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Diels–Alder Reactions of Epoxybutene Derivatives and Subsequent Synthetic Manipulations of the Cycloadducts

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Abstract:

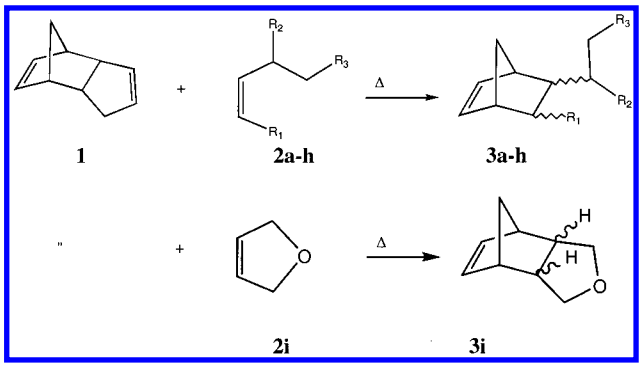
Diels–Alder reactions between cyclopentadiene, cyclohexadiene, and a number of epoxybutene derivatives are reported. The endo diastereomer from the Diels–Alder reaction of cyclopentadiene with 2,5-dihydrofuran was functionalized by additional oxidative transformations.

Introduction

3,4-Epoxy-1-butene (**2a**) is a synthetically interesting small molecule in that each of the four carbons is part of a reactive functional group and they all have significantly different reactivities. Epoxybutene is now commercially available on a multikilogram scale, and a variety of its derivatives are also available from Eastman for possible use as fine, specialty, or commodity chemicals. The ready access to large quantities of this alkenyl epoxide, coupled with the fact that Diels–Alder adducts of the derivatives with cyclic dienes might prove useful as ring-opening metathesis polymerization (ROMP) monomers,[1] prompted us to investigate Diels–Alder reactions of epoxybutene derivatives with several dienes. While the Diels–Alder reaction between epoxybutene and hexachlorocyclopentadiene is mentioned in the patent literature,[2] there has been no prior systematic study of Diels–Alder reactions of this compound and its derivatives. The alkenes studied here were not classical Diels–Alder dienophiles because the alkene was not substituted with a strong electron-withdrawing group. As such, they would be expected to be sluggish dienophiles in Diels–Alder reactions, possibly requiring more forcing reaction conditions used for other dienes[3] and dienophiles[4] of low reactivity.

Results and Discussion

Initial attempts to effect thermal Diels–Alder reactions between cyclopentadiene and epoxide (**2a**) as well as 4-vinyl-1,3-dioxolan-2-one (vinyl ethylene carbonate or VEC) (**2c**) produced only small amounts of Diels–Alder cycloadducts (**3**). However, the simple change of switching to the use of Ace Glass Pressure tubes as the reaction vessel produced a number of Diels–Alder cycloadducts. (Table 1). These tubes can be used to produce gram quantities of these cycloadducts. Two of these synthetic preparations were then scaled up further. Cycloadduct (**3a**) was produced on 120 g scale through the use of a steel autoclave (750 mL) equipped with a glass liner. Use of the glass liner was critical to the success of this reaction. Vinyl ethylene carbonate was considerably more reactive than **2a** as a dienophile, and the VEC/cyclopentadiene cycloadduct (**3c**) was synthesized on a 70 g scale using standard laboratory glassware under reflux at atmospheric pressure.



Endo/exo cycloadduct diastereomer ratios could be determined in all cases by analysis of their ^{1}H NMR spectra. Since this analysis was complicated by the existence of stereogenic centers in some of the racemic dienophiles we used, we chose to initiate analysis of the diastereoselectivity of these cycloadditions by looking at the cyclopentadiene/2,5-dihydrofuran cycloadducts (**3i**). ^{1}H NMR analyses of related cyclopentadiene Diels–Alder cycloadducts proved useful for determining diagnostic resonances in the endo and exo diastereomers reported in Table 1.[5] The exo and endo cycloadducts for the reaction of cyclopentadiene with dimethyl maleate (**4**, **5**), the endo cycloadduct for the reaction of cyclopentadiene with maleic anhydride (**6**), as well as the **3f** diastereomers are shown below. Two sets of ^{1}H NMR resonances, $H_{7s/7a}$ and $H_{2,3}$, are most diagnostic of these stereoisomers (Table 2). The $H_{2,3}$ protons in the exo diastereomer (**4**) are significantly shielded compared to the

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Table 1. **Thermal Diels−Alder reactions of cyclopentadiene with epoxybutene derivatives**

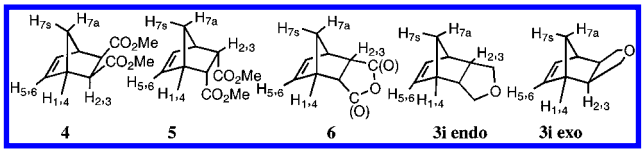
entry	R_1	R_2	R_3	cmpd	yield (%)	*endo:exo*	cmpd
1	H	$R_2 = R_3 = -O-$		**2a**	65	1.56:1	**3a**
2	H	$R_2 = R_3 = -O-C(Me)_2-O-$		**2b**	60	1.21:1	**3b**
3	H	$R_2 = R_3 = -O-C(O)-O-$		**2c**	95	1.18:1	**3c**
4	H	OH	OBz	**2d**	61	1.51:1	**3d**
5	H	OAc	OAc	**2e**	28	1.24:1	**3e**
6	H	OH	OH	**2f**	10	1.65:1	**3f**
7	H	H	OH	**2g**	28	2.42:1	**3g**
8	H	OMe	OAc	**2h**	39	1.30:1	**3h**
9	2,5-dihydrofuran			**2i**	87	2.39:1	**3i**

Table 2. **Proton NMR chemical shifts of endo and exo diastereomers**

$H_{1,4}$	3.12	3.10	3.50	2.89	2.67
$H_{2,3}$	2.62	3.23	3.56	2.86	2.26
$H_{5,6}$	6.22	6.15	6.29	6.21	6.16
H_{7a}	1.50	1.37	1.55	1.44	1.31
H_{7s}	2.14	1.37	1.77	1.53	1.83

$H_{2,3}$ protons in the endo diastereomer (**5**). The endo cycloadduct of cyclopentadiene with maleic anhydride (**6**) is similar to the dimethyl maleate endo cycloadduct, that is, H_{7s} and H_{7a} close in chemical shift and $H_{2,3}$ above 3 ppm. Since the $H_{7s/H7a}$ protons in these molecules are typically easily discernible, the ratios of $H_{7s/H7a}$ integrals for the endo and exo isomers were used to calculate diastereomer ratios.

2,5 -Dihydrofuran (**2i**) cyclized with cyclopentadiene in high chemical yield, 87%, (Table 1, entry 9) as a 2.39:1 mixture of diastereomers. The major diastereomer was determined to be the endo diastereomer (**3i *endo***) by ^{1}H NMR analysis as described above. Endo/exo ratios for the other cycloadducts listed in Table 1 were determined analogously. Dienophiles containing stereogenic centers were used as racemic mixtures. In general, epoxybutene derived dienophiles where the oxygen dienophile substituents (Table 1, entries 1−3, 9), were part of a ring provided Diels−Alder cycloadducts in the highest chemical yields.

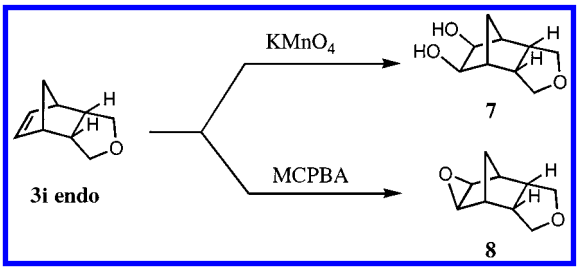


Epoxybutene (**2a**) is too reactive to be used as a possible substrate for Lewis acid-catalyzed Diels−Alder reactions. We made a number of attempts to improve endo/exo ratios by Lewis acid catalysis of the cyclopentadiene/VEC (**2c**) Diels−Alder reaction. A variety of aluminum, boron, and titanium containing Lewis acids were tried in CH_2Cl_2 and toluene over temperature ranges from −78 to 40 °C. In no case did we observe more than trace amounts of Diels−Alder cycloadducts (**3**).

As expected, these epoxybutene derivatives were less reactive with cyclohexadiene. The reaction of **2a** with cyclohexadiene required a temperature of 210 °C for 72 h to generate small amounts of product. Cyclohexadiene also reacted with VEC to provide a 1:1 mixture of endo/exo diastereomers in low isolated yield. Isoprene proved equally unreactive as a diene.

Organic Transformations of *endo*-4-Oxa-tricyclo [5.2.1.0]-dec-8-ene

The endo and exo diastereomers (**3i**) of the cyclopentadiene/2,5-dihydrofuran cycloadduct could be separated on a several gram scale using flash silica chromatography. Since several grams of the endo diastereomer (**3i *endo***) could be obtained easily, we decided to investigate some additional organic transformations of this compound. Treatment of **3i *endo*** with basic $KMnO_4$ yielded the expected diol (**7**) (64%) and treatment with MCPBA yielded the epoxide (**8**)(79%). These reactions appear to go with complete diastereoselectivity and addition of the oxygens to the exo face of **3i *endo*** was expected by analogy to other electrophilic additions to norbornenes which had been reported previously.[6]



Conclusions

Diels−Alder cycloadducts from reactions of cyclopentadiene with epoxybutene derivatives have been prepared in batch sizes of 1−100 g. One of the diastereomerically pure cycloadducts, *endo*-4-oxa-tricyclo[5.2.1.0]-dec-8-ene (**3i *endo***), was subsequently oxidized to a diol and an epoxide.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCE 300 or 500 MHz FT NMR. All absorptions are expressed in parts per million using residual protonated solvent as the reference. Infrared (IR) spectra were obtained using a Perkin-Elmer 1620 FTIR. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, Georgia. Melting points were obtained on a Mel Temp apparatus and are reported uncor-

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rected. Alumina (80-200) mesh was purchased from Fisher Scientific and deactivated with a 90:10 by volume acetone−water mixture. Flash silica gel was purchased from Universal Scientific Inc. All dienophiles were used as received from Eastman Chemical Company.

2-Bicyclo[2.2.1]hept-5-en-2-yl oxirane (3a). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.821 g, 12.42 mmol) and epoxybutene (8.21 g, 117.40 mmol). The contents were degassed by bubbling nitrogen through the solution for 5 min. The tube was equipped with a magnetic stirring bar and fitted with a Teflon screw cap. The reaction tube was placed into an oil bath (170 °C) for 66 h and then cooled to room temperature. The yellow solution was transferred to a 10 mL conical reaction vial, and epoxybutene (4.66 g, 66.49 mmol) was distilled from the solution at 63 °C. The conical reaction vial was then connected to a micro spinning band distillation apparatus. The distillation yielded a clear product (1.11 g, 8.15 mmol, 65%) at 75 °C (11 mmHg). The product contained 97% of the expected cycloadduct and 3% of dicyclopentadiene impurity. A second spinning band distillation at 75 °C (11 mmHg) can be performed to yield analytically pure material if desired. Diagnostic NMR resonances from the major product diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.70 (ddd, J = 11.63, 4.41, 4.43 Hz, 1H), 1.18 (m, 1H), 1.35 (m, 1H), 1.77 (dt, J = 11.28, 3.80 Hz, 1H), 2.62 (m, 1H), 2.80 (bs, 2H), 5.95 (dd, J = 2.9, 2.7 Hz, 1H) 6.13 (dd, J = 3.1, 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ) 28.88 (C3), 30.22 (C2), 45.27 (C4), 47.53 (C1), 50.10 (C7), 55.10 (C1′), 56.07 (C2′), 132.60 (C5), 137.28 (C6). IR (NaCl) 2964.07, 2871.50, 2448.21, 1730.81, 1455.03, 1234.22, 1196.62, 1079.94, 1049.09, 1023.05 cm^{-1}. Anal. Calcd for $C_9H_{12}O$ C, 79.37; H, 8.88. Found: C, 79.50; H, 8.84.

Scale-Up Preparation of 3a. A 750-ml steel autoclave equipped with a glass liner was charged with epoxybutene (175 g, 200 mL, 2.50 mol) and dicyclopentadiene (DCPD) (79 g, 80 mL, 0.60 mol). The autoclave was sealed, purged with nitrogen, and agitated at 185 °C for 48 h. After cooling the contents were discharged as a yellow-orange liquid which was analyzed by gas chromatography and immediately distilled through a 10-in. Vigreaux column. GC analysis (DB-5 capillary column, 30−200 °C @ 10 °C/min) disclosed the presence of residual epoxybutene, a trace of dicyclopentadiene, two diastereomeric product peaks, and four minor high-boiling byproducts. Distillation to a head temperature of 67−70 deg/760 mmHg provided unreacted epoxybutene (85 g, 49%). The pressure was then gradually lowered and a product cut (colorless liquid, 117.0 g, 0.86 mol) was taken at 73−75 °C/10−12 mmHg (72% yield based on DCPD charged, 68% based on epoxybutene consumed). This material was identical by spectroscopic comparison to the material (**3a**) reported above.

4-Bicyclo[2.2.1]hept-5′-2′-yl-2,2-dimethyl-1,3-dioxolane (3b). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.821 g, 12.42 mmol) and 2,2-dimethyl-4-ethenyl-1,3-dioxolane (10 g, 78 mmol). The contents were degassed, heated, and cooled as described above. The excess 2,2-dimethyl-4-ethenyl-1,3-dioxolane (7.97 g) was removed using vacuum distillation (30 °C, 11 mmHg). The product was further purified by bulb-to-bulb distillation yielding a clear liquid (1.39 g, 7.16 mmol, 58%) at 120 °C (7 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$) major diastereomer: 0.27 (ddd, J = 11.49, 4.50, 4.40 Hz, 1H), 1.19 (m, 1H), 1.41 (s, 3H), 1.54 (s, 3H), 1.95 (m, 1H), 2.10 (m, 1H), 2.40 (s, 1H), 3.51 (m, 1H), 3.91 (m, 1H), 6.07 (m, 1H), 6.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 26.25 (C4′), 27.41 (C5′), 31.30 (C3), 42.63 (C2), 43.86 (C4), 49.35 (C7), 45.85 (C1), 69.28 (C2′), 79.97 (C1′), 133.48 (C5), 137.36 (C6). Anal. Calcd. For $C_{12}H_{18}O_2$ C, 74.19; H, 9.34. Found: C, 74.36; H, 9.30. HRMS for $C_{12}H_{18}O_2$ *m/z* Calcd: 194.1307. Found: 194.1307.

4-Bicyclo[2.2.1]hept-5′-en-2′-yl-1,3-dioxolan-2-one (3c). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.411 g, 6.21 mmol) and 4-ethenyl-1,3 dioxolan-2-one (5.59 g, 48.99 mmol). The contents were degassed then heated at 138 °C for 48 h. The tube was then cooled to −78 °C to relieve any pressure from the possible formation of CO_2. The yellow solution was transferred to a round-bottom flask and cooled to −78 °C, and excess 4-ethenyl-1,3 dioxolan-2-one (3.78 g, 33.13 mmol) was removed by trituration with petroleum ether. The remaining product was a white solid (1.12 g, 5.55 mmol, 84%); mp = 32 °C; diagnostic NMR resonances from the major product diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.53 (ddd, J = 11.69, 4.50, 4.40 Hz, 1H), 1.08 (t, J = 3.6 Hz, 1H), 1.45 (m, 1H), 1.77 (dt, J = 5.6, 3.8 Hz, 1H), 2.31 (m, 1H), 2.82 (bs, 1H), 2.85 (bs, 1H), 5.97 (m, 1H) 6.16 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 31.30 (C3), 43.81 (C2), 43.86 (C4), 50.17 (C7), 45.85 (C1), 69.30 (C2′), 80.50 (C1′), 132.92 (C5), 138.77 (C6). IR (NaCl) 3060.20, 2966.21, 2872.24, 1801.51, 1478.96, 1366.77, 1337.37, 1260.91, 1166.93, 1067.06 cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_3$ C, 66.65; H, 6.71; Found: C, 66.65; H, 6.76.

Scale-Up Preparation of 3c. A 300 mL three-necked flask was equipped with thermometer, reflux condenser, magnetic stirrer, and argon atmosphere and was charged with vinyl ethylene carbonate (57 g, 0.50 mol), dicyclopentadiene (37 g, 0.28 mol, 12% excess), and *tert*-butylhydroquinone (0.10 g). The mixture was stirred under reflux for 2 h, during which time the pot temperature climbed from 160 to 220 °C. The heating was removed, and the cooled batch was sampled. Gas chromatographic analysis (DB-5 capillary column, 75 to 275 °C @ 15 °C/min) indicated that the reaction was about 65% complete. After standing under argon overnight at 25 °C, the mixture was reheated to 200−220 °C for 3 h, after which time GC analysis indicated more than 95% consumption of the vinylethylene carbonate. The flask was fitted with a short-path distillation head, and the material was distilled at 0.3 mmHg. A forerun of 16 g, bp to 125 °C, was discarded. Product was then obtained (67.7 g, 0.38 mol, 75% based on vinylethylene carbonate) bp 128−148 °C/0.3 mmHg. GC analysis disclosed the presence of at least three isomers. The product solidified upon standing in the refrigerator, but all attempts to separate the isomers by crystallization or column chromatography failed to provide

useful resolution. This material was identical by spectroscopic comparison to **3c** reported above.

2-Bicyclo[2.2.1]hept-5′-en-2′-yl-2-benzyloxyethanol (3d). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.841 g, 12.72 mmol) and 2-benzyloxy-3-buten-1-ol (9.06 g, 50.92 mmol). The contents were degassed, heated, and cooled as described above. The solution was transferred to a round-bottom flask, and the excess butenol (3.48 g) was removed using vacuum distillation (105 °C, 5 mmHg) followed by the product (1.924 g, 7.88 mmol, 62%) at 189 °C (1 mmHg). Diagnostic NMR resonances for the major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.53 (ddd, J = 11.53, 4.70, 4.60 Hz, 1H), 1.29 (d, J = 7.4 Hz, 1H), 1.44 (d, J = 2.0 Hz, 1H), 2.00 (m, 1H), 2.31 (m, 1H), 2.84 (bs, 2H), 5.81 (m, 1H) 6.15 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 29.30 (C3), 42.63 (C2), 44.48 (C4), 44.60 (C1), 49.54 (C7), 62.97 (C2′), 83.89 (C1′), 133.08 (C5), 138.01 (C6). IR (NaCl) 3038.71, 2954.52, 2872.21, 2343.23, 1260.95, 1102.22, 1037.60 cm^{-1}. HRMS for $C_{16}H_{20}O_2$ *m*/*z* Calcd 244.1463. Found 244.1467.

Acetic Acid 2-Acetoxy-1-bicyclo[2.2.1]hept-5-en-2-yl Ethyl Ester (3e). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.821 g 12.42 mmol) and 3,4-diacetoxybutene (21.90 g, 127.21 mmol). The contents were degassed, heated, and cooled as described above. The yellow solution was transferred to a round-bottom flask, and excess 3,4-diacetoxybutene (11.83 g, 68.17 mmol) was distilled from the solution at 60 °C (9 mmHg). Further purification via bulb-to-bulb distillation yielded a clear product (0.832 g, 3.49 mmol, 28%) at 180 °C (2 mmHg). Diagnostic NMR resonances for the major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.61 (ddd, J = 11.66, 4.50, 4.20 Hz, 1H), 1.22 (t, J = 4.8 Hz, 1H), 1.41(dd, J = 8.5, 1.8 Hz, 1H), 1.79 (m, 1H), 2.00 (s, 3H), 2.06 (s, 3H), 2.80 (bs, 2H), 3.93 (m, 1H) 4.23 (d, J = 6.7 Hz, 1H), 4.33 (d, J = 9.9 Hz, 1H), 4.49 (m, 1H), 5.84 (bs, 1H), 6.15 (bs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 29.41 (C3), 40.21 (C2), 45.55 (C4), 49.17 (C7), 50.17 (C1), 75.59 (C2′), 76.37 (C1′), 132.73 (C5), 138.26 (C6), 170.46 (C3′) 171.13 (C4′). IR (NaCl) 3017.10, 2968.89, 2394.24, 2286.21, 1737.55, 1588.10, 1318.11, 1236.15, 1152.26, 1047.16, 952.66 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2$: C, 65.53; H, 7.61. Found: C, 64.98; H, 7.54. HRMS (*m*/*z*) Calcd for $C_{14}H_{18}O_2$: 238.1205, found: 238.1201.

1-Bicyclo[2.2.1]hept-5′-en-2′yl-1,2-ethanediol (3f). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.841 g, 12.72 mmol) and 3-buten-1,2-diol (5.24 g, 59.42 mmol). The contents were degassed, heated, and cooled as described above. The solution was transferred to a 25 mL round-bottom flask, and the excess diol (2.89 g) was removed using vacuum distillation (104 °C, 12 mmHg). The remaining product was purified by bulb-to-bulb distillation yielding a clear product (0.205 g, 1.33 mmol, 10%) at 160 °C (1 mmHg). Diagnostic NMR resonances for the major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.49 (ddd, J = 11.50, 4.44, 4.40 Hz, 1H), 0.96 (dt, J = 4.8, 2.7 Hz, 1H), 1.70 (dd, 1H, J = 5.4, 3.8 Hz, 1H), 2.04 (m, 2H), 2.79 (bs, 1H), 2.81 (bs, 1H), 6.01 (m, 1H), 6.14 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 29.75 (C3), 42.56 (C2), 43.32 (C4), 45.38 (C1), 49.44 (C7), 66.31 (C2′), 76.89 (C1′), 132.75 (C5), 137.49 (C6). IR (NaCl) 3443.29, 3411.47, 3030.60, 2967.92, 2942.85, 2870.54, 2395.17, 933.38 cm^{-1}. Anal. Calcd for $C_9H_{14}O_2$ C, 70.10; H, 9.15. Found: C, 69.05; H, 9.17.

2-Bicyclo[2.2.1]hept-5-en-2-yl ethanol (3g). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.821 g, 12.42 mmol) and 3-butenol (8.84 g, 122.65 mmol). The contents were degassed, heated, and cooled as described above. The solution was transferred to a 10 mL conical reaction vial, and excess 3-butenol (8.06 g, 111.83 mmol) was distilled at 113 °C. Subsequent spinning band distillation yielded a clear product (0.421 g, 3.05 mmol, 28%) at 62 °C (7 mmHg). Diagnostic NMR resonances for the major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.52 (dt, J = 11.22, 4.10, 4.00 Hz, 1H), 1.21 (d, J = 8.05 Hz, 1H), 1.32 (m, 2H), 1.37 (m, 1H), 1.86 (dt, J = 12.20, 2.72 Hz, 1H), 2.07 (m, 1H), 2.26 (s, 1H), 2.76 (br, 2H), 3.59 (t, J = 6.95 Hz, 2H), 6.10 (m, 1H), 6.13 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) 32.34 (C3), 35.34 (C2), 42.84 (C1′), 45.89 (C4), 49.72 (C1), 49.93 (C7), 62.42 (C2′), 132.64 (C5), 137.52 (C6). IR (NaCl) 3507.14, 3011.32, 2964.07, 2940.93, 2869.57, 1047.16, 1006.66, 936.27 cm^{-1}. HRMS (*m*/*z*) Calcd for $C_9H_{14}O$ 138.1045; found 138.1049.

Acetic Acid 2-bicyclo[2.2.1]hept-5-en-2-yl-2-methoxy Ethyl Ester (3h). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.821 g, 12.42 mmol) and 1-acetoxy-2-methoxy-3-butene (7.08 g, 48.61 mmol). The contents were degassed, heated, and cooled as described above. The solution was transferred to a 25 mL round-bottom flask, and the excess 1-acetoxy-2-methoxy-3-butene (3.80 g) was removed using vacuum distillation (68 °C, 5 mmHg) followed by the clear product (1.049 g, 5.41 mmol, 40%) at 129 °C (5 mmHg). Diagnostic NMR resonances for the major diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 0.54 (ddd, J = 11.56, 4.52, 4.40 Hz, 1H), 1.16 (m, 1H), 1.36 (m, 1H), 1.71 (dt, J = 11.70, 3.84 Hz, 1H), 2.01 (s, 3H), 2.14 (m, 1H), 3.33 (s, 3H), 4.27 (dd, J = 11.23, 3.00 Hz, 1H), 5.90 (m, 1H), 6.15 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 29.41 (C3), 40.21 (C2), 45.55 (C4), 49.17 (C7), 50.17 (C1), 75.59 (C2′), 76.37 (C1′), 132.73 (C5), 138.26 (C6), 170.46 (OAc), 171.132 (OAc). IR (NaCl) 3009.39, 2966, 2870.54, 2830.04, 1733.70, 1453.10, 1271.83, 1042.34, 968.09 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_2$ C, 68.55; H, 8.63. Found: C, 68.60; H, 8.63.

4-Oxa-tricyclo[5.2.1.0]dec-8-ene (3i). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (0.821 g 12.42 mmol) and 2,5-dihydrofuran (8.70 g, 124.13 mmol). The contents were degassed, heated, and cooled as described above. The yellow solution was transferred to a 10 mL conical reaction vial and 2,5-dihydrofuran (7.07 g, 100.87 mmol) was distilled from the solution at 64 °C. The conical reaction vial was then connected to a micro spinning band distillation apparatus to produce a clear product[7] (1.10 g, 8.08 mmol, 65%) at 70 °C (25 mmHg); mp = 26 °C. Diagnostic NMR resonances for the major

(7) For a report of the reaction between cyclopentadiene and 2,5-dihydrofuran, see: Brace, N. O. *J. Am. Chem. Soc.* **1955**, *77*, 4157.

diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) 1.41 (d, J = 8.2 Hz, 1H), 1.49 (d, J = 8.2 Hz, 1H), 2.83 (s, 1H), 2.86 (t, J = 3.35 Hz, 2H), 3.40 (d, J = 2.2 Hz, 1H), 3.43 (s, 1H), 3.54 (m, 2H,). ^{13}C NMR (125 MHz, $CDCl_3$) 46.19 (C1, C4), 48.33(C7), 53.01(C2, C3), 70.39 (C1′), 135.44 (C5, C6). IR (NaCl) 3017.10, 2968.89, 2802.08, 1350.89, 1207.22, 1091.51, 998.95 cm^{-1}. Anal. Calcd for $C_9H_{12}O$ C, 79.37; H, 8.88. Found C, 79.37; H, 8.89.

Organic Transformations of Diasteromerically Pure *endo*-4-Oxatricyclo[5.2.1.0]dec-8-ene. Isolation of the Endo Diastereomer (3i *endo*). A thick-walled, high-pressure tube was charged with freshly cracked cyclopentadiene (4.11 g, 62.10 mmol) and 2,5 dihydrofuran (23.5 g, 335.24 mmol). The contents were degassed, heated, and cooled as described above. Excess 2,5-dihydrofuran (15.77 g) was removed by distillation at 80 °C (20 mmHg). Column chromatography of the remaining material (19:1 petroleum ether/diethyl ether) yielded 1.70 g of a mixture (1.5:1) of endo/exo cycloadduct, followed by 3.95 g (40.1%) of *endo*-4-oxa-tricyclo[5.2.1]-dec-8-ene (**3i *endo***) identical by spectroscopic comparison to the material reported above.

4-Oxa-tricyclo[5.2.1.0]decane-8,9-diol (7). A flask was charged with triethylbenzylammonium chloride (2.34 g, 10.23 mmol), $KMnO_4$ (1.62 g, 10.23 mmol), and CH_2Cl_2 (20 mL). The flask was cooled to 0 °C. A solution of *endo*-4-oxa-tricyclo[5.2.1]dec-8-ene (**3i *endo***) (0.93 g, 6.81 mmol) in methylene chloride (10 mL) was added to the stirring solution dropwise over a time period of 50 min while maintaining the temperature. The solution was stirred until most of the $KMnO_4$ had reacted (2 h), then treated with 20 mL of 3% NaOH, and stirred for 18 h at 25 °C. The solution was filtered through Celite to remove the potassium salts, and the organic layer and the aqueous layer were separated. The aqueous layer was extracted several times using ether; the extracts were dried and concentrated using rotary evaporation and high vacuum to yield a viscous liquid (0.739 g, 4.35 mmol, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) 1.30 (d, J = 8.4 Hz, 1H), 1.70 (bs, 2H), 1.93 (d, J = 10.1 Hz, 1H), 2.18 (m, 2H), 2.54 (m, 2H), 3.29 (m, 2H), 3.93 (d, J = 9.9 Hz, 2H), 4.05 (d, J = 9.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) 30.70(C7), 43.57 (C5, C6) 47.79 (C1,C4), 68.69-(C1′), 70.58 (C2, C3). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found C, 63.57; H, 8.02.

4-Oxa-tricyclo[5.2.1.0]-8,9-epoxydecane (8). A round-bottom flask was charged with *endo*-4-oxa-tricyclo[5.2.1]-dec-8-ene (**3i *endo***) (0.100 g, 0.735 mmol), $NaHCO_3$ (0.200 g, 2.38 mmol), and dry CH_2Cl_2 (10 mL). The flask was placed in an ice bath, and the solution was stirred while MCPBA (0.256 g, 1.483 mmol) dissolved in dry CH_2Cl_2 (15 mL) was added dropwise over a period of 20 min. After stirring (5 h) a white precipitate had formed. The solution was treated with aqueous Na_2CO_3 (10 mL) and stirred for 30 min. The aqueous layer was extracted using diethyl ether and dried using $MgSO_4$. The organic layer was concentrated using rotary evaporation and further dried under high vacuum to yield a white solid (0.088 g, 0.58 mmol, 79%); mp = 64−65 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 0.83 (d, J = 9.7 Hz, 1H), 1.45 (d, J = 9.7 Hz, 1H), 2.55 (m, 2H), 2.68 (m, 2H), 3.25 (s, 2H), 3.43 (dd, J = 12.5, 7.5 Hz, 2H), 3.75 (d, J = 12.5 Hz, 2H) ^{13}C NMR (125 MHz, $CDCl_3$) 29.91(C7), 40.17 (C5, C6) 46.55 (C1, C4), 49.89 (C2, C3), 68.49 (C1′). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.48; H, 8.00.

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