Direct Synthesis of Spiro δ-Lactones, Spiro γ-Lactones, and Alcohols from Substituted (2-Butene-1,4-diyl)magnesium Complexes

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A convenient, one-pot process for the synthesis of spiro δ- and γ-lactones and alcohols from conjugated dienes mediated by Rieke magnesium is described. This technique involves the treatment of a substituted (2-butene-1,4-diyl)magnesium complex with an epoxide or ketone at −78 °C, followed by the addition of carbon dioxide at 0 °C to room temperature. After acidic hydrolysis and subsequent warming, a spiro δ- or γ-lactone accommodating both a quaternary carbon center and vinyl moiety at the β-position is afforded in good isolated yield. Alternatively, acidic hydrolysis of the initially formed adduct at 0 °C furnishes an alcohol containing a quaternary carbon center in good to excellent chemical yield.

Introduction

In this manuscript, we describe a general approach for the synthesis of spiro δ- and γ-lactones and alcohols from 1,3-conjugated dienes. The obstacles associated with the synthesis of both spiro δ- and γ-lactones include the introduction of functionalities required for lactonization and the generation of a quaternary carbon center.[1] Considerable progress has been made in the development of more efficient synthetic routes for these classes of molecules due to the significant biological activity exhibited by them.[2] One of the more adept methods for the synthesis of δ- and γ-lactones involves the treatment of bis(bromomagnesio)alkanes with dicarboxylic anhydrides.[3]

Moreover, an assortment of synthons containing carbanions at the convenient position has been developed,[4] and their addition to aldehydes and ketones provided the skeletal arrangement which ultimately has been converted into δ- and γ-lactones. Also, 1,4- and 1,5-diols have been reported to undergo oxidative condensation upon treatment with a ruthenium catalyst and converted into the corrresponding γ- and δ-lactones, respectively.[5] In addition, radical cyclization strategies have also been reported leading to spiro δ- and γ-lactones.[6]

One of the recent significant accomplishments in organomagnesium chemistry is the development of a nontraditional approach to halide-free organomagnesium reagents based on the direct metalation of conjugated dienes with Rieke magnesium.[7] These substituted (2-butene-1,4-diyl)magnesium complexes contain two formal magnesium–carbon bonds and can serve as bis-nucleophiles.[8] This chemistry has been extended to exocyclic conjugated dienes utilizing Rieke magnesium,[9] providing a facile route to spirocarbocycles.[10] We have also developed direct syntheses of spiro δ-lactones,[11] spiro γ-lactones,[12] spiro γ-lactams,[13] and alcohols.[14] We recently reported a straightforward method to synthesize fused carbocyclic enols by reaction of 1,2-bis(methylene)cycloalkane–magnesium[15] reagents with carboxylic esters.[16] We now wish to report expanded details of this chemistry involving the direct synthesis of spiro δ- and γ-lactones.

Results and Discussion

Preparation of Substituted (2-Butene-1,4-diyl)-magnesium Complexes. In the preparation of 1,3-

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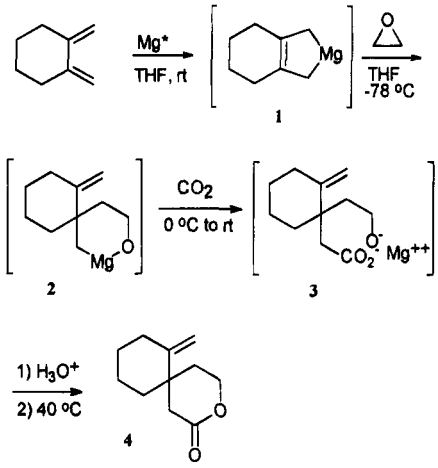
0022-3263/95/1960-5143$09.00/0

Scheme 1



diene–magnesium complexes, Rieke magnesium has been shown to be exceptional compared to ordinary magnesium in that the latter requires forcing conditions which leads to the dimerization, trimerization, and oligomerization of the 1,3-dienes. Prior to the advent of Rieke magnesium, the development of this class of organomagnesium reagents, especially the more difficult to form diene–magnesium complexes such as (2,3-dimethyl-2-butene-1,4-diyl)magnesium as well as all unsymmetrically substituted 1,3-dienes, was severely impeded. The problems associated with ordinary magnesium are avoided owing to the high reactivity of Rieke magnesium, which allows formation of the magnesium–diene complex under extremely mild conditions.

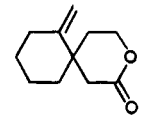
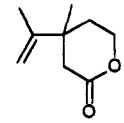
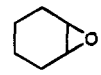
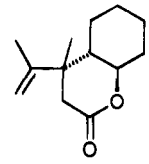
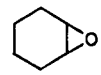
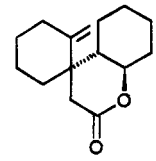
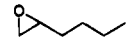
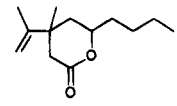
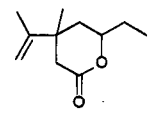
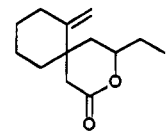
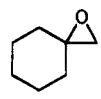
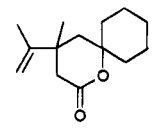
Highly reactive magnesium was prepared by the Rieke method[17] of metal activation. This method involves the reduction of anhydrous magnesium chloride with 2 equiv of lithium and a catalytic amount of naphthalene (electron carrier). The resulting finely divided black powder was treated with the appropriate diene at room temperature. The diene–magnesium complexes reported here are soluble in THF and formed between 4 and 8 h, depending on the diene incorporated.

While the magnesium complexes of 1,3-dienes appear to be bis-Grignard reagents, their reaction with various electrophiles demonstrate that they are powerful nucleophiles and exhibit a range of reactions not observed by ordinary Grignard reagents. Yet another peculiar feature of these reagents is that they react with 100% regioselectivity in the 2-position with soft carbon electrophiles. These electrophiles include imines, alkyl halides, aldehydes, esters, and lactones. In contrast, they react with 100% regioselectivity in the 1-position with harder electrophiles such as silicon, tin, or boron halides.

Synthesis of Spiro δ-Lactones and δ-Lactones. Studies indicated that treatment of the magnesium complex of 1,2-bis(methylene)cyclohexane[18] (**1**) with excess ethylene oxide at −78 °C resulted in the formation of adduct **2**, derived from a totally regioselective attack of ethylene oxide at the 2-position of the diene-magnesium complex, as shown in Scheme 1. This is agreeable with the attack mode observed with other soft carbon electrophiles. Significantly, **1** reacted with only one molecule of the ethylene oxide, even though it was added in excess. It was considered that upon warming, the intermediary Grignard reagent **2** should be able to undergo nucleophilic addition to a second electrophile. To that end, upon warming to 0 °C, **2** reacted smoothly with carbon dioxide to yield presumably the magnesium salt of a δ-hydroxy acid (**3**). Acidic hydrolysis of **3**, followed by warming to 40 °C, generated the spiro δ-lactone, 7-methylene-3-oxaspiro[5.5]undecan-2-one (**4**), containing both a quaternary carbon center and a vinyl moiety at the β-position, in 69% isolated yield (Table 1, entry 1).

Importantly, the approach described in Scheme 1 was used to prepare the fused ring spiro δ-lactone, octahydro-4-methyl-4-(1-methylethenyl)-2*H*-1-benzopyran-2-one (**11**)

Table 1. Reactions of Conjugated Diene–Magnesium Reagents with Epoxides followed by Carbon Dioxide. Formation of Spiro δ-Lactones

Entry	Diene[a]	Epoxide		Product[b]		% Yield[c]
1	A		4			69
2	B		10			39[d]
3	B		11			69[e]
4	A		12			63[e]
5	B		13			72[e]
6	B		14			58[e]
7	A		15			84[e]
8	B		16			66

[a] Dienes utilized: **A**: 1,2-dimethylenecyclohexane; **B**: 2,3-dimethyl-1,3-butadiene. [b] Elemental analysis, mass spectra, ^{1}H NMR, ^{13}C NMR, and FTIR were all consistent with the indicated formulation. [c] Isolated yields. [d] Yield was based on amount of active magnesium. [e] A 1:1 mixture of diastereomers as determined by ^{1}H NMR.

(17) (a) Furstner, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 164–189. (b) Rieke, R. D. *CRC Crit. Rev. Surf. Chem.* **1991**, *1*, 131–166.
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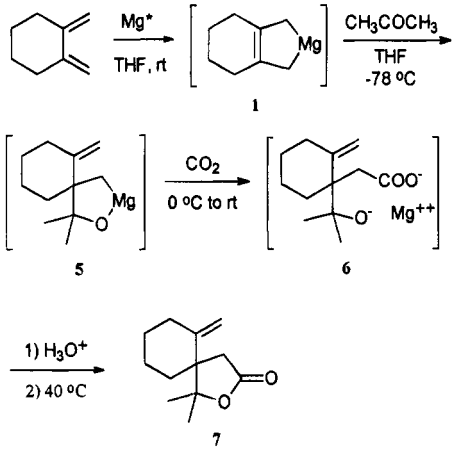
Scheme 2



in 69% isolated yield as a 1:1 mixture of diastereomers (Table 1, entry 3).

Similarly, treatment of the diene–magnesium complex **1** with cyclohexene oxide resulted in the formation of the fused tricyclic spiro δ-lactone, hexahydro-2′-methylenespiro[4*H*-1-benzopyran-4,1′-cyclohexan]-2(3*H*)-one (**12**) in 63% isolated yield as a 1:1 mixture of diastereomers (Table 1, entry 4).

High regioselectivity in the attack of unsymmetrically substituted epoxides was also realized. The formation of a δ-substituted δ-lactone, 6-butyltetrahydro-4-methyl-4-(1-methylethenyl)-2*H*-pyran-2-one (**13**) in 72% isolated yield (Table 1, entry 5), illustrates that the attack by the diene–magnesium complex of 1,2-epoxyhexane ocurred at the less sterically hindered carbon. Synthetic routes to δ-substituted δ-lactones are important because molecules of this class include many natural products that reveal significant biological activity.[19] For other examples of this regioselective attack of unsymmetric epoxides, see Table 1 (entries 6–8).

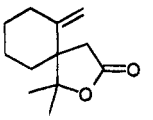
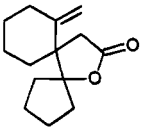
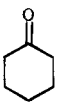
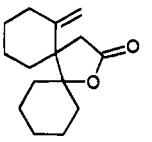
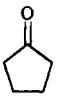
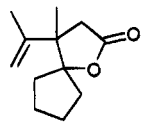
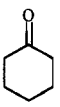
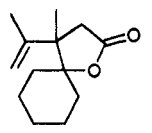
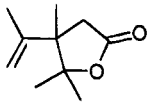
Significantly, this approach was equally applicable to open-chain diene-magnesium complexes. For example, treatment of (2,3-dimethyl-2-butene-1,4-diyl)magnesium with 1-oxaspiro[2.5]octane afforded the spiro δ-lactone, 4-methyl-4-(1-methylethenyl)-1-oxaspiro[5.5]undecan-2-one (**16**) in 66% isolated yield (Table 1, entry 8).

Synthesis of Spiro γ-Lactones and γ-Lactones. Scheme 2 illustrates a route for spiro γ-lactone synthesis from the magnesium complex of 1,2-dimethylenecyclohexane (**1**). Initially, it was observed that treatment of **1** with 1 equiv of acetone at −78 °C resulted in the formation of intermediate **5** derived from the incorporation of one molecule of acetone with the diene–magnesium complex. Again, the attack by the diene–magnesium complex of the acetone was totally regioselective for the 2-position of the complex. Intermediate **5** reacted cleanly with carbon dioxide at 0 °C to room temperature to afford presumably the magnesium salt of a γ-hydroxy acid (**6**). After acidic hydrolysis followed by slight warming, the spiro γ-lactone, 4,4-dimethyl-6-methylene-3-oxaspiro[4.5]decan-2-one (**7**), accommodating a quaternary carbon center and a vinyl group at the β-position, was obtained in 68% isolated yield (Table 2, entry 1).

It is imperative to note that when **1** was treated with only 1 equiv of acetone, no product derived from the reaction of **1** with two molecules of acetone was observed.

(19) Kobayashi, K.; Sasaki, A.; Kanno, Y.; Siginome, H. *Tetrahedron* **1991**, *47*, 7245–7258.

Table 2. Reactions of Conjugated Diene–Magnesium Reagents with Ketones Followed by Carbon Dioxide. Formation of Spiro γ-Lactones

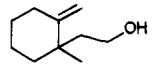
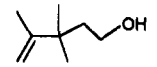
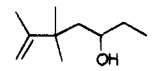
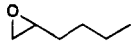
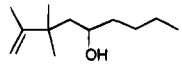
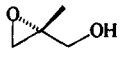
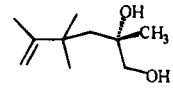
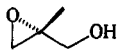
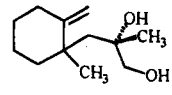
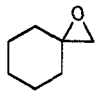
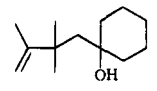
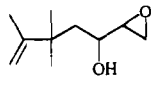
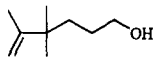
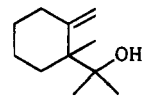
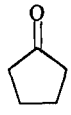
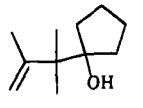
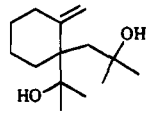
Entry	Diene[a]	Ketone	Product[b]	% Yield[c]
1	A		7 	68
2	A		17 	66
3	A		18 	60
4	B		19 	68
5	B		20 	61
6	B		21 	59

[a] Dienes utilized: **A**: 1,2-dimethylenecyclohexane; **B**: 2,3-dimethyl-1,3-butadiene. [b] Elemental analysis, mass spectra, ^{1}H NMR, ^{13}C NMR, and FTIR were all consistent with the indicated formulation. [c] Isolated yields.

This indicated that in the presence of **1**, the initially formed adduct **5** did not add competitively to the unreacted acetone. This feature allowed that both acetone and subsequently added carbon dioxide were delivered to the diene–magnesium complex at the desired positions. However, if excess acetone was used, **1** was found to undergo further nucleophilic attack of the ketone, yielding the diol 1-(1-hydroxy-1-methylethyl)-1-(2-hydroxy-2-methylpropyl)-2-methylenecyclohexane (**32**) in 50% yield (Table 3, entry 12). As a result, it is paramount to use not more than 1 equiv of acetone for the synthesis of **7**.

Importantly, the approach described in Scheme 2 was also used to prepare spiro γ-lactones accommodating two spiro centers. Representative examples of this dispiroannulation are listed in Table 2 (entries 2 and 3). For example, when **1** was treated with cyclopentanone at −78 °C, followed by charging the reaction mixture with carbon dioxide at 0 °C to room temperature and lactonization,

Table 3. Reactions of Conjugated Diene–Magnesium Reagents with Epoxides Followed by Acidic Hydrolysis. Formation of Alcohols

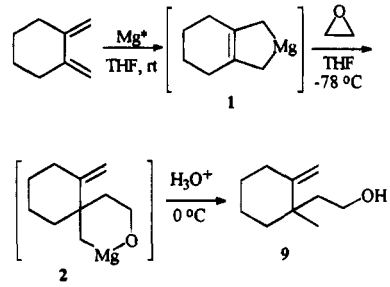
Entry	Diene[a]	Epoxide		Product[b]	% Yield[c]
1	A		9		86
2	B		22		60[d]
3	B		23		64
4	B		24		90
5	B		25		68[e]
6	A		26		62[e,f]
7	B		27		77
8	B		28		72
9	B		29		62
10	A		30		76
11	B		31		78
12	A		32		50[g]

[a] Dienes utilized: **A**: 1,2-dimethylenecyclohexane; **B**: 2,3-dimethyl-1,3-butadiene. [b] Elemental analysis, mass spectra, ^{1}H NMR, ^{13}C NMR, and FTIR were all consistent with the indicated formulation. [c] Isolated yields. [d] Yield was based on amount of active magnesium. [e] 0.5 equiv of epoxide was used. [f] A 1:1 mixture of diastereomers as determined by ^{1}H NMR. [g] 2 equiv of acetone was used.

7-methylene-14-oxadispiro[4.0.5.3]tetradecan-13-one (**17**) was produced in 66% isolated yield (Table 2, entry 2).

When this approach was applied to the magnesium complexes of acyclic 1,3-dienes, it provided a facile route to both spiro γ-lactones and γ-lactones. Treatment of (2,3-dimethyl-2-butene-1,4-diyl)magnesium with cyclopentanone at −78 °C, followed by carbon dioxide addition at 0 °C to room temperature and workup, a spiro γ-lactone, 4-methyl-4-(1-methylethenyl)-1-oxaspiro[4.4]-nonan-2-one (**19**) was afforded in 68% isolated yield (Table 2, entry 4).

Scheme 3



The use of acyclic ketones as initial electrophiles produced substituted γ-lactones. For example, treatment of (2,3-dimethyl-2-butene-1,4-diyl)magnesium with acetone followed by carbon dioxide afforded β,γ,γ-trimethyl-β-(1-methylethenyl)-γ-butyrolactone (**21**) in 59% isolated yield (Table 2, entry 6).

Synthesis of Alcohols. The construction of a quaternary carbon center is not a trivial undertaking in organic synthesis. Multiple synthetic steps are often required to generate a quaternary carbon. In the formation of the spiro δ- and γ-lactones reported here, the second electrophile introduced to the intermediary Grignard reagent was carbon dioxide. Subsequent lactonization generated the lactones. Instead of using carbon dioxide as the second electrophile, we concluded that the initially formed adduct could simply be protonated, affording an alcohol containing a quaternary carbon center.

As shown in Scheme 3, when the metallocycle **1** was treated with excess ethylene oxide, followed by protonation at 0 °C of intermediate (**2**), an alcohol 2-(β-hydroxyethyl)-2-methyl-1-cyclohexylidene (**9**), containing a quaternary carbon center, was generated in 86% isolated yield (Table 3, entry 1). Again, as in prior cases employing unsymmetrical epoxides, the attack of the diene–magnesium complex was entirely regioselective for the less hindered carbon of the epoxide, as indicated by the high isolated yields of the alcohols shown in Table 3 (entries 3, 4, and 7). When (2,3-dimethyl-2-butene-1,4-diyl)magnesium was treated with 1,2-epoxyhexane followed by acidic hydrolysis, the secondary alcohol, 2,3,3-trimethyl-1-nonen-5-ol (**24**) was afforded in 90% isolated yield (Table 3, entry 4).

When the unprotected unsymmetric chiral epoxide, (*R*)-2-methylglycidol,[20] was added to (2,3-dimethyl-2-butene-1,4-diyl)magnesium at −78 °C followed by protonation at 0 °C, the diol, 2,4,4,5-tetramethyl-(*S*)-5-hexene-1,2-diol (**25**) was afforded in 68% isolated yield (Table 3, entry 5).[21] Analogously, treatment of the metallocycle derived from 1,2-dimethylenecyclohexane with this chiral epoxide resulted in the formation of the diol, 2-methyl-3-(1-methyl-2-methylenecyclohexyl)-(*S*)-1,2-propanediol (**26**) in 62% isolated yield, as a 1:1 mixture of diastereomers (Table 3, entry 6). It was hoped that the attack of **1** could be induced to produce a single diastereomer. Unfortu-

(20) (*R*)-2-Methylglycidol was purchased from the Eastman Kodak Co.

(21) A 0.5 equiv amount of the chiral epoxide was added relative to the metallocycle. The first molecule of metallocycle presumably deprotonates the hydroxyl group and the second molecule attacks the deprotonated epoxide.

nately, the chiral epoxide did not have any significant influence on the diastereoselectivity of the attacking diene-magnesium complex. However, the reactions of an excess of the two metallocycles with (*R*)-2-methylglycidol proved that they will attack an epoxide in the presence of an unprototected proximal hydroxyl group with no epimerization of the chiral center in the epoxide.

A molecule containing both a hydroxyl and an epoxide group was also obtained when a diepoxide was added to the metallocycle. When (2,3-dimethyl-2-butene-1,4-diyl)-magnesium was treated with (±)-1,3-butadiene diepoxide at −78 °C followed by acidic hydrolysis at 0 °C, the secondary alcohol accommodating an epoxide, 2,3,3-trimethyl-6,7-epoxy-1-hepten-5-ol (**28**), was generated in 72% isolated yield (Table 3, entry 8). The initially formed Grignard adduct was not found to undergo nucleophilic attack of the proximal epoxide group, either at 0 °C or at refluxing conditions. This again proves that the 2-position of the diene−magnesium complexes is much more nucleophilic than the 1-position for these carbon electrophiles.

The less strained cyclic ether, trimethylene oxide, is less electrophilic than an epoxide.[22] The ring opening of this compound by traditional Grignard reagents has been reported by refluxing in benzene for several hours.[23] However, when the reactions were performed in the presence of 10% copper iodide at 20 °C for 20 h, the alcohols were formed in acceptable yield.[24] We observed that when trimethylene oxide was used as the initial electrophile, a primary alcohol, 2,3,3-trimethyl-1-hexen-6-ol (**29**) was afforded in 62% isolated yield (Table 3, entry 9). The fact that **29** formed at −78 °C in 30 min with no additive again demonstrates the exceptional nucleophilicity of these diene−magnesium complexes. However, treatment of the initial adduct with carbon dioxide and attempted lactonization to a seven-membered lactone ring was fruitless using our lactonization procedure.

Finally, addition of both cyclic and acyclic ketones followed by hydrolysis at 0 °C resulted in the formation of tertiary alcohols. For example, when (2,3-dimethyl-2-butene-1,4-diyl)magnesium was treated with cyclopentanone followed by acidic hydrolysis, 1-(1,1,2-trimethyl-2-propenyl)cyclopentanol (**31**) was afforded in 78% yield (Table 3, entry 11). Similarly, when the metallocycle derived from 1,2-dimethylenecyclohexane was treated with acetone at −78 °C followed by acidic hydrolysis, 1-(1-hydroxy-1-methylethyl)-1-methyl-2-methylenecyclohexane (**30**) was produced in 76% isolated yield (Table 3, entry 10).

Conclusion

The general procedure for the direct synthesis of spiro δ- and γ-lactones can be regarded as a molecular assembling operation in which three independent species, *i.e.*, a conjugated diene, an epoxide (or ketone), and carbon dioxide, mediated by Rieke magnesium, are converted into a complex organic molecule in a well-controlled fashion. The higher degree of nucleophilicity demonstrated by the 2-position of the diene−magnesium complex is exploited in these transformations. In the process, the introduction of both a hydroxyl and a carboxyl group required for lactonization is accomplished in one direct synthetic procedure. The resulting lactones also contain a quaternary carbon center as well as a vinyl moiety at the β-position. The vinyl group could be used for subsequent elaboration of the molecules. Alternatively, acidic hydrolysis of the initially formed adduct funishes an alcohol containing a quaternary carbon center in good to excellent chemical yield. Further studies are currently underway to define the scope and limitations of the process and to extend the present approach to include the synthesis of optically active spiro δ- and γ-lactones. Also, the discovery of novel diene−Rieke metal complexes which may find utility in organic synthesis is presently being investigated.

Experimental Section

General Methods. NMR spectra were obtained from a 360, 200, 500, or 300 spectrometer. All NMR samples were dissolved in $CDCl_3$. ^1H NMR spectral chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Fully decoupled ^{13}C NMR chemical shifts (δ) were reported in reference to the 77.00 ppm peak for $CDCl_3$. Mass spectra were performed by the Nebraska Center for Mass Spectrometry at the University of Nebraska−Lincoln. Elemental analyses were performed by Desert Analytics (Tucson, AZ).

All manipulations were carried out under an atmosphere of argon on a dual manifold vacuum/argon system. The Linde prepurified grade argon was further purified by passage over a BASF R3-11 catalyst column at 150 °C, a phosphorus pentoxide column, and a column of granular potassium hydroxide. Lithium, naphthalene, and $MgCl_2$ were weighed out and charged into reaction flasks under argon in a Vacuum Atmospheres Co. drybox. Tetrahydrofuran was distilled immediately before use from Na/K alloy under an atmosphere of argon.

Gas chromatographic analyses were done on a Hewlett-Packard 5890A chromatograph using stainless steel columns (12 ft x 1/8 in.) packed with GP 10% SP 2100 on 100/120 Supelcoport. Analytical thin-layer chromatography was performed using Merk 5735 indicating plates precoated with silica gel 60 F_{254} (layer thickness 0.2 mm). The product spots were visualized with either iodine or a solution of vanillin. Preparative thin-layer chromatographic separations were obtained using Analtech silical gel GF (layer thickness 2 mm) preparative plates. Liquid chromatographic purifications were performed by flash column chromatography using glass columns packed with Merck silical gel 60 (230−400 mesh). Low-temperature conditions were obtained by utilizing dry ice/acetone baths.

Preparation of Highly Reactive Magnesium (Mg*). Highly reactive magnesium was prepared by the reduction of anhydrous magnesium chloride with lithium using naphthalene as the electron carrier. In a typical preparation, lithium (9.68 mmol), naphthalene (1.48 mmol), and anhydrous magnesium chloride (4.71 mmol) were *vigorously* stirred in freshly distilled THF (15 mL) for 3.5 h at room temperature. After the addition of 10 mL of THF, the newly formed magnesium slurry (black powder) was allowed to settle for 2 h, and the supernatant was drawn off via cannula, leaving 4 mL of solvent covering the Mg*. Freshly distilled THF was added (10 mL), followed by the appropriate 1,3-diene. A volume of 1.5 mL of freshly distilled 2,3-dimethyl-1,3-butadiene (excess) was added to the magnesium. 1,2-Dimethylenecyclohexane was added in a Mg*/diene = 1.5−1.8:1. (Note: The number of millimoles of Mg* cited in this paper refers to the theoretical amount possible, based on the original amount of anhydrous magnesium chloride).

Preparation of Spiro δ-Lactone: 7-methylene-3-oxaspiro[5.5]undecan-2-one (4). 1,2-Dimethylenecyclohexane (0.330 g, 3.05 mmol) was added via a disposable syringe to the active magnesium (4.68 mmol) in freshly distilled THF (15 mL). After being stirred at ambient temperature for 4 h,

(22) Millon, J.; Linstrumelle, G. *Tetrahedron Lett.* **1976**, *14*, 1095−1098.
(23) Searles, S. *J. Am. Chem. Soc.* **1951**, *73*, 124−127.
(24) Huynh, C.; Derguini-Boumechal, F.; Linstrumelle, G. *Tetrahedron Lett.* **1979**, *17*, 1503−1506.

the reaction mixture was allowed to stand until the solution became transparent (ca. 2h). The yellow THF solution of the magnesium complex was then separated from the excess magnesium by cannulating the solution into another flask. The THF solution of newly formed magnesium complex of 1,2-dimethylenecyclohexane was cooled to −78 °C using a dry ice/acetone bath. Ethylene oxide (1 mL) was condensed into a small vial capped with a rubber septum (at −78 °C) and was subsequently added to the reaction mixture via cannula. The mixture was stirred at −78 °C for 30 min, gradually warmed to 0 °C, and charged with purified carbon dioxide for 10 min at 0 °C and continued for 10 min at room temperature. An aqueous solution of 3 N HCl (10 mL) was added via a syringe at 0 °C. The reaction mixture was then warmed to 40 °C for 1 h. After cooling to room temperature, the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and water (1 × 20 mL) and then dried over anhydrous $MgSO_4$. Evaporation of solvents and flash chromatography of the crude product using hexanes/ethyl acetate afforded 7-methylene-3-oxaspiro[5.5]undecan-2-one **(4)** (0.378 g) in 69% isolated yield: ^1H NMR δ 4.91 (s, 1H), 4.66 (s, 1H), 4.40−4.00 (m, 2H), 2.73−2.67 (m, 1H), 2.36−2.05 (m, 4H), 1.82−1.50 (m, 5H), 1.49−1.20 (m, 2H); ^{13}C NMR δ 171.0, 151.1, 108.6, 66.0, 41.7, 39.3, 38.9, 32.3, 30.7, 27.7, 21.3; IR (neat) 3082, 2929, 2858, 1732, 1639, 1448, 1404 cm^{-1}; HRMS calcd for $C_{11}H_{16}O_2$ 180.1151, found 180.1151. Anal. Calcd: C, 73.35; H, 8.95. Found: C, 73.17; H, 9.19.

4-Methyl-4-(1-methylethenyl)-2*H*-pyran-2-one (10): 39% yield; ^1H NMR δ 4.93 (s, 1H), 4.79 (s, 1H), 4.37−4.23 (m, 2H), 2.78−2.72 (m, 1H), 2.39−2.34 (m, 1H), 2.10−1.86 (m, 1H), 1.98 (s, 3H), 1.83−1.72 (m, 4H); ^{13}C NMR δ 170.7, 147.9, 111.3, 66.3, 41.9, 37.9, 32.7, 26.2, 18.5; IR (neat) 3086, 2951, 2871, 1738, 1637, 1448, 1402 cm^{-1}; HRMS calcd for $C_9H_{14}O_2$ 154.0994, found 154.0993. Anal. Calcd: C, 70.15; H, 9.16. Found: C, 69.96; H, 9.17.

Octahydro-4-methyl-4-(1-methylethenyl)-2*H*-1-benzopyran-2-one (11): 69% yield (1:1 mixture of diastereomers); ^1H NMR δ 5.06−4.71 (m, 4H), 4.16−4.02 (m, 2H), 2.81−2.65 (m, 2H), 2.31−2.21 (m, 2H), 2.20−2.12 (m, 2H), 1.82−1.72 (m, 9H), 1.71−1.60 (m, 3H), 1.59−1.20 (m, 7H), 1.19−0.85 (m, 6H), 1.10−0.83 (m, 3H); ^{13}C NMR δ 171.0, 170.9, 147.3, 146.7, 114.1, 114.0, 112.3, 79.3, 79.4, 49.2, 44.3, 44.2, 42.5, 44.0, 32.8, 32.77, 32.6, 25.8, 25.7, 25.6, 25.2, 24.7, 24.1, 24.0, 18.9, 18.6; IR (neat) 3084, 2939, 2863, 1737, 1633, 1450, 1381 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2$ 208.1464, found 208.1463. Anal. Calcd: C, 75.02; H, 9.68. Found: C, 75.07; H, 9.84.

Hexahydro-2′-methylenespiro[4*H*-1-benzopyran-4,1′-cyclohexan]-2(3*H*)-one (12): 63% yield (1:1 mixture of diastereomers); ^1H NMR δ 5.03−4.65 (m, 4H), 4.22−4.02 (m, 2H), 3.51−3.48 (m, 1H), 3.01−2.79 (m, 2H), 2.19−2.00 (m, 9H), 1.99−1.65 (m, 10H), 1.64−1.42 (m, 7H), 1.40−1.20 (m, 9H); ^{13}C NMR δ 172.5, 170.6, 150.2, 149.9, 111.6, 108.0, 80.0, 78.8, 49.0, 45.6, 44.1, 41.3, 40.7, 40.2, 40.1, 35.9, 33.4, 32.8, 32.6, 29.8, 28.1, 26.4, 26.2, 26.0, 25.4, 24.6, 24.5, 24.1, 22.5, 21.0; IR (neat) 3081, 2952, 2852, 1724, 1633, 1448, 1419, 1383 cm^{-1}; HRMS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1622. Anal. Calcd: C, 76.94; H, 9.47. Found: C, 76.58; H, 9.34.

6-Butyltetrahydro-4-methyl-4-(1-methylethenyl)-2*H*-pyran-2-one (13): 72% yield (1:1 mixture of diastereomers); ^1H NMR δ 4.93−4.77 (m, 4H), 4.41−4.39 (m, 1H), 4.20−4.10 (m, 1H), 2.86−2.78 (m, 1H), 2.50−2.45 (m, 2H), 2.27−2.20 (m, 1H), 2.05−1.97 (m, 1H), 1.86−1.77 (m, 1H), 1.75−1.72 (m, 6H), 1.71−1.25 (m, 14H), 1.24−1.17 (s, 3H), 1.16−1.12 (s, 3H), 0.95−0.85 (m, 6H); ^{13}C NMR δ 171.8, 171.5, 150.4, 147.7, 112.1, 109.4, 77.7, 77.2, 42.0, 41.3, 39.2, 39.0, 38.3, 37.4, 36.5, 35.7, 35.4, 27.8, 27.0, 26.9, 24.6, 22.5, 22.4, 18.9, 18.8, 13.8; IR (neat) 3087, 2956, 2931, 2871, 1735, 1639, 1455, 1380 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.19; H, 10.58.

6-Ethyltetrahydro-4-methyl-4-(1-methylethenyl)-2*H*-pyran-2-one (14): 58% yield (1:1 mixture of diastereomers); ^1H NMR δ 4.93−4.77 (m, 4H), 4.36−4.26 (m, 1H), 4.24−4.10 (m, 1H), 2.87−2.81 (m, 1H), 2.49 (m, 2H), 2.28−2.22 (m, 1H), 2.05−1.99 (m, 1H), 1.86−1.55 (m, 12H), 1.46−1.37 (m, 1H), 1.21 (s, 3H), 1.15 (s, 3H), 1.06−0.96 (m, 6H); ^{13}C NMR δ 171.6, 171.3, 150.3, 147.6, 111.9, 109.3, 78.8, 78.3, 41.9, 41.2, 38.6, 38.4, 38.1, 37.2, 28.8, 28.5, 27.7, 24.5, 18.8, 18.7, 9.2, 9.1; IR (neat) 3087, 2960, 2879, 1743, 1639, 1456 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.46; H, 10.05.

6-Ethyl-7-methylene-3-oxaspiro[5.5]undecan-2-one (15): 84% yield (1:1 mixture of diastereomers); ^1H NMR δ 4.95−4.58 (m, 4H), 4.34−4.22 (m, 1H), 4.15−4.05 (m, 1H), 2.76−2.66 (m, 1H), 2.60−2.47 (m, 2H), 2.32−2.03 (m, 7H), 1.88−1.77 (m, 1H), 1.76−1.53 (m, 10H), 1.52−1.24 (m, 7H), 1.07−0.95 (m, 6H); ^{13}C NMR δ 174.0, 171.6, 153.5, 151.1, 108.9, 106.1, 78.4, 77.6, 41.8, 40.5, 40.4, 38.9, 38.0, 37.3, 37.0, 35.9, 32.6, 32.5, 28.5, 28.4, 27.8, 27.5, 21.6, 21.2, 9.2, 9.1; IR (neat) 3083, 2965, 2937, 2881, 2859, 1733, 1641, 1448, 1386 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.95; H, 9.68. Found: C, 74.91; H, 9.83.

4-Methyl-4-(1-methylethenyl)-1-oxaspiro[5.5]undecan-2-one (16): 66% yield; ^1H NMR δ 4.82−4.80 (m, 2H), 2.75 (dd, J = 16.4, 1.7 Hz, 1H), 2.36 (dd, J = 16.4, 0.7 Hz, 1H), 2.08 (dd, J = 14.0, 1.7 Hz, 1H), 1.78 (m, 4H), 1.72−1.44 (m, 10H), 1.15 (s, 3H); ^{13}C NMR δ 171.3, 149.3, 110.6, 82.5, 41.3, 40.6, 27.9, 24.8, 21.9, 21.8, 21.7, 19.1; IR (neat) 3463, 3448, 3087, 2927, 2864, 1734, 1652, 1637, 1448, 1400, 1375, 1358, 1303, 1278, 1240, 1198, 999, 897 cm^{-1}; HRMS calcd for $C_{14}H_{22}O_2$ 222.1619, found 222.1614.

Preparation of Spiro γ-Lactone: 4,4-Dimethyl-6-methylene-3-oxaspiro[4.5]decan-2-one (7). 1,2-Dimethylenecyclohexane (0.239 g, 2.21 mmol) was added via a disposable syringe to the activated magnesium (3.53 mmol) in THF (20 mL). After being stirred at room temperature for 4 h, the reaction mixture was allowed to stand until the solution became transparent (ca. 2 h). The yellow THF solution of the complex was then separated from the excess magnesium by cannulating the solution to another flask. The THF solution of newly formed magnesium complex of 1,2-dimethylenecyclohexane was cooled to −78 °C using a dry ice/acetone bath, and acetone (0.122 g, 2.10 mmol) was slowly added via syringe. The mixture was stirred at −78 °C for 10 min and then gradually warmed to 0 °C. The reaction mixture was slightly heated at 40 °C for 1 h. After cooling to room temperature, the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and brine (20 mL) and dried over anhydrous $MgSO_4$. Evaporation of solvents and flash chromatography of the crude product using hexanes/ethyl acetate afforded 4,4-dimethyl-6-methylene-3-oxaspiro[4.5]decan-2-one **(7)** (0.279 g) in 68% isolated yield: ^1H NMR δ 4.99 (s, 1H), 4.79 (s, 1H), 2.97 (d, J = 17.2 Hz, 1H), 2.31 (d, J = 17.2 Hz, 1H), 2.18−2.07 (m, 2H), 1.92−1.83 (m, 1H), 1.68−1.55 (m, 3H), 1.42−1.35 (m, 2H), 1.53 (s, 3H), 1.33 (s, 3H); ^{13}C NMR δ 175.2, 148.4, 111.2, 88.3, 50.0, 42.8, 34.8, 34.7, 27.5, 26.1, 25.6, 22.9; IR (neat) 3081, 2981, 2937, 2860, 1782, 1639, 1469, 1456, 1389, 1373, 1263, 1134, 1119, 964 cm^{-1}; HRMS calcd for $C_{12}H_{18}O_2 - CH_3$ 179.1072, found 179.1067.

7-Methylene-14-oxadispiro[4.0.5.3]tetradecan-13-one (17): 66% yield; ^1H NMR δ 4.96 (s, 1H), 4.77 (s, 1H), 2.94 (d, J = 16.7 Hz, 1H), 2.30 (d, J = 16.7 Hz, 1H), 2.22−1.60 (m, 14H), 1.50−1.36 (m, 2H); ^{13}C NMR δ 175.3, 148.4, 110.6, 99.9, 49.0, 43.2, 35.2, 35.1, 34.3, 27.3, 22.9, 22.4, 21.9; IR (neat) 3084, 2937, 2873, 2858, 1772, 1637, 1450, 1431, 1336, 1246, 1167, 1142, 1115, 957, 939, 897 cm^{-1}; HRMS calcd for $C_{14}H_{20}O_2$ 220.1464, found 220.1474.

1-Methylene-13-oxadispiro[5.0.5.3]pentadecan-14-one (18): 60% yield; ^1H NMR δ 4.99 (s, 1H), 4.77 (s, 1H), 2.97 (d, J = 17.2 Hz, 1H), 2.38−2.32 (m, 1H), 2.24 (d, J = 17.2 Hz, 1H), 2.23−2.12 (m, 2H), 2.05−1.97 (m, 1H), 1.92−1.84 (m, 1H), 1.82−1.72 (m, 2H), 1.71−1.57 (m, 7H), 1.43−1.26 (m, 4H); ^{13}C NMR δ 175.4, 148.4, 111.5, 89.5, 50.5, 42.7, 34.9, 34.5, 34.3, 34.1, 27.4, 25.1, 22.9, 22.4, 22.3; IR (KBr) 3087, 2974, 2941, 2900, 2864, 2850, 1765, 1635, 1450, 1429, 1371, 1273, 1252, 1232, 1138, 960, 947, 930, 891 cm^{-1}; HRMS calcd for $C_{15}H_{22}O_2 - C_6H_{10}$ 136.0888, found 136.0893.

4-Methyl-4-(1-methylethenyl)-1-oxaspiro[4.4]nonan-2-one (19): 68% yield; ^1H NMR δ 4.93 (s, 1H), 4.82 (s, 1H), 2.97 (d, J = 16.6 Hz, 1H), 2.34 (d, J = 16.5 Hz, 1H), 1.97−1.92 (m, 2H), 1.86−1.83 (m, 2H), 1.80 (s, 3H), 1.75−1.67 (m, 4H), 1.27 (s, 3H); ^{13}C NMR δ 175.3, 146.0, 113.1, 99.9, 49.0, 42.6, 34.6,

33.9, 23.9, 23.5, 22.7, 20.8; IR (neat) 3087, 2966, 2873, 1780, 1637, 1452, 1435, 1379, 1336, 1242, 1167, 1111, 974, 933, 899 cm^{-1}; HRMS calcd for $C_{12}H_{18}O_2 - C_5H_8O$ 110.0732, found 110.0736.

4-Methyl-4-(1-methylethenyl)-1-oxaspiro[4.5]decan-2-one (20): 61% yield; ^1H NMR δ 4.99 (s, 1H), 4.81 (s, 1H), 3.06 (d, J = 16.3 Hz, 1H), 2.26 (d, J = 16.8 Hz, 1H), 2.01–1.94 (m, 1H), 1.82 (s, 3H), 1.73–1.47 (m, 9H), 1.19 (s, 3H); ^{13}C NMR δ 175.3, 145.4, 113.4, 88.6, 50.2, 41.5, 32.0, 31.5, 25.0, 22.5, 21.8, 21.6, 21.2; IR (neat) 3087, 2937, 2864, 1772, 1637, 1448, 1427, 1373, 1267, 1225, 1147, 1119, 958, 949, 931, 924 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2 - CO$ 180.1514, found 180.1512.

β,γ,γ-Trimethyl-β-(1-methylethenyl)-γ-butyrolactone (21): 59% yield; ^1H NMR δ 4.95–4.83 (m, 2H), 3.05 (d, J = 16.8 Hz, 1H), 2.29 (d, J = 16.8 Hz, 1H), 1.81 (s, 3H), 1.47 (s, 3H), 1.28 (s, 3H), 1.24 (s, 3H); ^{13}C NMR δ 174.9, 145.5, 113.1, 87.5, 49.9, 41.8, 24.0, 23.4, 22.2, 20.6; IR (neat) 3087, 2974, 2927, 2873, 1772, 1637, 1456, 1425, 1392, 1377, 1257, 1184, 1138, 1093, 1078, 972, 962, 935, 922, 899 cm^{-1}; HRMS calcd for $C_{10}H_{16}O_2 - C_3H_6O$ 110.0731, found 110.0728.

Preparation of Alcohol: 2-(β-Hydroxyethyl)-2-methyl-1-cyclohexylidene (9). 1,2-Dimethylenecyclohexane (0.211 g, 1.95 mmol) was added via a disposable syringe to the active magnesium (3.98 mmol) in freshly distilled THF (15 mL). After being stirred at ambient temperature for 4 h, the reaction mixture was allowed to stand until the solution became transparent (ca. 2 h). The yellow THF solution of the magnesium complex was then separated from the excess magnesium by cannulating the solution into another flask. The THF solution of newly formed magnesium complex of 1,2-dimethylenecyclohexane was cooled to −78 °C using a dry ice/acetone bath. Ethylene oxide (1 mL) was condensed into a small vial capped with a rubber septum (at −78 °C) and was subsequently added to the reaction mixture via cannula. The mixture was stirred at −78 °C for 30 min and gradually warmed to 0 °C and quenched by addition of aqueous solution of 3 N HCl (10 mL) at 0 °C. After warming to room temperature, the mixture was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and water (1 × 20 mL) and then dried over anhydrous $MgSO_4$. Evaporation of solvents and flash chromatography of the crude product using hexanes/ethyl acetate afforded 2-(β-hydroxyethyl)-2-methyl-1-cyclohexylidene **(9)** in 86% isolated yield: ^1H NMR δ 4.72–4.63 (m, 2H), 3.60–3.54 (m, 2H), 2.32 (s, 1H), 2.25–2.05 (m, 3H), 1.80–1.19 (m, 7H), 1.07 (s, 3H); ^{13}C NMR δ 155.2, 106.8, 59.6, 41.1, 39.6, 38.2, 33.1, 28.4, 25.7, 21.8; IR (neat) 3305 (br), 3081, 2925, 2854, 2840, 1635, 1448, 1371 cm^{-1}; HRMS calcd for $C_{10}H_{18}O$ 154.1358, found 154.1352. Anal. Calcd: C, 77.92; H, 11.77. Found: C, 77.67; H, 11.82.

2,3,3-Trimethyl-1-penten-5-ol (22): 60% yield; ^1H NMR δ 4.77–4.76 (m, 2H), 3.58 (t, J = 7.2 Hz, 2H), 1.86 (s, 1H), 1.77 (s, 3H), 1.71–1.66 (t, 2H), 1.1 (s, 6H); ^{13}C NMR δ 152.3, 109.7, 60.0, 42.9, 37.6, 27.4, 19.4; IR (neat) 3307 (br), 3085, 2965, 2854, 1633, 1447, 1400 cm^{-1}; HRMS calcd for $C_8H_{16}O$ 128.1202, found 128.0630. Anal. Calcd: C, 75.00; H, 12.59. Found: C, 74.86; H, 12.73.

2,3,3-Trimethyl-1-hepten-5-ol (23): 64% yield; ^1H NMR δ 4.87–4.83 (m, 2H), 3.65–3.60 (m, 1H), 2.04 (d, J = 7.4 Hz, 1H), 1.82 (s, 3H), 1.77–1.64 (m, 1H), 1.48–1.41 (m, 3H), 1.16 (s, 3H), 1.09 (s, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ 153.9, 110.3, 70.8, 47.5, 38.2, 31.1, 28.9, 26.7, 19.7, 9.9; IR (neat) 3288 (br), 3085, 2964, 2931, 2867, 1633, 1461, 1398. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.95; H, 12.53.

2,3,3-Trimethyl-1-nonen-5-ol (24): 90% yield; ^1H NMR δ 4.76–4.73 (m, 2H), 3.59–3.54 (m, 1H), 2.25 (s (br), 1H), 1.71 (s, 3H), 1.58–1.53 (m, 1H), 1.34–1.18 (m, 7H), 1.04 (s, 3H), 1.01 (s, 3H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 153.4, 109.9, 69.1, 47.8, 38.1, 38.0, 28.4, 27.6, 26.7, 22.5, 19.4, 13.8; IR (neat) 3373 (br), 3089, 2958, 2929, 2871, 2859, 1635, 1466, 1398. Anal. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12. Found: C, 78.23; H, 13.26.

2,4,4,5-Tetramethyl-(S)-5-hexene-1,2-diol (25): 68% yield; ^1H NMR δ 4.90–4.84 (m, 2H), 3.40–3.27 (m, 2H), 2.76 (s (br), 2H), 1.88–1.83 (m, 4H), 1.59–1.54 (m, 1H), 1.21 (s, 3H), 1.19 (s, 3H), 1.16 (s, 3H); ^{13}C NMR δ 153.6, 110.4, 74.1, 70.9, 46.7, 38.7, 29.7, 29.2, 24.7, 19.9; IR (neat) 3383 (br), 3090, 2962, 2929, 2877, 1633, 1458, 1379, 1169, 1047, 891 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.71; H, 11.71. Found: C, 69.86; H, 11.61.

2-Methyl-3-(1-methyl-2-methylenecyclohexyl)-(S)-1,2-propanediol (26): 62% yield; ^1H NMR δ 4.89 (s, 1H), 4.86 (s, 1H), 3.33–3.11 (m, 2H), 2.60 (s, 1H), 2.54–2.49 (m, 1H), 2.43–2.37 (m, 1H), 2.21–2.18 (m, 2H), 1.93–1.36 (m, 7H), 1.30 (s, 3H), 1.26 (s, 3H); ^{13}C NMR δ 157.3, 108.6, 74.2, 71.4, 44.6, 43.5, 36.5, 33.7, 28.9, 27.9, 25.9, 21.9; IR (neat) 3542 (br), 3238, 3081, 3000, 2883, 2840, 1635, 1464, 1456, 1381, 1155, 1043, 895, 735 cm^{-1}; HRMS calcd for $C_{12}H_{22}O_2$ 198.1619, found 198.1622.

1-(2,2,3-Trimethyl-3-butenyl)cyclohexanol (27): 77% yield; ^1H NMR δ 4.87–4.82 (m, 2H), 1.89 (s, 1H), 1.84 (s, 3H), 1.67–1.63 (m, 3H), 1.59–1.54 (m, 4H), 1.44–1.35 (m, 5H), 1.16 (s, 6H); ^{13}C NMR δ 154.0, 110.0, 72.5, 51.8, 39.2, 38.9, 29.7, 25.7, 21.9, 20.0; IR (neat) 3432 (br), 3087, 2958, 2927, 2859, 1633, 1446, 1375, 1263, 1172, 985, 891 cm^{-1}; HRMS calcd for $C_{13}H_{24}O$ 196.1827, found 196.1825.

2,3,3-Trimethyl-6,7-epoxy-1-hepten-5-ol (28): 72% yield; ^1H NMR δ 4.82–4.81 (m, 2H), 3.49–3.45 (m, 1H), 2.98–2.94 (m, 1H), 2.79–2.77 (m, 1H), 2.69–2.66 (m, 1H), 2.02–2.00 (m, 1H), 1.80–1.63 (m, 5H), 1.14 (s, 3H), 1.12 (s, 3H); ^{13}C NMR δ 152.4, 110.4, 69.8, 55.9, 45.3, 44.5, 38.1, 27.9, 27.6, 19.5; IR (neat) 3431 (br), 3087, 2966, 2929, 2875, 1635, 1446, 1400, 1378, 1159, 921, 890, 854 cm^{-1}; HRMS calcd for $C_{10}H_{18}O_2$ 170.1306, found 170.1300. Anal. Calcd: C, 70.53; H, 10.66. Found: C, 70.86; H, 10.68.

2,3,3-Trimethyl-1-hexen-6-ol (29): 62% yield; ^1H NMR δ 4.75–4.69 (m, 2H), 3.58 (t, J = 7.2 Hz, 2H), 2.27 (s (br), 1H), 1.69 (s, 3H), 1.39–1.37 (m, 4H), 1.04 (s, 6H); ^{13}C NMR δ 151.7, 109.6, 63.4, 38.4, 36.6, 27.9, 27.1, 19.3; IR (neat) 3328 (br), 3089, 2966, 2873, 1635, 1450, 1377, 1363, 1061, 1024, 891 cm^{-1}; HRMS calcd for $C_9H_{18}O$ 142.1357, found 142.1356.

1-(1-Hydroxy-1-methylethyl)-1-methyl-2-methylenecyclohexane (30): 76% yield; ^1H NMR δ 4.99–4.80 (m, 2H), 2.43–2.33 (m, 1H), 2.22–2.14 (m, 1H), 1.93–1.85 (m, 1H), 1.77–1.65 (m, 4H), 1.55–1.41 (m, 2H), 1.24 (s, 3H), 1.20 (s, 3H), 1.09 (s, 3H); ^{13}C NMR δ 154.3, 111.6, 75.2, 46.4, 34.4, 33.6, 26.8, 25.6, 25.2, 23.3, 20.9; IR (neat) 3481 (br), 3080, 2987, 2951, 2868, 1629, 1456, 1450, 1385, 1369, 1331, 1176, 1161, 1136, 1113, 1092, 943, 895, 843 cm^{-1}; HRMS calcd for $C_{11}H_{20}O - C_3H_6O$ 110.1096, found 110.1087.

1-(1,1,2-Trimethyl-2-propenyl)cyclopentanol (31): 78% yield; ^1H NMR δ 5.02–4.89 (m, 2H), 1.86 (s, 3H), 1.67–1.63 (m, 5H), 1.57–1.52 (m, 2H), 1.50–1.45 (m, 2H), 1.15 (s, 6H); ^{13}C NMR δ 151.3, 113.7, 85.7, 44.9, 35.3, 23.8, 23.7, 22.9; IR (neat) 3487 (br), 3087, 2962, 2871, 1652, 1628, 1456, 1437, 1377, 895 cm^{-1}; HRMS calcd for $C_{11}H_{20}O - CH_3$ 153.1279, found 153.1274.

1-(1-Hydroxy-1-methylethyl)-1-(2-hydroxy-2-methylpropyl)-2-methylenecyclohexane (32): 50% yield; ^1H NMR δ 5.43–5.04 (m, 2H), 4.40 (s (br), 2H), 2.29 (m, 3H), 1.80 (d, J = 15.8 Hz, 1H), 1.60–1.51 (m, 6H), 1.45 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR δ 149.9, 114.4, 76.2, 71.9, 50.9, 44.1, 35.9, 35.1, 34.2, 29.0, 27.3, 27.2, 26.5, 21.5.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **7, 17–21, 27,** and **29–32** (24 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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