Asymmetric Synthesis at Prochiral Centers: Substituted 1,3-Dioxolanes

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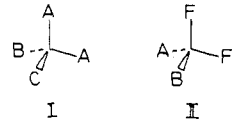
Asymmetric substitution at the prochiral carbon atom of two series of 2-substituted 4,5-dimethyl-1,3-dioxolanes is studied; the hydroxy ethers formed by reaction with the "mixed hydride reagent" $LiAlH_4/AlCl_3$ show a marked influence of the substitutents on the asymmetric induction, i.e., from 4% to 98% diastereomeric excess (de). The dioxolanes are studied by both ^{13}C NMR and ^1H NMR spectroscopy and their chemical shift inequivalences correlate well with the de, provided that no unsaturated residues are present. The proposed mechanism is based on preferred complexation of the hydride reagent with one of the diastereotopic oxygen atoms. This is supported by a drastic decrease of the de if further ether groups are introduced into the substrate molecules.

Research on asymmetric synthesis involving prochiral trigonal centers is being actively pursued; asymmetric induction is achieved by preferential addition of the reagent to one of the prochiral faces of the substrate molecule[1a,2] (C=C, C=O, and C=N). However, reactions starting from prochiral tetrahedral centers remain scarcely studied. Indeed, the statement of Morrison and Mosher[1b] that "the number of asymmetric synthesis resulting from preferential attack at either one or the other of the prochiral ligands of a molecule is much smaller but perhaps even more interesting" still holds today. This contribution reports a systematic study of asymmetric reactions at prochiral tetrahedral carbon atom centers were the ligands themselves are chiral. Two series of substituted 1,3-dioxolanes serve as model compounds; they were studied by ^{13}C and ^1H NMR spectroscopy, and the preferred reactivity of the paired chiral ligands was tested by their reactivity toward "mixed hydride" reagents ($LiAlH_4/AlCl_3$).[3]

Background

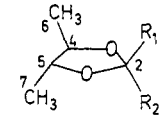
The formal notation of stereochemical relationship introduced by Prelog[4] allows an easy classification of chiral and prochiral centers; two dimensional symmetrical capital letters (e.g., A, B, C) represent achiral ligands, whereas two dimensional asymmetric ones (e.g., F, G) represent chiral ligands. Two relevant prochiral substituent patterns are given in formulas I and II. In formula I the ligands A and A′ are enantioptic, whereas in formula II F and F′ are diastereotopic.[5]



I II

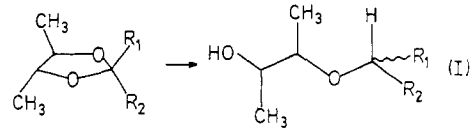
Most asymmetric reactions at prochiral centers proceed from a situation exemplified by formula I: a chiral center is generated by substituting one of the A's by either a chiral ligand F or by an additional achiral ligand D. Experimentally the latter route has been used successfully in the synthesis of optically active silanes starting from $R_1R_2SiH_2$.[6] The second type of prochiral center requires substitution of one of the chiral ligands F by an achiral ligand C to generate an additional chiral center. This approach has been successful for the asymmetric synthesis of silanes and phosphanes[7,8] but has not been applied to carbon compounds.

From previous work using menthyl groups as ligands at the prochiral center it was concluded[7] that rotating diastereotopic ligands yield a pattern of chemical shift inequivalences not interpretable up to now. Additionally, there was no correlation found between the observed anisochrony[10] of the ligands and the degree of asymmetric induction. Therefore we turned to cyclic chiral molecules where the diastereotopic ligands form a chelate. A five-membered ring seemed to be particularly appropriate since the energy barrier between different conformers is presumably low. 2-Substituted 4,5-dimethyl-1,3-dioxolanes



appeared to be the logical choice. Their easy accessibility from racemic or (–)-2,3-butanediol and ketones or aldehydes and their well-established reactivity toward several reducing agents like the "mixed hydride reagent" made them ideal for this study.[9] Since the carbon atoms C-4 and C-5 are homochiral, e.g., either 4*R*,5*R* or 4*S*,5*S*, different substituents at carbon atom 2 generate diastereotopism of the carbon atoms C-4 and C-5 as well as C-6 and C-7, respectively.

The resulting chemical shift inequivalence was measured and related to the substitution pattern of the prochiral centre. Two series of compounds were studied; series **1** with $R_1 = CH_3$ and various groups for R_2, amounting to 13 examples, and series **2**, with R_1 being hydrogen and six different residues for R_2. Additionally the prefered reactivities of the paired chiral ligands were tested by their reactivity toward "mixed hydride reagents" ($LiAlH_4/AlCl_3$) according to the following scheme:



Diastereotopic Chemical Shift Nonequivalence in 1,3-Dioxolanes

Since the two ligands F at a prochiral center are diastereotopic, they will in principle give nonequivalent NMR

(1) (a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, NJ, 1971; (b) *ibid.*, p 419.
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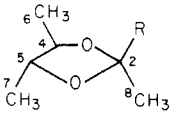
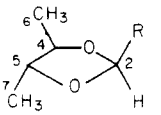
Table I. ^{13}C NMR Chemical Shifts of the Compounds 1a-m (± 0.01 ppm)



compd	R	C-2	C-4	C-5	$\Delta\delta_{4,5}$	C-8	C-6	C-7	$\Delta\delta_{6,7}$
1a	CH_3	107.60	78.42	78.42		27.35	16.95	16.95	
1b	$C\equiv CH$	99.38	79.46	79.38	0.09	27.52	17.67	16.42	1.25
1c	$CH_2C(CH_3)_3$	109.81	77.99	77.83	0.16	27.79	17.46	16.62	0.84
1d	$CH_2C_6H_5$	108.63	78.47	78.17	0.30	26.17	16.78	16.23	0.55
1e	$CH_2CH(CH_3)_2$	109.87	78.78	78.14	0.64	26.15	17.32	16.72	0.60
1f	$CH=CH_2$	106.46	78.90	78.13	0.77	25.97	16.86	16.48	0.38
1g	$CH_2CH_2CH_3$	109.24	78.83	78.04	0.79	25.70	17.19	16.55	0.64
1h	CH_2CH_3	109.51	78.92	78.10	0.82	25.24	17.25	16.59	0.66
1i	$CH(CH_3)_2$	111.35	78.99	77.99	1.00	22.37	17.52	16.43	1.07
1j	C_6H_5	107.85	79.29	78.25	1.04	29.07	17.10	16.56	0.54
1k	C_6H_{11}	110.86	78.94	77.79	1.15	23.01	17.35	16.31	1.04
1l	$C(CH_3)_3$	112.99	79.54	77.88	1.66	20.96	17.91	16.04	1.87
1m	$C_{10}H_{15}$ [a]	112.43	79.43	77.55	1.88	28.43	17.74	15.91	1.83

[a] Adamantyl.

Table II. ^{13}C NMR Chemical Shifts of the Compounds 2a-f (± 0.01 ppm)



compd	R	C-2	C-4	C-5	$\Delta\delta_{4,5}$	C-6	C-7	$\Delta\delta_{6,7}$
2a	$C(CH_3)_3$	109.26	79.63	78.59	1.04	17.27	16.57	0.70
2b	C_6H_{11}	106.42	79.56	78.20	1.36	17.26	16.79	0.47
2c	CH_2CH_3	104.18	79.80	78.24	1.56	17.34	16.99	0.65
2d	$CH_2C_6H_5$	103.40	79.68	78.09	1.59	17.08	16.87	0.21
2e	C_6H_5	102.62	80.30	78.55	1.75	17.15	16.90	0.25
2f	CH_3	100.19	80.04	78.18	1.85	17.38	17.15	0.23

chemical shifts and couplings; given sufficient resolution, a $^{13}C\{^1H\}$ NMR spectrum should show a doubling of all resonances attributed to the ligand F.

In our previous studies on siloxanes of the general formula[7] $R_1R_2Si(OMen)_2$ (Men = menthyl) we have demonstrated that while this chemical shift nonequivalence strongly depends on the nature of the ligands R_1 and R_2, we were not able to uncover a correlation between the two. Turning to cyclic compounds like the substituted 1,3-dioxolanes, the situation becomes more transparent as outlayed in Tables I and II. On the one hand, the ^{13}C NMR chemical shifts of the diastereotopic carbon atoms C-4 and C-5 and of C-6 and C-7, respectively, in the compounds **1b–m** show only negligible substituent effects in contrast to carbon atoms C-2 and C-8. The mean values of the chemical shifts are close to the chemical shift of the parent compound **1a**, which implies that no strong electronic effect is present.[11] The actual ground-state conformations of 4,5-disubstituted 1,3-dioxolanes are an equilibrium between different twist or envelope conformations. Depending on the substituent in C-2, envelope conformations will become more dominant in this equilibrium, forcing one of the methyl groups at C-4 or C-5 to spend more of its time in a pseudoaxial position. Steric interaction of the methyl group with the different ligands R_1 and R_2 will play a minor role in causing the chemical shift difference. A widely accepted measure for sterical bulk are the $-\Delta G°$ values derived from cyclohexanes; the ratio of equatorial and axial conformations of a given

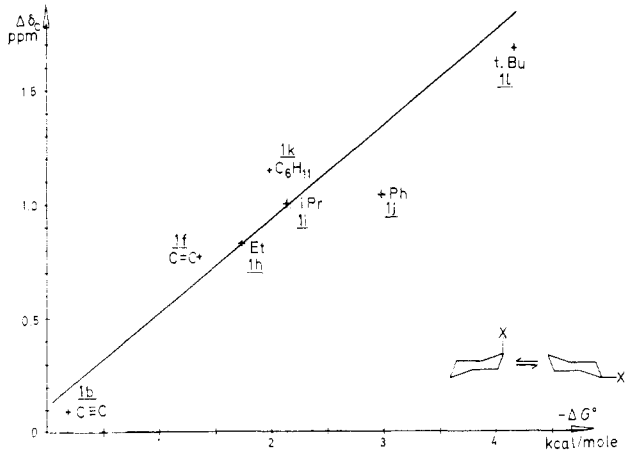


Figure 1. Plot of $\Delta\delta_C$ vs. $-\Delta G°$.

isomer allows an ordering of substituents according to their relative "size".[12] A plot of these $-\Delta G°$ values vs. the difference in chemical shifts ($\Delta\delta_{4,5}$) for the ethynyl, vinyl, ethyl, isopropyl, cyclohexyl and *tert*-butyl groups (e.g., compounds **1b,f,h,1i–l**) indicates a monotonously increasing function and suggests physical correspondance between the two phenomena (Figure 1). The 2,4,5-trisubstituted 1,3-dioxolanes derived from aldehydes differ markedly in their $\Delta\delta$ values (Table II). From the sparse data available, these $\Delta\delta$ values for atoms C-4 and C-5 show no similar correlation. The small second substituent at carbon atom C-2 (H vs. CH_3) may account for dominant

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Table III. Reduction of 2-Substituted 2,4,5-Trimethyl-1,3-dioxolanes

compd	R	$\Delta\delta_{4,5}$, ppm	product	isomer ratio	de,[a] %
1a	CH_3		3c		
1b	$C{\equiv}CH$	0.09	3b	15.2:16.3	3.4
1c	$CH_2C(CH_3)_3$	0.16	3c	64.0:35.9	28.1
1d	$CH_2C_6H_5$	0.30	3d	57.3:38.9	19.1
1e	$CH_2CH(CH_3)_2$	0.64	3e	71.6:22.9	51.5
1f	$CH{=}CH_2$	0.77	3f	44.7:53.3	8.8
1g	$CH_2CH_2CH_3$	0.79	3g	59.0:26.1	38.6
1h	CH_2CH_3	0.82	3h	73.0:23.6	51.1
1i	$CH(CH_3)_2$	1.00	3i	76.4:20.7	57.4
1j	C_6H_5	1.04	3j	50.6:45.8	4.9
1k	C_6H_{11}	1.15	3k	69.3:22.9	50.3
1l	$C(CH_3)_3$	1.66	3l	85.0:11.9	73.1
1m	$C_{10}H_{15}$[b]	1.88	3m	88.5:11.4	77.2

[a] Diastereometric excess. [b] Adamantyl.

envelope conformations, thus reversing the $\Delta\delta$ values for the *tert*-butyl and the ethyl groups (**2a** and **2c** vs. **1l** and **1h**).

Reduction of 2,2,4,5-Tetrasubstituted 1,3-Dioxolanes with $LiAlH_4/AlCl_3$

The reduction of the substituted 1,3-dioxolanes was performed as described in the literature.[9] Since variation of the molarity of the various reagents affected the asymmetric induction, standardized conditions were employed, all reactions were quenched after 2 h, after which the reactions were generally complete. The ratio of the diastereomers formed was determined by GC while in some cases the ratios could be evaluated from the integrals of the ^1H NMR spectra (e.g., **3d–g,j,i**). However, in view of the complexity of the spectra of many of them, they were not analyzed in detail, and the integrals could not be accurately measured. The GC results summarized in Table III show that the asymmetric induction varies widely in this system, showing a remarkable dependence of the ligand R_2. The lowest induction is found with the ethynyl group (3.4% de) and the largest (ca. 80% de) with the adamantyl group **3m**, the asymmetric induction. We also find a correlation between the $\Delta\delta_{4,5}$ values of these compounds and the de; generally, the larger $\Delta\delta$ value also indicates a larger induction, with a few characteristic exceptions, namely, **3b,d,f,j**, all bearing unsaturated ligands. The relation between the $\Delta\delta_{4,5}$ value and the asymmetric induction also holds for compounds having neopentyl (**1c**) and isobutyl (**1e**) residues, the relative "sizes" of which are difficult to estimate.

If we explain the $\Delta\delta_{4,5}$ values with preferred envelope conformations generated by the different substituents at C-2, the same rational holds for the asymmetric induction with saturated 1,3-dioxolanes. The reaction scheme taken from the literature[14] (Scheme I) states that first an equilibrium between free and complexed AlH_2Cl is established, while the formation of a dialkyloxocarbonium ion is considered to be the rate-determining step, and hydride transfer fixes the chirality of the dialkylalkoxycation, whereas ring closure would reestablish the prochiral center C-2.

In addition, changing the nature of the substituents R_1 and R_2 at C-2 will alter the stability of the oxocarbonium ion and may influence the stereochemical course of the reaction. Unsaturated ligands like the ethynyl group (**1b**), the vinyl group (**1f**), the phenyl group (**1j**), and to a lesser extent the benzyl group (**1d**) tend to stabilize the intermediate oxocarbonium ion. Given sufficient lifetime, the carbonium ion will lose its chirality by pyramidal flattening before the hydride transfer is effected.[13] This is in accordance with the finding of low asymmetric induction with the above compounds.

In the series **2**, where one of the residues is hydrogen, a secondary alkoxycarbonium ion could be formed, but as a result of reduced stability, the deuterium transfer in this case successfully competes with formation of a free carbonium ion, and the asymmetric induction is generally higher than in series **1** except for unsaturated ligands (see below).

Scheme I

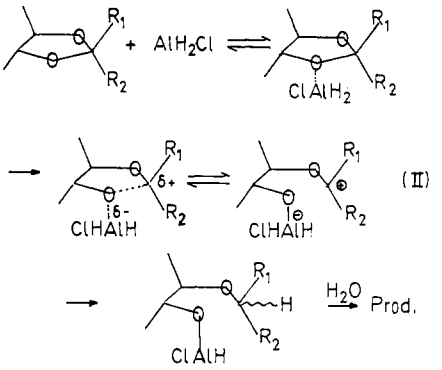


Table IV. Reduction of 2-Substituted 4,5-Dimethyl-1,3-dioxolanes

compd	R	$\Delta\delta_{4,5}$, ppm	product	isomer ratio	de, %
2a	$C(CH_3)_3$	1.04	4a	22:78	56.0
2b	C_6H_{11}	1.36	4b	10:90	80.0
2c	CH_2CH_3	1.56	4c	1:99	98.0
2d	$CH_2C_6H_5$	1.59	4d	9.4:90.6	81.2[a]
2e	C_6H_5	1.75	4e	14:86	72.0
2f	CH_3	1.85	4f	2:98	96.0

[a] For details see ref 16.

Table V. ^{13}C NMR Chemical Shifts (ppm) of the Compounds 5a,b and 6

compd	C-2	C-4	C-5	$\Delta\delta_{4,5}$	C-6	C-7	$\Delta\delta_{6,7}$
5a	111.57	77.93	77.17	0.76	73.66	73.35	0.31
5b	115.19	79.04	77.36	1.68	73.99	73.21	0.78
6	108.00	79.23	78.64	0.59	16.77	16.63	0.14

Reduction of 2,4,5-Trisubstituted 1,3-Dioxolanes

Reduction of 1,3-dioxolanes with only one substituent at C-2 (series **2**) gives no new center of chirality if $LiAlH_4/AlCl_3$ is used; however, reaction with $LiAlD_4/AlCl_3$ generates a new chiral center, owing its chirality to isotopic labeling. Such centers can be characterized with respect to enantiomeric excess.[15] Both GC methods and the ^{13}C NMR spectra at 25 MHz of the reduced products (**4a–f**) gave no resolution of species diastereomeric by virtue of deuterium substitution; on the other hand, 270-MHz ^1H NMR as well as ^2H NMR spectra gave reliable results consistent with each other.

These results are summarized in Table IV. The de's are the mean values determined by both two NMR methods. As Table V shows, the de's in this series are generally higher than for tetrasubstituted 1,3-dioxolanes.

(14) H. A. Davis and R. K. Brown, *Can. J. Chem.*, **49**, 2563 (1971).

(15) M. Raban and K. Mislow, *Tetrahedron Lett.* **33**, 3961 (1966); D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

(16) R. Benn and W. Riemer, Z. Naturforsch., *B: Anorg. Chem., Org. Chem.*, *36B*, 488 (1981).

The methyl and ethyl substituents (**2f** and **2d**) yield almost exclusively one isomer upon reduction: since the integrals of the minor components (98%) lie within the range of the accuracy of integration (2%), the reactions may well be stereospecific.

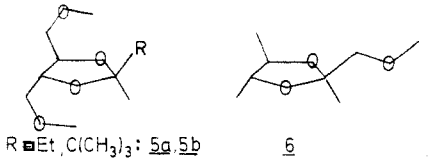
Again, the relationship of the $\Delta\delta_{4,5}$ value to the de is obvious: if $\Delta\delta$ exceeds 1.5 ppm, then, generally, a high selectivity is found. The phenyl and benzyl groups (**4d** and **4e**) exhibit a lower induction as anticipated from their $\Delta\delta$ value; resonance stabilization of the oxocarbonium ion serves as a reasonable explanation for the lower de's.

Conclusions

From our experiments we conclude that the $\Delta\delta$ values of substituted 1,3-dioxolanes can serve as a measure of the asymmetric induction reached with this system, provided that only saturated ligands are present. While these residues leading to preferred conformations allow selective complexation of the hydride reagent and fast fixation of the chirality at carbon atom 2, unsaturated ligands give deviating results by forming stabilized carbocation intermediates.

The higher induction found in the series **2** as opposed to series **1** may be partly due to the small size of the hydrogen residue compared to all other residues, since selective complexation at one of the two neighboring oxygen atoms may be faciliated. On the other hand, the enhanced reactivity of secondary alkylalkoxycarbonium ions as intermediates favor the high induction according to the reaction scheme discussed above.

In principle both lone-pair orbitals of the two diastereotopic oxygen atoms are capable of complexing the AlH_2Cl molecule; complexation then leads to chemical nonequivalence and thus to chirality at C-2. Model studies suggest that the lone-pair orbitals to O-1 and O-3 eclipsed with the methyl groups at C-4 and C-5 are less favored for nucleophilic attack than those which are staggered. The latter experience a steric shielding different from that of the different groups R_1 and R_2 at the prochiral center, making one lone-pair orbital more accessible toward complexation. Thus the larger the difference between R_1 and R_2, the larger the de becomes. It follows that any further complexation between the reacting molecules will disturb the subtle balance of selective complexation and presumably will change the de. To test the above assumption, we prepared and reduced the molecules **5a** and **5b**



[(4*S*,5*S*)-2-ethyl- and (4*S*,5*S*)-2-*tert*-butyl-4,5-bis(methoxymethyl)-2-methyl-1,3-dioxolane] and (4*R*,5*R*)-2-(methoxymethyl)-2-methyl-1,3-dioxolane (**6**), all of which can form a five-membered chelate. Their $\Delta\delta_{4,5}$ values (0.76, 1.51, 0.59 ppm) correspond closely to those of the compounds **1h**, **1l**, and **1g** with no oxygen in the substituent present (0.82, 1.66, and 0.79 ppm; see Table V).

However, upon reduction the de is only one-tenth of the induction observed with the corresponding molecules **1h**,**l**,**g**, namely, 5.2% 5.1%, and 8.5% de for **7a**, **7b**, and **8**. In all three molecules the methoxymethyl substituent apparently serves as an additional complexing ligand; the energetically favored five-membered chelate dominates the subtle balance of selective complexation of AlH_2Cl at either O-1 or O-3, and thus destroys the high asymmetric induction.

Experimental Section

The ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer at 25.16 MHz with an internal deuterium lock (10–20% solutions in C_6D_6 with Me_4Si as an internal standard). The ^1H NMR spectra were recorded in 1–3% solutions in $CDCl_3$ on a Bruker WP-80 and on a Varian WH-270. A CH-5 mass spectrometer was used; an italic entry designates the *m/e* value of the base peak. Gas chromatography was done on a Becker-Packard instrument under the following typical conditions: 50-m CW 20M column, FID, injection temperature 250 °C, column temperature 50–250 °C, detector temperature 270 °C, 5 °C/min, N_2 pressure at 0.1 bar, 1 mV recorder, chart speed 1 cm/min.

The 1,3-dioxolanes were prepared from readily available ketones (**1a–m**), aldehydes (**2a–f**), and 2,3-butanediol. Racemic butanediol (Bayer) contained 2% of the meso compound. The reductions were performed as described in the literature; the reaction was quenched after 2 h. The molar ratio of 2:1:4 for the reactants (ketal/$LiAlH_4$/$AlCl_3$) was carefully maintained.[9] The substituted (4*R*,5*R*)- and (4*S*,5*S*)-4,5-dimethyl-1,3-dioxolanes constitute an A_3XYB_3 spin system, for which a full spectral simulation has not been carried out. Thus we report here only the proton signals of the substituents at carbon atom 2.

2,2,4,5-Tetramethyl-1,3-dioxolane (1a), bp 109 °C.[17]

2-Ethynyl-2,4,5-trimethyl-1,3-dioxolane (1b): bp 105 °C; n^{20}_D 1.4369; mass spectrum, *m/e* 140, 125, 96, *43*; ^1H NMR ($CDCl_3$) δ 2.47 (s, 1 H, ≡CH), 1.61 (s, 3 H, CH_3). Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.23; H, 8.75.

2-Neopentyl-2,4,5-trimethyl-1,3-dioxolane (1c): bp 65 °C (10 mm); n^{20}_D 1.4205; mass spectrum, *m/e* 171, *115*, 56, 73, 57, 43; ^1H NMR ($CDCl_3$) δ 1.70 (d, 2 H, CH_2), 1.38 (s, 3 H, CH_3), 1.06 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.66; H, 11.83.

2-Benzyl-2,4,5-trimethyl-1,3-dioxolane (1d): bp 114 °C (13 mm); n^{20}_D 1.4875; mass spectrum, *m/e* 150, 134, 115, **91**, 60, *43*; ^1H NMR ($CDCl_3$) δ 7.27 (s, 5 H, C_6H_5), 2.88 (s, 2 H, CH_2), 1.32 (s, 3 H, CH_3). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.50; H, 8.33.

2-Isobutyl-2,4,5-trimethyl-1,3-dioxolane (1e): bp 50 °C (10 mm); n^{20}_D 1.4202; mass spectrum, *m/e* (relative intensity) MS: 157, 115 (80), 73, 57, *43*; ^1H NMR ($CDCl_3$) δ 1.80 (m, 1 H, CH), 1.52 (d, 2 H, CH_2), 1.31 (s, 3 H, CH_3), 0.93 (d, 6 H, $C(CH_3)_2$). Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.96; H, 11.51.

2-Vinyl-2,4,5-trimethyl-1,3-dioxolane (1f): bp 25 °C (0.2 mm); n^{20}_D 1.4138; mass spectrum, *m/e* 127, 115, 73, 56, *43*; ^1H NMR ($CDCl_3$) δ 5.92 (q, 1 H, CH=), 5.38 (q, 1 H, $=CH_2$, trans), 5.06 (q, 1 H, $=CH_2$, cis), 2.4 (s, 3 H, CH_3). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.26; H, 9.48.

2-Propyl-2,4,5-trimethyl-1,3-dioxolane (1g): bp 26 °C (0.1 mm); n^{20}_D 1.4115; mass spectrum, *m/e* (relative intensity) 143, 129, 115 (70), 99, 86, 71, 57, *43*; ^1H NMR ($CDCl_3$) δ 1.58 (m, 4 H, CH_2CH_2), 1.31 (s, 3 H, CH_3), 0.95 (t, 3 H, CH_3). Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.05; H, 11.06.

2-Ethyl-2,4,5-trimethyl-1,3-dioxolane (1h): bp 45 °C (25 mm); n^{20}_D 1.4025; mass spectrum, *m/e* 129, 115, 100, 72, 57, *43*; ^1H NMR ($CDCl_3$) δ 1.63 (q, 2 H, CH_2), 1.30 (s, 3 H, CH_3), 0.92 (t, 3 H, CH_3). Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.23; H, 11.10.

2-Isopropyl-2,4,5-trimethyl-1,3-dioxolane (1i): bp 42 °C (15 mm); n^{20}_D 1.4147; mass spectrum, *m/e* 143, 115, 86, 71, 55, *43*; ^1H NMR ($CDCl_3$) δ 1.81 (septet, 1 H, CH), 1.26 (s, 3 H, CH_3), 0.92 (d, 6 H, $C(CH_3)_2$). Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.02; H, 11.15.

2-Phenyl-2,4,5-trimethyl-1,3-dioxolane (1j): bp 70 °C (0.01 mm); n^{20}_D 1.4898; mass spectrum, *m/e* (relative intensity) 192, 177 (80), 147, 115, *105*, 77; ^1H NMR ($CDCl_3$) δ 7.55, 7.29 (m, 5 H, C_6H_5), 1.61 (s, 3 H, CH_3). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.02; H, 8.25.

2-Cyclohexyl-2,4,5-trimethyl-1,3-dioxolane (1k): bp 72 °C (2 mm); n^{20}_D 1.4524; mass spectrum, *m/e* 183, 154, 139, 126, *115*, 83, 71; ^1H NMR ($CDCl_3$) δ 1.73 (m, 11 H, C_6H_{11}), 1.24 (s, 3 H, CH_3). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.95; H, 11.48.

(17) J. J. Plattner and H. Rapoport, *J. Am. Chem. Soc.*, **93**, 1758 (1971).

2-*tert*-Butyl-2,4,5-trimethyl-1,3-dioxolane (1l): bp 25 °C (0.001 mm); n^{20}_D 1.4193; mass spectrum, *m/e* 157, 128, 115, 100, 73, 57, *43*; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 3 H, CH_3), 0.96 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.60; H, 11.70.

2-Adamantyl-2,4,5-trimethyl-1,3-dioxolane (1m): bp 128 °C (0.1 mm); n^{20}_D 1.4957; mass spectrum, *m/e* 250, 235, 206, 135, *115*, 73; ^{1}H NMR ($CDCl_3$) δ 1.94 (s, 3 H, CH), 1.64 (s, 12 H, CH_2), 1.20 (s, 3 H, CH_3). Anal. Calcd for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.13; H, 10.09.

2-*tert*-Butyl-4,5-dimethyl-1,3-dioxolane (2a): bp 30 °C (20 mm); n^{20}_D 1.4180; mass spectrum, *m/e* 157, 130, 114, *101*, 73, 55, 41; ^{1}H NMR ($CDCl_3$) δ 4.65 (s, 1 H, CH), 0.88 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.16; H, 11.06.

2-Cyclohexyl-4,5-dimethyl-1,3-dioxolane (2b): bp 54 °C (1 mm); n^{20}_D 1.4522; mass spectrum, *m/e* 184, 183, 140, 111, *101*, 73, 55; ^{1}H NMR ($CDCl_3$) δ 4.81 (d, 1 H, CH), 1.52 (m, C_6H_{11}). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.16; H, 10.90. Found: C, 70.85; H, 11.08.

2-Ethyl-4,5-dimethyl-1,3-dioxolane (2c): bp 28 °C (15 mm); n^{20}_D 1.4061; mass spectrum, *m/e* 131, 102, *57*, 45, 29; ^{1}H NMR ($CDCl_3$) δ 4.77 (dd, 1 H, CH), 2.3 (m, 2 H, CH_2), 1.1 (m, CH_3). Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.20; H, 11.01.

2-Benzyl-4,5-dimethyl-1,3-dioxolane (2d): bp 66 °C (0.1 mm); n^{20}_D 1.4990; mass spectrum, *m/e* 191, 177, 164, 148, 133, 119, *101*, 91, 43; ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 5 H, C_6H_5), 5.21 (t, 1 H, CH), 2.89 (d, 2 H, CH_2). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.61; H, 8.03.

2-Phenyl-4,5-dimethyl-1,3-dioxolane (2e): bp 75 °C (1 mm); n^{20}_D 1.4998; mass spectrum, *m/e* 177, 133, *106*, 90, 77, 56, 43; ^{1}H NMR ($CDCl_3$) δ 5.97 (s, 1 H, CH), 7.4 (m, 5 H, C_6H_5). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.86; H, 7.83.

2,4,5-Trimethyl-1,3-dioxolane (2f): bp 107 °C (760 mm).[18]

1,2,4-Trimethyl-3-oxa-1-pentanol (3a): bp 25 °C (1 mm); n^{20}_D 1.4093; mass spectrum, *m/e* 115, 101, 87, *45*; ^{1}H NMR ($CDCl_3$) δ 3.5 (s, 1 H, OH), 3.66, 3.48 and 3.20 (m, CH groups), 1.10 and 1.05 (m, CH_3 groups), 1.13, 1.12 (m, 6 H, $C(CH_3)_2$); mass spectrum, *m/e* 87, *45*. Anal. Calcd for $C_7H_{16}O_2$: C, 63.60; H, 12.20. Found: C, 63.15, H, 11.95.

1,2,4-Trimethyl-3-oxa-5-hexyn-1-ol (3b): bp 55 °C (15 mm); n^{20}_D 1.4239; GC indicates 15.2% + 16.3% + 68% **1b**; mass spectrum, *m/e* 127, 98, 45, in addition to fragments of **1b**.

1,2,4,6,6-Pentamethyl-3-oxa-1-heptanol (3c): bp 48 °C (0.1 mm); n^{20}_D 1.4281; GC indicates 64.0% + 35.9%; mass spectrum, *m/e* 143, 117, 99, 73, 57, 45; ^{1}H NMR ($CDCl_3$) δ 2.88 (s, 1 H, OH), CH groups at 3.6, 3.29 (m), and 1.5, 1.3 (m, 2 H, CH_2), CH_3 groups at 1.09, 1.08, and 1.06 (m), 0.91 (s, 9 H, $C(CH_3)_3$). Anal. Calcd for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 69.86; H, 12.50.

5-Phenyl-1,2,4-trimethyl-3-oxa-1-pentanol (3d): bp 66 °C (0.01 mm); n^{20}_D 1.4884, GC indicates 38.9% + 57.4% + 3% **1d**; mass spectrum, *m/e* 208, 163, 119, 91, *73*, 55, 45; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5 H, C_6H_5), CH groups at 3.5 (m), and 2.75, 2.58 (m, 2 H, CH_2), CH_3 groups at 1.12, 1.06, 0.95 (isomer I), 1.07, 1.02, and 0.86 (isomer II), ratio of isomers 1:1. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 7.68. Found: C, 75.10; H, 8.01.

1,2,4,6-Tetramethyl-3-oxa-1-heptanol (3e): bp 30 °C (0.1 mm) n^{20}_D 1.4131; GC indicates 71.6% + 22.9% + 5% **1e**; mass spectrum, *m/e* 129, 113, 55, *45*; ^{1}H NMR ($CDCl_3$) δ 4.77 (s, 1 H, OH), CH groups at 3.55 and 3.22 (m), CH_3 groups at 1.15 (m) and 0.9 (m, 6 H, $CH(CH_3)_2$), 1.5 (d, 2 H, CH_2).

1,2,4-Trimethyl-3-oxa-5-hexen-1-ol (3f): bp 45 °C (15 mm); n^{20}_D 1.4241; GC indicates 44.7% + 53.3%; mass spectrum, *m/e* 129, 115, 99, 73, *55*, 45. ^{1}H NMR ($CDCl_3$) δ 5.83 (octet, 1 H, CH=), 5.19 (dt, 1 H, $=CH_2$), 5.16 (dt, 1 H, $=CH_2$), CH groups at 3.98, 3.55, and 3.27 (q), CH_3 groups at 1.2, 1.1, and 1.04 (d), 3.85 (s, 1 H, OH) (isomer I), 5.70 (octet, 1 H, CH=), 5.15 (dt, 1 H, $=CH_2$), 5.08 (dt, 1 H, $=CH_2$), CH groups at 3.98, 3.58, and 3.25 (q), CH_3 groups at 1.20, 1.08, and 1.03 (d), 3.85 (s, 1 H, OH) (isomer II), ratio of isomers 1:1. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.50; H, 10.93.

1,2,4-Trimethyl-3-oxa-1-heptanol (3g): bp 60 °C (4 mm); n^{20}_D 1.4211; GC indicates 59.0% + 26.1%; mass spectrum, *m/e* 115, 71, 55, *45*, 29; ^{1}H NMR ($CDCl_3$) δ CH groups at 3.5 and 3.2 (m), 2.74 (s, 1 H, OH), 1.4 (m, 4 H, 2 CH_2), CH_3 groups at 1.06, 1.1, 1.0, and 0.88 (m, 3 H, CH_3 terminal). Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.09; H, 12.16.

1,2,4-Trimethyl-3-oxa-1-hexanol (3h): bp 62 °C (15 mm); n^{20}_D 1.4159; GC indicates 73% + 23.7%; mass spectrum, *m/e* 117, 101, 73, 57, *45*, 41; ^{1}H NMR ($CDCl_3$) δ CH groups at 3.5 and 3.18 (m), 2.88 (s, 1 H, OH), 1.49 (m, 2 H, CH_2), CH_3 groups at 1.1, 1.09, and 1.04 (d), ratio of 2:1. Anal. Calcd for $C_8H_{18}O_2$: C, 65.70; H, 12.40. Found: C, 65.46; H, 12.14.

1,2,4,5-Tetramethyl-3-oxa-1-hexanol (3i): bp 70 °C (15 mm); n^{20}_D 1.4202; GC indicates 76.5% + 20.7%; mass spectrum, *m/e* ^{1}H NMR ($CDCl_3$) CH groups at δ 3.5, 3.24, and 3.19 (q), 2.79 (s, 1 H, OH), 1.65 (sextet, 1 H, $CH(CH_3)_2$, $J_{4,5}$ = 5.6 Hz), CH_3 groups at 1.14, 10.8, 1.06, 0.9, and 0.89 (d) (isomer I), CH groups at 3.54, 3.34, and 3.22, 2.76 (s, 1 H, OH), 1.80 (sextet, 1 H, $CH(CH_3)_2$, $J_{4,5}$ = 4.8 Hz), CH_3 groups at 1.10, 1.08, 1.06, 0.91, 0.90 (d) (isomer II), ratio of isomers 3:1. Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.58. Found: C, 67.15; H, 12.42.

4-Phenyl-1,2,4-trimethyl-3-oxa-1-pentanol (3j): bp 59 °C (0.01 mm); GC indicates 50.7% + 45.8%; n^{20}_D 1.4988; mass spectrum, *m/e* 149, 121, *105*, 91, 77, 51, 45; ^{1}H NMR ($CDCl_3$) δ 7.31 (s, 5 H, C_6H_5), 4.45 (q, 1 H, CHC_6H_5), 3.51 (dq, 1 H, CH), 3.08 (dq, 1 H, CH) (isomer I), 3.28 (dq, 1 H, CH) (isomer II), CH_3 groups at 1.42, 1.09, and 1.01 (d), ratio of isomers 1.2:1. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.53.

4-Cyclohexyl-1,2,4-trimethyl-3-oxa-1-pentanol (3k): bp 56 °C (0.01 mm); n^{20}_D 1.4578; GC indicates 69.4% + 22.9% + 8% **1k**; mass spectrum, *m/e* 155, 117, *111*, 73, 69, 55, 45; ^{1}H NMR ($CDCl_3$) δ CH groups at 3.49 (isomer I), 3.53 (isomer II), 3.22, and 3.18 (q), 2.77 (s, 1 H, OH), 1.74 (m, C_6H_{11}), 1.3 (m, 1 H, CH), CH_3 groups at 1.13, 1.07, and 1.05 (d). Anal. Calcd for $C_{12}H_{21}O_2$: C, 71.95; H, 12.08. Found: C, 71.43; H, 11.86.

1,2,4,5,5-Pentamethyl-3-oxa-1-hexanol (3l): bp 42 °C (1 mm); n^{20}_D 1.4268; GC indicates 11.9% + 85.0%; mass spectrum, *m/e* 129, *85*, 73, 55, 43; ^{1}H NMR ($CDCl_3$) CH groups at δ 3.56, 3.23, and 3.14 (q), 2.76 (s 1 H, OH), CH_3 groups at 1.11, 1.06, and 1.04 (m), 0.88 (s, 9 H, $C(CH_3)_3$) (isomer I), 0.86 (s, 9 H, $C(CH_3)_3$) (isomer II), ratio of isomers 9:1. Anal. Calcd for $C_{10}H_{22}O_2$: C, 68.92; H, 12.72. Found: C, 69.13; H, 12.44.

4-(1-Adamantyl)-1,2-dimethyl-3-oxa-1-pentanol (3m): bp 110 °C (0.01 mm); n^{20}_D 1.4972; GC indicates 88.5% + 11.4%; mass spectrum, *m/e 163*, 135, 107, 81, 73, 41; ^{1}H NMR ($CDCl_3$) CH groups at δ 3.57, 3.20, and 3.00 (q), 3.05 (t, 1 H, OH), CH_3 groups at 1.15, 1.09, and 1.05 (d), 1.66 (m, 15 H, $C_{10}H_{15}$) (isomer I), CH groups at 3.50, 3.15, and 2.95 (q), CH_3 groups at 1.14, 1.10, and 1.03 (d) (isomer II), ratio of isomers 6.3:1. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 75.86; H, 11.06.

1,2,5,5-Tetramethyl-3-oxa-1-hexanol-*4-d* (4a): bp 77–78 °C (20 mm); n^{20}_D 1.4138; mass spectrum, *m/e* 161, 116, *72*, 55, 44; ^{1}H NMR ($CDCl_3$; silylated with $(CH_3)_3SiCl$) δ 3.81 (dq, 1 H, CH, $^3J_{1,2}$ = 5.2 Hz) 3.23 (dq, 1 H, CH, $^3J_{2,CH_3}$ = 6.3 Hz), 3.04 (t, 1 H, CHD, $^2J_{4,D}$ = 1.2 Hz) (isomer I), 3.10 (t, 1 H, CHD, $^2J_{4,D}$ = 1.2 Hz) (isomer II), ratio of isomers 78:22, 0.89 (s, 9 H, $C(CH_3)_3$), 0.11 (s, 9 H, $Si(CH_3)_3$). Anal. Calcd for $C_9H_{19}DO_2$: C, 67.03; H, 13.13. Found: C, 67.40; H, 12.88.

4-Cyclohexyl-1,2-dimethyl-3-oxa-1-butanol-*4-d* (4b): bp 50 °C (0.01 mm); n^{20}_D 1.4552; mass spectrum, *m/e* 189, 142, *98*, 55, 45; ^{1}H NMR ($CDCl_3$; WH 270; **4b**/Eu(fod)$_3$ ratio of 1:6.9) δ 5.53, 4.07 (2 CH), 3.61 (t, CHD) (isomer I), 3.80 (t, CHD) (isomer II), ratio of isomers 90:10, 2.15 (CH_3), 1.65 (CH_3), 1.75, 1.50 (C_6H_{11}), 9.51 (OH). Anal. Calcd for $C_{11}H_{23}DO2$: C, 69.79; H, 13.31. Found: C, 69.66; H, 12.90.

1,2-Dimethyl-3-oxa-1-hexanol-*4-d* (4c): bp 42 °C (20 mm); n^{20}_D 1.4103; mass spectrum, *m/e* 133, 118, 102, 88, *45*; 270-MHz ^{1}H NMR ($CDCl_3$) δ 3.49 (q, 1 H, CH), 3.08 (q, 1 H, CH), 3.22 (t, 1 H, CHD, $^2J_{4,D}$ = 1.4 Hz), 2.86 (s, 1 H, OH), 1.57 (q, 2 H, CH_2), 1.12, 1.08 (dd, 6 H, 2 CH_3), 0.92 (t, 3 H, CH_3), no other isomer detected. Anal. Calcd for $C_7H_{15}DO_2$: C, 63.12; H, 12.86. Found: C, 62.93; H, 12.96.

5-Phenyl-1,2-dimethyl-3-oxa-1-pentanol-*4-d* (4d): bp 80 °C (0.1 mm); n^{20}_D 1.4969; mass spectrum, *m/e* 195, 150, *106*, 73, 45; ^{1}H NMR ($CDCl_3$; silylated with Me_3SiCl) δ 3.77 (dq, 1 H, CH, $^3J_{1,2}$ = 5.4 Hz, $^3J_{1,CH_3}$ = 6.3 Hz), 3.27 (dq, 1 H, CH, $^3J_{2,CH_3}$ = 6.3 Hz), 3.70 (tt, 1 H, CHD $^2J_{4,D}$ = 1.6 Hz) (isomer I), 3.61 (tt, 1 H, CHD) (isomer II), ratio of isomers 90.6:9.4, 1.04 (d, 3 H, CH_3), 1.06 (d, 3 H, CH_3), 2.84 (d, 2 H, CH_2), 7.22 (m, 5 H, C_6H_5), 0.10

(18) H. K. Garner and H. J. Lucas, *J. Am. Chem. Soc.*, 72, 5497 (1950).

(s, 9 H, $Si(CH_3)_3$). Anal. Calcd for $C_{12}H_{17}DO_2$: C, 73.81; H, 9.80. Found: C, 73.52; H, 9.57.

4-Phenyl-1,2-dimethyl-3-oxa-1-butanol-4-*d* (4e): bp 59 °C (0.01 mm); n^{20}_D 1.5044; mass spectrum, *m/e* 181, 136, *92*, 66, 45; ^1H NMR ($CDCl_3$) δ 7.27 (m, 5 H, C_6H_5), 3.58 (dq, 1 H, CH), 3.26 (dq, 1 H, CH), 4.37 (t, 1 H, CHD, $^2J_{4,D}$ = 1.5 Hz) (isomer I), 4.36 (t, 1 H, CHD, $^2J_{4',D}$ = 1.5 Hz) (isomer II), ratio of isomers 86:14, 2.89 (s, 1 H, OH), 1.11 (d, 6 H, 2 CH_3); 30.7-MHz ^2H NMR ($CDCl_3$) Δδ = 0.12 ppm (ratio of isomers I and II of 86:14). Anal. Calcd for $C_{11}H_{15}DO_2$: C, 72.89; H, 9.45. Found: C, 72.60; H, 9.22.

1,2-Dimethyl-3-oxa-1-pentanol-4-*d* (4f): bp 37 °C (10 mm); n^{20}_D 1.4102; mass spectrum, *m/e* 119, 104, 89, 74, *45*; 270-MHz ^1H NMR ($CDCl_3$; silylated with $(CH_3)_3SiCl$) δ 3.79 (dq, 1 H, CH, $^3J_{1,2}$ = 5.3 Hz, $^3J_{1,CH_3}$ = 6.3 Hz), 3.72 (dq, 1 H, CH, $^3J_{2,CH_3}$ = 6.3 Hz), 3.48 (qt, 1 H, CHD, $^2J_{4,D}$ = 1.3 Hz) (isomer I), 3.33 (qt, 1 H, CHD, $^2J_{4',D}$) = 1.3 Hz) (isomer II), ratio of isomers 84.5:2.6, 1.09 (d, 3 H, CH_3), 1.06 (d, 3 H, CH_3), 1.17 (dt, 3H, CH_3, $^3J_{CH_3,D}$ = 1.5 Hz), 0.11 (s, 9 H, $Si(CH_3)_3$); 30.7-MHz ^2H NMR ($CDCl_3$) 3.54, 3.65 ppm (ratio of isomers I and II of 86:1.7). Anal. Calcd for $C_6H_{13}DO_2$: C, 60.47; H, 12.68. Found: C, 60.62; H, 12.28.

(4*S*,5*S*)-(−)-4,5-Bis(methoxymethyl)-2-ethyl-2-methyl-1,3-dioxolane (5a). Compound **5a** was made from (*S,S*)-(−)-1,4-dimethoxy-2,3-butanediol[19] and butan-2-one: bp 62 °C (20 mm); n^{20}_D 1.4401; mass spectrum, *m/e* 189, 175, 115, *84*, 59, 47; ^1H NMR ($CDCl_3$) δ 4.0, 3.9 (m, 2 H, CH), 3.49 (d, 4 H, 2 CH_2), 3.40 (s, 6 H, 2 CH_3), 1.70 (q, 2 H, CH_2), 1.36 (s, 3 H, CH_3), 0.93 (t, 3 H, CH_3); $[\alpha]^{20}_D$ −4.5° (*c* 3.5, $CHCl_3$). Anal. Calcd for $C_{10}H_{20}O_4$: C, 58.79; H, 9.86. Found: C, 58.66; H, 8.98.

(4*S*,5*S*)-(+)-4,5-Bis(methoxymethyl)-2-*tert*-butyl-2-methyl-1,3-dioxolane (5b) was made from (*S,S*)-(−)-1,4-dimethoxy-2,3-butanediol and 3,3-dimethylbutan-2-one: bp 105 °C (14 mm); n^{20}_D 1.4358; mass spectrum, *m/e* 217, 187, 175, *115*, 101, 85, 59, 43; ^1H NMR ($CDCl_3$) δ 4.04 (m, 1 H, CH, $^3J_{4,5}$ = 8.5 Hz, $^3J_{4,CH_2}$ = 5.0 Hz), 3.6 (m, 5 H, CH, 2 CH_2), 3.36, 3.35 (d, 6 H, OCH_3), 1.28 (s, 3 H, CH_3), 0.95 (s, 9 H, $C(CH_3)_3$); $[\alpha]^{20}_D$ +1.4° (*c* 18.0, $CHCl_3$). Anal. Calcd for $C_{12}H_{24}O_4$: C, 61.98; H, 10.17. Found: C, 62.03; H, 10.41.

2-(Methoxymethyl)-2,4,5-trimethyl-1,3-dioxolane (6) was made from racemic 2,3-butanediol and methoxyacetone: bp 42 °C (6 mm); n^{20}_D 1.3940; mass spectrum, *m/e* 145, 115, 73, 59, *43*; ^1H NMR ($CDCl_3$) δ 3.65 (m, 2 H, CH), 3.40 (s, 3 H, OCH_3), 3.32 (s, 2 H, CH_2), 1.38 (s, 3 H, CH_3), 2.55 (d, 6 H, 2 CH_3). Anal. Calcd for $C_8H_{16}O_3$: C, 59.97; H, 10.06. Found: C, 59.95; H, 10.42.

1,2-Bis(methoxymethyl)-4-methyl-3-oxa-1-hexanol (7a): bp 81 °C (0.1 mm); n^{20}_D 1.4313; GC indicates 47.2% + 42.5% + 10% **5a**; mass spectrum, *m/e* 189, 175, 161, 143, 131, 115, 105, 87, 75, 57, *45*; ^1H NMR ($CDCl_3$) δ 3.8, 3.5 (m, 5 H, CH, CH_2), 3.38, 3.37, 3.36 (s, 6 H, OCH_3), 2.89 (s, 1 H, OH), 1.5 (m, 2 H, CH_2), 1.15, 1.12 (dd, 3 H, CH_3), 0.92 (t, 3 H, CH_3).

1,2-Bis(methoxymethyl)-4,5,5-trimethyl-3-oxa-1-hexanol (7b): bp 120 °C (6 mm); n^{20}_D 1.4360; GC indicates 46.49% + 41.94%; mass spectrum, *m/e* 189, 177, 101, 85, 75, 59, 43; ^1H NMR ($CDCl_3$) δ 3.33, 3.32 (2 s, 6 H, OCH_3), 3.3, 3.3 (m, 7 H, CH, CH_2), 3.0 (s, 1 H, OH), 1.05 (dd, 3 H, CH_3), 0.88 (s, 9 H, $C(CH_3)_3$) (isomer I), 1.02 (dd, 3 H, CH_3), 0.87 (s, 3 H, CH_3) (isomer II), ratio of isomers 1:1. Anal. Calcd for $C_{12}H_{26}O_4$: C, 61.54; H, 11.11. Found: C, 61.53; H, 10.94.

1,2,4-Trimethyl-1,3,6-dioxa-1-heptanol (8): bp 68 °C (10 mm); n^{20}_D 1.4175; GC indicates 45.5% + 54.2%; mass spectrum, *m/e* 117, *73*, 55, 45; ^1H NMR ($CDCl_3$) δ 4.12 (s, 1 H, OH), 3.7 (m, 5 H, CH, CH_2), 3.34 (s, 3 H, CH_3) (isomer I), 3.33 (s) (isomer II), ratio of isomers 1:1, 1.09, 1.08, 1.12, 1.07 (d, 9 H, 3 CH_3). Anal. Calcd for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 59.50; H, 10.83.

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Registry No. 1a, 5660-61-7; **1b**, 79449-66-4; **1c**, 79449-67-5; **1d**, 5406-60-0; **1e**, 4351-14-8; **1f**, 79449-68-6; **1g**, 6414-04-6; **1h**, 4359-51-7; **1i**, 79449-69-7; **1j**, 5413-61-6; **1k**, 79449-70-0; **1l**, 79449-71-1; **1m**, 79449-72-2; **2a**, 24382-65-8; **2b**, 74793-11-6; **2c**, 24382-63-6; **2d**, 5468-06-4; **2e**, 4359-31-3; **2f**, 3299-32-9; **3a**, 79449-73-3; **3b**, 79449-74-4; **3c**, 74810-44-9; **3d**, 74810-46-1; **3e**, 74810-45-0; **3f**, 79449-75-5; **3g**, 74810-43-8; **3h**, 79449-76-6; **3i**, 79449-77-7; **3j**, 79449-78-8; **3k**, 79449-79-9; **3l**, 79449-80-2; **3m**, 79449-81-3; **4a**, 79449-82-4; **4b**, 79449-83-5; **4c**, 79449-84-6; **4d**, 79449-85-7; **4e**, 79449-86-8; **4f**, 79449-87-9; **5a**, 79449-88-0; **5b**, 79449-89-1; **6**, 79449-90-4; **7a**, 79449-91-5; **7b**, 79449-92-6; **8**, 79449-93-7; butan-2-one, 78-93-3; (*S,S*)-(−)-1,4-dimethoxy-2,3-butanediol, 50622-10-1; 3,3-dimethylbutan-2-one, 75-97-8; (±)-2,3-butanediol, 6982-25-8; methoxyacetone, 5878-19-3.

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