Fatty Alcohols Through Hydroxylation of Symmetrical Alkenes with Selenium Dioxide/*tert.*-Butylhydroperoxide

G. Knothe*, M.O. Bagby and D. Weisleder
NCAUR, USDA, Peoria, Illinois 61604

ABSTRACT: Several symmetrical alkenes were reacted with the selenium dioxide/*tert.*-butylhydroperoxide system to give three hydroxylated products each. These products were those of allylic mono- and dihydroxylation (*meso* and *threo* dihydroxy compounds) of the double bond. Some dihydroxy products were hydrogenated to give saturated 1,4-diols. The compounds were characterized by nuclear magnetic resonance. The products have potential for application in commercial products, such as biodiesel, lubricants, greases, and cosmetics.
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KEY WORDS: Hydroxylation, nuclear magnetic resonance, selenium dioxide, symmetrical alkene, *tert.*-butylhydroperoxide.

Recently we reported on the reaction of isolated double bonds in fatty compounds with the selenium dioxide (SeO_2)/*tert.*-butylhydroperoxide (TBHP) system (1–3). Four hydroxylated products, by monohydroxylation of either allylic position and by dihydroxylation of both allylic positions to give *erythro/threo* diastereomers, were obtained. In our continuing efforts to synthesize novel hydroxy fatty compounds, we were interested in obtaining compounds with hydroxy groups near the center of pure hydrocarbon chains. Therefore, several symmetrical alkenes were reacted with the SeO_2/TBHP system to give three hydroxylated products, the monohydroxy compound and two diastereomers of dihydroxy compounds.

The reaction of SeO_2/TBHP with alkenes can also offer a route to novel fatty alcohols where the hydroxy group is not at carbon atom #1 (C_1). Fatty alcohols are of considerable interest as surfactants (4), and have potential as components in microemulsions for vegetable oil-based alternative diesel fuels (5–7). Accordingly, we are seeking novel fatty alcohols that might serve the aforementioned purposes. Allylic hydroxy fatty compounds (with functional groups at C_1), such as those obtained previously (1–3), exhibit good surfactant properties (8).

Besides synthesis and properties of these compounds, we also were interested in the nuclear magnetic resonance (NMR) characterization of these compounds. The previous compounds with carboxylic acid, methyl ester, or hydroxy groups at C_1 displayed interesting effects, especially in ^{13}C NMR (2,3,9). The present products enable the study of the allylic mono- and dihydroxy functionalities without the influence of other functional groups.

*To whom correspondence should be addressed at NCAUR, 1815 North University St., Peoria, IL 61604.

MATERIALS AND METHODS

4(*E*)-Octene was purchased from Sigma Chemical Co. (St. Louis, MO). 5(*E*)-Decene and 7(*E*)-tetradecene were obtained from Aldrich Chemical Co. (Milwaukee, WI). Solvents were obtained either from EM Science (Gibbstown, NJ) or Fisher Scientific (Fairlawn, NJ).

NMR spectra were obtained with $CDCl_3$ as solvent on a Bruker (Rheinstetten, Germany) ARX-400 spectrometer operating at 400 MHz (^1H NMR) or 100 MHz (^{13}C NMR).

Gas chromatography/mass spectrometry (GC/MS) analyses were conducted on a Hewlett-Packard (Palo Alto, CA) 5890/5970 benchtop GC/MS system, operated with electron ionization (EI) and equipped with a J&W Scientific (Folsom, CA) DB-1 column. Derivatizations for GC/MS were carried out by silylating at ambient temperature with a Supelco (Bellefonte, PA) Sylon BTZ mixture that contained trimethylchlorosilane, *N,O-bis*(trimethylsilyl)acetamide and *N*-trimethylsilylimidazole.

Fourier transform infrared (FTIR) spectra were recorded on a Mattson (Madison, WI) Polaris spectrometer as film on NaCl plates (for liquids), or with KBr as matrix in diffuse reflectance technique (for solids). Melting points (uncorrected) were determined on an Electrothermal (Southend, England) 9300 or a Fisher-Johns apparatus.

The high-performance liquid chromatography (HPLC) system was sequentially comprised of a Gilson (Madison, WI) Model 303 pump, a Rainin (Woburn, MA) Dynamax-60A silica column (25 cm × 21.4 mm i.d.), a Kratos (Perkin-Elmer Corp., Norwalk, CT) Spectroflow 757 absorbance detector, a Waters (Millipore Corp., Milford, MA) R401 differential refractometer, and an NGI Servogor 124 (Fisher Scientific, Pittsburgh, PA) chart recorder. The flow rate was 25 mL/min, and fractions were collected manually. All runs were conducted isocratically.

6(Z)-Dodecene. This material was prepared by Wittig reaction of hexanal and hexyltriphenylphosphonium bromide (both from Aldrich) by following a published procedure (10).

Butyllithium (2.5*M* solution in hexanes; Aldrich) was used in this reaction. Differing from the literature (10), in the present work the product was purified after work-up by HPLC by means of the system described previously with hexane as eluent. The product was obtained as a colorless liquid. Yields were in the range of 45–50% for repeated reactions. ^{1}H NMR ($CDCl_3$): 5.35 (*m*, 2H, C*H*=C*H*, *J* = 4.7 Hz), 2.01 (*q*, 4H, CH_2–CH=CH–CH_2), 1.26-1.35 (*m*, 12H, CH_2), 0.88 (*t*, 6H, CH_3); ^{13}C-NMR ($CDCl_3$): 129.89, 31.54, 29.46, 27.17, 22.58, 14.11; EI-MS: 41 (100%), 168 (11%, M^+); IR (NaCl): 3006, 2960, 2929, 2859, 1462, 725 cm^{-1}. The product contained some 6(*E*)-dodecene, as evidenced by small ^{13}C NMR peaks at 130.36 and 32.58 ppm.

8(Z)-Hexadecene. A Wittig reaction of octanal (Aldrich) with octyltriphenylphosphonium bromide (Lancaster Synthesis, Windham, NH), analogous to the procedure used for 6(*Z*)-dodecene, afforded 8(*Z*)-hexadecene. Purification was again carried out by HPLC with hexane as eluent to give the product as a colorless liquid. Yields were similar to the synthesis of 6(*Z*)-dodecene. ^{1}H NMR ($CDCl_3$): 5.34 (*m*, 2H, C*H*=C*H*, *J* = 4.7 Hz), 2.01 (*q*, 4H, CH_2–CH=CH–CH_2), 1.36–1.26 (*m*, 20H, CH_2), 0.87 (*t*, 6H, CH_3); ^{13}C NMR ($CDCl_3$): 129.88, 31.87, 29.77, 29.27, 29.22, 27.19, 22.67, 14.09; EI-MS:41 (100%), 224 (4%, M^+); IR (NaCl): 3006, 2956, 2925, 2856, 1462, 722 cm^{-1}. The product also contained some 8(*E*)-hexadecene as shown by small ^{13}C NMR peaks at 130.36 and 32.62 ppm.

9(Z)-Octadecene. This compound was synthesized from oleyl alcohol (Nu-Chek-Prep, Elysian, MN) by a published procedure (11) employing tosylation and reduction with lithium aluminum hydride (LAH). *p*-Toluenesulfonyl chloride and 1*M* LAH in tetrahydrofuran, both from Aldrich, were used in this procedure. The colorless liquid product obtained after work-up did not require further purification as determined by GC/MS. Overall yield was 85%. ^{1}H NMR ($CDCl_3$): 5.34 (*m*, 2H, C*H*=C*H*, *J* = 5.3 Hz), 2.01 (*q*, 4H, CH_2–CH=CH–CH_2), 1.26–1.34 (*m*, 24H, CH_2), 0.88 (*t*, 6H, CH_3); ^{13}C NMR ($CDCl_3$): 129.89, 31.92, 29.79, 29.55, 29.34, 27.21, 22.69, 14.11; EI-MS: 41 (100%), 252 (2%, M^+); IR (NaCl): 3006, 2925, 2856, 1462, 722 cm^{-1}.

Hydroxylation reaction. This reaction with SeO_2 (Aldrich) and TBHP (90% solution in water; Aldrich) was conducted as described (1–3). Stoichiometric ratios of alkene to SeO_2/TBHP (alkene/SeO_2, 1.03:1) were unchanged. Reaction time usually was 48 h. Two HPLC runs purified the products after work-up. An 80:20:1 hexane/ethyl acetate/acetic acid purified the monohydroxy compound. The column was washed with methanol and filled with ethyl acetate for the time between runs. A subsequent run of the material in the wash with 95:5 methylene chloride/methanol separated and purified the dihydroxy diastereomers. FTIR (general for liquid products; cm^{-1}): 3360, 2960, 2925, 2860, 1462, 970; FTIR (general for solid products; cm^{-1}): 3310, 3325, 2960, 2925, 2860, 1462, 1138, 1070, 970, 910. EI-MS: All products were derivatized for mass spectral analyses, *m/z* 73 [= $(CH_3)_3Si$] was the base peak in all spectra; monohydroxy products: *m/z* 199 [3-trimethylsilyloxy (tmso)-4(*E*)-octene, $M^+ - H$], *m/z* 185 [4-tmso-5(*E*)-decene], *m/z* 199 [5-tmso-6(*E*)-dodecene], *m/z* 213 [6-tmso-7(*E*)-tetradecene], *m/z* 241 [8-tmso-9(*E*)-octadecene]; dihydroxy compounds (*meso* and *threo* had indistinguishable patterns): *m/z* 259, 169, 131 [3,6-*bis*(tmso)-4(*E*)-octene], *m/z* 273, 183, 145 [4,7-*bis*(tmso)-5(*E*)-decene], *m/z* 287, 197, 159 [5,8-*bis*(tmso)-6(*E*)-dodecene], *m/z* 301, 211, 173 [6,9-*bis*(tmso)-7(*E*)-tetradecene], *m/z* 315, 225, 187 [7,10-*bis*(tmso)-8(*E*)-hexadecene], and *m/z* 329, 239, 201 [8,11-*bis*(tmso)-9(*E*)-octadecene].

Hydrogenation reaction. These reactions were carried out as described (1–3) with the hydrazine (64% solution in water; Sigma Chemical Co.)/air system for the unsaturated 1,4-diols as starting materials at reaction times of 48 h. All products were obtained as white solids. FTIR (general; cm^{-1}): 3265, 2955, 2925, 2855, 1465, 1340, 1125, 1045, 910. EI-MS: All products silylated, *m/z* 73 again base peak; *m/z* 275, 185, 145 [4,7-*bis*(tmso)-decane], *m/z* 289, 199, 159 [5,8-*bis*(tmso)-dodecane], *m/z* 303, 213, 173 [6,9-*bis*(tmso)-tetradecane], *m/z* 317, 227, 187 [7,10-*bis*(tmso)-hexadecane], *m/z* 331, 241, 201 [8,11-*bis*(tmso)-octadecane].

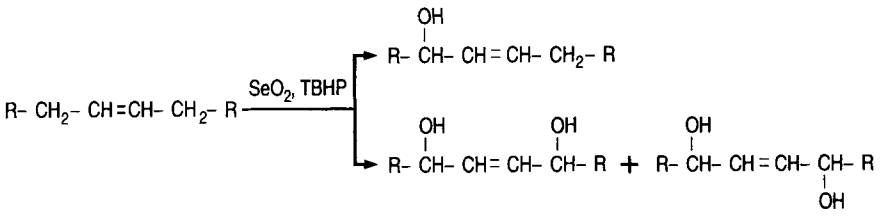
RESULTS AND DISCUSSION

Symmetrical alkenes, 4(*E*)-octene, 5(*E*)-decene, 6(*Z*)-dodecene, 7(*E*)-tetradecene, 8(*Z*)-hexadecene, and 9(*Z*)-octadecene, reacted with SeO_2/TBHP to afford three hydroxylated products separable by HPLC. These products were one monohydroxy compound and two fractions of dihydroxy compounds. All products had *trans* double bond configuration, regardless of the double bond configuration of the starting material. This effect is known to arise in SeO_2-based hydroxylations (12; for a review of SeO_2based allylic hydroxylation, see Ref. 13). Table 1 lists reactions, as well as yields

TABLE 1
Yields and Melting Points of Products Obtained from the Allylic Mono- and Dihydroxylation of Unsubstituted Symmetrical Alkenes with Selenium Dioxide/*tert.*-Butylhydroperoxide

	Products				
		Dihydroxy			
	Monohydroxy[a]	*meso*		*threo*	
Starting material	Yield[b] (%)	Yield[b] (%)	m.p. (°C)	Yield[b] (%)	m.p. (°C)
4(*E*)-Octene	38	2	50–51	5	liq.[c]
5(*E*)-Decene	50	7	37–39	13	liq.
6(*Z*)-Dodecene[d]	31	9	59–60	13	liq.
7(*E*)-Tetradecene	55	12	69–70	12	liq.
8(*Z*)-Hexadecene[d]	45	10	70–71	10	38–39
9(*Z*)-Octadecene	35	6	82–83	12	40–41

[a]All monohydroxy products were clear liquids at ambient temperature. No melting points determined.
[b]Yields determined by gas chromatography/mass spectrometry (GC/MS). Ratios of dihydroxy products were determined gravimetrically after high-performance liquid chromatography purification and applied to GC/MS.
[c]liq. = Liquid at room temperature.
[d]Contain smaller amounts of the *E*-isomer. This does not affect the outcome of the hydroxylation reactions because all hydroxylated products have the same configuration (*E*).



SCHEME 1

and melting points, of the products. Scheme 1 depicts the procedure for the synthesis of the hydroxy products.

The formation of two dihydroxy products corresponds with previous results (1–3) on the reaction of C_1-functionalized monoalkenoic long-chain compounds with SeO_2/TBHP. However, due to the symmetry of the present compounds, the products are the *meso* compound [corresponding to the *erythro* diastereomer when functional groups at C_1 are present (1–3); absolute configuration *R,S*] and the *threo* (absolute configurations *R,R* and *S,S*) diastereomer. In other work on hydroxylation of compounds with double bonds, including straight-chain terminal alkenes, only one monohydroxylated product was obtained (13).

Corresponding to previous results on reactions of C_1-functionalized long-chain compounds, in most reactions the *threo* diastereomer was formed in moderately higher yield than the *meso* counterpart. This effect was less regular here than with the compounds containing functional groups at C_1.

Mass-spectral characterization of the products. The EI mass spectra of the silylated products obey a fragmentation pattern discussed in the literature (2). Diagnostic peaks of the products are listed in the Materials and Methods section. Combination of mass and NMR spectra identified the position of the functional group.

NMR characterization: allylic monohydroxy products. The ^{13}C NMR peaks of the monohydroxy products are given in Table 2.

The differences in the chemical shifts of the olefinic carbons range between 0.42 and 0.92 ppm. These differences are virtually identical to those observed for C_1-functionalized compounds in which the sole hydroxy group is on the side of the C_1 functional group (referred to as position I; Ref. 2). When the hydroxy group is on the terminal methyl side in C_1-functionalized compounds (referred to as position II), there is a regular trend in the shift values and differences of the olefinic carbon signals (2), which can be evaluated as rational functions (9). The shift values and differences depend directly on the position of the double bond in the chain. The differences in the olefinic carbons observed here and in the C_1-functionalized compounds with the OH on the C_1 side correspond to the differences in the correction factor between rational functions deduced for unsubstituted octadecenoic acids and position II allylic hydroxy fatty acids (9).

The chemical shifts of the other signals are mainly influenced by the proximity of the enol functionality to the terminal methyl groups. As expected, at greater chainlengths this influence diminishes. The downfield olefinic carbon in the

TABLE 2
^{13}C Nuclear Magnetic Resonance (NMR) Signals of the Monohydroxy Products (solvent: $CDCl_3$)

Compound	^{13}C NMR signals[a] (ppm)			
	CH=CH	CHOH	CH_2	CH_3
4(*E*)-Octen-3-ol	132.62(4) 132.20(5)	74.59	34.22(2) 29.98(6) 22.28(7)	13.57(8) 9.69(1)
5(*E*)-Decen-4-ol	132.99(5) 132.07(6)	72.92	39.42(3) 31.83 31.82 22.15(9) 18.65(2)	13.95 13.87
6(*E*)-Dodecen-5-ol	132.91(6) 132.22(7)	73.23	36.95(4) 32.12(8) 31.33(10) 28.83(9) 27.63(3) 22.59 22.47	14.01[b]
7(*E*)-Tetradecen-6-ol	132.91(7) 132.12(8)	73.19	37.18(5) 32.14(9) 31.71 31.65 29.10 28.77 25.11(4) 22.56(2,13)[b]	14.01 13.95
8(*E*)-Hexadecen-7-ol	132.92(8) 132.28(9)	73.29	37.29(6) 32.17(10) 31.82(3,14)[b] 29.21 29.17 29.14 29.09 25.43(5) 22.64 22.59	14.07[b]
9(*E*)-Octadecen-8-ol	132.88(9) 132.34(10)	73.33	37.26(7) 32.18(11) 31.87 31.80 29.50 29.44 29.27[b] 29.16[b] 25.47(6) 22.65(2,17)[b]	14.09[b]

[a]The numbers in parentheses assign signals to specific carbon atoms. Where no parentheses appear, the assignments are either straightforward (for example, the hydroxy-bearing carbons) or could not be made unambiguously (CH_2 carbons). The assignment of the olefinic carbons by two-dimensional heteronuclear correlation was reported in Reference 2.
[b]Signal of two carbons.

^{13}C NMR spectra is the one adjacent to the hydroxy-bearing carbon (2).

NMR characterization: allylic dihydroxy products. The *erythro/threo* diastereomers discussed previously (2) were readily distinguishable by ^{1}H and ^{13}C NMR. Similar distinguishing features were observed here (Tables 3 and 4). In ^{13}C NMR, the signals of the olefinic and hydroxy-bearing carbons are shifted downfield in the *threo* isomers compared to the *meso*. The CH_2 group α to the hydroxy-bearing carbon is shifted slightly upfield in the *threo* isomer. In ^{1}H NMR, the olefinic protons and the proton attached to the hydroxy-bearing carbons are shifted downfield in the *meso* compound compared to *threo* (signal of terminal CH_3 used as reference).

In previous work (2), we discussed how the allylic dihydroxy *erythro* and *threo* diastereomers could be distinguished by the resonances of the olefinic protons. The diastereomers could not be distinguished, however, by the resonances of the protons attached to the hydroxy-bearing carbons because of poorer resolution of the signals. For the present compounds, however, we also distinguished *meso* (or *erythro*) and *threo*

TABLE 3
^{13}C NMR Signals of the Unsaturated 1,4-Diols (solvent: $CDCl_3$)[a]

Compound[b]	^{13}C-NMR signals[c] (ppm)			
	*C*H=*C*H	*C*HOH	CH_2	CH_3
m-4(*E*)-Octene-3,6-diol	133.40	73.49	30.03	9.64
t-5(*E*)-Octene-3,6-diol	133.88	73.88	29.90	9.70
m-5(*E*)-Decene-4,7-diol	133.44	71.87	39.32(3,8) 18.58(2,9)	13.93
t-5(*E*)-Decene-4,7-diol	134.09	72.29	39.14(3,8) 18.64(2,9)	13.95
m-6(*E*)-Dodecene-5,8-diol	133.52	72.21	36.92(4,9) 27.54(3,10) 22.58(2,11)	14.01
t-6(*E*)-Dodecene-5,8-diol	134.00	72.53	36.78(4,9) 27.59(3,10) 22.55(2,11)	14.02
m-7(*E*)-Tetradecene-6,9-diol	133.54	72.26	37.21(5,10) 31.73(3,12) 25.05(4,11) 22.59(2,13)	14.01
t-7(*E*)-Tetradecene-6,9-diol	133.98	72.54	37.06(5,10) 31.68(3,12) 25.08(4,11) 22.57(2,13)	13.98
m-8(*E*)-Hexadecene-7,10-diol	133.57	72.24	37.27(6,11) 31.76(3,14) 29.19(4,13) 25.32(5,12) 22.57(2,15)	14.06
t-8(*E*)-Hexadecene-7,10-diol	133.84	72.50	37.22(6,11) 31.77(3,14) 29.16(4,13) 25.36(5,12) 22.57(2,15)	14.05
m-9(*E*)-Octadecene-8,11-diol	133.54	72.26	37.25(7,12) 31.78(3,16) 29.49 29.23 25.37(6,13) 22.62(2,17)	14.06
t-9(*E*)-Octadecene-8,11-diol	133.82	72.52	37.20(7,12) 31.78(3,16) 29.46 29.24 25.42(6,13) 22.62(2,17)	14.06

[a]Abbreviations as in Table 2.
[b]The letters *m* and *t* denote *meso* and *threo*, respectively.
[c]The numbers in parentheses assign signals to specific carbon atoms. Where no parentheses appear, the assignments are either straightforward (for example, the hydroxy-bearing carbons) or could not be made unambiguously (CH_2 carbons).

TABLE 4
^{1}H NMR Signals of the Unsaturated 1,4-Diols (solvent: $CDCl_3$)[a]

Compound[b]	^{1}H NMR signals[c] (ppm)		
	CH=*CH*	*CH*OH	CH_3
m-4(*E*)-Octene-3,6-diol	5.68	4.04	0.93
t-5(*E*)-Octene-3,6-diol	5.60	3.97	0.91
m-5(*E*)-Decene-4,7-diol	5.66	4.09	0.90
t-5(*E*)-Decene-4,7-diol	5.55	4.01	0.88
m-6(*E*)-Dodecene-5,8-diol	5.67	4.09	0.88
t-6(*E*)-Dodecene-5,8-diol	5.60	4.05	0.87
m-7(*E*)-Tetradecene-6,9-diol	5.68	4.10	0.87
t-7(*E*)-Tetradecene-6,9-diol	5.57	4.02	0.87
m-8(*E*)-Hexadecene-7,10-diol	5.68	4.10	0.86
t-8(*E*)-Hexadecene-7,10-diol	5.64	4.08	0.87
m-9(*E*)-Octadecene-8,11-diol	5.68	4.11	0.86
t-9(*E*)-Octadecene-8,11-diol	5.63	4.07	0.86

[a]Abbreviation as in Table 2.
[b]The letters *m* and *t* denote *meso* and *threo*, respectively.
[c]The numbers in parentheses assign signals to specific carbon atoms. Where no parentheses appear, the assignments are either straightforward (for example, the hydroxy-bearing carbons) or could not be made unambiguously (CH_2 carbons)

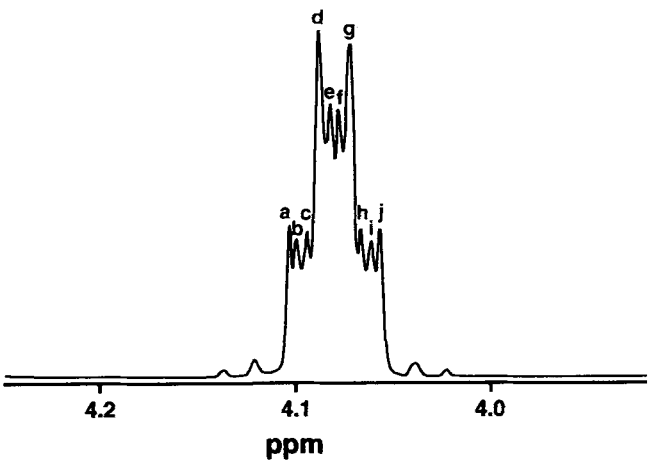


FIG. 1. ^{1}H Nuclear magnetic resonance signals of the protons attached to the hydroxy-bearing carbons (solvent $CDCl_3$) in allylic dihydroxy compounds. The resonance differences (in Hz) of the peaks can be used to distinguish diastereomers (see text and Table 7).

diastereomers by the resonances (400 MHz ^{1}H NMR spectra) of the protons attached to the hydroxy-bearing carbons.

Figure 1 depicts a resolved multiplet for these protons. The diastereomers are easily distinguished by overall peak width (for *m*, 17.61–17.87 ppm; for *t*, 18.65–19.28 ppm), as well as differences within the peak fine structure (Table 5).

Hydrogenations. Several unsaturated 1,4-diols were hydrogenated with the hydrazine/air system to give the corresponding saturated compounds. This reaction had been used previously to affect hydrogenations (1–3). Tables 6 and 7 contain NMR data of the saturated 1,4-diols.

Generally, the ^{13}C NMR data of the present saturated 1,4-diols are similar to those of the unsaturated 1,4-diols and previously reported saturated and unsaturated 1,4-diols (1–3). The signals of the hydroxy-bearing carbons and all carbons adjacent to these are shifted downfield in the *threo* diastereomers. This effect is strongest for the 2,3-carbons located between the OH-bearing carbons, where the difference is about 0.8 ppm.

The ^{13}C NMR of saturated, enantiomerically pure 1,4-diols with *R,R* or *S,S* configuration correspond well with the present values obtained for *threo* diastereomers. Machinaga and Kibayashi (14) report signals at 72.40 ppm for the hydroxy-bearing carbons and 34.08 ppm for the 2,3-carbons in *R,R*- and *S,S*-5,8-tridecanediol. Burk *et al.* (15) state 74.0 ppm for the hydroxy-bearing carbons and 34.1 for the 2,3-carbons in (3*R*,6*R*)-3,6-octanediol. In another study, Burk *et al.* (16) also report ^{13}C NMR shifts of 72.18, 40.24, 34.31, 19.13, and 14.28 ppm and ^{1}H NMR shifts of 3.48 (C*H*OH) and 0.92 (CH_3) in (4*S*,7*S*)-4,7-decanediol (*threo* diastereomer). The other diastereomer *(meso)* and diastereomer discernment by NMR were not reported.

These and other authors (17–23) investigated the synthesis of 1,4-diols by various methods. Lengthy synthetic sequences

TABLE 5
Average Peak Distances (in Hz) of Multiplets Caused by the Protons Attached to the Hydroxy-Bearing Carbons in the ^{1}H NMR Spectra of the Allylic Dihydroxy Products[a]

A)	a–b	b–c	c–d	d–e	e–f	f–g	g–h	h–i	i–j
m	1.57	1.84	2.89	1.57	1.89	1.53	3.18	1.77	1.58
t	1.94	1.98	2.38	2.09	2.04	2.14	2.43	2.03	1.96

B)	a–d[b]	g–d[b]	j–g[b]
m	6.30	5.01	6.55
t	6.33	6.23	6.42

C)	a–j[c]
m	17.61–17.87
t	18.65–19.28

[a]The averages were deduced from the spectra of the compounds reported in Tables 3 and 4. The peaks are denoted by letters according to Figure 2. *m, meso; t, threo.*
[b]The sums of the differences reported in A do not always correspond to the differences reported in B, because most of the smallest or largest differences according to A may occur in one spectrum, thus shifting the results.
[c]For the total differences a–j, observed ranges are given for the reasons stated in footnote b.

TABLE 6
Melting Points and ^{13}C NMR Signals of Saturated 1,4-Diols (solvent: $CDCl_3$)[a]

Compound[b]	Melting point (°C)	^{13}C NMR signals[c] (ppm) CHOH	CH_2	CH_3
m-Decane-4,7-diol	85	71.66	39.70(3,8) 33.29(5,6) 18.90(2,9)	14.09
t-Decane-4,7-diol	65	72.05	39.93(3,8) 34.01(5,6) 18.90(2,9)	14.10
m-Dodecane-5,8-diol	91–91.5	71.93	37.21(4,9) 33.25(6,7) 27.90(3,10) 22.72(2,11)	14.06
t-Dodecane-5,8-diol	68.5–69.5	72.31	37.47(4,9) 34.00(6,7) 27.93(3,10) 22.72(2,11)	14.06
m-Tetradecane-6,9-diol	99	71.94	37.47(5,10) 33.23(7,8) 31.86(3,12) 25.40(4,11) 22.63(2,13)	14.03
t-Tetradecane-6,9-diol	67	72.33	37.75(5,10) 34.01(7,8) 31.87(3,12) 25.40(4,11) 22.63(2,13)	14.04
m-Hexadecane-7,10-diol	103–104	71.96	37.54(6,11) 33.28(8,9) 31.81(3,14) 29.33(4,13) 25.68(5,12) 22.61(2,15)	14.08
t-Hexadecane-7,10-diol	81–82	72.32	37.78(6,11) 33.98(8,9) 31.81(3,14) 29.33(4,13) 25.68(5,12) 22.61(2,15)	14.08
m-Octadecane-8,11-diol	92–93	71.88	37.47(7,12) 33.15(9,10) 31.81(3,16) 29.63 29.27 25.74(6,13) 22.64 (2,17)	14.08
t-Octadecane-8,11-diol	75	72.33	37.78(7,12) 33.98(9,10) 31.81(3,16) 29.63 29.28 25.72(6,13) 22.64(2,17)	14.09

[a]Abbreviation as in Table 2.
[b]The letters *m* and *t* denote *meso* and *threo*, respectively.
[c]The numbers in parentheses assign signals to specific carbon atoms. Where no parentheses appear, the assignments are either straightforward (for example, the hydroxy-bearing carbons) or could not be made unambiguously (CH_2 carbons).

TABLE 7
Selected ^{1}H NMR Signals of Saturated 1,4-Diols (solvent: $CDCl_3$)[a]

Compound[b]	^{1}H NMR signals (ppm)	
	CHOH	CH_3
m-Decane-4,7-diol	3.64	0.92
m-Dodecane-5,8-diol	3.63	0.89
t-Dodecane-5,8-diol	3.60	0.89
m-Tetradecane-6,9-diol	3.63	0.88
t-Tetradecane-6,9-diol	3.60	0.88
m-Hexadecane-7,10-diol	3.63	0.87
t-Hexadecane-7,10-diol	3.61	0.87
m-Octadecane-8,11-diol	3.62	0.86
t-Octadecane-8,11-diol	3.60	0.87

[a]Abbreviation as in Table 2.
[b]The letters *m* and *t* denote *meso* and *threo*, respectively.

were required in some cases. SeO_2/TBHP-based dihydroxylation with subsequent hydrogenation may be an alternative in some cases, although all possible enantiomers (diastereomers) are formed. However, the reduction in the number of reaction steps and a conceivable development of ligands or coreactants for enhancing yields of dihydroxy products and/or increasing enantio- or diastereoselectivity or possible development of enantiomer separation by chiral chromatography may facilitate application of this reaction. All starting materials were commercially available or easily accessible by reactions, such as reduction by LAH or Wittig reaction. Also, both the unsaturated (in *trans* configuration) and saturated 1,4-diol functionalities are accessible in the same sequence.

In conclusion, the reaction of symmetrical alkenes (and also unsymmetrical alkenes, although these were not studied here) with the SeO_2/TBHP system offers rapid access to novel hydroxylated compounds with potential uses in commercial products. NMR characterization of these compounds is also especially interesting. *Meso* and *threo* isomers were distinguished. The SeO_2/TBHP system may be of interest for the synthesis of other saturated 1,4-diols.

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