54178 | 1.54178 |
| Crystal system | orthorhombic | orthorhombic |
| Space group | $P2_12_12_1$ | $P22_12_1$ |
| Unit cell dimensions (Å) | a = 4.7871(8)<br>b = 16.585(1)<br>c = 36.121(1) | a = 4.909(1)<br>b = 18.118(2)<br>c = 28.224(3) |
| Volume ($Å^3$) | 2867.8(5) | 2510.3(6) |
| Z | 4 | 4 |
| Density (calculated) ($Mg/m^{-3}$) | 1.104 | 1.266 |
| Absorption coefficient ($mm^{-1}$) | 0.650 | 0.743 |
| F(000) | 1008 | 1016 |
| Crystal size (mm.) | 0.28x0.50x0.77 | 0.11x0.11x0.70 |
| θ range for data collection (°) | 2.45 to 74.67 | 2.90 to 73.85 |
| Index ranges | 0≤ h ≤5, -20≤ k ≤0, 0≤ l ≤44, | -6 ≤h≤ 0, 0≤ k ≤22, -35 ≤l ≤0 |
| Reflections collected | 1700 | 1636 |
| Independent reflections | 1700 | 1636 |
| Refinement method | Full-matrix l.s. on $F^2$ | |
| Data / restraints / parameters | 1700 / 0 / 276 | 1627 / 0 / 330 |
| Goodness-of-fit on $F^2$ | 1.134 | 1.005 |
| Final R indices [I>2σ(I)] | $R_1$=0.1212, w$R_2$=0.3353 | $R_1$=0.0368, wR2=0.0822 |
| R indices (all data) | $R_1$=0.1243, w$R_2$=0.3433 | $R_1$=0.0438, w$R_2$=0.0871 |
| Δρ max & min (e $Å^{-3}$) | 0.68 and -0.39 | 0.11 and -0.12 |

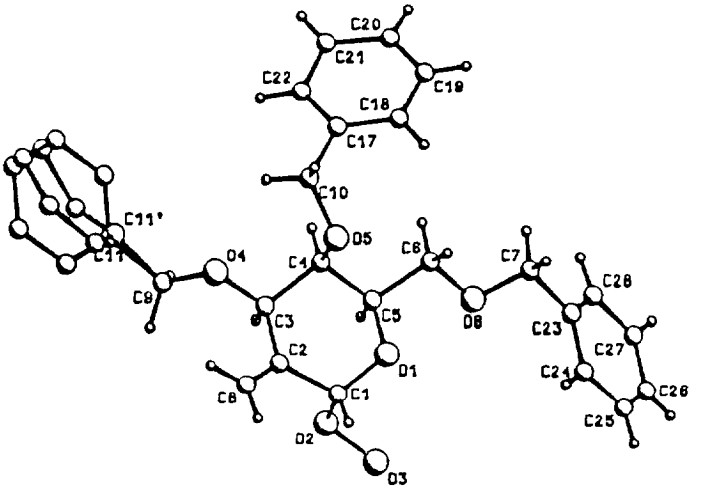



Fig. 1. The arbitrarily oriented molecule of hydroperoxide **5** with crystallographic labelling of atoms.

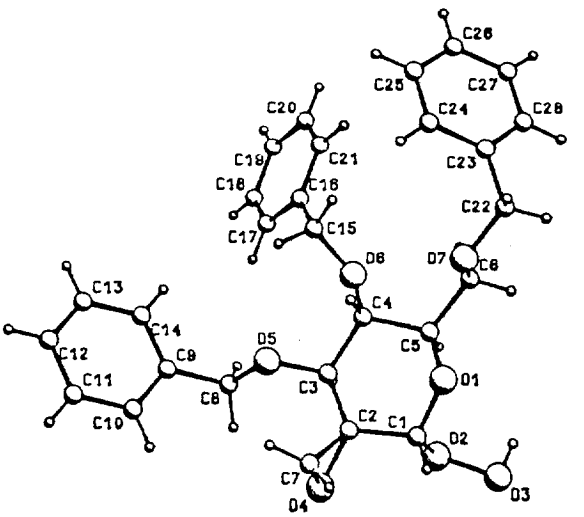



Fig. 2. The arbitrarily oriented molecule of epoxide **8** with crystallographic labelling of atoms.

**Transformation of the hydroperoxide 4 in the presence of Ti(O-i-Pr)$_4$.**

Hydroperoxide **4** (0.2 g, 0.4 mmol) in dichloromethane (5mL) was treated with Ti(O-i-Pr)$_4$ (0.012g, 0.04 mmol). After disappearance of the substrate (45 min), the solvent was evaporated and the residue was separated on a silica gel column using hexan/ethyl acetate 8:2 v/v as an eluent to afford **10** (0.067 g, 36%) and **9** (0.034 g, 19%).

**(10)**: $[\alpha]_D$ +5.6 °(*c* 0.8, $CH_2Cl_2$), IR (film): 3404 cm$^{-1}$; $^1$H NMR ($CDCl_3$) selected signals; **(10a)** : 5.17 (t,1H, *J* 1.4, 1.4 Hz, = C**H$_A$**CH$_B$), 5.28 (dd,1H, *J* 1.3, 2.0 Hz, = CH$_A$C**H$_B$**), 5.56 (s, 1H, H-1); **(10b)**: 5.12 (s, 1H, H-1) 5.34 (quintet, 1H, *J* 0.9, 0.9, 18 Hz , = C**H$_A$**CH$_B$), 5.41 (m,1H, *J* 1.3, 1.3, 1.7 Hz, CH$_A$C**H$_B$**); **(10c)**: 6.16 (s, 1H, =C**H$_A$**CH$_B$), 6.61 (t, 1H, *J* 1.1, 1.1 Hz, =CH$_A$C**H$_B$**), 9.48 (s, 1H, CHO); MS (LSIMS) m/z : 445(M-H)$^+$, 469 ( M+Na )$^+$.

**Preparation of lactones. General procedure. 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-methylene-D-arabino and D-lyxo-hexono-1,5-lactone (11) and (12).**

Hydroperoxide **4** or **5** (0.93 g, 2.0 mmol) was dissolved in dry methylene chloride (20 mL), cooled and treated dropwise with the mixture of acetic anhydride / pyridine 1:2 v/v (1.8 mL) in methylene chloride (10 mL). The mixture was left overnight in refrigerator. Subsequently it was poured into ice/ water and extracted with methylene chloride. The extract was washed with water, sodium hydrogen carbonate and brine, dried and evaporated. The residue was purified on a silica gel column by flash chromatography using hexane/ t-butyl methyl ether 6.5:3.5 v/v as eluent to give lactone **11** or **12**, respectively, ( 0.72 g, 81% ). Both compounds exhibited the same spectral data as those obtained earlier.[6]

**Enantioselective epoxidation by hydroperoxides 4 and 5. General procedure.**

All reactions were carried out using hydroperoxide (0.1 mmol), allylic alcohol (0.1 mmol) and aryl sulfide (0.1 mmol), respectively with 20 mol % Ti(O-i-Pr)$_4$ in the presence of powdered 3Å molecular sieves in dichloromethane (3 mL). After complete conversion of the hydroperoxide (detected by TLC) the e.e. of the epoxy alcohol formed was estimated in the resulting reaction mixture by GLC on cyclodextrin stationary phases.[2,8] The enantiomeric excess of the sulfoxide was determined by HPLC on CHIRALCEL OD or CHIRALCEL OB,[9] respectively. Peak assignment to the **R** and **S** configuration of the sulfoxides has been made with authentic sample from FLUKA.

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**References**

1. Chmielewski, M.; Jurczak, J.; Maciejewski, S. *Carbohydr. Res.*, **1987**,*165*, 111-115.
2. Hamann, H.- J.; Höft, E.; Chmielewski, M.; Maciejewski, S. *Chirality*, **1993**, *5*, 338-340.
3. Booma, C.; Balasubramanian, K.K. *J. Chem. Soc., Chem. Commun.*, **1993**, 1394-1395.
4. Ramesh, N.G.; Balasubramanian, K.K. *Tetrahedron*, **1995**, *51*, 255-272 .
5. Chmielewski, M. *Polish J. Chem.*, **1980** , 54, 1913-1921.
6. Kast, J.; Hoch, M.; Schmidt, R.R.; *Liebigs Ann. Chem.*, **1991**, 481-485.
7. Giese, B.; Hoch, M.; Lamberth, C.; Schmidt, R.R. *Tetrahedron Lett.*, **1988**, 29, 1375-1378.
8. Schurig,V.; Nowotny, H.P., *Angew. Chem.* **1990**, *102*, 969-1106; Reiher, T.; Hamann, H.-J., *HRC* **1992**, *15, 346-349.*
9. Finn, M.G.; Sharpless, K.B.; in *" Asymmetric Synthesis "* Ed. Morrison , J.D,: Academic Press, New York, Vol.5, **1985**, 247-308 .
10. Takata, T.; Ando, W. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1275-1276 .
11. Fu, H.; Kondo, H.; Ichikawa, Y.; Lock, G.C.; Wong, C.-H. *J.Org.Chem.***1992**, *57*, 7265-7270.

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