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Diels-Alder Reactions of [(S)*R*]-(1*E*,3*E*)-1-*p*-Tolylsulfinyl-1,3-pentadiene: The Unexpected Evolution of Maleic Anhydride Adducts.

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Abstract: The Diels-Alder adducts resulting in the reaction of enantiomerically pure [(S)*R*]-(1*E*,3*E*)-1-*p*-tolylsulfinyl-1,3-pentadiene with maleic anhydride evolved stereoselectively in situ through several intramolecular tandem reactions, involving [2,3]-sigmatropic sulfoxide-sulfenate rearrangement, acylation of the sulfinyl oxygen, and elimination of the sulfur function through a S_N2' process yielding lactones **3** and **4**.

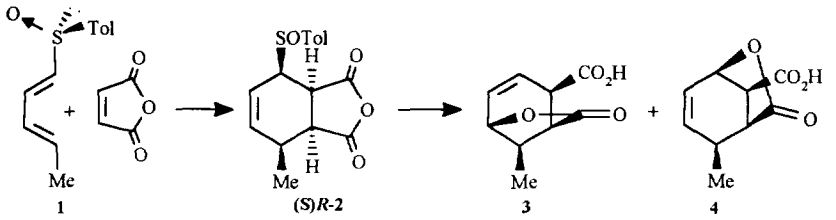
Since the first publication of Diels and Alder,[1] adducts resulting from maleic anhydride and their derivatives have been widely used as versatile intermediates in total synthesis of complex molecules.[2,3] The production of these adducts in optically active form has been mainly achieved by using chiral maleic anhydride derivatives[2a] as dienophiles in the cycloadditions. Resolution of racemic adducts[4] also provided the desired optically active synthons. To our knowledge, few examples of the use of chiral dienes as a tool to enantiomerically pure maleic anhydride adducts have been reported.[3b]

In continuation with our investigations related to the study of Diels-Alder reactions of enantiomerically pure 1-*p*-tolylsulfinyl-1,3-dienes we thought of using maleic anhydride as dienophile in order to open easy access to homochiral derivatives containing the anhydride moiety. The cycloadditions previously studied by us on these chiral dienes,[5] demonstrated the efficiency of the sulfinyl group in the control of π-facial diastereoselectivity. The presence in the resulting adducts of an allylic sulfoxide facilitated a series of tandem reactions[5,6] giving rise to highly functionalized compounds. In this paper we report that the reaction between (*R*)-1-*p*-tolylsulfinyl-1,3-pentadiene **1** and maleic anhydride results in the stereoselective formation of an adduct which evolves into lactones **3** and **4**.

Enantiomerically pure diene **1** was synthesized following the method previously described by us. [7] Reactions with maleic anhydride were carried out in thermal conditions, at high pressure and in the presence of different Lewis acids ($ZnCl_2$, $TiCl_4$, $BF_3.OEt_2$, $Eu(fod)_3$). In the latter conditions complex reaction mixtures without utility were always formed. The results of thermal and high pressure reactions are shown in Table 1. In the reactions run at normal pressure (entries 1-4) the initial cycloadduct [(S)*R*]-**2** was not observed: instead, the lactones **3** and **4** were directly obtained in different ratios depending on the temperature. Long reaction times were required at room temperature or at 40°C (entries 1-3), but a substantial increase of the reaction rate was observed upon heating at 70°C the acetonitrile solution (2 days, entry 4) and when the cycloaddition was performed under high pressure (13 Kbar, 1 day, entry 5). In the latter a 70:30 mixture of *endo*-adduct [(S)*R*]-**2** and γ-lactone **3** was formed. On standing in CH_2Cl_2 solution at rt, this mixture slowly evolved into a new mixture of compounds [(S)*R*]-**2**, [(S)*S*]-**2**, **3** and **4**. After 10 days both epimers **2** disappeared to yield a stable

mixture of compounds **3** and **4** in a 90:10 ratio. The separation of adducts [(S)*R*]-**2** and [(S)*S*]-**2** was not possible due to their instability and they were characterized from the ^{1}H-NMR of the crude mixture as both epimers at sulfur. The isolation of pure lactone **3** was achieved after $NaHCO_3$ extraction of the 90:10 crude mixture (Table 1, entry 1) and further successive fractional crystallization. All these results indicated that both **3** and **4** proceeded from the initially formed adduct [(S)*R*]-**2**, only detected in the reactions performed under high pressure.

Table 1. Diels-Alder reactions of diene **1** and maleic anhydride.



Entry	Solvent([a])	Temperature	Time (days)	Pressure	2 : 3 : 4 ratio	Yield (%)[b]	3 (% ee)
1	CH_2Cl_2 (3)	rt	40		0 : 90 : 10	65	0
2	CH_2Cl_2 (3)	40°C	30		0 : 80 : 20	60	-
3	CH_3CN (3)	rt	36		0 : 85 : 15	40	-
4	CH_3CN (3)	70°C	2		0 : 70 : 30	60	50
5	CH_2Cl_2 (1.2)	rt	1	13 Kbar	70 : 30 : 0	90	82

[a] Equivalents of maleic anhydride. [b] Calculated from the crude reaction mixture

The configurational assignment of both epimers **2** was established on the basis of their ^{1}H-NMR parameters and by comparison with those of the adduct resulting from reaction of **1** and N-methyl maleimide **5**.[5a] The most significant data are collected in Table 2. The evidence that Diels-Alder adducts **2** resulted from *endo*-cycloaddition followed from the coupling constant observed between the bridge-head hydrogens H_{3a} H_{7a} ($J_{3a\text{-}7a}$=8.2-9.3 Hz) which suggested the "extended" boat conformation [8] for the cyclohexene ring represented. As can be seen, all the chemical shifts and multiplicity of protons of compound (S)*R*-**2** are quite similar to those of compound **5** already described[5a] suggesting a very similar structure (relative and absolute configurations) for both. The low δ values of H_5 and H_6 (δ 5.80 and 5.56) when compared with the corresponding absortions in compound (S)*S*-**2** (m 6.00) and other similar cyclohexene systems (δ 6.2-5.9)[9] may be due to the rigid disposition of the sulfinyl group in the adduct (S)*R*-**2** (Figure 1), where the aromatic tolyl system exerts a net shielding effect. Moreover H_{7a} is deshielded in (S)*R*-**2** and **5** (δ 3.94-4.30) and shielded in (S)*R*-**2** (δ 2.90) with respect to H_{3a} (δ 3.18-3.53) in both **2** and **5**. Thus, for (S)*R*-**2** and **5** the 1,3-parallel disposition of the S-O and C-H_{7a} is responsible of the deshielding of the latter whereas the tolyl ring is shielding the olefinic protons. In the case of the (S)*S*-**2**, the disposition of the tolyl ring is shielding H_{7a}. These effects, already reported in the literature,[10] suggests the indicated absolute configuration at the sulfinyl group for (S)*R*-**2** and (S)*S*-**2** respectively.

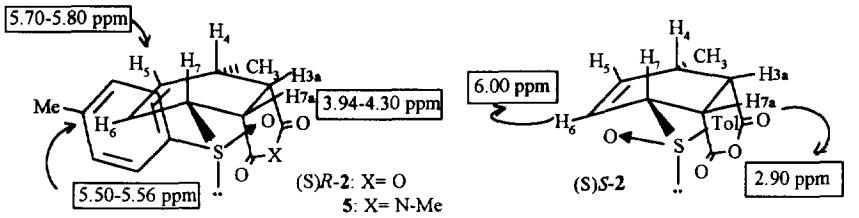


Figure 1

Table 2. ^{1}H-NMR data for compouds (S)*R*-**2**, (S)*S*-**2** and **5**.

Proton	(S)*R*-**2**	(S)*S*-**2**	**5**
H_{3a}	3.53, dd, 9.3, 8.1	3.30,dd, 6 y 3.6	3.18, t, 8.2
H_4	2.55-2.30, m	2.75, m	2.36,m
H_5	5.80, ddd, 9.4, 6.2, 3.1	6.00, m	5.70, ddd, 9.3, 3.1, 3.1
H_6	5.56, ddd,9.4, 6.4,3.2	6.00, m	5.50, ddd, 9.3, 3.3, 3.3
H_7	3.69-3.58, m	3.70, m	3.44,m
H_{7a}	4.30, dd, 9.3, 4.9	2.90, dd 5 y 3.6	3.94, dd, 8.7, 5.3
CH_3	1.35, d, 7.4	1.22,d,7	1.38, d, 7.5
CH_3-Ar	2.43, s	2.39,s	2.4, s
AA'BB' sistem	7.72 and 7.37	7.64 and 7.32	7.71 and 7.30

The structure of lactone **4** was deduced from a 28:72 mixture of **3** and **4** obtained from the mother liquors, once **3** had been fully identified. Their configurational assignment has been also based on the ^{1}H-NMR parameters indicated in figure 2. As can be seen, the multiplicity and coupling constant of H_8 (2.51, q, $J_{3\text{-}8}$=6.9 Hz) in lactone **3**, indicated a rigid disposition where the dihedral angles H_1-C_1-C_8-H_8 and H_5-C_5-C_8-H_8 should be 90° to justify the absence of coupling between H_8 and its vicinal protons at C_1 and C_5. This situation is only possible if compound **3** shows the bicyclic structure represented in figure 2, where the carboxylic group at C_2 is lactonized with the *cis*-carbinol at C_5. The long range coupling constants existent between H_1 and H_3, H_1 and H_5, and between H_5 and H_3 respectively, ($J_{1\text{-}3}$= $J_{1\text{-}5}$ =$J_{3\text{-}5}$=1.4 Hz) corroborated the proposed structure. In the case of lactone **4**, the multiplicity of H_8 (3.17, s) is also indicating a dihedral angle with its neighbouring protons, (H_1 and H_5) of 90° in a very rigid structure. The long range coupling constants of 1.2-1.4 Hz observed between H_1 and H_5, H_1 and H_3, H_3 and H_5, confirmed the bridged structure represented in figure 2 for lactone **4**.

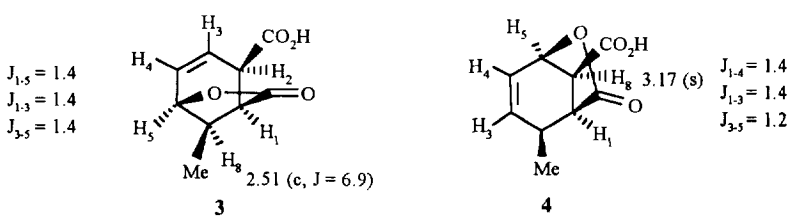
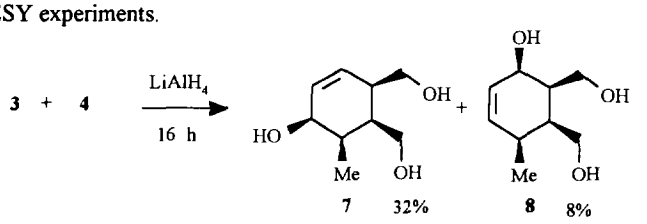


Figure 2

The configurational assignment of compounds **3** and **4** was confirmed by transforming the 70:30 mixture which resulted from conditions of entry 4 (Table 1) into polyhydroxy derivatives **7** [32 % overall yield from **1**, $[\alpha]_D^{20}$= -24 (c=0.37 acetone), 50% ee by ^{1}H-NRM with Pirkle's alcohol and **8** (8% overall yield from **1**) by $LiAlH_4$ reduction (Scheme 1). The structure of **7** and **8** could be unequivocally establised from their ^{1}H-NMR spectra including NOESY experiments.

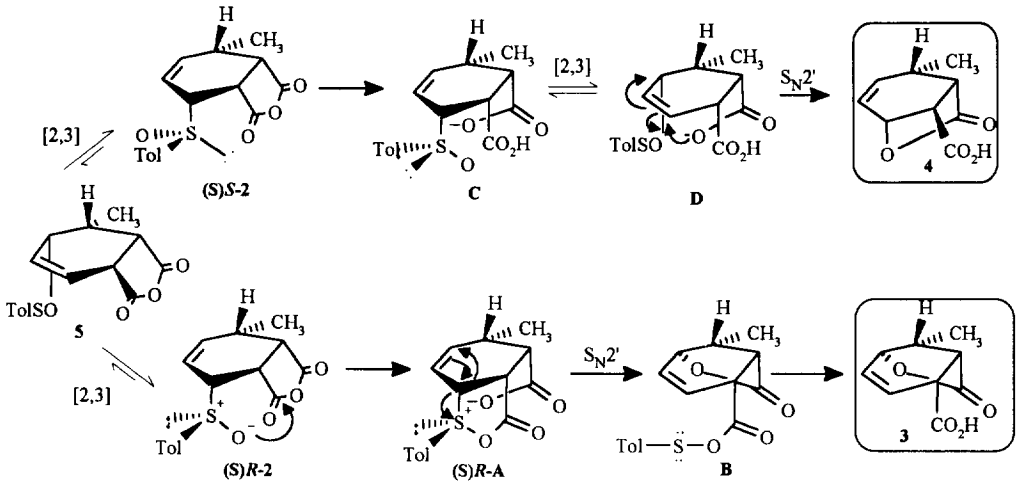


Scheme 1

The epimerization of the initially formed [(S)*R*]-**2** into [(S)*S*]-**2** can be understood from the equilibration through the sulfenate **5**, resulting in the [2,3]-sigmatropic rearrangement of the initially formed allylic sulfoxide [(S)*R*]-**2** (See Scheme 2). This rearrangement is reversible in the absence of a thiophilic agent and occurs with a complete transfer of chirality at the carbonated framework.[11]

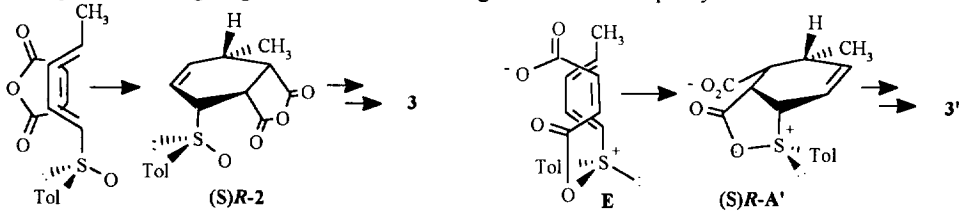
The transformation of adduct [(S)*R*]-**2** into lactones **3** and **4** could be rationalized as indicated in Scheme 2. The relative stereochemistry of the sulfinyl and anhydride groups in [(S)*R*]-**2** could determine an easy intramolecular acylation of the sulfinyl oxygen, giving the allylic acyloxysulfonium intermediate [(S)*R*]-**A**. A nucleophilic intramolecular attack of the free carboxylate with allylic rearrangement pushing out the the sulfur function (S_N2' process) explains the formation of **B** readily converted into the lactone **3** in a slow hydrolytic process. A similar evolution could be expected from [(S)*S*]-**2**. When long reaction times are required to complete the whole transformation, traces of water can be present and the hydrolytic opening of the intermediate **A** could take place to give **C**.[12] The evolution of **C** through a new sulfoxide-sulfenate rearrangement and further intramolecular S_N2' of the resulting sulfenate **D** (Scheme 2) account for the formation of lactone **4**. The sealed tube and shorter time required under high pressure (entry 5) would minimize the amount of water present in the reaction medium justifying the absence of **4** in the resulting mixtures.

More intriguing is the dependence of the enantiomeric purity of **3** and the reaction conditions. Shorter reaction times (reactions run at high pressure or heating) yielded samples of higher ee (compare entries 1, 4 and 5 in Table 1). Once disregarded the partial racemization of the starting diene after long times in solution,[13] the enantiomeric purity of **3** must reflect the π-facial selectivity of the initial cycloaddition. The absence of π-facial diastereoselectivity at rt (ee≅0) and the moderate diastereoselectivity observed in the reactions run in acetonitrile at 70° (ee≅50) are not consistent with the reactivity-selectivity principle. Taking into account the high π-facial diastereoselectivity of cycloadditions between of diene **1** and N-methyl maleimide,[5a] the null π-facial selectivity of cycloadditions with the structurally similar maleic anhydride is difficult to explain. In the latter, two different cycloaddition processes could compete. One is the expected intermolecular Diels-Alder reaction, which as in the case of maleimide, should be totally stereoselective. The increase of pressure and



Scheme 2

temperature must accelerate such intermolecular cycloaddition (bimolecular process). The competing process could result after an intermolecular acylation of the sulfinyl group, yielding an acyloxysulfonium species **E**. The evolution of **E** through an intramolecular cycloaddition (unimolecular process as rate limiting step) into [(S)*R*]-**A'**, would explain the formation of lactone **3'**, enantiomer of **3**. (Scheme 3). The higher influence of temperature and mainly pressure on the bimolecular processes justify the predominant evolution of the system through the former giving rise to a lactone **3** of higher enantiomeric purity.



Scheme 3

Acknowledgements. We thank Dirección General de Investigación Científica y Técnica (Grants PB92-161 and PB92-162) and Comunidad Autónoma de Madrid (Grant AE 244/95) for financial support.

EXPERIMENTAL

Melting points were determined with a Gallenkamp apparatus in open capillary tubes. ^{1}H-NMR and ^{13}C-NMR spectra were recorder in the FT mode on a Bruker WP-200-SY instrument coupled to an Aspect 2000 computer. Both chemical shifts (ppm downfield from internal tetramethylsilane) and coupling constants (Hz) were obtained by first order analysis of spin patterns. Mass spectra were recorded on a VG Autospec spectrometer in the electron impact (EI, 70eV) ionization mode. Mass data are reported in mass unit (m/z) and the values in brackets regard the relative intensity from base peak (as 100%). Infrared (IR) spectra were recorder on a Philips Pu-9716 spectrometer. Elemental analysis were performed at the Universidad Autónoma de Madrid (SIDI) Microanalitical Laboratory with a Perkin-Elmer 2400 CHN Elemental analyzer. Optical

rotations were measured with a Perkin-Elmer 141 polarimeter. The Diels-Alder reactions under high pressure conditions were carried out in a Unipressequipment 101. Ether and dichloromethane were predried on $CaCl_2$ and distilled from sodium-benzophenone.and P_2O_5 respectivelly. Maleic anhydride was freshly sublimed. $LiAlH_4$ was purchased from Aldrich and used without further purification. DMF was directely used from SDS. Flash chromatography was performed by using silica gel (SDS 60, 230-400 mesh).

General procedure for Diels-Alder reactions.

To a 0.25 M solution of 2g of diene **1**, in the required solvent (Table 1) maleic anhydride (3 eq) was added. The reaction mixture was stirred at the temperature indicated in Table 1 and monitored by TLC (ethyl acetate-hexane 7:3). After completion of the reaction (see Table 1 for reaction times) the solvent was evaporated in vacuo and the resulting mixture was disolved in EtOAc and washed with a $NaHCO_3$ solution (x2). The aqueous phase was acidified until pH=1 with a HCl (35 %) solution. After extraction with EtOAc (x3) the organic phase was dried ($NaSO_4$) and concentrated in vacuo. A mixture of lactones **3** and **4** in the proportions shown in table 1 was obtained contaminated with maleic acid resulting from the opening of the excess of maleic anhydride used. The yields shown in table 1 has been calculated at this point discounting the maleic acid through the integration of the olefinic protons with respect to the lactones in the ^{1}H-NMR spectrua. Pure lactone **3** was obtained by successive triturations in ether and subsequent crystallization in acetone (475 mg , 28% isolated yield from diene **1** in the reaction conditions of entry 4, table 1). The solution of trituration processes were concentrated and triturated with $CHCl_3$.in order to separate the remaining maleic acid. The solid (264 mg) was filtered and characterized as a mixture **3**:**4**:maleic acid in the ratio 20 : 50 : 30.

Diels-Alder reactions under high pressure conditions.

Diene **1** (60 mg) and of maleic anhydride (29 mg 1 eq) were solved in CH_2Cl_2 (2 ml). The solution was kept under 13 kbar for 24 h. The solvent was then evaporated at reduced pressure and after ^{1}H-NMR ($CDCl_3$) the resulting crude was characterized as a mixture of (S)R-2 and lactone 3 (90% yield, Table 1 entry 5).

[3a*R*,4*S*,7*R*,7a*S*,(S)*R*]-4-Methyl-7-(*p*-tolylsulfinyl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione ((S)*R*-2) ^{1}H-NMR ($CDCl_3$) d: 7.72 y 7.37 (AA'BB' system, 4H, p-tolyl), 5.80 (ddd, 1H, $J_{5\text{-}6}$=9.4, $J_{5\text{-}4}$=6.2, $J_{5\text{-}7}$=3.1, H_5), 5.56 (ddd, 1H, $J_{6\text{-}5}$=9.4, $J_{6\text{-}7}$ =6.4, J $_{6\text{-}4}$=3.2, H_6), 4.30 (dd, 1H, $J_{7a\text{-}3a}$=9.3, $J_{7a\text{-}7}$ =4.9, H_{7a}), 3.69-3.58 (m, H_7), 3.53 (dd, 1H, $J_{3a\text{-}7a}$=9.3, $J_{3a\text{-}4}$=8.1, H_{3a}), 2.55-2.30 (m, H_4), 2.43 (s, 3H, CH_3-Ar), 1.35 (d, 3H, J=7.4, CH_3).

[3a*R*,4*S*,7*R*,7a*S*,(S)*S*]-4-Methyl-7-(*p*-tolylsulfinyl)-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione ((S)*S*-2) ^{1}H-NMR ($CDCl_3$) d 7.64 y 7.32 (AA'BB' system, 4H, p-tolyl), 6,00 (m, 2H, H_5 y H_6), 3,70 (m, 1H, H_7), 3,30 (dd, 1H, $J_{3a\text{-}4}$=6.0, J $_{3a\text{-}7a}$=3.6 H_{3a}), 2.90 (dd, 1H, J $_{7a\text{-}7}$=5.0 $J_{7a\text{-}3a}$=3.6, H_{7a}), 2.75 (m, 1H, H_4), 2.39 (s, 3H, CH_3-Ar), 1.12 (d, 3H, J=7.0, CH_3).

(+)-(1*S*,2*R*,5*S*,8*R*)-8-Methyl-7-oxo-bicyclo[3.2.1]oct-3-ene-2-carboxylic acid (3). IR ($CHCl_3$): 1770, 1700 cm^{-1}. ^{1}H-NMR (Acetone D_6) d 6.36 (ddd, 1H, $J_{4\text{-}3}$ =9.5; $J_{4\text{-}5}$=5.6; $J_{4\text{-}2}$=2.6; H_4); 5.99 (ddt, 1H, $J_{3\text{-}4}$=9.5; $J_{3\text{-}2}$=2.6; J $_{3\text{-}5}$=$J_{3\text{-}1}$=1.4; H_3); 4.46 (dt 1H, $J_{5\text{-}4}$=5.6, $J_{5\text{-}3}$=$J_{5\text{-}1}$=1.4, H_5); 3.71 (dt 1H, $J_{2\text{-}1}$=4.6, $J_{2\text{-}3}$=$J_{2\text{-}4}$=2.6, H_2); 2.94 (dt 1H, $J_{1\text{-}2}$=4.6, $J_{1\text{-}5}$=$J_{1\text{-}3}$=1.4, H_1); 2.51 (q, 1H, $J_{3\text{-}CH3}$ =6.9, H_8); 1.15 (d, 3H, $J_{CH3\text{-}8}$=6.9, CH_3); ^{13}C-NMR (50,3

MHz, Acetone D6): d 176.2, 171.5, 131.5, 129.3, 77.9, 48.4, 45.9, 42.9, 16.7. Anal. Calc for $C_9H_{10}O_4$: C: 59.32 H:5.54,. Found: C: 59.30 H:5.56

(1*S*, 2*S*, 5*R*, 8*S*)-2-Methyl-7-oxo-6-oxa-bicyclo [3.2.1] oct-3-ene-8-carboxylic acid (4). ^{1}H-NMR: (Acetone D6) d: 6.28 (ddd, 1H, J_{4-3}=9.3, J_{4-5}=5.7, J_{4-2}=2.6, H_4),5.82 (dddd, 1H, J_{3-4}=9.3, J_{3-2}=2.6, J_{3-1}=1.4, J_{3-5}=1.2, H_3), 4.98 (bd, 1H, J_{5-4}=5.7, H_5), 3.17 (s, 1H, H_8), 3.01 (dt, J_{1-2}=4.5, J_{1-5}=J_{1-3}=1.4, H_1), 2.95-2.80 (m, 1H, H_2), 1.13 (d, 2H, J=7.2, CH_3).

Reduction of lactones 3 and 4

To a suspension of $AlLiH_4$ (900 mg) in dry ether (50 ml) a solution of lactones **3** and **4** (405 mg of the mixture resulting from conditions of Table 1 entry4) in dry ether (15 ml) was added dropwise at 0°C. The mixture was allowed to reach room temperature and stirred for 24 h. Then, under vigorous stirring at 0°C, 0.9 ml of water, 0.9 ml of a NaOH solution (10%) and 2.7 ml of water were added slowly and sequentially. This mixture was stirred at 0°C for 20 min, filtered, washed with ether (200 ml) and the solvent eliminated in vacuo. The residue was purified by chromatography [hexane: EtOAc 1 :3]. Overall yield from diene **1** 95 mg of triol **7** (30%) and 22 mg of triol **8** (7%). This product is contaminated with a 10 % of 1,4-butanediol, resulting from the reduction of maleic acid present in the starting mixture.

(-)-(1*S*,4*R*,5*S*,6*R*)-4.5-Bis-hydroxymethyl-6-methyl-cyclohex-2-enol (7)

Colorless oil, [a]= -24° (c=0.37, acetone); IR ($CHCl_3$): 3320 , 2860; 1660 , 1430, 1020. cm^{-1}.^{1}H-NMR: (200MHz, $CHCl_3$) d; 5.95 (ddd, J_{2-3}=10.1, J_{2-1}=4.7, J_{2-4}=3.1, H_2), 5.76 (dd, J_{3-2}=10.1, J_{3-4}=1.5, H_3), 3.92 (m, 1H, H_1), 3.90 (m, 2H, C_4-CH_2), 3.82 (m, 2H, C_5-CH_2), 2.70-2.57 (m, 1H, H_4), 2.17-1.98 (m, 1H, H_6), 1.84-1.72 (m, 1H, H_5), 1.17 (d, 3H, J=7.2, CH_3). ^{13}C-NMR (50,3 MHz, $CHCl_3$) d: 130.7, 130.6, 65.8, 63.8, 58.4, 41.2, 41.1, 35.9, 15.1.

(-)-(1*R*,4*S*,5*S*,6*R*)-5,6-Bis-hydroxymethyl-4-methyl-cyclohex-2-enol (8)

Colorless oil: IR ($CHCl_3$): 3390, 2960, 1700, 1410, 1350, 1160 cm^{-1}. ^{1}H-NMR (200MHz, $CHCl_3$) 5.80 (ddd, J_{2-3}=9.9, J_{2-1}=4.1, J_{2-4}=2.8, H_2), 5.68 (dd, J_{3-2}=9.7, J_{3-4}=1.5, H_3), 4.34-4.26 (m, 1H, H_1), 4.12-3.72 (m, 4H, $2CH_2$), 2.61-2.39 (m, 1H, H_4), 2.16-2.0 (m, 1H, H_6), 1.94-1.82 (m, 1H, H_5), 1.14 (d, J=7.6, 3H, CH_3).^{13}C-NMR (50,3 MHz, $CHCl_3$) d: 135.5, 127, 64.5, 63.5, 59.2; 44.1, 39.2, 33.7 17.6.

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12 .- Intermediate **C** could also arise from the hydrolytic attack at sulfur, opening the acyloxysulfonium intermediate (S)*R*-**A**.

13 .- The diene recovered from reactions interrupted before completion was enantiomerically pure.

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