spectrum, m/e 269.1044 ($C_{16}H_{15}NO_3$ requires 269.1052) 268 (base).

7-Oxo-α-lycorane (23a). A solution of the lactam **4** (15 mg, 0.05 mmol) in glacial acetic acid (1.5 mL) containing 10% Pt/C (10 mg) was stirred under H_2 (1 atm) at room temperature for 4 h. The catalyst was removed by suction filtration and washed with hot ethanol (20 mL). The combined filtrates were concentrated under reduced pressure, and the residue was dissolved in CH_2Cl_2 (10 mL). The solution was then washed with saturated aqueous $NaHCO_3$ (2 × 5 mL) and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was recrystallized from hexane to give 14 mg (94%) of **23a** which was identical in all respects with that obtained previously.

7-Oxo-β-lycorane (23b). The lactam **31** (20 mg, 0.08 mmol) was hydrogenated as described above to give 19 mg (95%) of **23b**, which was identical in all respects with that obtained previously.

Acknowledgment. This research was generously supported by grants from the National Institutes of Health (GM-25439) and the Robert A. Welch Foundation, to whom we are extremely grateful. We also thank Dr. Franz Scheidl of Hoffmann-La Roch, Inc., for performing the combustion analyses.

Registry No. **4**, 53951-02-3; **8**, 82281-20-7; **11**, 82281-21-8; **12**, 82281-22-9; **15**, 82281-23-0; **16**, 82293-68-3; **17a**, 82281-24-1; **17b**, 82281-25-2; **17c**, 82281-26-3; **18**, 82281-27-4; **19a**, 63814-02-8; **19b**, 71630-03-0; **19c**, 10313-53-8; **20a**, 82281-28-5; **20b**, 82281-29-6; **20c**, 82281-30-9; **21a**, 82281-31-0; **21b**, 82281-32-1; **21c**, 82281-33-2; **22a**, 82281-34-3; **22b**, 82281-35-4; **22c**, 82281-36-5; **23a**, 66816-53-3; **23b**, 78512-55-7; **23c**, 82398-31-0; **24a**, 78456-83-4; **24b**, 78456-84-5; **26**, 78456-78-7; **27a**, 78479-41-1; **27b**, 78456-80-1; **29a**, 78456-81-2; **29b**, 78456-82-3; **30**, 78456-85-6; **31**, 78512-54-6; benzylamine, 100-46-9; phenylacetaldehyde, 122-78-1; homopiperonal, 6543-34-6; *p*-methoxybenzylamine, 2393-23-9.

Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

Reactions of the Formaldehyde–Trimethylaluminum Complex with Alkenes

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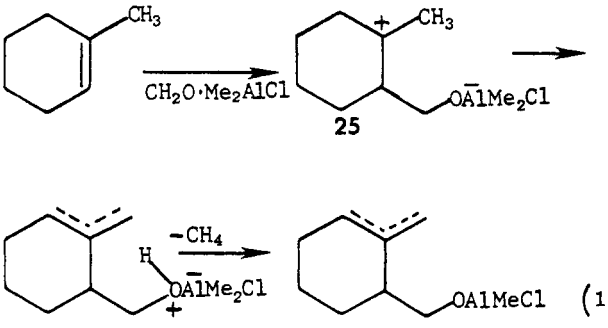
Reaction of $CH_2O{\cdot}Me_3Al$ with electron-rich alkenes gives a zwitterion that reacts further to give homoallylic alcohols (ene adducts), allylic alcohols, and the product of cis addition of a hydroxymethyl and a methyl group to the double bond. The stereochemistry and effect of alkene structure on the nature of the reaction are examined.

The acid-catalyzed addition of aldehydes to alkenes, the Prins reaction, has been extensively investigated over the past 60 years.[2] 1,3-Diols and *m*-dioxanes are the major products in aqueous media. Homoallylic alcohols resulting from a stepwise or concerted ene reaction are the major products from the Lewis acid catalyzed reaction of electron-deficient aldehydes, e.g., chloral and formaldehyde, with electron-rich alkenes, i.e., those that can give a tertiary carbenium ion.

We have recently found the use of Me_2AlCl as the Lewis acid extends the scope of this reaction.[3] Ene adducts can now be obtained in good yield from aliphatic and aromatic aldehydes and reactive alkenes that give a tertiary carbenium ion. With Me_2AlCl as a catalyst, formaldehyde also reacts with alkenes that give a secondary carbenium ion to give ene adducts and varying amounts of chloro alcohol resulting from the cis addition of hydroxymethyl and chloride groups to the double bond. The success of these reactions is due to the fact that Me_2AlCl is a proton scavenger as well as a Lewis acid.[4]

The reactions of $CH_2O{\cdot}Me_3Al$ with alkenes were explored to determine the suitability of a weaker Lewis acid as the catalyst and to prevent the formation of chloride-containing byproducts. To our surprise, the reaction of $CH_2O{\cdot}Me_3Al$ with 1-methylcyclohexene (see Table I) gave only 5% of ene adducts **4a** and **5a**, the exclusive products with $CH_2O{\cdot}Me_2AlCl$[3b] (see eq 1). The major products were



(1)

the alcohol **2a**, resulting from cis addition of the hydroxymethyl and methyl groups to the double bond, and the allylic alcohol **3a**. Both of these products appear to result from a common zwitterionic intermediate that can undergo a 1,5 methyl shift to give **2a**[5] or a 1,5 proton shift with loss of methane to give **3a** (see eq 2). The enhanced basicity and nucleophilicity of the methyl groups of **26** as compared to those for **25** are apparently responsible for the difference between these reactions. The product mixtures obtained from a variety of alkenes are shown in Table I.

1-Phenylcyclohexene (run 3) gives a single adduct **7**, which results from methyl addition to the zwitterion. Formation of the allylic alcohol would require that the oxyalkyl group be equatorial so that the hydrogen being

(1) (a) Brandeis University. (b) Princeton University.
(2) Adams, D. R.; Bhatnagar, S. P. *Synthesis* **1977**, 661.
(3) (a) Snider, B. B.; Rodini, D. J. *Tetrahedron Lett.* **1980**, *21*, 1815. (b) Snider, B. B.; Rodini, D. J.; Kirk, T. C.; Cordova, R. *J. Am. Chem. Soc.* **1982**, *104*, 555.
(4) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927.
(5) For related reactions see: Yamamoto, H.; Nozaki, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 169.

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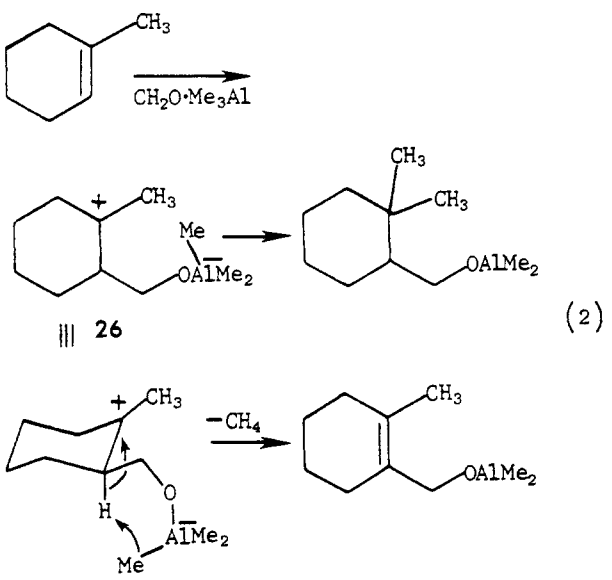


abstracted is eclipsed with the vacant p orbital (eq 2). This conformation cannot be adopted since a large equatorial substituent will force the phenyl group out of conjugation with the p orbital of the carbenium ion. Reaction of $CH_2O{\cdot}Me_2AlCl$ with **6** gives the ene adduct in 96% yield.

The low yield of **7** results from a competing addition of a methyl group to formaldehyde to give Me_2AlOEt. Steric hindrance and lack of conjugation make **6** less reactive than **1a**. Attempted reaction of $CH_2O{\cdot}Me_3Al$ with monosubstituted, 1,2-disubstituted, or tetrasubstituted alkenes gives only Me_2AlOEt. We have also noted a slight decrease in yield for run 3 when the reaction is scaled up. Clearly, the formation of Me_2AlOEt is competitive with the addition of an alkene to $CH_2O{\cdot}Me_3Al$ to give a zwitterion analogous to **26**. We have been unable to obtain comparable products from the reaction of $CH_2O{\cdot}Et_3Al$ or $CH_2O{\cdot}(i\text{-}Bu)_2AlH$ with alkenes.

The reaction of $CH_2O{\cdot}Me_3Al$ with **2a** (run 2) occurs equally from both faces of the cyclohexene since **3b** must result from β attack that gives the equatorial oxyalkyl group. The reaction with *tert*-butylmethylenecyclohexane (run 10) shows similar lack of selectivity.

Run 5 establishes the stereochemistry of the reaction. The quaternary methyl group of **9b** absorbs at δ 0.79 in the NMR spectrum. The upfield methyl group of **9a**, which is shielded by the cis hydroxymethyl, absorbs at δ 0.83. The downfield methyl group of **9a**, which is trans to the hydroxymethyl group, absorbs at δ 1.07. Therefore, the methyl group of **9b** is cis to the hydroxymethyl group.

Reaction of $CH_2O{\cdot}Me_3A$] with dihydropyran (**22**; run 11) gives a 75% yield of a 92:8 mixture of **23** and **24**. The stereochemistry was rigorously established by NMR decoupling experiments at 270 MHz that indicate coupling constants of 2.8 and 8.8 Hz for the hydrogens shown in **23** and **24**, respectively. Examination of models indicates that formation of the trans isomer by intramolecular delivery of the methyl group is possible.

The allylic alcohols **15** obtained from (*Z*)- and (*E*)-3-methyl-2-pentene (runs 7 and 8) are a 4:1 mixture of regioisomers. In both cases the major alcohol results from bond rotation in the intermediate zwitterion of 60°, rather than 120°, to align the hydrogen with the vacant p orbital. The ene reaction to give **16** and **17** shows an even higher preference for abstraction of a hydrogen from the alkyl group syn to the vinylic hydrogen than was observed with Me_2AlCl.[3b]

A cursory examination of Table I indicates that the ratio of methyl addition product to allylic alcohol to ene adduct varies widely with alkene structure. This results from a complicated interplay of factors affecting the reactivity of the zwitterionic intermediate common to all three reactions. The stability of the double bond of the ene adduct affects the rate of its formation. Alkene **13b** (run 7), which would prefer for steric reasons[3b] to give the ene adduct **16b** with a less stable disubstituted double bond, gives a 51% yield of ene adducts and a 23% yield of **14b**, whereas alkene **13c** (run 8), which gives the ene adduct **16c** with a more stable trisubstituted double bond, gives a 74% yield of ene adducts and only a 3% yield of **14b**. Similar effects can be observed in runs 4 and 5.

Steric hindrance to delivery of the methyl group to the cationic center is factor in run 7. Run 6 gives mainly methyl addition product. Run 7, which gives an ene adduct of similar stability, nevertheless gives less methyl addition product due to steric hindrance by the ethyl group.

Substrates in which the 1,5 proton shift to give ene adduct is sterically hindered give more of the other two products. Cycloalkenes are poor substrates for ene reactions as compared to the analogous acyclic compound.[6] Therefore, run 7 gives more ene adduct than run 1.

These results extend the scope of the Prins reaction. Further studies with enol ethers, which appear to have the most synthetic potential, will be reported shortly.

Experimental Section

NMR spectra were obtained on a Varian EM-390, a Perkin-Elmer R32, a JEOL FX90Q, a Bruker WH90, or a homemade 270-MHz NMR spectrometer. IR spectra were obtained on a Perkin-Elmer 283 spectrometer. GC analyses were carried out on the following 0.25-in. columns on 60/80 mesh supports at a flow rate of 55 mL/min: A (12 ft, 8% UCON LB-550X on Chromosorb WNAW), B (10 ft, 10% Carbowax 20M on Chromosorb WNAW), C (9 ft, 10% DEGS on Chromosorb PNAW), D (15 ft, 7% DEGS on Chromosorb WNAW).

Dihydropyran was distilled from sodium/benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2. Me_3Al was obtained from Alfa as a 2.35 M solution in hexane.

Run 1. General Procedure. Me_3Al (1.75 mL, 2.35 M in hexane, 4.0 mmol) was added to a stirred solution of 1-methylcyclohexene (0.19 g, 2.0 mmol) and paraformaldehyde (0.120 g, 4 mmol) in 10 mL of CH_2Cl_2, under nitrogen at 25 °C. After 15 min, 10 mL of water was added followed by 10 mL of 10% aqueous hydrochloric acid to dissolve precipitated alumina. The layers were separated, and the aqueous phase was extracted with three 10-mL portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated at reduced pressure to give 0.15 g (60%) of a colorless oil, which GC (A, 130 °C) showed to consist of **2a**, **3a**, **4a**, and **5a** in the yields indicated in Table I. Pure samples of **2a** and **3a** were isolated by preparative GC.

The data for **2a** are as follows: NMR ($CDCl_3$) δ 3.84 (dd, 1, J = 10.5, 3.4 Hz), 3.30 (dd, 1, J = 10.5, 8.1 Hz), 2.17 (s, 1, OH), 1.8–1.0 (m, 9), 0.97 (s, 3), 0.80 (s, 3); ^{13}C NMR ($CDCl_3$) δ 64.4, 49.1, 42.0, 32.3, 30.7, 26.1, 25.6, 22.4, 20.4; IR ($CDCl_3$) 3630, 1365, 1030, 1010, 980 cm^{-1}; MS, m/e (relative intensity) 142 (M^+, 0.4), 127 (1), 124 (16), 111 (17), 110 (6), 109 (31), 96 (7), 95 (12), 82 (28), 81 (31), 69 (82), 68 (24), 64 (47), 55 (55), 41 (100); GC (A, 130 °C) t_R 22.8 min.

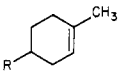
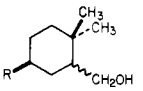
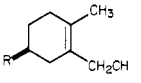
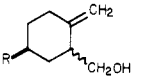
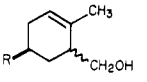
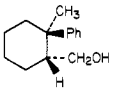
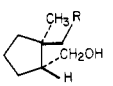
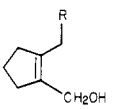
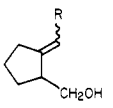
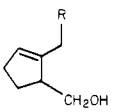
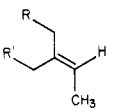
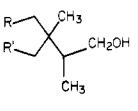
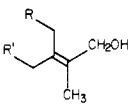
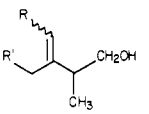
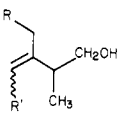
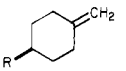
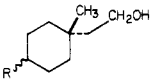
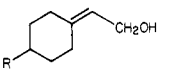
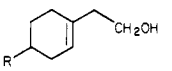
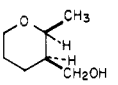
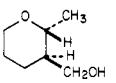
The data for **3a** are as follows: NMR ($CDCl_3$) δ 4.11 (s, 2), 2.18 (s, 1, OH), 2.1–1.8 (m, 4), 1.75 (br s, 3), 1.8–1.11 (m, 4); IR ($CDCl_3$) 3620; MS, m/e (relative intensity) 126 (M^+, 42), 111 (71), 108 (37), 97 (31), 95 (46), 93 (84), 67 (96), 55 (80); GC (A, 130 °C) t_R 18.2 min.

The GC data for ene adducts **4a**[3b] and **5a**[3b] are as follows (A, 130 °C): **4a**, t_R 13.5 min; **5a**, t_R 16.2 min).

Run 2 gave a quantitative recovery that was shown by GC to consist of the products shown in Table I, which were isolated by preparative GC, and recovered starting material.

(6) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

Table I. Reactions of $CH_2O{\cdot}Me_3Al$ with Alkenes

run	alkene	products and % yield			
	 1	 2	 3	 4	 5
1	a, R = H	38	14	4	
2	b, R = $CH(CH_3)_2$	24[a]	11	2	
	 6	 7			
3		11[b]			
	 8	 9	 10	 11	 12
4	a, R = H	24	21	6	1
5	b, R = CH_3	10	18	29[c]	
	 13	 14	 15	 16	 17
6	a, R = R′ = H	45		12	
7	b, R = H; R′ = CH_3	23	4 (1% **15c**)	36[d]	15[d]
8	c, R = CH_3; R′ = H	3	2 (0.5% **15b**)	73[d]	0.5[d]
	 18	 19	 20		 21
9	a, R = H	28	13		31
10	b, R = *t*-Bu	25[e]	15		31
11	 22	 23	 24		
		69	6		

[a] 75% α-CH_2OH, 25% β-CH_2OH. [b] 79% of **6** was recovered. [c] 29% of a mixture which may contain some **12b**. [d] Note that **16b** = **17c** and **16c** = **17b**. [e] 56% α-*t*-Bu, 44% β-*t*-Bu.

The data for **2b** are as follows: 270-MHz NMR ($CDCl_3$) δ 3.7–3.8 (m, 1), 3.51 (dd, 0.75 × 1, J = 10, 10 Hz, α-CH_2OH), 3.30 (dd, 0.25 × 1, J = 10, 10 Hz, β-CH_2OH), 1.60-1.37 (m, 3), 1.37–1.00 (m, 6), 0.98 (s, 3), 0.88 (d, 6, J = 6 Hz), 0.87 (s, 0.75 × 3, α-CH_2OH), 0.75 (s, 0.25 × 3, β-CH_2OH); IR (CCl_4) 3620, 1385, 1365 cm^{-1}; GC (B, 150 °C) t_R 24.9 min. The stereochemistry is assigned by comparison of the NMR spectra to those of *cis*- and *trans*-4-*tert*-butyl-2,2-dimethylcyclohexanemethanol.[7]

The data for **3b** are as follows: mp 29.0–30.5 °C; NMR ($CDCl_3$) δ 4.12 (br, 2), 2.37–1.76 (m, 4), 1.70 (s, 3), 1.65–1.08 (m, 4), 0.94 (s, 1, OH), 0.91 (d, 6, J = 6.2 Hz); IR (CCl_4), 3600, 1604, 1380, 1365 cm^{-1}; GC (B, 150 °C) t_R 29.7 min.

Run 3 on a 2-mmol scale gave 0.36 g of which 0.301 g was purified by chromatography on silica gel (hexane–ether, 3:1) to give 0.213 g (79%) of recovered **6** and 0.040 g (11%) of **7**: NMR ($CDCl_3$) δ 7.45–7.08 (m, 5), 3.28 (dd, 1, J = 4.1, 10.7 Hz), 3.08 (dd, 1, J = 8.0, 10.7 Hz), 2.2–1.2 (m, 10), 1.24 (s, 3); ^{13}C NMR ($CDCl_3$) δ 150.0, 128.1, 125.6, 124.8, 64.5, 47.5, 42.6, 40.0, 25.9, 25.5, 22.4, 17.1; IR ($CDCl_3$) 3550, 1604, 1370 cm^{-1}.

Run 4 on a 5-mmol scale gave, after evaporative distillation [50 °C (0.02 torr)], 347 mg (62%) of the mixture indicated in Table I. Pure samples were isolated by preparative GC.

The data for **9a** are as follows: NMR ($CDCl_3$) δ 3.8–3.2 (m, 2), 2.0–1.8 (m, 8), 1.07 (s, 3), 0.83 (s, 3); ^{13}C NMR ($CDCl_3$) δ 64.8, 51.7, 42.5, 40.3, 29.2, 28.6, 22.2, 21.7; IR ($CDCl_3$) 3620, 1462, 1378, 1079, 987 cm^{-1}; GC (B, 125 °C) t_R 19.5 min.

The data for **10a** are as follows: NMR ($CDCl_3$) δ 4.19 (s, 2), 2.35 (br t, 4, J = 7 Hz), 1.81 (quintet, 2, J = 7 Hz), 1.70 (br s, 3), 1.20 (br s, 1, OH); ^{13}C NMR ($CDCl_3$) δ 135.9, 134.1, 59.2, 38.8, 34.1, 21.6, 13.7; IR ($CDCl_3$) 3620, 1600, 1365, 1075, cm^{-1}; GC (B, 125 °C) t_R 25.4 min.

The GC data (B, 125 °C) for ene adducts **11a**[3b] and **12a**[3b] are t_R 18.2 min.

Run 5 on a 5-mmol scale gave, after evaporative distillation [70 °C (0.03 torr)], 0.368 g (57%) of the mixture indicated in Table I. Pure samples were obtained by preparative GC.

The data for **9b** are as follows: NMR ($CDCl_3$) δ 3.8–3.4 (m, 2), 1.8–1.2 (m, 10), 0.86 (t, 3, J = 8.5 Hz), 0.79 (s, 3); IR ($CDCl_3$) 3625, 1040 cm^{-1}; MS, m/e (relative intensity) 124 (7, $M^+ - H_2O$), 113 (10), 112 (5), 109 (14), 96 (27), 95 (100); GC (A, 120 °C) t_R 26.1 min.

The data for **10b** are as follows: NMR ($CDCl_3$) δ 4.18 (br s, 2), 3.40 (br s, 1, OH), 2.45–1.50 (m, 8), 1.1–0.9 (m, 3); IR ($CDCl_3$) 3625, 1670, 1030 cm^{-1}; MS m/e (relative intensity) 126 (12, M^+), 108 (10), 97 (6), 96 (9), 95 (100); GC (A, 120 °C) t_R 19.1 min.

The GC data (A, 120 °C) for ene adducts **11b** and **12b** are t_R 18.1 min.

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Run 6 on a 1-mmol scale gave 68 mg (68%) of the mixture indicated in Table I. Pure products were isolated by preparative GC (C, 100 °C).

The data for **14a** are as follows: NMR ($CDCl_3$) δ 3.79 (dd, 1, J = 3.9, 10.3 Hz), 3.27 (dd, 1, J = 8.8, 10.3 Hz), 2.03 (s, 1, OH), 1.30 (m, 1), 0.92 (d, 3, J = 7.8 Hz), 0.86 (s, 9); ^{13}C NMR ($CDCl_3$) δ 65.1 (t), 45.5 (d), 32.0 (s), 27.6 (q) and 12.3 (q); IR (neat) 3350, 1395, 1367, 1030 cm^{-1}; GC (C, 100 °C) t_R 17.4 min. These data correspond well to those previously reported.[8]

The data for **16a** are as follows: NMR ($CDCl_3$) δ 4.87 (br, 1), 4.81 (br, 1), 3.51 (d, 2, J = 7.5 Hz), 2.38 (tq, 1, J = 7.5, 7.5 Hz), 1.72 (br, 3), 1.40 (br s, 1, OH), 1.00 (d, 3, J = 7.3 Hz); GC (C, 100 °C) t_R 12.5 min. The IR data are identical with those previously reported.[9]

Run 7 on a 2-mmol scale gave, after evaporative distillation [50 °C (0.05 torr)], 182 mg (81%) of the mixture indicated in Table I. Pure samples were obtained by preparative GC.

The data for **14b** are as follows: NMR (CCl_4) δ 3.82 (dd, 1, J = 10, 4 Hz), 3.33 (dd, 1, J = 10, 8 Hz), 1.87–1.1 (m, 4), 0.93 (d, 3, J = 7 Hz), 0.86 (s, 3), 0.82 (s, 3), 0.82 (t, 3, J = 7 Hz); IR (neat) 3320, 1389, 1378, 1364 cm^{-1}; GC (A, 100 °C) t_R 38.3 min.

The data for **15b** and **15c** are as follows: NMR ($CDCl_3$) δ 4.12 (d, 2, J = 4.4 Hz), 2.06 (q, 2, J = 7.3 Hz), 1.74 (s, 6), 1.07 (t, 1, J = 4.4 Hz, OH), 0.97 (t, 3, J = 7.3 Hz); IR ($CDCl_3$) 3600, 1602, 1455, 1370, 1245 cm^{-1}; GC (A, 100 °C) t_R (**15b**) 26.6 min, t_R (**15c**) 25.0 min. The stereochemistry is assigned on the basis of GC retention times. The hydroxyl group of **15b** is more sterically accessible and **15b** elutes slower.[10]

The data for ene adducts **16b**[3b] and **17b**[3b] are as follows (A, 100 °C): **16b**, t_R 16.1 min; **17b**, t_R 17.6 min.

Run 9 on a 5-mmol scale gave, after evaporative distillation [70 °C (0.05 torr)], 0.477 g (72%) of the products indicated in Table I. Pure samples were obtained by preparative GC.

The data for **19a**[11] are as follows: NMR ($CDCl_3$) δ 3.69 (t, 2, J = 7.5 Hz), 1.54 (t, 2, J = 7.5 Hz), 1.4–1.3 (m, 11), 0.90 (s, 3); IR ($CDCl_3$) 3625, 1040 cm^{-1}, GC (A, 120 °C) t_R 29.8 min.

The data for **20a**[12] are as follows: NMR ($CDCl_3$) δ 5.37 (tt, 1, J = 7.3, 1.1 Hz), 4.14 (d, 2, J = 7.3 Hz), 2.25–2.07 (m, 4), 1.61–1.55 (m, 6), 1.20 (br s, 1, OH); IR ($CDCl_3$) 3630, 3015, 1665, 1025 cm^{-1}; GC (A, 120 °C) t_R 22.8 min.

The data for **21a**[3b] is as follows: GC (A, 120 °C) t_R 18.8 min.

Run 10 on a 1.71-mmol scale gave, after evaporative distillation [100 °C (0.15 torr)], 208 mg (71%) of the products indicated in Table I. Pure samples were obtained by preparative GC.

The data for **19b**[13] (β-*t*-Bu) are as follows: mp 63.5–65.5 °C; lit.[13] mp 65.0–65.5 °C; the spectral data are identical with those previously reported; GC (A, 150 °C) t_R 73.7 min.

The data for a 1:1.2 mixture of **19b**[13] (α-*t*-Bu) and **20b**[14] are as follows: NMR ($CDCl_3$) δ 5.36 (t, 1, J = 7 Hz, **20b**), 4.14 (d, 2, J = 7 Hz, **20b**), 3.67 (t, 2, J = 7.5 Hz, **19b**), 0.85 (s, 3, **19b**); IR (CCl_4) 3610, 1667 cm^{-1}; GC (A 150 °C) t_R 65.3 min.

Run 11. Me_3Al (0.87 mL, 2.34 M in hexane, 2.0 mmol) was added to a solution of dihydropyran (**22**; 170 mg, 2 mmol) in 10 mL of anhydrous CH_2Cl_2 at 0 °C under nitrogen. The solution was stirred for 5 min at 0 °C and 60 mg (2 mmol) of paraformaldehyde was added. The solution was warmed to 25 °C and stirred for 40 h. Normal workup gave 0.207 g (88%) of crude product. Evaporative distillation [75 °C (0.05 torr)] gave 175 mg (75%) of a 92:8 mixture of **23** and **24**. Pure samples were obtained by preparative GC.

The data for **23** are as follows: 270-MHz NMR ($CDCl_3$) δ 3.96 (ddd, 1, J = 11.3, 4, 4 Hz), 3.83 (d, 2, J = 6.3 Hz), 3.77 (qd, 1, J = 6.8, 2.8 Hz) 3.49 (ddd, 1, J = 11.3, 11.3, 2.6 Hz), 2.38 (s, 1, OH) 2.2–1.15 (m, 5), 1.22 (d, 3, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 75.6, 73.9, 66.6, 59.9, 39.8, 24.3, 21.7, 17.0; IR (neat) 3380, 1382, 1104, 1077 cm^{-1}; GC (D, 110 °C) t_R 27.3 min.

The data for **24** are as follows: 270-MHz NMR ($CDCl_3$) δ 3.91 (br d, 1, J = 11 Hz), 3.59 (br d, 1, J = 10 Hz), 3.47 (br d, 1, J = 10 Hz), 3.35 (ddd, 1, J = 10, 11, 4.1 Hz), 3.24 (qd, 1, J = 6.0, 8.8 Hz), 1.96–1.22 (m, 5), 1.55 (s, 1, OH), 1.24 (d, 3, J = 6.0 Hz); IR (CCl_4) 3600, 1381, 1099 cm^{-1}; GC (d, 110 °C) t_R 31.0 min.

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Registry No. **1a**, 591-49-1; **1b**, 5502-88-5; **2a**, 81980-07-6; **2b** (isomer 1), 82495-04-3; **2b** (isomer 2), 82495-15-6; **3a**, 29474-11-1; **3b**, 6007-05-2; **6**, 771-98-2; **7**, 82495-05-4; **8a**, 693-89-0; **8b**, 2146-38-5; **9a**, 82495-06-5; **9b**, 82495-07-6; **10a**, 81328-62-3; **10b**, 82495-08-7; **13a**, 513-35-9; **13b**, 922-62-3; **13c**, 616-12-6; **14a**, 36794-64-6; **14b**, 66576-25-8; **15b**, 82495-09-8; **15c**, 82495-10-1; **16a**, 1708-93-6; **16b**, 77103-98-1; **17b**, 3778-92-5; **18a**, 1192-37-6; **18b**, 13294-73-0; **19a**, 82495-11-2; **19b** (isomer 1), 82495-12-3; **19b** (isomer 2), 82495-16-7; **20a**, 932-89-8; **20b**, 41498-18-4; **22**, 110-87-2; **23**, 82495-13-4; **24**, 82495-14-5; CH_2O-Me_3Al, 82495-17-8.

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