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Zirconocene-Catalyzed Cationic Diels-Alder Reactions

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Abstract: *In situ* prepared $Cp_2ZrCl^{\oplus}$ catalyzes the formation of dioxolenium ions from α,β-unsaturated epoxy esters. As a consequence of this activation process, acrylate, methacrylate and crotonate derivatives undergo a rapid and stereoselective cationic [4+2] cycloaddition with a wide range of dienes. Ring-extended carboxylic acid derivatives are formed in 1-7 h at 0-21 °C and in 50-90% yield after saponification of the intermediate diol esters. Simple Lewis acid catalysis by $Cp_2ZrCl^{\oplus}$ can be excluded on the basis of the experimental results.

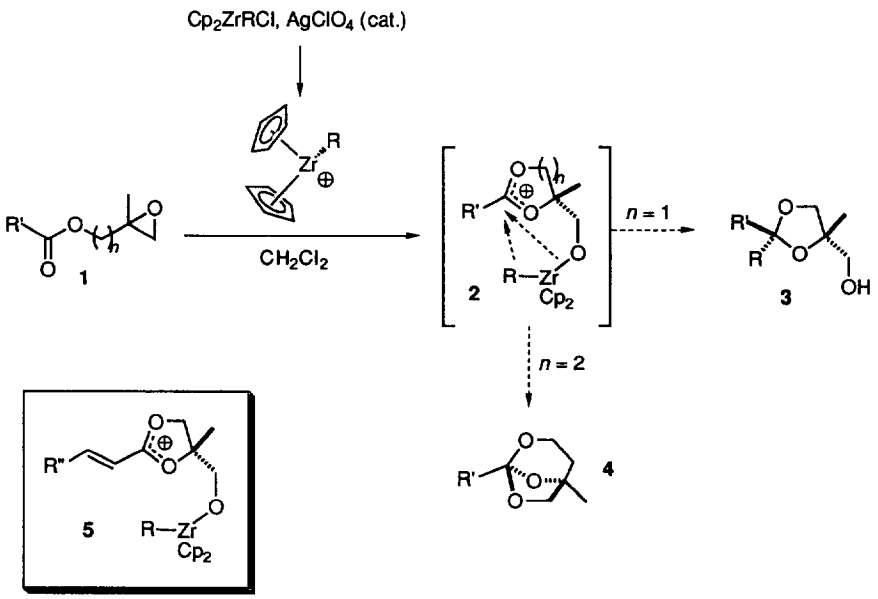
Introduction

Diels-Alder reactions[2] are among the most efficient methods for stereocontrolled C,C-bond formations, and particularly research aiming at extending the scope of the Lewis-acid catalyzed and the intramolecular versions of the [4+2] cycloaddition has surged during the last decade.[3,4] In the normal-electron-demand Diels-Alder reaction, the main orbital interaction is between the HOMO of an electron-rich diene and the LUMO of an electron-deficient dienophile. Since the most powerful electron-withdrawing group is a carbocation, cycloadditions between neutral dienes and cationic dienophiles would be expected to be both extremely facile and highly selective. The considerable synthetic potential of cycloadditions with ionic components, e.g. polar cycloadditions,[5] has been recognized by a number of groups. Early studies of the chemistry of allyl cations established the feasibility of ionic Diels-Alder processes.[6] In 1976, Baum and Viehe found that the reactivity of α,β-unsaturated alkoxy iminium ions in pericyclic reactions exceeded that of acid chlorides and aldehydes.[7] Subsequently, Bauld and coworkers used tris(*p*-bromophenyl)aminium hexachloroantimonate for the *in situ* ionization of conjugated dienes, styrenes, and enol ethers as well as vinyl sulfides and *N*-vinyl amides in cation radical pericyclic reactions.[8,9] Fast turnover at low temperatures and high stereoselectivity were observed by Roush and Gassman in the acid promoted ionic Diels-Alder reaction of 2-hydroxyethyl esters, acrolein acetals, and triethyl orthoacrylate.[10,11] The cation radical protocol as well as the use of allyl cations were also found to promote excellent levels of *endo* selectivity in intramolecular Diels-Alder reactions.[10,12] Recently, Saigo and coworkers have used the Lewis acid ($TiCl_4$, TMSOTf) induced formation of dioxolenium ions from unsaturated 2,2-dimethoxyethyl and 2-oxoalkyl esters for the preparation of Diels-Alder adducts with a variety of cyclic and acyclic dienes.[13]

In prior studies, we have found that the cationic zirconocene species prepared *in situ* from organozirconocene and catalytic amounts of $AgClO_4$ were efficiently initiating tandem epoxide rearrangement-aldehyde addition cascades[14] and were compatible with a wide range of functional

groups in the formation of dioxolanes[15] and ortho esters[16] from epoxy esters. In the latter reactions, it was likely that dioxolenium ions **2** were formed as intermediate species preceding C,C- or C,O-bond formations (Scheme I).

Scheme I



Dienophile in Cationic Diels-Alder Reactions

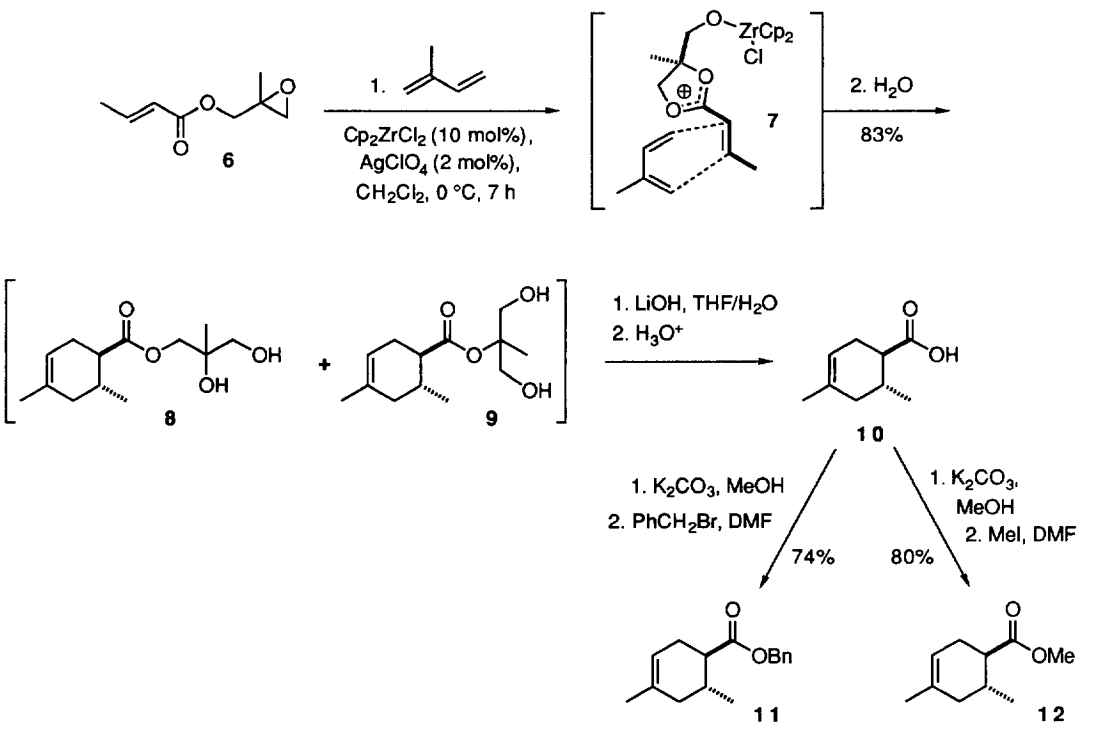
This chemistry offers the intriguing prospect to use α,β-unsaturated dioxolenium ions of type **5** as dienophiles in cationic Diels-Alder processes. Dioxolane formation could be suppressed by the use of non-transferable substituents R on zirconium, and the use of glycidol esters with $n = 1$ should minimize ortho ester formation and thus provide cationic intermediates of sufficient lifetime for intermolecular addition reactions to occur. Furthermore, the ready accessibility of glycidols of high enantiomeric purity and the considerable steric bulk exercised by the zirconocene moiety would allow for face-selective attack of the diene on the activated π-bond. In the present paper, we report on our exploratory studies of the generation and the reactivity of dienophiles **5** in the ionic Diels-Alder reaction.

Results and Discussion

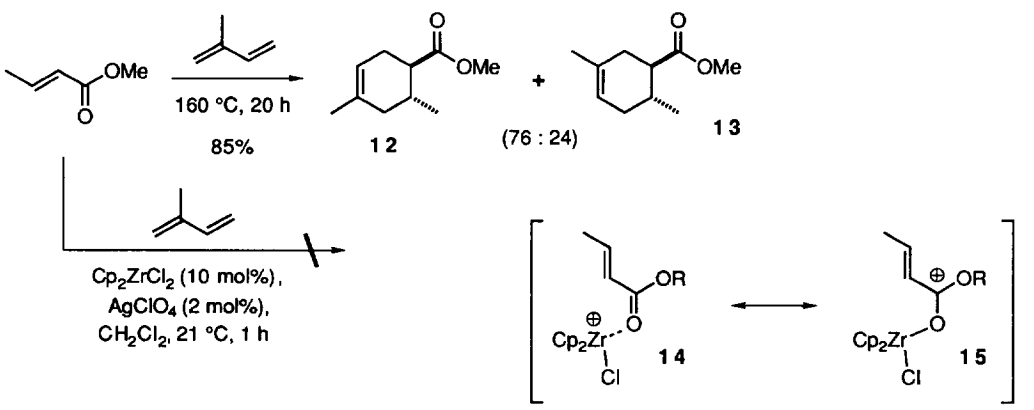
Treatment of a solution of crotonate **6** and 10 equiv of isoprene in CH_2Cl_2 with catalytic amounts of zirconocene dichloride (10 mol%) and silver(I) perchlorate (2 mol%) followed by an aqueous quench resulted in the formation of an approximately 2.5 : 1 mixture of cyclohexenes **8** and **9** in 83% yield (Scheme II). Hydrolysis provided cyclohexenecarboxylic acid **10**, which was converted to the known[17] benzyl ester **11** and methyl ester **12**. During the cycloaddition, the reaction conditions

have to be strictly anhydrous to avoid quenching of the reactive species, $Cp_2ZrCl^{\oplus}$.[18] In the presence of coordinating solvents such as THF, for example, no product is formed. The reaction also failed if Lewis acids such as BF_3-etherate were used in place of zirconocene dichloride and Ag(I) salts.

Scheme II



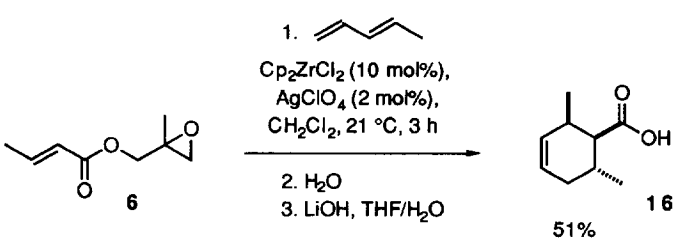
Scheme III



The para/meta regioselectivity of the zirconocene-catalyzed Diels-Alder reaction of **6** and isoprene was excellent. It exceeded 96% (GC, 500 MHz NMR). In contrast, the thermal, uncatalyzed cycloaddition provided a 76 : 24 mixture of regioisomers **12** and **13** (Scheme III).

It is important to note that $Cp_2ZrCl^{\oplus}$ does not simply function as a Lewis acid in the activation of the ester carbonyl group as shown in the resonance structures **14** and **15**. Titanocene- and zirconocene-based catalysts have been used in the Diels-Alder and Mukaiyama reactions with α,β-unsaturated aldehydes and ketones,[19] as well as acrylates.[20] However, the activity of these complexes is generally low, and long reaction times or the use of highly reactive diene components are necessary to effect significant cycloaddition. Indeed, exposure of methyl crotonate and isoprene to the zirconocene dichloride/silver perchlorate mixture led only to extensive polymerization of the diene, and no cycloadduct was isolated after 1 h at 21 °C (Scheme III). Accordingly, the reactivity of the cationic dienophile **7** appears to be considerably higher than that of the corresponding Lewis acid adduct **14**. Conversion of epoxy ester **6** with the relatively unreactive piperylene, for example, provided 51% of the 3-cyclohexene-1-carboxylic acid **16** after 3 h at room temperature in the presence of 2 mol% of *in situ* prepared $Cp_2ZrCl^{\oplus}$ (Scheme IV). The general scope of the zirconocene-catalyzed cationic Diels-Alder reaction of epoxy esters and 1,3-dienes is summarized in Table I.

Scheme IV



Scheme V

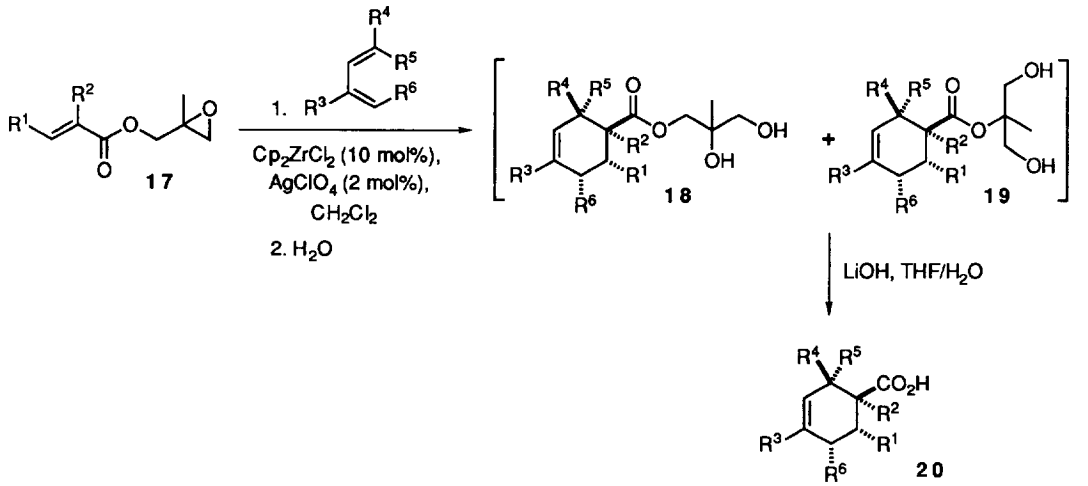
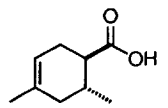
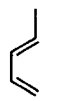
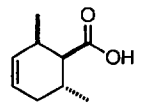
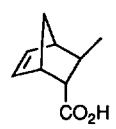
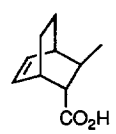
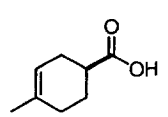
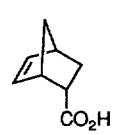
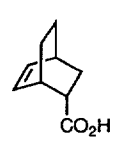
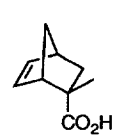


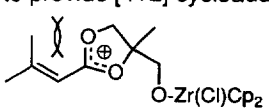
Table I. Cationic Diels-Alder Reaction Promoted by Catalytic $Cp_2ZrCl_2/AgClO_4$ (Scheme V).

entry	epoxy ester			diene		reaction	product[a]		*endo / exo*	yield
	R^1	R^2	No.	structure	No.	time / temp.	structure	No.	ratio[b]	(%)[c]
1	CH_3	H	**6**		**21**	7 h / 0 °C		**10**	-[d]	83
2	CH_3	H	**6**		**22**	3 h / 21 °C		**16**	-[e]	51
3	CH_3	H	**6**		**23**	1.5 h / 0 °C		**24**	2.7 : 1	80
4	CH_3	H	**6**		**25**	6 h / 21 °C		**26**	30 : 1	70
5	H	H	**27**		**21**	1 h / 21 °C		**28**	-	83
6	H	H	**27**		**23**	1.5 h / 0 °C		**29**	8 : 1	87
7	H	H	**27**		**25**	6 h / 21 °C		**30**	110 : 1	60
8	H	CH_3	**31**		**23**	2.5 h / 0 °C		**32**	8 : 1	74

[a]Only the major product is shown. [b]Ratios of the carboxylic acid products were determined by integration in ^1H NMR and verified by GC analysis of the corresponding methyl esters. [c]Yields are based on epoxy ester and refer to chromatographically purified carboxylic acids; a five- to tenfold excess of diene was used. [d]Ratio of regioisomers exceeded 98 : 2. [e]Only one regioisomer was observed in ^1H NMR.

The yields of the cycloaddition reaction of crotonate, acrylate, and methacrylate derivatives and cyclic and acyclic dienes ranged from 51 to 87% based on epoxy ester and chromatographically purified acid. As expected, cyclopentadiene was the most reactive diene in this series and the starting material was consumed within 1-3 h at 0 °C. In general, however, the reactivity differences between the dienes as well as the dienophiles in this cationic process tended to be quite small. Cyclohexadiene (**25**) provided bicyclic addition products **26** and **30** with very high *endo* selectivities (entries 4 and 7). In contrast, the use of cyclopentadiene (**23**) lead only to a surprisingly low 2.7 : 1 *endo/exo* selectivity with crotonate **6** (entry 3). The preference for the *endo* addition product increased to 8 : 1 for acrylate **27** and methacrylate **31** (entries 6 and 8). The thermal cycloaddition of methacrylates is known to provide an excess of the *exo* addition product,[21] and Lewis catalyst variants tend to result in low *endo/exo* selectivities with this dienophile.[17a] It is therefore quite remarkable that in the cationic version methacrylate showed the same *endo* selectivity as acrylate and considerably improved selectivity over crotonate in the cycloaddition to cyclopentadiene.

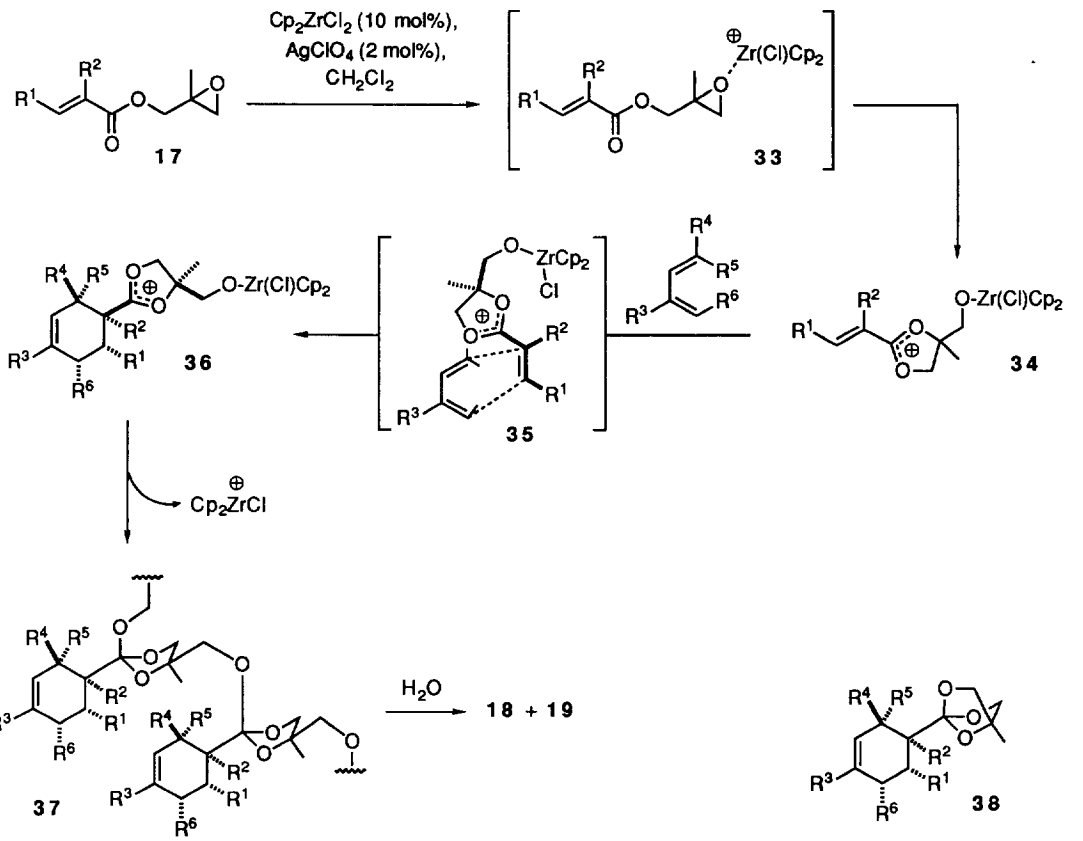
Another dienophile that was examined, the methylglycidol ester of β,β-dimethylacrylate, failed to provide [4+2] cycloaddition products with isoprene and cyclohexadiene.



Under the standard conditions, only rapid decomposition of the parent epoxy ester was detected. A considerable destabilizing $A^{1,3}$-strain in the dioxolenium ion is probably responsible for this negative result.

The initial generation of only 2 mol% of $Cp_2ZrCl^{\oplus}$ by activation of zirconocene dichloride with silver (I) salts was generally sufficient for all of these reactions to proceed to completion. Therefore, the cationic catalyst must be efficiently regenerated once the intramolecular cyclization - Diels-Alder addition process has occurred. Similar to the pathways postulated for epoxide rearrangements and ortho ester formation,[14,15] we propose that, after the cycloaddition of **34** and diene, an intermolecular attack of the zirconium alkoxide on the dioxolenium ion **36** leads to the formation of the ortho ester oligomer **37** and regenerates $Cp_2ZrCl^{\oplus}$ (Scheme VI).[22] Hydrolysis of the ortho ester functionalities upon aqueous workup provides diol esters **18** and **19**. We have not found any spectroscopic evidence for intramolecular charge recombination of **36** by formation of the trioxabicyclo[2.2.1]heptane **38**.[23,24] However, it is not unlikely that **38** is indeed the kinetically formed product and is subsequently rapidly oligomerized by the cationic catalyst to give **37**. Due to the increased stability of the more highly delocalized dioxolenium ion **34** vs. **36**,[15,23c] we would expect the inter- or intramolecular ortho ester formation of **34** to be slow relative to diene capture. This difference in the rate of the charge-trapping reaction of **34** and **36** is a crucial feature for the use of catalytic quantities of cationic zirconocene in dienophile activation.

Scheme VI



Conclusions

Cationic and cation-radical induced Diels-Alder reactions are synthetically useful modifications of [4+2] cycloadditions. The exceptional reactivity that is associated with a charge-activation of the dienophile allows normally inert substrates to participate readily in the pericyclic process. Regio- and stereoselectivity of the cycloaddition are greatly enhanced over the thermal reaction and often comparable or superior to Lewis-acid catalyzed procedures. The use of cationic zirconocene and α,β-unsaturated epoxy esters in the Diels-Alder reaction is especially attractive, since the preparation of the dienophile is synthetically straightforward and stoichiometric amounts of zirconocene dichloride are not necessary. The catalytically active species, $Cp_2ZrCl^{\oplus}$, prepared *in situ* by addition of 2 mol% of $AgClO_4$, promotes the rearrangement of the epoxy ester to the dioxolenium ion which participates as a cationic dienophile in the accelerated Diels-Alder process. $Cp_2ZrCl^{\oplus}$ is probably continuously recycled by intermolecular ortho ester formation of the Diels-Alder adduct. The mild reaction conditions and the specificity of this novel cationic cycloaddition for epoxy ester moieties are promising features for applications in the synthesis of highly functionalized target molecules. We are currently extending our studies to asymmetric as well as intramolecular variants of this protocol.

Experimental Section

General. Anhydrous solvents were freshly distilled from either sodium benzophenone ketyl, P_2O_5, or CaH_2. All reactions were performed in oven-dried glassware under an argon or nitrogen atmosphere. IR spectra were recorded on an IBM IR/32 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Bruker AC-300 NMR spectrometer (300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR) and are reported in ppm relative to tetramethylsilane (δ). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constants. Mass spectra were obtained on a VG-70-70 HF. Analytical TLC used Merck silica gel 60 F-254 plates, and flash silica gel chromatography was used to separate and purify the crude reaction mixtures. GC analysis was performed on a Perkin-Elmer 8500 gas chromatograph with an Econo-Cap SE-54, 0.54 mm ID, 30 m / 1.2 μ column.

General Procedure for Zr-Catalyzed Diels-Alder Additions: (*trans*)-4,6-Dimethyl-3-cyclohexene-1-carboxylic acid (10). A solution of 30 mg (0.19 mmol) of crotonate **6** in 1 mL of CH_2Cl_2 was treated at 0 °C with 130 mg (1.9 mmol) of isoprene, 6 mg (0.02 mmol) of Cp_2ZrCl_2 and finally 1 mg (0.004 mmol) of $AgClO_4$. The reaction mixture was stirred for 7 h at 0 °C , treated with saturated aqueous $NaHCO_3$ solution, and extracted with EtOAc (3x). The combined organic layers were dried (Na_2SO_4) and filtered through a pad of florisil. The solvent was removed *in vacuo*, and the residue was purified by chromatography on SiO_2 (EtOAc/hexanes, 1 : 2) to give 38 mg (83%) of a 2.5 : 1 mixture of diol esters **8** and **9** as a corlorless oil.

8: IR (neat) 3416, 2961, 2924, 1730, 1456, 1381, 1234, 1165, 1057 cm^{-1}; ^1H NMR δ 5.33 (br s, 1 H), 4.14 (d, 1 H, J = 11.2 Hz), 3.99 (d, 1 H, J = 11.3 Hz), 3.47, 3.40 (AB, 2 H, J = 11.5 Hz), 2.9-2.7 (br, 2 H), 2.3-2.15 (m, 3 H), 2.1-1.9 (m, 2 H), 1.75-1.6 (m, 1 H), 1.63 (s, 3 H), 1.17 (s, 3 H), 0.90 (d, 3 H, J =7.3 Hz); ^{13}C NMR δ 177.0, 133.5, 118.5, 72.0, 67.7, 66.9, 47.0, 37.9, 30.9, 28.9, 23.3, 21.3, 19.8; MS (EI) *m/z* (relative intensity) 224 ([M-H_2O]$^+$, 2), 211 (4), 154 (15), 137 (20), 108 (100), 93 (50), 55 (20); HRMS (EI) *m/z* calcd. for $C_{12}H_{19}O_3$ (M-CH_2OH): 211.1334, found: 211.1340.

A solution of 38 mg of **8** and **9** in 2 mL of THF was treated with 2 mL of 1 M LiOH, stirred at room temperature overnight, concentrated *in vacuo*, and washed with Et_2O. The aqueous layer was acidified to pH 1 by addition of 3 M HCl, and extracted with Et_2O (2x). The combined ether layers were dried (Na_2SO_4), concentrated, and chromatographed on SiO_2 (EtOAc/hexanes, 1 : 3) to give 24 mg (100%) of **10** as a white solid: mp 80-82.5 °C (lit.[25] 84 °C); ^1H NMR δ 5.36 (br s, 1 H), 2.25-2.15 (m, 3 H), 2.10-1.90 (m, 2 H), 1.75-1.60 (m, 1 H), 1.65 (s, 3 H), 1.02 (d, 3 H, J = 6.2 Hz); ^{13}C NMR δ 182.6, 133.5, 118.5, 46.8, 37.9, 30.8, 28.8, 23.4, 19.8; MS (EI) *m/z* (relative intensity) 154 (M$^+$, 20), 120 (80), 108 (30), 93 (40), 70 (100).

Phenylmethyl (*trans*)-4,6-Dimethyl-3-cyclohexene-1-carboxylate (11). To a solution of 18 mg (0.12 mmol) of acid **10** in 1 mL of dry methanol was added 8 mg (0.06 mmol) of powdered K_2CO_3. The mixture was stirred until the solid had dissolved, methanol was removed, and 1 mL of dry DMF was added followed by 25 mg (0.14 mmol) of benzyl bromide. The reaction mixture was stirred overnight, H_2O was added, and the solution was extracted with Et_2O (2x). The combined ether layers were dried (Na_2SO_4), concentrated *in vacuo*, and chromatographed on SiO_2 (EtOAc/hexanes, 1 : 10) to yield 21 mg (74%) of **11**[17a] as a corlorless oil: ^1H NMR δ 7.5-7.3 (m, 5 H), 5.35 (s, 1 H), 5.14 (s, 2 H), 2.3-1.6 (m, 6 H), 1.64 (s, 3 H), 0.94 (d, 3 H, J = 6.3 Hz).

Methyl (*trans*)-4,6-Dimethyl-3-cyclohexene-1-carboxylate (12). To a solution of 20 mg (0.13 mmol) of acid **10** in 1 mL of dry methanol was added 9 mg (0.065 mmol) of powdered K_2CO_3. The mixture was stirred until the solid had dissolved, methanol was removed, and 1 mL of dry DMF was added followed by 22 mg (0.15 mmol) of iodomethane. The reaction mixture was stirred

overnight, H_2O was added, and the solution was extracted with Et_2O (2x). The combined ether layers were dried (Na_2SO_4), concentrated, and chromatographed on SiO_2 (EtOAc/hexanes, 1 : 10) to give 18 mg (80%) of **12**[17b] as a corlorless oil: ^1H NMR δ 5.34 (s, 1 H), 3.68 (s, 3 H), 2.3-1.65 (m, 6 H), 1.64 (s, 3 H), 0.94 (d, 3 H, J = 6.2 Hz).

(1,2-*cis*-1,6-*trans*)-2,6-Dimethyl-3-cyclohexene-1-carboxylic acid (16). According to the general procedure, 70 mg (0.45 mmol) of crotonate **6**, 300 mg (4.48 mmol) of piperylene, 13 mg (0.045 mmol) of Cp_2ZrCl_2 and 2 mg (0.009 mmol) of $AgClO_4$ afforded 35 mg (51%) of **16** as a white solid: mp 76.5-77.5 °C (lit.[17a] 74-75.5°C); IR (neat) 3017, 2965, 2930, 2872, 2829, 1705, 1659, 1460, 1417, 1306, 1236, 1186, 1116, 933, 910, 713 cm^{-1}; ^1H NMR δ 5.70-5.50 (m, 2 H), 2.65-1.60 (m, 5 H), 1.04 (d, 3 H, J = 6.7 Hz), 0.99 (d, 3 H, J = 7.1 Hz); ^{13}C NMR δ 180.8, 131.2, 125.2, 50.6, 33.3, 31.6, 24.7, 20.2, 17.3; MS (EI) *m/z* (relative intensity) 154 (M^+, 25), 109 (100), 93 (40), 68 (70), 55 (40); HRMS (EI) *m/z* calcd. for $C_9H_{14}O_2$: 154.0994, found: 154.0989.

(2-*endo*,3-*exo*)-3-Methylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid (24). According to the general procedure, 50 mg (0.32 mmol) of crotonate **6**, 210 mg (3.2 mmol) of cyclopentadiene, 9 mg (0.032 mmol) of Cp_2ZrCl_2 and 1 mg (0.006 mmol) of $AgClO_4$ afforded 41 mg (80%) of a 2.7 : 1 mixture of **24** and its (3-*endo*,2-*exo*)-isomer as a white solid.

24:[26] ^1H NMR δ 6.27 (dd, 1 H, J = 5.6, 3.1 Hz), 6.03 (dd, 1 H, J = 5.6, 2.8 Hz), 3.13 (br s, 1 H), 2.48 (br s, 1 H), 2.45-2.35 (m, 1 H), 1.85-1.75 (m, 1 H), 1.55 (d, 1 H, J = 8.6 Hz), 1.45 (d, 1 H, J = 8.6 Hz), 1.18 (d, 3 H, J = 7.1 Hz).

(2-*endo*,3-*exo*)-3-Methylbicyclo[2.2.2]oct-5-ene-2-carboxylic acid (26). According to the general procedure, 50 mg (0.32 mmol) of crotonate **6**, 250 mg (3.2 mmol) of 1,3-cyclohexadiene, 9 mg (0.032 mmol) of Cp_2ZrCl_2 and 1 mg (0.006 mmol) of $AgClO_4$ afforded 37 mg (70%) of a 30 : 1 mixture of **26**[27] and its (3-*endo*,2-*exo*)-isomer as a white solid: mp 101.2-102.4 °C; IR (neat) 3049, 2959, 2928, 2874, 1699, 1471, 1458, 1319, 1296, 1261, 949, 866, 696 cm^{-1}; ^1H NMR δ 6.42 (t, 1 H, J = 7.3 Hz), 6.15 (t, 1 H, J = 7.3 Hz), 2.9-2.8 (m, 1 H), 2.3-2.2 (m, 1 H), 2.05-2.0 (m, 1 H), 1.9-1.0 (m, 5 H), 1.12 (d, 3 H, J = 6.9 Hz); ^{13}C NMR δ 181.9, 137.0, 130.9, 51.4, 35.7, 35.6, 32.8, 25.8, 19.8, 17.8; MS (EI) *m/z* (relative intensity) 166 (M^+, 10), 93 (10), 80 (100), 66 (30).

4-Methyl-3-cyclohexene-1-carboxylic acid (28). According to the general procedure, 50 mg (0.35 mmol) of acrylate **27**, 230 mg (3.5 mmol) of isoprene, 10 mg (0.035 mmol) of Cp_2ZrCl_2 and 2 mg (0.007 mmol) of $AgClO_4$ afforded 40 mg (83%) of **28** as a white solid: mp 95.8-96.6 °C (lit.[28] 97-99 °C); ^1H NMR δ 5.37 (br s, 1 H), 2.60-2.50 (m, 1 H), 2.3-2.20 (m, 2 H), 2.1-1.95 (m, 3 H), 1.8-1.6 (m, 1 H), 1.65 (s, 3 H); ^{13}C NMR δ 182.8, 133.9, 119.1, 39.1, 29.2, 27.4, 25.3, 23.5.

(2-*endo*)-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (29). According to the general procedure, 50 mg (0.35 mmol) of acrylate **27**, 230 mg (3.5 mmol) of cyclopentadiene, 10 mg (0.035 mmol) of Cp_2ZrCl_2 and 2 mg (0.007 mmol) of $AgClO_4$ afforded 42 mg (87%) of an 8 : 1 mixture of **29** [29]and its (2-*exo*)-isomer as a corlorless oil: IR (neat) 2974, 1701, 1419, 1336, 1275, 1236, 1111, 910, 839, 708 cm^{-1}; ^1H NMR δ 6.20 (dd, 1 H, J = 5.6, 3.0 Hz), 5.99 (dd, 1 H, J = 5.6, 2.9 Hz), 3.23 (br s, 1 H), 3.05-2.85 (m, 2 H), 2.0-1.85 (m, 1 H), 1.5-1.2 (m, 3 H); ^{13}C NMR δ 181.4, 138.0, 132.5, 49.8, 45.8, 43.3, 42.6, 29.2; MS (EI) m/z (relative intensity) 138 (M^+, 5), 91 (10), 66 (100), 43 (40).

(2-*endo*)-Bicyclo[2.2.2]oct-5-ene-2-carboxylic acid (30). According to the general procedure, 50 mg (0.35 mmol) of acrylate **27**, 280 mg (3.5 mmol) of 1,3-cyclohexadiene, 10 mg (0.035 mmol) of Cp_2ZrCl_2 and 2 mg (0.007 mmol) of $AgClO_4$ afforded 32 mg (60%) of a 110 : 1 mixture of **30** and its (2-*exo*)-isomer as a white solid: mp 53.0-54.2 °C (lit.[30] 56-57 °C); ^1H NMR δ 6.32 (t, 1 H, J = 7.7 Hz), 6.17 (t, 1 H, J = 7.7 Hz), 3.1-2.9 (m, 1 H), 2.75-2.55 (m, 2 H), 2.0-1.15 (m, 6 H).

2-*exo*-Methylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid (32). According to the general procedure, 50 mg (0.32 mmol) of methacrylate **31**, 210 mg (3.2 mmol) of cyclopentadiene, 9 mg (0.032 mmol) of Cp_2ZrCl_2 and 1 mg (0.006 mmol) of $AgClO_4$ afforded 36 mg (74%) of an 8 : 1 mixture of **32**[30] and its 2-*endo*-methyl isomer as a white solid: ^{1}H NMR δ 6.23 (dd, 1 H, J = 5.6, 3.1 Hz), 6.09 (dd, 1 H, J = 5.6, 3.1 Hz), 3.05-3.02 (m, 1 H), 2.88-2.75 (m, 1 H), 2.43 (dd, 1 H, J = 12.1, 3.9 Hz), 1.5-1.4 (m, 2 H), 1.16 (s, 3 H), 0.86 (d, 1 H, J = 12.1 Hz); ^{13}C NMR δ 185.8, 138.8, 133.6, 50.5, 49.6, 49.1, 42.9, 37.4, 24.3.

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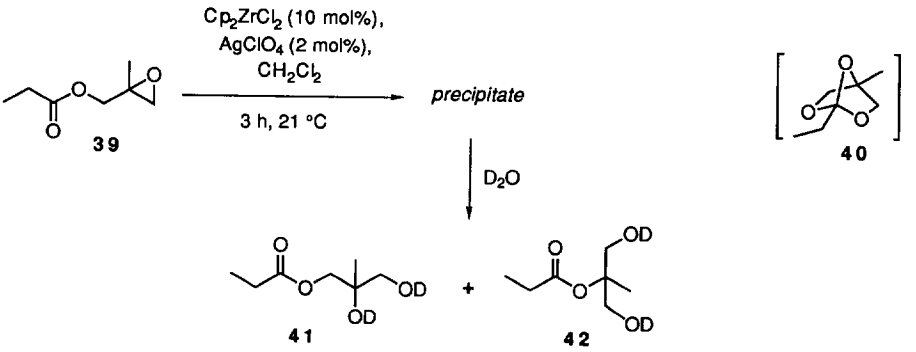
the CH_2Cl_2 solution. The precipitate was soluble in DMSO-d_6, and showed complex signals in ^1H and ^{13}C NMR. No ester carbonyl function was detectable. Upon addition of D_2O, two ester signals appeared at 174.0 and 173.8 ppm. The NMR data were in accordance with a mixture of diol esters **41** and **42**.



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