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Stereochemical Studies of Cyclononyl Systems

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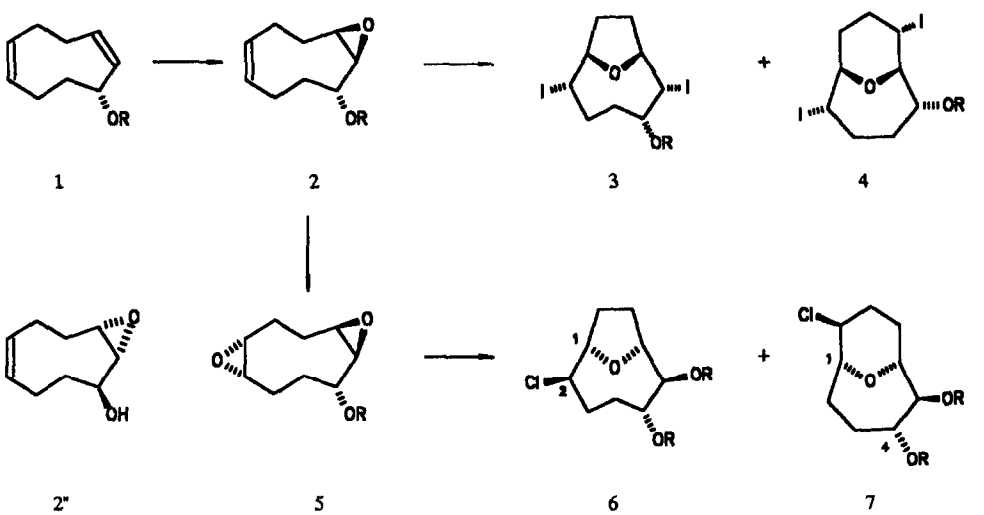
Abstract: The kinetically controlled electrophilic additions to (Z,Z)-1-hydroxy-cyclonona-2,6-diene and to (Z)-*threo*-1-hydroxy-2,3-epoxy-6-cyclononene are studied. The stereoselectivity of these reactions can be explained by the conformational preferences of the cyclononyl systems, which are revealed by the CD exciton chirality methodology and molecular mechanics calculations. An absolute configurational study is also included

Medium- and macrocyclic compounds have conformational properties which are quite useful for stereochemical control in synthesis of natural products[1] In an effort to utilize (Z,Z)-2,6- cyclononadien-1-ol (±)-1, R=H as a readily available[2] starting material for the stereocontrolled synthesis of substituted oxepanes,[3] we have studied the iodine-induced transannular ring expansion of racemic 1-acetyl-2,3-epoxy-cyclonon-6-ene (±)-2, R=Ac, to give the iodine containing oxacycles (±)-3, R=Ac and (±)-4, R=Ac, the latter being an obvious precursor of valuable α,α'-dialkyl β,β'-oxygenated oxepanes,[2a] provided the iodine functions can be further manipulated in a regio- and stereocontrolled fashion (Scheme 1)



Scheme 1

To use satisfactorily this methodology in the syntheses of bioactive molecules in enantiomerically pure form it is necessary to utilize chiral compounds of known absolute configuration and it is desirable to have a better understanding of their reaction mechanism. In this paper we report on a study of kinetically controlled electrophilic additions to (Z,Z)-1-hydroxy-cyclonona-2,6-diene and to (Z)-*threo*-1-hydroxy-2,3-epoxy-6-cyclononene, the kinetic resolution of the former, and the absolute configurational and conformational studies of these cyclononyl systems

The kinetic resolution of the racemic allylic alcohol (Z,Z)-1-hydroxy-cyclonona-2,6-diene, (±)-**1**, R=H, which can easily be prepared from 1,5-cyclooctadiene in two steps,[4] was performed by enantioselective Sharpless epoxidation[5]

The results observed in Table I reveal a small relative rate difference, about seven,[5a] for the epoxidation of the pair of enantiomers of **1**, R=H, and show the advantage of going for the remaining alcohol (-)-**1**, R=H instead of going for the *threo* epoxy-alcohol **2'** The enantiomeric excesses were determined by conversion to the MTPA ester followed by GLC analysis[6]

The conditions shown in entry 8 were used for the 2 g scale kinetic resolution of the racemic allylic alcohol (±)-**1**, R=H, leading to the enantiomerically pure (-)-(Z,Z)-1-hydroxy-cyclonona-2,6-diene

Table I

						% ee[c]	
Entry	TBHP	Tartrate	Time	Conv	Yield	(-)-1	2'
1	0 7	(+)-DCHT	24 h	49	67	-	32
2	0 4	(+)-DCHT	24 h	30	83	-	67
3	0 4	(+)-DET	24 h	21	82	-	78
4[a]	0 7	(+)-DET	2 weeks	27	-	-	-
5	0 7	(+)-DET	7 days	62	80	69	-
6	0 7	(+)-DCHT	2 days	67	74	84	-
7	2 0	(+)-DIPT	36 h	80	75	90	-
8[b]	1 5	(+)-DCHT	10 h	83	75	>99	-

These kinetic resolutions were carried out as described in the literature[5] on a 1 mmol scale 1 0 equiv of $Ti(O\text{-}i\text{-}Pr)_4$ and 1 2 equiv of tartrate were added in all cases, except for entry 4 [a]Catalytic conditions, 0 2 equiv of $Ti(O\text{-}i\text{-}Pr)_4$ and 0 24 equiv of (+)-DET [b] This reaction was also run on a 2 g scale [c] The enantiomeric excesses were determined by conversion to the MTPA ester (0 1 mmol scale)[5b,6] followed by GLC analysis

Although the absolute configuration of (-)-**1**, R=H can be determined by the allylic benzoate method in circular dichroism,[7] we have preferred to convert it into the more rigid and X-ray determined bicyclo **6**, R=H[2b] and then apply the dibenzoate chirality method[8] These two methods belong to the more general CD exciton chirality method, a valuable chiroptical tool for determining absolute stereochemistry based upon the chiral exciton coupling mechanism, which has been exten-

sively applied to various natural and synthetic organic compounds [9]

The transformation of chiral compound (-)-1, R=H into the 10-oxabicyclo [5 2 1] decane 6, R=H was carried out following the sequence of reactions shown in Squeme 1 Sharpless asymmetric epoxidation of (-)-1, R=H using (-)-DET led to the *threo*-epoxy-alcohol 2, R=H, which was treated with mCPBA to give the *trans*-bisepoxy-alcohol 5, R=H. The reaction of this compound with $TiCl_2(O\text{-}Pr^i)_2$ in CH_2Cl_2 at -78 °C led to a mixture of the expected[2b] 10-oxabicyclo 6, R=H and the newly isolated and tentatively assigned structure 7

In order to determine the absolute stereochemistry of compound 6, R=H by applying the dibenzoate chirality method, the di-*p*-bromobenzoyl derivative was prepared The UV and CD spectra of 6, R=BrBz are shown in Figure 1, the UV spectrum exhibits the intense intramolecular charge transfer band or ^1L_a band of the benzoate chromophores at 243 nm, the electric transition moment of which are polarized along the long axis of the chromophores [9]

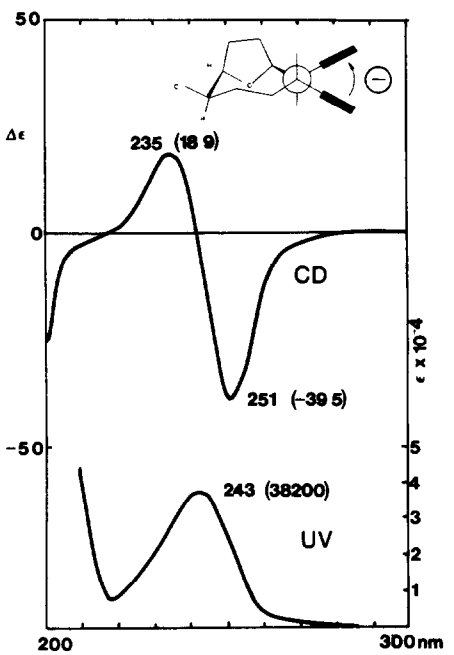


Figure 1 UV and CD Spectra of Compound 6, R=BrBz

Its CD spectrum exhibits intense split Cotton effects of the exciton coupling type The observed negative first and positive second Cotton effects lead to the conclusion that the exciton chirality between transition moments of the two benzoate chromophores is negative and of left-handed screwness. This unambiguously leads to the absolute configuration shown for 6, R=BrBz[8,9] and, by extension, to the absolute stereochemistries shown for compounds (-)-1 - 5 The present conclusion is in accordance with the fact that when (+)-tartrates are used in the kinetic resolution of racemic allylic alcohols[5] the fast reacting enantiomer is normally that related to the S configuration.

In order to have a deeper knowledge of electrophilic additions to the cyclononyl systems, we carried out a conformational analysis This study was performed mainly by the circular dichroism exciton chirality method and by molecular mechanics calculations

MM2 molecular mechanics calculations[10] of 1, R=H revealed five energy minima, conformers 1A-1E. Their strain energy differences, the distribution of conformers, and the dihedral angles $O\text{-}C_1\text{-}C_2\text{-}C_3$ are given in Table II. The symmetry of the polar map[11] of conformer 1A (Figure 2) agrees for the more stable one, having the same conformation as that obtained by MM2 for 1,5-cyclo-nonadiene [12]

Table II

Conformer	Strain energy (kcal/mol)	Dihedral angle $O\text{-}C_1\text{-}C_2\text{-}C_3$	Distribution of conformers
1A	0.00	-135	86.0
1B	1.57	-149	6.5
1C	1.85	-130	4.1
1D	2.23	47	2.7
1E	2.96	27	0.7

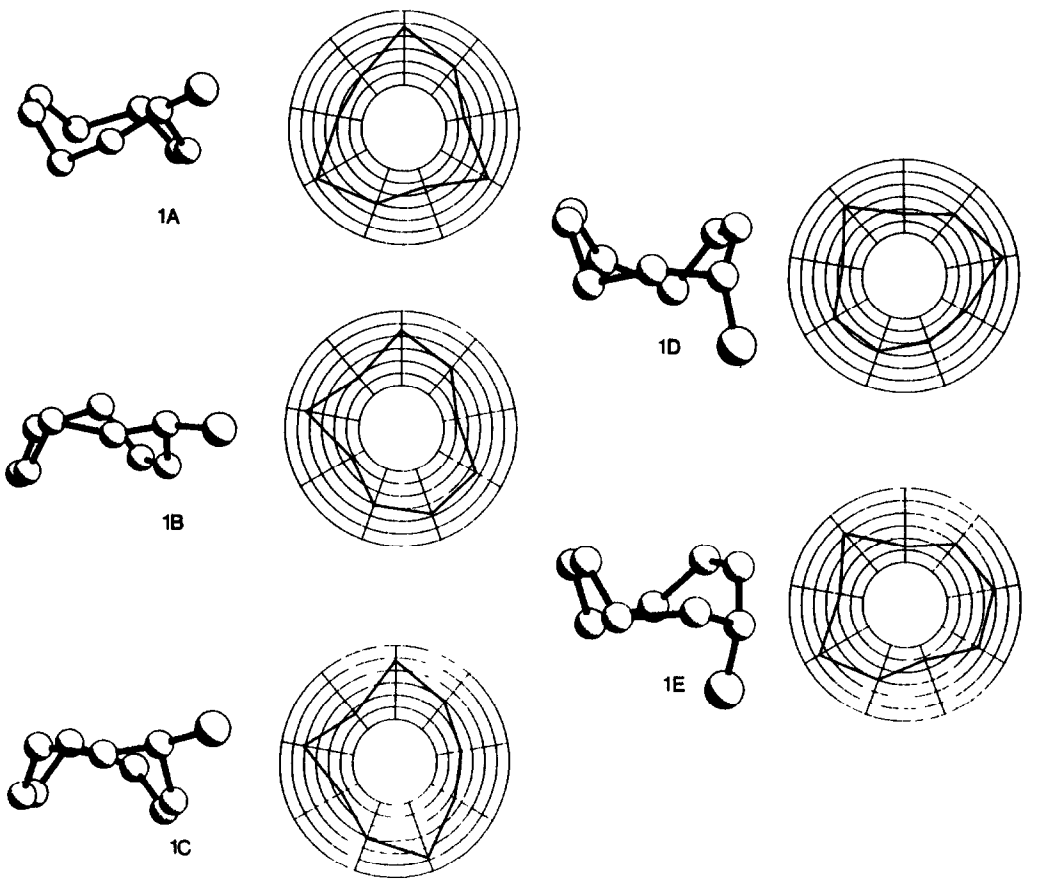


Figure 2 Five Lowest Energy Conformations of (Z,Z)-1-Hydroxy-Cyclonona-2,6-Diene (1)

This conformational analysis obtained by molecular mechanics calculations has been correlated with the observed at room and low-temperature circular dichroism data.

When an absolute configuration has been determined, as in the case of the (R)-(-)-1, R=H, circular dichroic spectroscopy is a powerful tool for conformational studies. Thus, we applied the allylic benzoate method in CD[7] to the *p*-bromobenzoyl derivative of (-)-1, R=BrBz, λ_{max} 243.0 nm. Its CD spectrum (CH_3CN, r.t.) exhibited two negative Cotton effects, λ_{ext} 241 7 nm, ($\Delta\varepsilon$ = -5 7) and 208 5 nm, ($\Delta\varepsilon$ = -14.6).[13] The negative sign of the CD Cotton effect at longer wavelengths is in accordance with a negative exciton chirality between the benzoate and allylic double bond chromophores. The existence of the mentioned exciton coupling was confirmed by the small negative Cotton effect exhibited at λ_{ext} 248.4 nm, ($\Delta\varepsilon$ = -1 5) by the *p*-bromobenzoyl derivative of compound 2, R=BrBz, lacking the allylic double bond. This small value also indicates a non-appreciable exciton interaction between the benzoate and the non-allylic double bond.[14] Therefore, it is concluded that the dihedral angle formed by the benzoate and allylic double bond chromophores in (-)-1, R=BrBz, is in between -120 and -160 degrees.[9]

To study the expected dependence of the conformation on the temperature, it seemed worthwhile to realize CD measurements at low temperature. The CD spectra of (-)-1, R=BrBz (EtOH) showed (Figure 3), upon lowering the temperature to -110 °C,[15] a red shift (239 nm to 243 nm) and a small increase ($\Delta\varepsilon$ -5 4 to -6 2) of the Cotton effect at longer wavelength, together with a blue shift (211 nm to 205 nm) and an important increase of the Cotton effect at shorter wavelength ($\Delta\varepsilon$ -6 6 to -15.7).[16]

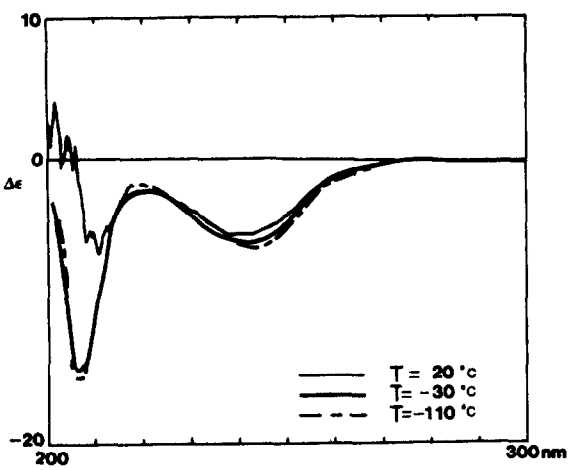


Figure 3 CD Spectra of Compound (-)-1, R=BrBz

An analysis of the observed temperature-dependence CD spectra shows the following: (a) The CD curve at room temperature is composed of a population-weighted average of the rotational strengths of the species involved (b) The small increase of the Cotton effect corresponding to the exciton coupling between the benzoate and double bond chromophores can be correlated with the elimination of conformers 1D and 1E, with positive contributions, in the conformational population (c) Lastly, the increase observed for the band at 208 nm, assigned to a double bond, suggests the elimination of conformers 1B and 1C.

The stereostructure of the three most stable conformers 1A-1C, representing 96% of the conformational population, adequately explains the ***threo*** stereostructure of the epoxy-alcohols 2, R=H and 2' obtained in the asymmetric epoxidation of compound 1, R=H, showing that the stereochemistry obtained is conformationally controlled.

To examine the electrophilic additions to the epoxy acetate **2**, **R=Ac**, a conformational analysis would be desirable.

The two relevant conformations of **2**, **R=H** are shown in Figure 4, along with their calculated strain energies.[17] In their corresponding polar maps can be observed the structural similarity between conformers **1A** and **2A**, and **1B** and **2B**.

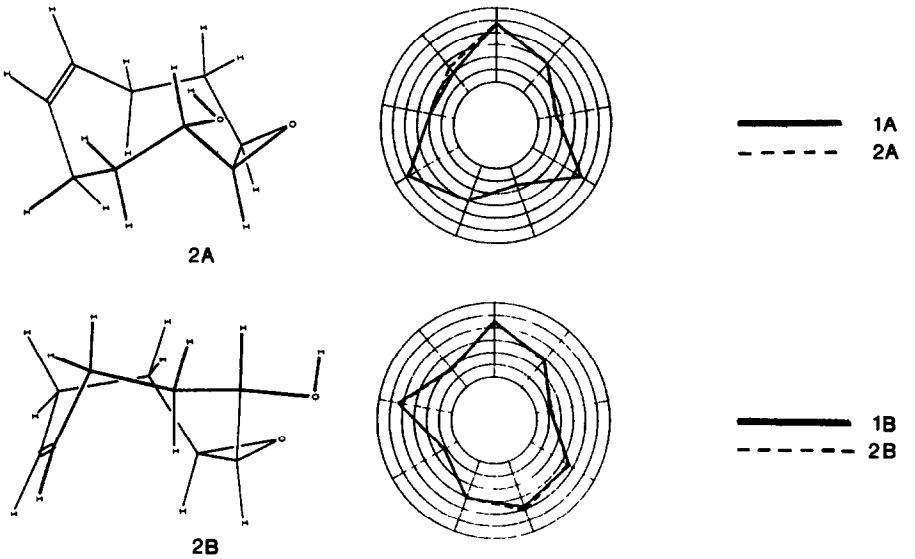


Figure 4: Two Lowest Energy Conformations of (Z)-*threo*-2,3-Epoxycyclonona-6-en-1-ol (2)

It is clear that the two faces of the olefinic π-systems in **2A** and **2B** are sterically differents and therefore the electrophilic additions would occur only from the less hindered, peripheral face of the olefinic linkage.[18] The stereochemistries of the *trans*-bisepoxide **5**, **R=H** and that of the iodonium ion, formed by treatment of **2**, **R=Ac** with mCPBA or iodine respectively, can be satisfactorily explained by the peripheral attack on conformer **2A**. The stereochemistry of the iodonium ion allows the regio- and stereo-selective transannular expansion of the epoxide ring, leading the iodine atom to the alpha configuration shown in the reaction products **3**, **R=Ac** and **4**, **R=Ac**.

Experimental Section

General. UV spectra were performed on a Perkin-Elmer Model 550D CD spectra were recorded on a JASCO J-600 spectropolarimeter Low temperature CD measurements were obtained by introducing a Jobin-Yvon Variocryostat system Optical rotations were determined with a Perkin-Elmer Model 241 polarimeter ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Model WP 200SY spectrometer (δ scale). Low and high resolution MS data were obtained with a VG Micromass Model ZAB-2F. GLC was performed on a HP Model 5790A gas chromatograph, SGE capillary column, OV-1, 25 m x 0.22 mm ID Prior to measurement of CD spectra, all compounds were purified by HPLC, Waters 6000A LC with a μ-Porasil column, 30 cm x 7 8 mm ID, 254 nm, EtOAc/n-hexane solvent systems. The concentrations of the CD samples were ascertained from the UV spectra, using the standard values of 21300 and 38200 for the mono- and di-*p*-bromobenzoate, respectively

General Procedure for Benzoylation. The solution of the starting material in dry pyridine with DMAP as catalyst is treated with a 1 5 x excess of *p*-bromobenzoyl chloride The resulting pale yellow solution is heated at 60 °C and stirred overnight The reaction is quenched with a few drops of MeOH, and the excess solvent is removed under reduced pressure in the presence of n-heptane or toluene The residue is then spotted on preparative TLC or fractionated on flash column chromatography to give the benzoate

General Procedure for Acetylation. The starting material dissolved in dry pyridine is treated with an excess of acetic anhydride, leaving the solution with stirring at room temperature overnight The mixture is quenched with MeOH and worked up similarly to the benzoylation

(Z,Z)-1-Hydroxy-cyclonona-2,6-diene, (±)-1, R=H. This compound was prepared by hydroboration of the 1,2,6-cyclononatriene, which was synthetized from 1,5-cyclooctadiene, according to published procedures[4] Oil, ^{1}H-NMR ($CDCl_3$) δ 1.80-2 10 (m, 6H), 2 18 (m, 2H), 4 32 (ddd, J = 11 5, 9 9 & 4 1 Hz, H_1), 5 41 (t, J = 9.9 Hz, H_2), 5 60 (m, 2H), 5.83 (q, J = 9.9 Hz, H_3); ^{13}C-NMR ($CDCl_3$) δ 24 1 (t), 26 2 (t), 27 3 (t), 36.9 (t), 67 5 (d), 129.7 (d), 130 1 (d), 130 7 (d), 134 4 (d), MS (EI) *m/z* (relative intensity) 138 (M^+, 1 6), 120 (M^+-H_2O, 4.3), 109 (35), 95 (42), 79 (64), 70 (76), HRMS calcd for $C_9H_{14}O$ 138 1045, found 138 1049, calcd for C_9H_{12} 120 0938, found 120 0929

(-)-(Z,Z)-1-Hydroxy-cyclonona-2,6-diene, (-)-1, R=H. This enantiomeric pure compound was obtained by enantioselective epoxidation of the racemic **1, R=H** on a 2 g scale, under the reaction conditions shown in entry 8, Table I $[\alpha]_D^{25}$= -145 6° (c 0 6, $CHCl_3$).

(Z,Z)-1-Acetoxy-cyclonona-2,6-diene (1, R=Ac) ^{1}H-NMR ($CDCl_3$) δ 2 01 (s, 3H), 5 30 (ddd, J = 12 5, 9 3 & 3.9 Hz, H_1), 5 37 (t, J = 9 3 Hz, H_2), 5 58 (ddd, J = 10.5, 10 5 & 5 4 Hz, 1H), 5 73 (m, 1H), 5 90 (q, J = 9 3 Hz, H_3)

***p*-Bromobenzoyl derivative of (-)-1, R=BrBz.** ^{1}H-NMR ($CDCl_3$) δ 5 53 (m, H_1 & H_2), 5 62 (m, 1H), 5 78 (m, 1H), 5 99 (q, J = 9 5 Hz, H_3), 7.55 (d, J = 8.6 Hz, 2H), 7 88 (d, J = 8.6, 2H), MS (EI) *m/z* (relative intensity) 322, 320 (M^+, 1 1), 241 (M^+-Br, 1), 185,183 (100 100), 120 (28), UV (CH_3CN) λ_{max} 243 0 nm (ε 21300), CD (CH_3CN) λ_{ext} 241 7 nm ($\Delta\varepsilon$ = - 5 7), 208 5 nm ($\Delta\varepsilon$ = - 14 6), UV (CH_2Cl_2) λ_{max} 244 0 nm , CD (CH_2Cl_2) λ_{ext} 241 9 nm ($\Delta\varepsilon$ = - 5 3)

Preparation of (-)-(Z)-*threo*-2,3-epoxycyclonona-6-en-1-ol (2, R=H). This epoxide was prepared by asymmetric epoxidation of (-)-1, R=H (100 mg, 0.72 mmol) as described in the literature,[19] using (-)-DET. Conversion 100%. Yield 83%. $[\alpha]_D^{25}$= -93.0° (c 0.9, CH_3Cl); ^{1}H-NMR ($CDCl_3$) δ 1.20 (m, 2H), 1.75 (m, 2H), 2.04 (m, 2H), 2.31 (m, 2H), 2.86 (dd, J = 9.3 & 4.3 Hz, H_2), 3.20 (ddd, J = 10.3, 4.3 & 4.3 Hz, H_3), 3.52 (ddd, J = 9.3, 9.3 & 4.9 Hz, H_1), 5.42 (ddd, J = 10.9, 10.9 & 5.6, 1H), 5.67 (ddd, J = 10.9, 8.5 & 8.5 Hz, 1H).

***p*-Bromobenzoyl derivative of compound (-)-2, R=BrBz.** ^{1}H- NMR ($CDCl_3$) δ 1.25 (m, 2H), 1.95 (m, 2H), 2.15 (m, 2H), 2.42 (m, 2H), 3.12 (ddd, J = 9.6 & 4.2 Hz, H_2), 3.25 (ddd, J = 9.5, 4.2 & 4.2 Hz, H_3), 5.00 (ddd, J = 9.7, 9.7 & 4.7 Hz, H_1), 5.53 (ddd, J = 10.9, 10.9 & 5.3, 1H), 5.81 (ddd, J = 10.9, 8.1 & 8.1 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.9 (d, J = 8.5 Hz, 2H), UV (CH_3CN) λ_{max} 243.0 nm (ε 21300), CD (CH_3CN) λ_{ext} 248.4 nm ($\Delta\varepsilon$ = - 1.5), 231.2 ($\Delta\varepsilon$ = 0.0), 216.1 ($\Delta\varepsilon$ = 1.0), 203.5 ($\Delta\varepsilon$ = 6.9)

Acetyl derivative of compound 2, R=Ac ^{1}H-NMR ($CDCl_3$) δ 1.15 (m, 2H), 1.75 (m, 2H), 2.07 (s, 3H), 2.10 (m, 2H), 2.31 (m, 2H), 2.98 (dd, J = 9.7 & 4.3 Hz, H_2), 3.19 (ddd, J = 9.7, 4.3 & 4.3, H_3), 4.75 (ddd, J = 9.7, 9.7 & 4.5 Hz, H_1), 5.48 (ddd, J = 10.9, 10.9 & 5.5 Hz, 1H), 5.77 (ddd, J = 10.9, 8.3 & 8.3 Hz, 1H)

***Trans*-bisepoxide 5, R=H.** To a solution of (-)-2, R=H (76 mg, 0.49 mmol) in CH_2Cl_2 (5 ml) was added mCPBA (94 mg, 0.54 mmol) under N_2 at room temperature After 7 h, the reaction was quenched with KF (36 mg) and left with stirring for 1 h. The mixture was filtered and purified on a gel column, hexane/EtOAc (6:4), to afford the desired bisepoxide (63.6 mg) ^{1}H-NMR ($CDCl_3$) δ 1.28-1.06 (m, 3H), 1.85 (m, 2H), 2.14 (m, 1H), 2.35 (m, 2H), 2.82 (m, 2H), 2.96 (ddd, J = 9.8, 4.5 & 4.5 Hz, 1H), 3.15 (ddd, J = 9.8, 4.5 & 4.5 Hz, H_3), 3.59 (ddd, J = 10.5, 9.3 & 4.5 Hz, H_1)

Preparation of bicyclos 6 and 7, R=H To a room temperature solution of $TiCl_4$ 1M in CH_2Cl_2 (2 ml, 2 mmol) containing powdered and activated 3Å sieves (20 wt %) was added Ti(O-i-Pr)$_4$ (600 μl, 2 mmol) in CH_2Cl_2 (3 ml) The resulting solution of $TiCl_2$(O-i-Pr)$_2$, maintained under an inert atmosphere, was cooled to -65 °C and the *trans*-bisepoxide 5, R=H (53.6 mg, 0.31 mmol) was added. The reaction was monitored by GLC and quenched by adding 3 ml of an aqueous solution of tartaric acid 15% The two-phase mixture was stirred for 10 min and then transferred to a separatory funnel The phases were separated and the aqueous phase was extracted with two 5 ml portions of CH_2Cl_2 The combined organic layers were dried over sodium sulfate, filtered, and concentrated The residue obtained was submitted to chromatography (silica gel, hexane/ EtOAc, 7:3) to afford compounds 6, R=H (28.8 mg, 0.14 mmol) and 7 (16.5 mg, 0.08 mmol) (ratio 7:4) **Compound 6, R=H** $[\alpha]_D^{25}$= +32.5 (c 0.2, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 1.90 (m, 2H), 2.10 (m, 2H), 3.57 (m, H_5 & H_6), 4.12 (m, H_2), 4.46 (br s, H_1 & H_7), ^{13}C-NMR ($CDCl_3$) δ 24.6 (t), 25.4 (t), 31.6 (t), 33.1 (t), 61.5 (d), 75.0 (d), 77.3 (d), 81.4 (d), 82.7 (d), MS (EI) *m/z* (relative intensity) 188, 190 (M^+-H_2O, 4.1:2), 170, 172 (M^+-2H_2O, 0.9:0.3), 171 (M^+-Cl, 0.4), 153 (M^+-Cl-H_2O, 8), 135 (M^+-Cl-2H_2O, 12), 114 (17), 97 (33), 79 (56), 70 (93), 57 (100), HRMS (EI) *m/z* calcd for $C_9H_{15}O_3{}^{35}Cl$ 206.0710, found 206.0717, calcd for $C_9H_{13}O_2{}^{35}Cl$ 188.0604, found 188.0630 **Compound 7, R=H** ^{1}H-NMR ($CDCl_3$) δ 1.90 (m, 4H), 3.57 (m, H_4 & H_5), 4.08 (m, H_6), 4.16 (m, 1H), 4.46 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 21.5 (t), 23.9 (t), 26.0 (t), 28.9 (t), 57.7 (d), 69.3 (d), 70.8 (d), 74.9 (d), 77.2 (d),

MS (EI) *m/z* (relative intensity) 188, 190 (M^+-H_2O, 9 3), 170, 172 (M^+-$2H_2O$, 1·1), 171 (M^+-Cl, 1), 153 (M^+-Cl-H_2O, 17), 135 (M^+-Cl-$2H_2O$, 13), 114 (15), 97 (29), 83 (62), 79 (44), 70 (70), 57 (100), HRMS (EI) *m/z* calcd for $C_9H_{13}O_2{}^{37}Cl$ 190 0574, found 190.0605; calcd for $C_9H_{13}O_2{}^{35}Cl$ 188 0604, found 188.0613.

di-*p*-Bromobenzoyl derivative of bicyclo 6, R=BrBz. ^{1}H-NMR ($CDCl_3$) δ 2.36-2 01 (m, 8H), 4 16 (m, H_2), 4.55 (m, H_1, H_7), 5 37 (br t, J = 9.4 Hz, H_5), 5.58 (dd, J = 10 0 & 4 7 Hz, H_6), 7 45 (d, J = 8 6 Hz, 2H), 7.47 (d, J = 8 5 Hz, 2H), 7 70 (d, J = 8.5, 2H), 7 72 (d, J = 8 6, 2H), MS (EI) *m/z* (relative intensity) 539, 537, 535 (M^+-Cl, 0 1.0 2 0 1), 374, 372, 370 (M^+-BrBzOH, 2 0.7.5 5.7), 337, 335 (2 3:2.3), 185, 183 (100.100); HRMS (EI) *m/z* calcd for $C_{23}H_{21}O_5{}^{79}Br_2$ 534 9754, found 534 9758; calcd for $C_{16}H_{16}O_3{}^{79}Br$ 335 0282, found 335.0292; UV (CH_3CN) λ_{max} = 243 0 nm (ε 38200); CD (CH_3CN) λ_{ext} 251 1 nm ($\Delta\varepsilon$ = - 39 5), 242 0 nm ($\Delta\varepsilon$ = 0.0), 234 5 nm ($\Delta\varepsilon$ = 18 9)

di-Acetyl derivative of bicyclo 6, R=Ac ^{1}H-NMR ($CDCl_3$) δ 2 16-1 80 (m, 8H), 1 99 (s, 3H), 2 01 (s, 3H), 4 08 (m, H_2), 4.35 (m, 1H), 4 49 (m, 1H), 5 00 (m, H_5), 5 17 (dd, J = 10 0 & 4 8 Hz, H_6)

di-*p*-Bromobenzoyl derivative of bicyclo 7, R=BrBz ^{1}H-NMR ($CDCl_3$) δ 2 20-1 90 (m, 8H), 4 28 (m, 3H), 5 41 (m, H_4), 5 45 (dd, J = 5 7 & 11 2 Hz, H_5), 7 48 (d, J = 8 6 Hz, 2H), 7 50 (d, J = 8 6 Hz, 2H), 7 75 (d, J = 8 6 Hz, 2H), 7 77 (d, J = 8 6 Hz, 2H), MS (EI) *m/z* (relative intensity) 539, 537, 535 (M^+-Cl, 1 1 1), 374, 372, 370 (M^+-BrBzOH, 3 11 7), 337, 335 (7 7), 185, 183 (100·98), UV (CH_3CN) λ_{max} = 243 0 nm (ε 38200); CD (CH_3CN) λ_{ext} 251 0 nm ($\Delta\varepsilon$ = - 41 5), 240 8 nm ($\Delta\varepsilon$ = 0 0), 233 8 nm ($\Delta\varepsilon$ = 16.1).

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