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Studies in Lewis Acid and $LiClO_4$ (or Nafion-H) Catalysed Ionic Diels-Alder Reactions of Chiral and Achiral Olefinic Acetals Respectively[1,2,▽]

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Abstract : Chiral olefinic acetals derived from crotonaldehyde undergo ionic Diels-Alder reaction giving the corresponding cycloadducts in moderate to good diastereoselectivities. A variety of achiral olefinic acetals react with isoprene and cyclopentadiene to form the cycloadducts in good to excellent yields when catalysed by 4M $LiClO_4$ in nitromethane or by Nafion-H in dichloromethane.

The Ionic Diels-Alder reaction using olefinic acetals, discovered by Gassman *et al.*,[3] is an excellent method to procure the corresponding cycloadducts with carbonyl groups already protected and without the polymerisation of dienophiles. In elaborate studies Gassman *et al.*[3] reported that cyclic acetals give better yields of the cycloadducts than acyclic acetals of the same dienophilic carbonyl compounds. Following their discovery, Alexakis and Mangeney[4] reported ionic Diels-Alder reactions with chiral acetal containing dienophiles in an attempt to obtain optically pure cycloadducts. However, the maximum diastereoselectivity obtained was only 13%. More recently, Sammakia and Berliner[5] have reported ionic Diels-Alder reactions of dienophiles bearing chiral acetals with Lewis acids instead of protic acids. In some cases, with Lewis acids such as $TiCl_2(iPrO)_2$, a high degree of diastereoselectivity was observed.

Our own interest[6] in asymmetric synthesis using chiral acetals led us to further explore their potential in ionic Diels-Alder reactions. For this purpose, we chose dienophiles with acetals bearing side chains such as $-CO_2Et$, $-CH_2OMe$ and $-CH_2OBn$. These were chosen to provide chelation (eq. 1, Scheme 1) through the oxygen atoms to the Lewis acids and thereby possibly affecting the diastereoselectivities. The dienophiles were derived from crotonaldehyde[7] and the dienes used were isoprene and cyclopentadiene. The Lewis acids employed for the initial study with **1a** were $TiCl_4$, $BF_3.OEt_2$ and $TiCl_2(iPrO)_2$ and the reactions were generally performed at -78°C and brought to 0°C. It was found that the catalyst $TiCl_2(iPrO)_2$ was better than $TiCl_4$ and $BF_3.Et_2O$ both in terms of yield and the d/e.[8a] Thus, using this catalyst 72% yield of the cycloadduct **2a** was obtained (eq. 2, Scheme 1) in 76% d/e whereas $TiCl_4$ and $BF_3.Et_2O$ gave only 65% and 50% d/e with chemical yields of 64% and 62% respectively. Similarly, cyclopentadiene reacted with the dienophile **1a** to

▽***(This paper is respectfully dedicated to Professor B. D. Tilak on the occasion of his 80th birthday)***

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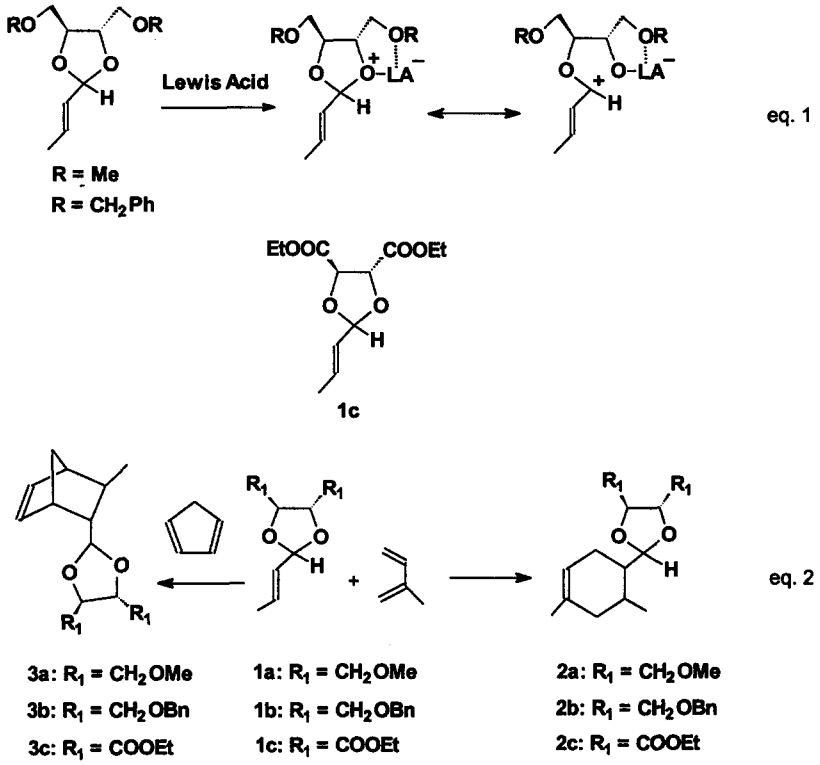
form the cycloadduct **3a** in 76% yield with d/e being 78% of the major product. The *endo/exo* ratio was found to be 74/26 on the basis of the peaks of the -CH_3 protons in its ^{1}H NMR spectrum and its comparison with literature data.[8b] This methyl group was found to appear as a set of four doublets at δ 0.84, 0.9, 1.03 and 1.12. Doublets at δ 1.12 and 1.03 belong to the diastereomer with 3-*exo* methyl (or the 2-*endo* acetal) group whereas doublets at δ 0.9 and 0.84 represent the diastereomer with 3-*endo* methyl (or the 2-*exo* acetal) group. This *endo/exo* ratio was further confirmed on the basis of its HPLC analysis using SH.ODS reverse phase column in acetonitrile-water (75:25) solvent system at 250 nm wavelength. Likwise, cycloadditions were carried out with the two other dienophiles **1b** and **1c** and the results of this study are summarised in Table 1.



Scheme 1

In an attempt to explore other catalysts for similar reactions we considered using $LiClO_4$-diethyl ether.[9] However, the ionic Diels-Alder reaction with dienophiles **1a-1c** did not occur. It is likely that the low nucleophilicity of the acetal oxygens, due to the side chain oxygens in **1a** and **1b** and due to the ester groups in **1c**, does not let them chelate with Li^+ sufficiently strongly for the reaction to proceed. We, therefore, turned our attention towards the more nucleophilic corresponding achiral acetals viz. **4a-9a** (Table 2) for $LiClO_4$ catalysed cycloaddition reactions. Initial attempts to use 5M solution of $LiClO_4.Et_2O$ did not yield any desired product. While our work was in progress Ayerbe and Cossio[10] reported that Diels-Alder reactions of

nitroalkenes in 4M $LiClO_4$ in nitromethane (LPNM) proceeded more smoothly than in diethyl ether. The high dipole moment of nitromethane (3.40 D) in comparison to diethyl ether (1.33 D) has been attributed as the cause of rate acceleration. We, therefore, presumed that the failure of the ionic Diels-Alder reaction using both chiral and achiral olefinic acetals in our case could well be due to the low dipole moment of ether. Clearly, the ionic Diels-Alder reactions involve intermediates which are charged species and therefore nitromethane may be the solvent of choice. Indeed, the reaction proceeded well with a variety of olefinic acetals **4a-9a** forming

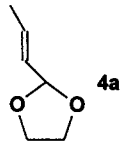
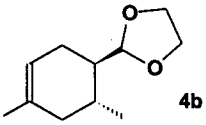
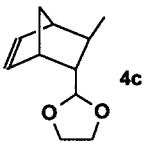
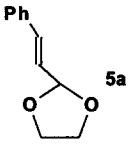
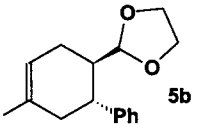
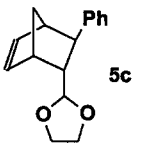
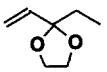
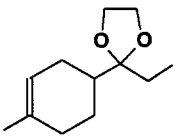
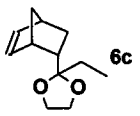
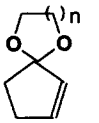
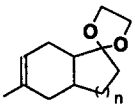
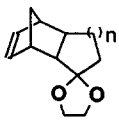
TABLE 1. LEWIS ACID CATALYSED IONIC DIELS-ALDER REACTION

Entry	Dienophile	Diene	Lewis Acid	Cyclo-adduct	Reaction Time (h)	% Yield	d/e (%)	Endo: Exo Ratio
1	**1a**	Isoprene	$TiCl_4$	**2a**	3	64	65	--
2	**1a**	Isoprene	$TiCl_2(iPrO)_2$	**2a**	3	72	76	--
3	**1a**	Isoprene	$BF_3.Et_2O$	**2a**	3	62	50	--
4	**1a**	Cyclopenta-dine	$TiCl_4$	**3a**	3	67	68*	60:40
5	**1a**	Cyclopenta-diene	$TiCl_2(iPrO)_2$	**3a**	2.5	76	78*	74:26
6	**1a**	Cyclopenta-diene	$BF_3.Et_2O$	**3a**	3	59	60*	60:40
7	**1b**	Isoprene	$TiCl_2(iPrO)_2$	**2b**	3	68	56	--
8	**1b**	Cyclopenta-diene	$TiCl_2(iPrO)_2$	**3b**	3	71	62*	60:40
9	**1c**	Isoprene	$TiCl_2(iPrO)_2$	**2c**	3	68	20	--
10	**1c**	Cyclopenta-diene	$TiCl_2(iPrO)_2$	**3c**	2.5	65	54*	65:35

* This represents d/e of the major *endo* isomer.

the corresponding cycloadducts in good yields in nitromethane. The cycloadducts were hydrolysed (Table 3) to obtain the corresponding carbonyl compounds whose spectral and HPLC analytical data assisted in determining the *endo/exo* ratio. Unfortunately, chiral acetal bearing dienophiles again did not react under these conditions. While this work was in progress Grieco *et al.*[11] reported ionic Diels-Alder reaction using 4M (or 5M) $LiClO_4$-diethyl ether containing 1% camphorsulfonic acid. Their intial observation, like ours, was failure of the reaction with 5M $LiClO_4$-Et_2O alone. The use of 1% camphorsulfonic acid dramatically permitted the reaction to occur, presumably by increasing its acid strength due to the coordination with Li^+. On the other hand, our success appears to be purely due to the favorable formation of the charged intermediates in more polar nitromethane medium. The 2-cyclohexenone acetal **8a** also reacted smoothly giving good yields of the cycloadducts **8b** and **8c**. In view of the resistance[12] of cyclohexenones to undergo Diels-Alder reactions, it is believed that the present method is useful in organic synthesis. Our results are

TABLE 2. LITHIUM PERCHLORATE AND NAFION-H CATALYSED IONIC DIELS-ALDER REACTIONS

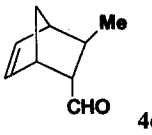
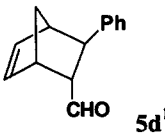
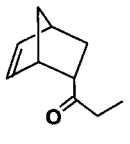
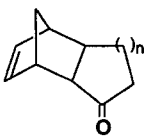
Entry	Dienophile	Diene	Cycloadduct	$LiClO_4$ Time (h)/%Yield[$]/ (*Endo/Exo* Ratio)#	Nafion-H Time (h)/%Yield[$]/ (*Endo/Exo* Ratio)#
1	 **4a**	Isoprene	 **4b**	--	7/80
2	**4a**	Cyclopentadiene	 **4c**	--	10/81/(85:15)
3	 **5a**	Isoprene	 **5b**	6.5/65	8/79
4	**5a**	Cyclopentadiene	 **5c**	6/84/(79:21)	12/84/(90:10)
5	 **6a**	Isoprene	 **6b**	5/72	--
6	**6a**	Cyclopentadiene	 **6c**	4.5/70/(93:7)	--
7 8 9	 n = 1, **7a** n = 2, **8a** n = 3, **9a**	Isoprene	 n = 1, **7b** n = 2, **8b** n = 3, **9b**	5/73 4.5/66 5/62	4/68 3/92 4/94
10 11 12	**7a** **8a** **9a**	Cyclopentadiene	 n = 1, **7c** n = 2, **8c** n = 3, **9c**	5/70/ (85/15) 4/75/ (81/19) 4.5/ 65 (78:22)	4/68/(96:4) 4/89/(95:5) 4/91/(80:20)

The *endo/exo* ratio was determined by HPLC analysis of these products and/or hydrolysed products.

[$] All the compounds were colourless oil.

summarised in Table 2.

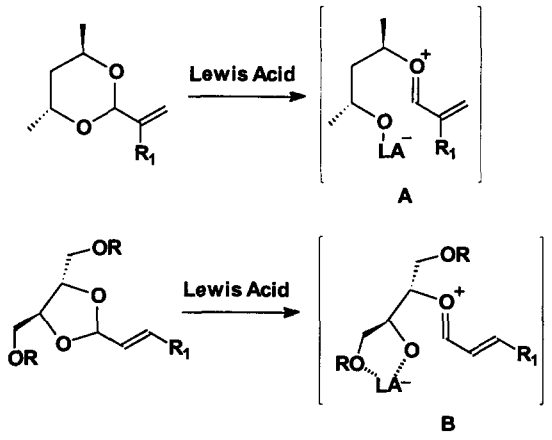
TABLE 3. HYDROLYSIS OF BICYCLIC ACETALS 4c-9c

Entry	Bicyclic Acetal	Hydrolysed Compound	% Yield
1	**4c**	 **4d**[14]	87
2	**5c**	 **5d**[14,15]	82
3	**6c**	 **6d**	75
4	**7c**	 n = 1, **7d**[16]	74
5	**8c**	n = 2, **8d**[17]	81
6	**9c**	n = 3, **9d**[16]	78

Nafion-H has been introduced[13] as an excellent solid acid catalyst for a variety of organic transformations. Since the acidity of Nafion-H is closer to H_2SO_4[13] we anticipated that ionic Diels-Alder reactions would proceed under these conditions. Further, since the work up merely involves filtration of the acid catalyst we expected that the reaction, if it works, will be better than using $LiClO_4$ or any other catalyst which require normal aqueous work up. As per our expectations, in our hands, the reaction worked very well with Nafion-H (200 mg per 5 mmol of the acetal) in CH_2Cl_2 in 3-10 h with a variety of substrates to yield the corresponding cycloadducts in good to excellent yields (Table 2). But, as with $LiClO_4$, Nafion-H also did not catalyse the cycloadditions of chiral acetals *viz.* **1a-1c**.

It was further observed that with less than 200 mg of Nafion-H per 5 mmol of the acetal the reaction proceeded slowly. Interestingly, larger amounts of Nafion-H did not cleave the acetal group. Further, among many solvents used for this reaction, CH_2Cl_2 appeared to be the best. The recovered Nafion-H was used several times (4-5) without affecting the yields of the cycloadducts.

In summary, although our studies using chiral acetals do not show any improvement in terms of selectivity in comparison to Sammakia and Berliner's experiments,[5] who used acetals which were devoid of oxygen atoms in the side chain appendages, this work indicates that due to the non-rigid nature of the allyl cation '**A**' or '**B**' (Scheme 2) the selectivity is not higher even if there are extra oxygens in the side chain. It is likely that the intermediate '**B**' could become more selective towards (2+4) cycloaddition if the size of the Lewis acid or that of group 'R' or both is increased considerably. Work towards this end is in progress in our laboratory. Further, our work also indicates that the polarity of the medium, in which $LiClO_4$ catalysed reactions are conducted, is important and nitromethane is an ideal solvent for such ionic Diels-Alder reactions. Finally, the usefulness of Nafion-H as an excellent solid acid catalyst is further documented for the ionic Diels-Alder reaction in CH_2Cl_2 giving high yields of the cycloadducts.



Scheme 2

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 1320 model spectrometer and ^{1}H NMR spectra were recorded on PMX60 from Jeol, WP80 and WM-400 from Bruker spectrometers. ^{13}C NMR spectra were recorded on Bruker WP200, 300 and WM 400 spectrometers at 50, 75.5 and 100 MHz respectively. Optical rotations were measured on Rudolph Autopol II polarimeter. Column chromatography was performed using 100-200 mesh (Acme, India) silica gel whereas thin layer chromatography was done using silica gel 60 F_{254} plates (E. Merck, Germany). The HPLC data were obtained on Perkin-Elmer LC135 instrument with SH ODS reverse phase column in acetonitrile-water (75:25) solvent system.

Ethanol and DMSO were stored over activated CaO, distilled and stored over 4 Å molecular sieves. Benzene and THF were distilled over Na-benzophenone. CH_2Cl_2 was distilled over CaH_2 and stored over 4 Å molecular sieves. Ethylene glycol was stored over anhydrous K_2CO_3 and distilled under reduced pressure. Nitromethane was stored over $CaCl_2$, distilled and again stored over 4 Å molecular sieves. $LiClO_4$ was prepared according to a literature procedure[18] from LiOH and 70% $HClO_4$ and dissolved in CH_3NO_2 instead of Et_2O to make a 4M solution. Compound **1c** was prepared according to literature procedure.[7]

(4S, 5S)-4,5-Bis(methoxymethyl) 2-(2-methylethenyl)-1,3-dioxolane (1a):

A solution of the diester **1c** (1.6g, 6.2 mmol) in anhydrous THF (6 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (1.41g, 37.2 mmol) in THF at 0°C under N_2 atmosphere. After the addition was complete, the reaction mixture was refluxed for 6h. On completion of the reaction (TLC monitoring), excess of $LiAlH_4$ was destroyed by successive addition of ethyl acetate and water. It was filtered through a pad of celite and the celite pad washed throroughly with ethyl acetate (70 ml). Usual work up followed by column chromatographic (SiO_2, hexane/ethyl acetate: 65/35) separation gave the diol in 76% yield. A solution of this diol (1.42g, 8.17 mmol) in anhydrous THF (5 ml) was added dropwise to a stirred suspension of NaH (0.784g,

32.68 mmol) in THF (8 ml) at 0°C and stirring continued under N_2 atmosphere. A solution of MeI (2 ml, 32.68 mmol) in THF (3 ml) was then added to the reaction mixture and further stirred for 8h. After the completion of the reaction (TLC monitoring), the reaction was worked up in the usual manner with Et_2O. Column chromatograpic (SiO_2, hexane/ethyl acetate: 90/10) purification of the crude product gave the dimethyl ether **1a** (1.12g, 68%) as a colourless oil . IR (CCl_4, cm^{-1}) 2900, 1460. ^1H NMR (60 MHz, CCl_4) δ 1.75 (d, J = 6 Hz, 3H), 3.35 (s, 6H), 3.45 (d, J = 6Hz, 4H), 3.7-4.0 (m, 2H, 2 methines), 5.15 (d, J = 4 Hz, 1H), 5.35-5.61 (m, 2H). Anal. Calcd. for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 58.91; H, 8.79%. $[\alpha]_D^{25} = -1°$ (C = l, CH_2Cl_2).

(4S, 5S)-4,5-Bis(benzyloxymethyl) 2-(2-methylethenyl)-1,3-dioxolane (1b):

This compound was prepared in an analogous manner as **1a** except that benzyl bromide was used in place of MeI. Yield : 83% as a colourless, viscous oil. IR (neat, cm^{-1}) 2920, 1670. ^1H NMR (60 MHz , CCl_4) δ 1.75 (d, J = 6 Hz, 3H), 3.55 (d, J = 4 Hz, 4H), 3.8-4.12 (m, 2H, 2 methines), 4.5 (s, 4H) 5.25 (d, J = 2 Hz, 1H), 5.4-6.05 (m, 2H), 7.25 (s, 10H). $[\alpha]_D^{25} = -3°$ (C = l, CH_2Cl_2). Anal. Calcd. for $C_{22}H_{26}O_4$: C,74.55; H, 7.39. Found: C, 74.87; H, 7.11%.

General Procedure for the Lewis Acid Catalysed Ionic Diels-Alder Reaction:

A solution of freshly distilled diene (isoprene or cyclopentadiene) (10 mmol) and a dienophile **1a**, **1b** or **1c** (1 mmol) in anhydrous CH_2Cl_2 (3 ml) was cooled to -78°C under Ar atmosphere for 10 min. Freshly distilled Lewis acid [$TiCl_4$ (10 mol%), $TiCl_2(iPrO)_2$ (1 mmol)[19] or $BF_3.OEt_2$ (10 mol %)] was added to the cooled mixture and stirred for the time indicated in Table 1. On completion of the reaction, the mixture was quenched with saturated $NaHCO_3$ (3-4 ml) and worked up with CH_2Cl_2 (3×20 ml) in the usual manner. The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate: 95/5).

(4S,5S)-Bis(methoxymethyl)-2-(4,6-dimethyl-3-cyclohexen-1-yl)-1,3-dioxolane (2a):

Yield: 64% as a colourless oil [ex. $TiCl_4$]; 72% [ex. $TiCl_2(iPrO)_2$]; 62% [ex. $BF_3.OEt_2$]. IR (neat, cm^{-1}): 1640, 1445. ^1H NMR (300 MHz , $CDCl_3$) δ 0.87, 0.99 (2d, J = 5.5 Hz, 3H), 1.57, 1.6 (2s, 3H), 1.75-2.2 (m, 4H), 3.4 (s, 6H), 3.45-3.7 (m, 4H), 3.75-4.0 (m, 4H), 5.1-5.2 (m, 1H), 5.3 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 19.4, 23.3, 23.8, 23.9, 29.3, 38.4, 42.4, 59.4, 73.2, 73.3, 105.2, 119.6, 132.6. MS m/z: 270 (M^+). Anal. Calcd. for $C_{15}H_{26}O_4$: C, 66.64; H, 9.69. Found: C, 66.32; H, 9.42%. $[\alpha]_D^{25} = -8°$ (C = l, CH_2Cl_2) [ex. $TiCl_4$]; -30° (C = l, CH_2Cl_2) [ex. $TiCl_2(iPrO)_2$]; -3° (C = l, CH_2Cl_2) [ex. $BF_3.Et_2O$].

(4S,5S)-4,5-Bis(methoxymethyl)-2-[3-methylbicylco(2.2.1)-hept-5-en-2-yl]-1,3-dioxolane (3a):

Yield: 67% as a colourless oil [ex. $TiCl_4$]; 76% [ex. $TiCl_2(iPrO)_2$]; 59% [ex. $BF_3.Et_2O$]. IR (neat, cm^{-1}): 2960, 1440. ^1H NMR (300 MHz , $CDCl_3$) δ 0.84, 0.9, 1.03, 1.12 (4d, J = 6 Hz, 3H), 1.2-1.4 (m, 2H), 1.4-1.5 (m, 1H), 1.6 (br s, 1H), 2.35 (br s, 1H), 2.9 (br s, 1H), 3.4 (s, 6H), 3.5 (br s, 4H), 3.9 (br s, 2H), 4.3-4.5 (m, 1H), 6.0 (br

s, 1H), 6.2 (br s, 1H). ^{13}C NMR (20 MHz, $CDCl_3$) : δ 36.3, 44.7, 46.04, 47.2, 48.8, 52.8, 59.4, 73.1, 73.6, 108.7, 133.3, 134.8, 138.3. Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.87; H, 9.34%. $[\alpha]_D^{25}$ = -4° (C = l, CH_2Cl_2) [ex. $TiCl_4$]; -16° (C = l, CH_2Cl_2) [ex. $TiCl_2(iPrO)_2$]; -1° (C = l, CH_2Cl_2) [ex. $BF_3.OEt_2$].

(4S,5S)-2-Bis(benzyloxymethyl)-2-(4,6-dimethyl-3-cyclohexen-1-yl)-1,3-dioxolane (2b):

Yield: 68% as a viscous, colourless oil. IR (CCl_4, cm^{-1}): 2960, 1640. ^1H NMR (400 MHz, $CDCl_3$) δ 1.0 (d, J = 5 Hz, 3H), 1.55-1.72 (m, 4H), 1.62 (s, 3H), 1.8-2.2 (m, 2H), 3.5-3.75 (m, 4H), 3.9-4.1 (m, 2H), 4.6 (s, 4H), 5.17 (d, J = 5 Hz, 1H), 5.35 (br s, 1H), 7.2-7.45 (m, 10H). MS m/z : 422 (M^+). Anal. Calcd. for $C_{27}H_{34}O_4$: C, 76.75; H, 8.11. Found: C, 76.16; H, 7.88%. $[\alpha]_D^{25}$ = -3.5° (C = l, CH_2Cl_2).

(4S,5S)-4,5-Bis(benzyloxymethyl)-2-[3-methyl bicylco(2.2.1)-hept-5-en-2-yl]-1,3-dioxolane (3b):

Yield: 71% as a viscous, colourless oil. IR (CCl_4, cm^{-1}): 1630. ^1H NMR (400 MHz , $CDCl_3$) δ 0.8, 1.15 (2d, J = 7.5 Hz, 3H), 1.25-1.4 (m, 2H), 1.45-1.57 (m, 1H), 1.57-1.8 (m, 1H), 2.45, 2.65, 2.77, 2.9 (4 br s, 2H), 3.45-3.75 (m, 4H), 3.95-4.15 (m, 2H), 4.45 (d, J = 10 Hz, 1H), 4.5-4.7 (m, 4H), 6.0 (br s, 1H), 6.17-6.27 (m, 1H), 7.2-7.6 (m, 10H). MS m/z : 420 (M^+). Anal. Calcd. for $C_{27}H_{32}O_4$: C, 77.11; H, 7.67. Found: C, 76.89; H, 7.47%. $[\alpha]_D^{25}$ = -4° (C = l, CH_2Cl_2).

(4S,5S)-2-Bis(carboethoxy)-2-(4,6-dimethyl-3-cyclohexen-1-yl)-1,3-dioxolane (2c):

Yield: 68% as a colourless oil. IR (CCl_4, cm^{-1}): 1740, 1650. ^1H NMR (300 MHz , $CDCl_3$) δ 1.0 (d, J = 4 Hz, 3H), 1.3 (t, J = 5 Hz, 6H), 1.45-1.85 (m, 4H), 1.6 (s, 3H), 1.85-2.35 (m, 2H), 4.2 (q, J = 6 Hz, 4H), 4.5-4.8 (m, 2H), 5.35 (br s, 2H). MS m/z : 326 (M^+). Anal. Calcd. for $C_{17}H_{26}O_6$: C, 62.56; H, 8.03. Found: C, 62.03; H, 7.86%. $[\alpha]_D^{25}$ = -2° (C= l, $CHCl_3$).

(4S,5S)-4,5-Bis(carboethoxy)-2-[3-methyl bicylco(2.2.1)-hept-5-en-2-yl]-1,3-dioxolane (3c):

Yield: 65% as a colourless oil. IR (CCl_4, cm^{-1}): 1740. ^1H NMR (300 MHz , $CDCl_3$) δ 1.3 (t, J = 5.5 Hz, 6H), 1.5 (d, 3H, J = 11 Hz), 1.6 (br s, 2H), 1.9 (br s, 1H), 1.95-2.15 (m, 1H), 2.15-2.45 (m, 1H), 2.45-2.7 (m, 1H), 4.3 (q, J = 6 Hz, 4H), 4.6-4.8 (m, 2H), 5.3 (m, 1H), 5.42 (br s, 1H), 5.7 (br s, 1H). MS m/z: 324 (M^+). Anal. Calcd. for $C_{17}H_{24}O_6$: C, 62.94; H, 8.08. Found: C, 62.68; H, 7.89%. $[\alpha]_D^{25}$ = -5° (C = l, CH_2Cl_2).

Preparation of dienophiles 4a-9a:

Compounds **4a** and **5a** were prepared by acetalisation of crotonaldehyde and cinnamaldehyde in a standard way using pyridinium p-toluenesulfonate (PPTS) as a catalyst till the water-benzene azeotrope formation stopped. Usual work up led to the expected products. Compounds **6a-9a** were synthesised according to a literature procedure.[20]

General Procedure for the $LiClO_4$ Catalysed Diels-Alder Reaction:

To a stirred solution of 4M LPNM (5 ml) at room temperature, 1 mmol of a dienophile was added and the reaction mixture was stirred for 30 min. under Argon. To this mixture was slowly added a diene (15 mmol) by syringe and the reaction mixture stirred for the time indicated in Table 2. On completion of the reaction (TLC monitoring), the reaction mixture was worked up in the usual manner with Et_2O. The crude product obtained was purified by column chromatography (SiO_2, hexane/ethyl acetate: 95/5).

General Procedure for Nafion-H Catalysed Diels-Alder Reaction:

To a stirred solution of a dienophile (5 mmol) was added Nafion-H (200 mg) followed by a freshly distilled diene (15 mmol). The mixture was vigorously stirred for the time indicated in the Table 2. After the completion of the reaction (TLC monitoring) the dichloromethane layer was decanted into another flask and the residue was washed several times with CH_2Cl_2. The combined organic layers were concentrated in vacuo to obtain a crude product which was purified by column chromatography (SiO_2, hexane/ethyl acetate: 95/5).

2-(4,6-Dimethyl-3-cyclohexen-1-yl)-1,3-dioxolane (4b):

IR (CCl_4, cm^{-1}): 2900, 1670. ^1H NMR (60 MHz , CCl_4) δ 1.0 (d, J = 6 Hz, 3H), 1.6 (s, 3H), 1.7-2.2 (m, 6H), 3.76 (d, J = 3 Hz, 4H), 4.76 (d, J = 6 Hz, 1H), 5.26 (br s, 1H). MS m/z : 182 (M^+), 167 (M^+-15), 120 (M^+- 62), 73 (M^+-109). Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.94; H, 9.37%.

2-[(3-Methyl bicyclo(2.2.1)-hept-5-en-2-yl]-1,3-dioxolane (4c):

IR (CCl_4, cm^{-1}): 2840, 2980. ^1H NMR (200 MHz , $CDCl_3$) δ 0.87 (d, J = 6 Hz, *endo* Me), 1.14 (d, J = 6 Hz, *exo* Me), 1.16-1.62 (m, 4H), 2.4 (br s, 1H), 2.88 (br s, 1H), 3.74-3.98 (m, 4H), 4.24 (d, J= 8 Hz, *endo* acetal methine), 4.8 (d, J = 8 Hz, *exo* acetal methine), 5.99-6.22 (m, 2H). MS m/z: 180 (M^+), 165 (M^+-15), 114 (M^+-166). Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.95; H, 8.87%.

2-[4-Methyl-6-phenyl-3-cyclohexen-1-yl]-1,3-dioxolane (5b):

IR (CCl_4, cm^{-1}): 2900. ^1H NMR (60 MHz , CCl_4) δ 1.66 (s, 3H), 1.93-2.3 (m, 5H), 2.83 (br s, 1H), 3.56-4.0 (m, 4H), 4.4 (br s, 1H), 5.43 (br s, 1H), 7.16 (s, 5H). MS m/z: 244 (M^+), 182 (M^+-62), 167 (M^+-77), 73 (M^+-171). Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78. 23; H, 7.96%.

2-[3-Phenyl bicyclo(2.2.1)hept-5-en-2-yl]-1,3-dioxolane (5c):

IR (neat, cm^{-1}): 1660. ^1H NMR (200 MHz, $CDCl_3$) δ 1.5-1.75 (m, 2H), 2.3-2.58 (m, 2H), 2.96-3.06 (m, 2H), 3.75-3.97 (m, 4H), 4.46 (d, J = 8 Hz, *endo* acetal methine), 4.95 (d, J = 8 Hz, *exo* methine), 6.18-6.36 (m, 2H), 7.18-7.4 (m, 5H). MS m/z: 242 (M^+), 176 (M^+-66), 175 (M^+-67), 165 (M^+-77), 104 (M^+-138), 66 (M^+-176). Anal. Calcd. for $C_{16}H_{18}O_2$: C,79.3; H,7.49. Found: C,79.24; H, 7.37%.

2-Ethyl-2-(4-methyl-3-cyclohexen-1-yl)-1,3-dioxolane (6b):

IR (CCl_4, cm^{-1}): 1640, 2900. ^1H NMR (60 MHz , CCl_4) δ 0.95 (t, J = 6 Hz, 3H), 1.2-2.3 (m, 9H), 1.6 (s, 3H), 3.85 (s, 4H), 5.2-5.5 (m, 1H). MS m/z: 196 (M^+), 181 (M^+-15). Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43: H, 10.27.

Found: C, 73.03; H, 9.89%.

2-Ethyl-2-[bicyclo (2.2.1)-hept-5-en-2-yl)-1,3-dioxolane (6c):

IR (CCl_4, cm^{-1}): 2970, 1630. ^1H NMR (200 MHz , $CDCl_3$) δ 0.85 (t, J = 6 Hz, *exo* Me), 1.0 (t, J = 6 Hz, *endo* Me),1.5-2.0 (m, 6H), 2.0-2.6 (m, 1H), 2.6-3.0 (br s, 2H), 3.8 (s, 3H), 5.65-6.1 (m, 2H). MS m/z: 194 (M^+). Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73. 79; H, 8.93%.

2,3,3a,4,7,7a-Hexahydro-5-methyl-ind-5-en-1-one ethylene ketal (7b):

IR (CCl_4, cm^{-1}): 2940, 1650. ^1H NMR (60 MHz, CCl_4) δ 1.0-2.3 (m, 10H), 1.65 (s, 3H), 3.8 (s, 4H), 5.3 (br s, 1H). MS m/z : 194 (M^+), 179 (M^+-15), 132 (M^+-62), 68 (M^+-126). Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73. 81; H, 9.01%.

Cis-3',4', 4'a, 5',8',8'a-Hexahydro-6'-methyl spiro [1,3-dioxolane-2,1'(2'H)-naphthalene (8b):

IR (CCl_4, cm^{-1}): 2940, 1650. ^1H NMR (60 MHz, CCl_4) δ 1.0-2.3 (m, 12H), 1.53 (s, 3H), 3.85 (s, 4H), 5.26 (br s, 1H). MS m/z: 208 (M^+), 193 (M^+-15),146 (M^+-62), 131 (M^+-77). Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74. 37; H, 9.29%.

Cis-1,4,4a,6,7,8,9,9a-Octahydro-2-methyl spiro[5H-benzocycloheptene-5,2'-[1,3] dioxoalane] (9b):

IR (CCl_4, cm^{-1}): 2940, 1625. ^1H NMR (60 MHz, CCl_4) δ 0.95-2.7 (m, 14H), 1.65 (s, 3H), 3.8 (s, 4H), 5.3 (br s, 1H). MS m/z: 222 (M^+), 160 (M^+-62), 154 (M^+-68), 105 (M^+-77). Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.28; H, 9.57%.

Cycloadduct (7c):

IR (CCl_4, cm^{-1}): 2940, 1625. ^1H NMR (400 MHz, $CDCl_3$) δ 1.2-1.45 (m, 2H), 1.5-1.8 (m, 4H), 2.55-2.65 (m, 1H), 2.65-2.77 (m, 1H), 2.8 (br s, 1H), 2.9 (br s, 1H), 3.85-4.05 (m, 4H), 6.05-6.3 (m, 2H). MS m/z: 193 $(M+1)^+$, 192 (M^+), 127 (M^+-65), 125 (M^+-67), 66 (M^+-126). Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74. 97; H, 8.39. Found: C, 74.63; H, 7.99%.

Cycloadduct (8c):

IR (CCl_4, cm^{-1}): 2940, 1640. ^1H NMR (400 MHz, $CDCl_3$) δ 0.95-1.8 (m, 8H), 2.3-2.45 (m, 2H), 2.8 (br s, 1H), 2.95 (br s, 1H), 3.85-4.25 (m, 4H), 6.05-6.15 (m, 1H), 6.15-6.25 (m, 1H). MS m/z: 206 (M^+), 146 (M^+-60), 141 (M^+-65), 140 (M^+-66), 112 (M^+-94), 66 (M^+-140). Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.37; H, 8.52%.

Cycloadduct (9c):

IR (CCl_4, cm^{-1}): 2930, 1625. ^1H NMR (60 MHz, CCl_4) δ 0.95-1.9 (m, 10H), 2.35, 2.6, 2.85 (3 br s, 4H), 3.9 (s, 4H), 5.91 (br s, 1H). MS m/z : 220 (M^+), 155 (M^+-65), 154 (M^+-66), 125 (M^+-95), 66 (M^+-154). Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76. 32; H, 9.15. Found: C, 75.89; H, 8.84%.

Hydrolysis of Bicyclic Acetals:

To a stirred solution of a bicyclic acetal (1 mmol) in acetone (3 ml) at 0°C was added a 3N HCl solution (2 ml). The reaction mixture was slowly brought to room temperature during 15-20 min and the completion of the reaction was monitored by TLC. It was then neutralised with saturated $NaHCO_3$ solution and extracted with diethyl ether (3×15 ml) in the usual manner. The crude product was purified by column chromatography (SiO_2, hexane/ethyl acetate: 96/4).

Compunds **4d**,[14] **5d**[14,15] and **8d**[17] were characterised by spectral means and compared these data with the literature ones.

1-Bicyclo(2.2.1)-hept-5-en-2-yl propanone (6d):

Colourless oil, IR (CCl_4, cm^{-1}): 2930, 1700, 1625. ^1H NMR (400 MHz, $CDCl_3$) δ 0.9 (exo), 1.05 (endo) (2t, J = 5 Hz, 3H), 1.2-1.9 (m, 4H), 2.12-2.2 (endo) and 2.35-2.51 (exo) (m, 2H), 2.9 (br s, 1H), 2.95-3.08 (m, 1H), 3.25 (br s, 1H), 5.8-6.2 (m, 2H). MS m/z: 150 (M^+). Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79. 67; H, 9.02%.

2,3,3a,4,7,7a-Hexahydro-4,7-methano-1H-inden-1-one (7d)[16]:

Colourless oil, IR (CCl_4, cm^{-1}): 1700. ^1H NMR (300 MHz, $CDCl_3$) δ 0.7-1.0 (m, 1H), 1.41 (d, J = 8 Hz, 1H), 1.54 (dt, J = 8 Hz, 1H), 1.95-2.64 (m, 3H), 3.2 (s, 1H), 2.72-3.18 (m, 3H), 6.11 (dd, J = 6 Hz, 3 Hz, 1H), 6.22 (dd, J = 6 Hz, 3 Hz, 1H). ^{13}C NMR for the *endo* isomer (100 MHz, $CDCl_3$): 222.6, 136.6, 135.1, 54.7, 52.7, 47.9, 47.4, 41.6, 40.9, 23.1. MS m/z: 148 (M^+), 147 (M^+-1), 130 (M^+-18), 120 (M^+-28), 82 (M^+- 66). Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.15. Found: C, 81.0; H, 8.09%.

1,4,4a,6,7,8,9,9a-Octahydro-1,4-methano-5H-benzocycloheptene-5-one (9d)[16]:

Colourless oil, IR (CCl_4, cm^{-1}): 2940, 1700. ^1H NMR (300 MHz, $CDCl_3$) δ 1.02-1.1 (m, 1H), 1.35 (br d, J = 6 Hz, 1H), 1.21-2.71 (m, 10H), 2.86 (br d, J = 6 Hz, 1H), 3.15 (br d, J = 6 Hz, 1H), 5.78 (dd, J = 7 Hz, 4 Hz, 1H), 6.23 (dd, J = 7 Hz, 4 Hz, 1H). ^{13}C NMR for the *endo* isomer (50 MHz, $CDCl_3$): 213.76, 137.84, 132.61, 58.59, 48.89, 48.17, 45.19, 42.99, 41.83, 33.81, 27.7, 23.26. MS m/z: 176 (M^+), 111 (M^+-65), 98 (M^+-78), 66 (M^+-110). Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.45; H, 8.86%.

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