The Formation of Ethers from Unsaturated Aliphatic Alcohols in the Presence of Boron Trifluoride Etherate

Kimiko NAGAI,* Mitsuru NAKAYAMA,** and Shûichi HAYASHI**

Yasuda Women's University, Kamiyasu, Yasufuruichi-cho, Hiroshima 731-01

** *Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730*

(Received February 3, 1978)

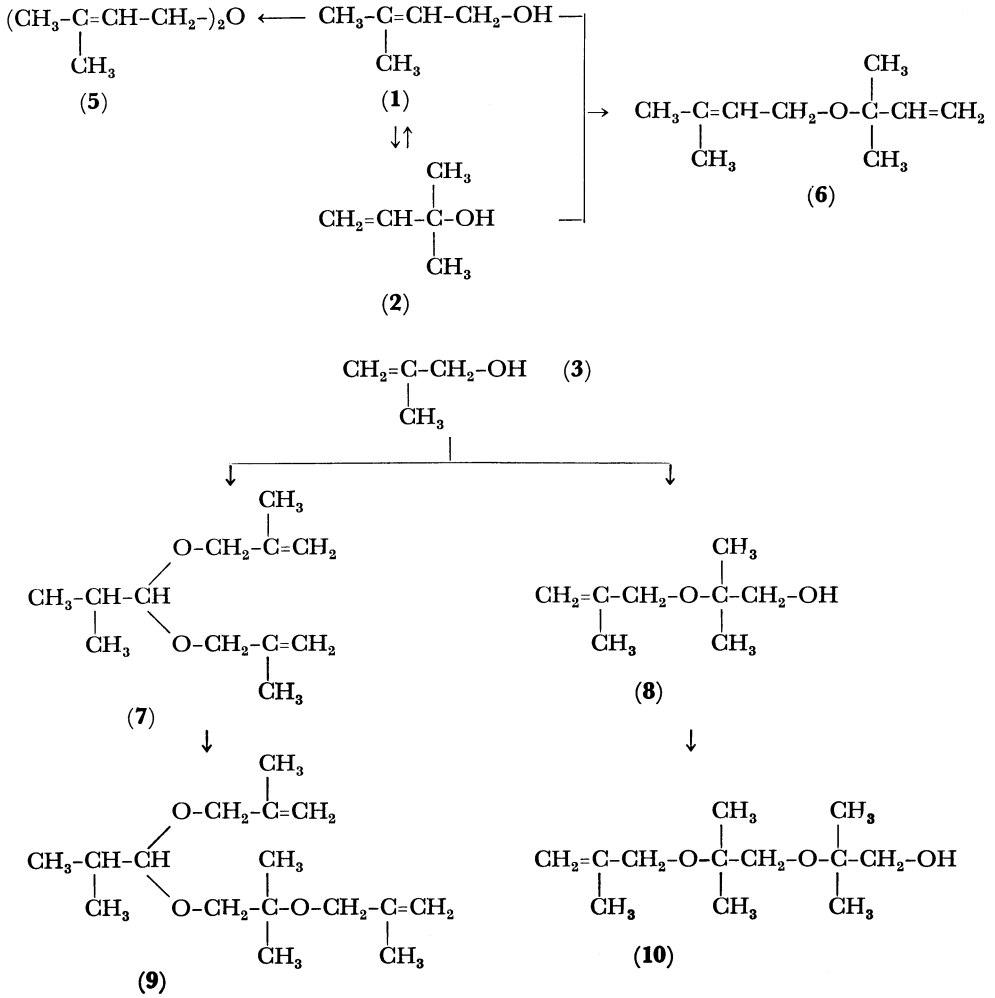
Unsaturated acyclic alcohols of carbon numbers four and five reacted with boron trifluoride etherate to give eight ethers. Of these ethers, novel acyclic di- and tri-ethers were found in the reaction products of 2-methyl-2-propen-1-ol. Boron trifluoride etherate catalyzes double-bond migration, allylic rearrangement, intermolecular dehydration, and Markownikov addition reactions in unsaturated aliphatic alcohols.

In previous papers it has been reported that ethers of several types were obtained by reactions of monoterpene alcohols, of allylic geraniol,[1] nerol,[2] homoallylic *l*-isopulegol,[3] saturated bicyclic *d*-borneol,[4] and *dl*-isoborneol[4] with boron trifluoride etherate in the acid-catalyzed intermolecular dehydration of these alcohols and/or their isomers. Citronellol, in which one double bond is at the ζ-position for the hydroxyl group, gave cyclic and acyclic ethers upon intermolecular addition.[5]

In the present work, studies of analogous acid-catalyzed reactions of four unsaturated acyclic alcohols, allylic 3-methyl-2-buten-1-ol (**1**), 2-methyl-3-buten-2-ol (**2**), 2-methyl-2-propen-1-ol (**3**), and homoallylic 3-methyl-3-buten-1-ol (**4**), will be reported.

Results and Discussion

Upon treatment with boron trifluoride etherate at room temperature, **1** of a primary alcohol was dimerized to give two ethers, one symmetrical and one unsymmetrical, in yields of 4 and 32% respectively, by means of the intermolecular dehydration of the starting material and/or its isomer. On the other hand, **2** of a tertiary alcohol gave only a unsymmetrical ether in a 40% yield. The structures of these ethers were determined to be bis(3-methyl-2-butenyl) ether (**5**) for the symmetrical ether and 3-methyl-2-butenyl 1,1-dimethyl-2-propenyl ether (**6**) for the other one on the basis of their spectral data and chemical behavior.



In these reactions, on double-bond migration occurs, the allylic rearrangement of the hydroxyl group takes place at a high rate, and the equilibrium is probably shifted from **1** to **2**.

2-Methyl-2-propen-1-ol (**3**), which contains a isopropenyl group, gave two kinds of polyethers (**7** and **9**) and two kinds of hydroxyl ethers (**8** and **10**). The novel ethers (**7** and **9**) are thought to be produced by the method of double-bond migration, followed by the dehydration condensation with **3** *via* the aldehyde form. On the other hand, the hydroxyl ethers appear to be formed by the Markownikov addition of the hydroxyl group to the double bond.

On the other hand, 3-methyl-3-buten-1-ol (**4**), which has two methylene groups between the double bond and the hydroxyl group, gave two hydroxyl ethers (**11** and **12**) according to the Markownikov rule and no di- or tri-ether (**7** or **9**), as has been mentioned in the case of the **3** alcohol.

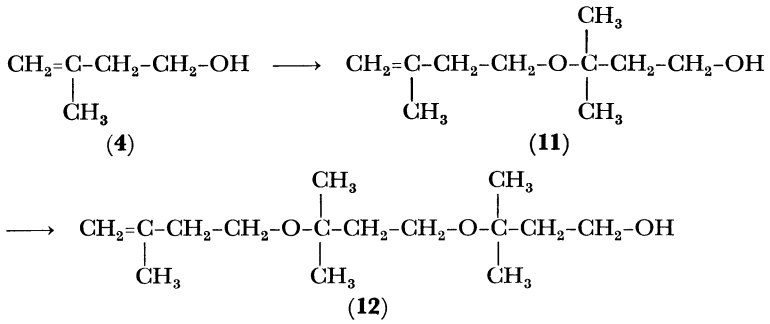


Table 1. Reaction conditions and reaction products of unsaturated aliphatic alcohols with boron trifluoride etherate

Reaction conditions					Reaction products		
Sample	(g)	$BF_3 \cdot Et_2O$ (ml)	React temp (°C)	React period (h)	Product	Yield (%)	n_D (°C)
1	10	0.6	20	24	**5**	4	1.4491 (22)
					6	32	1.4415 (22)
2	10	0.6	20	24	**6**	40	1.4403 (20)
3	10	0.5	23	72	**7**	12	1.4272 (20)
					8	28	1.4315 (20)
					9	5	1.4329 (20)
					10	20	1.4340 (20)
4	10	0.5	28	72	**11**	35	1.4371 (20)
					12	5	1.4427 (20)

Experimental

Apparatus. The GLC analyses were carried out using a Hitachi-063 apparatus, equipped with an FID detector, a stainless-steel separating column (3 mm×3 m) packed with Carbowax 6000 (10%) on Diasolid L (60—80 mesh) and Carbowax 20 M (10%) on Diasolid L (60—80 mesh); the flow rate of the nitrogen carrier gas was 20 ml/min. The mass spectra were recorded on a Hitachi RMS-4 spectrometer at an ionization voltage of 80 eV, an ion-accelerating voltage of 1800 eV, and an ionization chamber temperature of 100 °C. The PMR spectra were measured in CCl_4 solutions using a 60 MHz spectrometer, Hitachi R-20, with TMS as the internal reference. The CMR spectrum was obtained in a $CDCl_3$ solution on a JEOL FX-60 spectrometer under those conditions: pulse repetition, 3 s; accumulation, 1200 times, and frequency range, 4 kHz. The preparative-GLC separations were carried out by means of a Yanagimoto G-80 apparatus, with Carbowax 20 M (10%) on Diasolid L (6 mm×2 m); temperature program: 5 °C/min, from 150 °C to 200 °C.

Materials. Commercial **2**, **3**, and **4** were used without purification. These alcohols exhibited single peaks in GLC with DEGS and Carbowax 6000.

$BF_3 \cdot Et_2O$ of a chemical grade (BF_3 47%) was used without any purification.

*1) Reaction of **1** with $BF_3 \cdot Et_2O$.* Ten grams of **1**[6] were submitted to a reaction with $BF_3 \cdot Et_2O$ (0.6 ml) at room temperature (*ca.* 20 °C) for 24 h, and then extracted with ether after being diluted with water (50 ml). The extract was washed with a 10% aqueous solution of sodium carbonate and then with water, and dried over anhydrous sodium sulfate. The reaction mixture showed the presence of two compounds upon GLC and TLC, these compounds (**5** and **6**) were separated by means of a silica-gel column using a mixed solvent of hexane containing 5% ethyl acetate.

*Bis(3-methyl-2-butenyl) Ether (**5**)*: One of the above-mentioned compounds was isolated as a colorless oil: Rast's molecular weight, 158 (Calcd, 154); IR (liq.) 1070 (C–O–C), 1675, 830 cm^{-1} (–CH=$\overset{|}{C}$–); PMR (CCl_4) δ 1.61, 1.70 (each 6H, br s, CH_3–$\overset{|}{C}$=$\overset{|}{C}$–×4), 3.79 (4H, d, J=7 Hz, –$\overset{|}{C}$=CH–CH_2–O–×2), 5.24 ppm (2H, m, –CH=$\overset{|}{C}$–×2).

*Catalytic Hydrogenation of **5**:* Compound **5** (250 mg) was hydrogenated over PtO_2 (25 mg) in acetic acid (5 ml) to take up two equivalent moles of hydrogen. The spectral data of tetrahydro-**5** were superimposable on those of the diisopentyl ether synthesized from 3-methyl-1-butanol (1.0 g)

and diisopentyl bromide (0.5 g). Colorless oil; bp 171—172 °C, d_4^{20} 0.776. IR (liq.) 1385, 1371 (CH_3–$\underset{|}{C}H$–CH_3), 1130, 1111 cm^{-1} (C–O–C); PMR (CCl_4) δ 0.89 (12H, d, J= 6 Hz, CH_3–$\underset{|}{C}H$–$CH_3\times2$), 1.49 (4H, t, J=7 Hz, –$\underset{|}{C}H$–CH_2 –CH_2–$\times2$), 1.30—1.78 (2H, m, CH_3–$\underset{|}{C}H$–$CH_3\times2$), 3.40 ppm (4H, t, J=7 Hz, –CH_2–CH_2–O–$\times2$).

*3-Methyl-2-butenyl 1,1-Dimethyl-2-propenyl Ether (**6**)*: The second compound was obtained as a colorless oil. Rast's molecular weight (155) and the molecular ion (M^+ 154) in the mass spectrum corresponded to a molecular formula of $C_{10}H_{18}O$. Mass *m/e* 41 (75%), 55 (20), 57 (25), 69 (base), 85 (33), 110 (15), 124 (24), 137 (7, M^+-CH_3), 154 (5, M^+, $C_{10}H_{18}O$); IR (liq.) 1145, 1060 (C–O–C), 1680, 830 (–$\underset{|}{C}H$=$\underset{|}{C}$–), 3080, 1645, 1001, 920 cm^{-1} (CH_2=CH–); PMR (CCl_4) δ 1.20 (6H, s, –O–$\underset{|}{C}$–$\underset{|}{C}$=$\underset{|}{C}$–), 1.62, 1.71 (6H, br s, CH_3–$\underset{|}{C}$=$\underset{|}{C}$–$\times2$), 3.82 (2H, d, J=7 Hz, =CH–CH_2–O–), 4.91—5.80 ppm (4H, q and m, CH_2=CH– and –CH=$\underset{|}{C}$–).

*Tetrahydro Derivative of **6***: Colorless oil. IR (liq.) 1390, 1371, 1368 (CH_3–$\underset{|}{C}H$–CH_3), 1088 cm^{-1} (C–O–C); PMR (CCl_4) δ 0.82 (3H, t, J=6 Hz, CH_3–CH_2–$\underset{|}{C}$–), 0.88 (6H, d, J=6 Hz, CH_3–$\underset{|}{C}H$–CH_3), 1.10 (6H, s, $(CH_3)_2$–$\underset{|}{C}$–O–), 1.43 (2H, t, J=6 Hz, $(CH_3)_2$–CH–CH_2–CH_2–), 3.31 ppm (2H, t, J=6 Hz, –O–CH_2–CH_2–).

*2) Reaction of **2** with $BF_3\cdot Et_2O$.* The **2** alcohol (10 g) was allowed to react with $BF_3\cdot Et_2O$ (0.6 ml) according to the procedure previously described. A colorless oil was thus obtained; Rast's molecular weight, 156 (Calcd, 154). The spectral data of the compound and its tetrahydro derivative were identical with those of Compound **6** and its tetrahydro-**6** respectively.

*3) Reaction of **3** with $BF_3\cdot Et_2O$.* The **3** alcohol (10 g) was submitted to a reaction with $BF_3\cdot Et_2O$ (0.5 ml) at room temperature (*ca.* 20 °C) for 72 h. The reaction mixture showed the presence of four compounds (**7**, **8**, **9**, and **10**) by GLC with Carbowax 20 M; these compounds were separated into individual compounds by means of preparative-GLC.

*2,8-Dimethyl-5-isopropyl-4,6-dioxa-1,8-nonadiene (**7**)*: The first compound was isolated from the reaction mixture as a colorless oil. The molecular formula corresponded to $C_{12}H_{22}O_2$, judging from the molecular weight (Rast's 200; Calcd, 198). Mass *m/e* 55 (base), 71 (31%, C_4H_7O), 127 (9, M^+-CH_2=$\underset{|}{C}$–CH_2–O–), 155 (12H, $M^+-C_3H_7$), 198 (trace, $C_{12}H_{22}O_2$); IR (CCl_4), 3081, 1665, 905 (CH_2=$\underset{|}{C}$–), 1397, 1380 (CH_3–$\underset{|}{C}H$–CH_3), 1311, 1111, 1071, 1041 cm^{-1} (C–O–C); PMR (CCl_4) δ 0.91 (6H, d, J=7 Hz, CH_3–$\underset{|}{C}H$–CH_3), 1.75 (6H, br s, CH_3–$\underset{|}{C}$=$\underset{|}{C}$–$\times2$), 1.70—2.10 (1H, m, $(CH_3)_2$–$\underset{|}{C}H$–CH–), 3.84 (4H, br s, –O–CH_2–$\underset{|}{C}$=$\underset{|}{C}$–$\times2$), 4.09 (1H, d, J=7 Hz, –O–$\underset{|}{C}H$–CH–), 4.81, 4.91 ppm (each 2H, br s, CH_2=$\underset{|}{C}$–$\times2$). The CMR spectrum of the compound was reasonably explained by the following assignments.

*Tetrahydro Derivative of **7***: Colorless oil. Mass *m/e* 57 (base), 73 (28%, C_4H_9O), 125 (10, $M^+-(CH_3)_2$–CH–CH_2–O–); IR (CCl_4) 1384, 1370 (CH_3–$\underset{|}{C}H$–CH_3), 1080, 1050 cm^{-1} (C–O–C); PMR (CCl_4) δ 0.89, 0.92 (12H and 6H, each d, J=6 Hz, CH_3–$\underset{|}{C}H$–$CH_3\times3$), 1.51—2.05 (3H, m, $(CH_3)_2$–$\underset{|}{C}H$–$CH_2\times2$ and $(CH_3)_2$–$\underset{|}{C}H$–CH–), 3.10 (4H, d, J=6 Hz, –$\underset{|}{C}H$–CH_2–O–$\times2$), 4.09 ppm (1H, d, J=7 Hz, –O–$\underset{|}{C}H$–$\underset{|}{C}H$–O–).

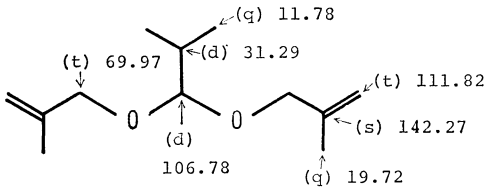
*2,2,5-Trimethyl-3-oxa-5-hexen-1-ol (**8**)*: The second compound was isolated as a colorless oil. The Rast's molecular weight, 145 (Calcd, 144), corresponded to the molecular formula of $C_8H_{16}O_2$. Mass *m/e* 55 (base), 113 (32%, M^+-CH_2OH), 126 (3, M^+-H_2O), 144 (trace, M^+, $C_8H_{16}O_2$); IR (liq.) 3480, 1155 (–OH), 1103, 1060 (C–O–C), 3080, 1664, 905 (CH_2=$\underset{|}{C}$–), 1380, 1370 cm^{-1} (CH_3–$\underset{|}{C}H$–CH_3); PMR (CCl_4) δ 1.15 (6H, s, CH_3–$\underset{|}{C}$–CH_3), 1.72 (3H, br s, CH_3–$\underset{|}{C}$=$\underset{|}{C}$–), 1.91 (1H, br s, –OH), 3.30 (2H, s, –$\underset{|}{C}$–CH_2–OH), 3.47 (2H, br s, =$\underset{|}{C}$–CH_2–O–), 4.78, 4.90 ppm (each 1H, br s, CH_2=$\underset{|}{C}$–).

*Acetyl Derivative of **8***: The acetylation of Compound **8** (300 mg) was carried out with acetic anhydride (1 ml) in dry pyridine (3 ml) at room temperature for 72 h. Colorless oil. IR (CCl_4) 1746, 1236 (CH_3COO–), 3080, 1660, 901 (CH_2=$\underset{|}{C}$–), 1100, 1050 cm^{-1} (C–O–C); PMR (CCl_4) δ 1.10 (6H, s, –O–$\underset{|}{C}$–$(CH_3)_2$), 1.72 (3H, br s, CH_3–$\underset{|}{C}$=$\underset{|}{C}$–), 2.00 (3H, s, CH_3COO–), 3.75 (2H, br s, –$\underset{|}{C}$=$\underset{|}{C}$–CH_2–O–), 3.92 (2H, s, CH_3COO–CH_2–$\underset{|}{C}$–), 4.73, 4.92 ppm (each 1H, br s, CH_2=$\underset{|}{C}$–).

*Dihydro Derivative of **8***: Colorless oil. IR (CCl_4) 3580, 3420, 1152 (–OH), 1080, 1057 (C–O–C), 1383, 1371 cm^{-1} (CH_3–$\underset{|}{C}H$–CH_3); PMR (CCl_4) δ 0.90 (6H, d, J=6 Hz, CH_3–$\underset{|}{C}H$–CH_3), 1.17 (6H, s, CH_3–$\underset{|}{C}$–CH_3), 1.60—2.01 (1H, m, $(CH_3)_2$–$\underset{|}{C}H$–CH_2–), 2.20 (1H, br s, –OH), 3.10 (2H, d, J=6 Hz, –$\underset{|}{C}H$–CH_2–O–), 3.40 ppm (2H, m, –$\underset{|}{C}$–CH_2–OH.)

*2,5,5,11-Tetramethyl-8-isopropyl-4,7,9-trioxa-1,11-dodecadiene (**9**)*: The third compound was also obtained as a colorless oil. The molecular formula had $C_{16}H_{30}O_3$ from Rast's molecular weight, 274 (Calcd, 270). Mass *m/e* 55 (base), 71 (15%), 81 (7), 101 (12), 115 (27), 155 (31), 227 (2, $M^+-C_3H_7$), 270 (trace, M^+, $C_{16}H_{30}O_3$); IR (CCl_4) 1110, 1060 (C–O–C), 3080, 1165, 903 (CH_2=$\underset{|}{C}$–), 1391, 1380, 1370 cm^{-1} (CH_3–$\underset{|}{C}H$–CH_3); PMR (CCl_4) δ 0.92 (6H, d, J=7 Hz, CH_3–$\underset{|}{C}H$–CH_3), 1.20 (6H, s, –$\underset{|}{C}H$–C–O–), 1.65 (6H, br s, –$\underset{|}{C}$=$\underset{|}{C}$–$\times2$), 1.76—2.10 (1H, m, $(CH_3)_2$–$\underset{|}{C}H$–CH–), 3.22, 3.40 (each 1H, d, J_{AB}=12 Hz, –O–CH_2–$\underset{|}{C}$–O–), 3.69, 3.89 (each 2H, s, =$\underset{|}{C}$–CH_2–O–$\times2$), 4.09 (1H, d, J=7 Hz, –O–$\underset{|}{C}H$–CH–), 4.80, 4.90 ppm (each 2H, br s, CH_2=$\underset{|}{C}$–$\times2$).

*Tetrahydro Derivative of **9***: Colorless oil. IR (CCl_4) 1390, 1384, 1370 (CH_3–$\underset{|}{C}H$–CH_3 and CH_3–$\underset{|}{C}$–CH_3), 1111, 1058 cm^{-1} (C–O–C); PMR (CCl_4) δ 0.89, 0.91 (18H, each d, J=6 Hz, CH_3–$\underset{|}{C}H$–$CH_3\times3$), 1.19 (6H, s, CH_3–$\underset{|}{C}$–CH_3), 1.70—2.05 (3H, m, $(CH_3)_2$–$\underset{|}{C}H$–$\underset{|}{C}H$–$\times3$), 3.15 (4H, d, J=



6 Hz, -O-C**H**$_2$-CH-×2), 3.20, 3.39 (each 1H, d, J_{AB}= 12 Hz, -O-C**H**$_2$-C-O-), 4.09 ppm (1H, d, J=7 Hz, -O-C**H**-CH-).

*2,2,5,5,8-Pentamethyl-3,6-dioxa-8-nonen-1-ol (**10**)*: The last compound was isolated as a colorless oil; Rast's mol wt, 220 (Calcd, 216, $C_{12}H_{24}O_3$). Mass *m/e* 55 (base), 73 (22%), 101 (9), 113 (28), 127 (7), 143 (4), 185 (4, M^+-CH_2OH), 216 (trace, M^+, $C_{12}H_{24}O_3$); IR (liq.) 3480, 1071 (-OH), 1170, 1095, 1068 (C-O-C), 3080, 1662, 903 (CH_2=C-), 1397, 1370 cm^{-1} (CH_3-C-CH_3); PMR (CCl_4) δ 1.10, 1.16 (each 6H, s, **C**H_3-C(O-)-**C**H_3×2), 1.73 (3H, br s, **C**H_3-C=C-), 2.33 (1H, br s, -O**H**), 3.18 (2H, s, -C-C**H**$_2$-O-), 3.28 (2H, s, -C-C**H**$_2$-OH), 3.78 (2H, br s, -C=C-C**H**$_2$-O-), 4.76, 4.90 ppm (each 1H, br s, C**H**$_2$=C-).

*Acetyl Derivative of **10***: Colorless oil. IR (CCl_4) 1746, 1235 (CH_3COO-), 1170, 1095, 1045 (C-O-C), 3080, 1660, 900 cm^{-1} (CH_2=C-); PMR (CCl_4) δ 1.10, 1.18 (each 6H, s, -O-C-(C**H**$_3$)$_2$×2), 1.73 (3H, br s, **C**H_3-C=C-), 2.01 (3H, s, **C**H_3COO-), 3.15 (2H, s, -C-C**H**$_2$-O-), 3.78 (2H, br s, =C-C**H**$_2$-O-), 3.96 (2H, s, CH_3COO-C**H**$_2$-C-), 4.78, 4.93 ppm (each 1H, br s, C**H**$_2$=C-).

*Dihydro Derivative of **10***: Colorless oil. IR (CCl_4) 3470, 1070 (-OH), 1088, 1060 (C-O-C), 1389, 1375 cm^{-1} (CH_3-C-CH_3 and CH_3-CH-CH_3); PMR (CCl_4) δ 0.90 (6H, d, J=6 Hz, **C**H_3-CH-C**H**$_3$), 1.13, 1.18 (each 6H, s, **C**H_3-C(O-)-**C**H_3×2), 1.65—1.98 (1H, m, $(CH_3)_2$-C**H**-CH_2-), 2.24 (1H, br s, -O**H**), 3.10 (2H, d, J=7 Hz, -CH-C**H**$_2$-O-), 3.17 (2H, br s, -C-C**H**$_2$-O-C-), 3.40 ppm (2H, m, -C-C**H**$_2$-OH).

*4) Reaction of **4** with $BF_3 \cdot Et_2O$.* The reaction of **4** (10 g) was carried out with $BF_3 \cdot Et_2O$ (0.5 ml) according to the procedure described above.

*3,3,7-Trimethyl-4-oxa-7-octen-1-ol (**11**)*: The compound from the first eluate was obtained as a colorless oil. The molecular formula was $C_{10}H_{20}O_2$ (M^+ 172, Rast's mol wt, 176). Mass *m/e* 31 (41%), 41 (30), 59 (6), 69 (base), 87 (22), 99 (16), 117 (5), 127 (5), 155 (3), 172 (2, M^+, $C_{10}H_{20}O_2$); IR (CCl_4) 3510, 1145 (-OH), 1170, 1075, 1035 (C-O-C), 1652, 899 (CH_2=C-), 1380, 1369 cm^{-1} (CH_3-C-CH_3); PMR (CCl_4) δ 1.27 (6H, s, $(CH_3)_2$-C(O-)-), 1.65 (2H, t, J=6 Hz, -C-C**H**$_2$-CH_2-OH), 1.72 (3H, br s, **C**H_3-C=C-), 2.20 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-C=C-), 2.67 (1H, br s, -O**H**), 3.47 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-O-), 3.62 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-OH), 4.80 ppm (2H, br s, C**H**$_2$=C-).

*Acetyl Derivative of **11***: Colorless oil. IR (CCl_4) 1745, 1245, 1239 (CH_3COO-), 1387, 1378 (CH_3-C-CH_3), 3081, 1653, 893 (CH_2=C-), 1171, 1035 cm^{-1} (C-O-C); PMR (CCl_4) δ 1.26 (6H, s, $(CH_3)_2$-C(O-)-), 1.65 (2H, t, J=6 Hz, -C-C**H**$_2$-CH_2-), 1.70 (3H, br s, -C(**C**H_3)=C-), 2.00 (3H, s, **C**H_3COO-), 2.20 (2H, t, J=6 Hz, =C-C**H**$_2$-CH_2-), 3.40 (2H, t, J= 6 Hz, -CH_2-C**H**$_2$-O-), 4.10 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-$COOCH_3$), 4.68 ppm (2H, br s, C**H**$_2$=C-).

*Dihydro Derivative of **11***: Colorless oil. Mass *m/e* 41 (32%), 43 (85), 59 (55), 69 (43), 70 (11), 71 (base), 89 (18), 129 (59, $M^+-(CH_2-CH_2-OH)$), 159 (7, M^+-CH_3), 174 (trace, M^+, $C_{10}H_{22}O_2$); IR (CCl_4) 3490, 1148 (-OH), 1079 (C-O-C), 1391, 1371 cm^{-1} ($(CH_3)_2$-CH-, CH_3-C-CH_3); PMR (CCl_4) δ 0.90 (6H, d, J=6 Hz, $(CH_3)_2$-CH-), 1.23 (6H, s, $(CH_3)_2$-C(O-)-), 1.50 (2H, t, J=6 Hz, -CH-C**H**$_2$-CH_2-O-), 1.66 (2H, t, J=6 Hz, -O-C(O-)-C**H**$_2$-CH_2-OH), 2.16 (1H, br s, -O**H**), 3.40 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-O-), 3.78 ppm (2H, t, J=6 Hz, -CH_2-C**H**$_2$-OH).

*3,3,7,7,11-Pentamethyl-4,8-dioxa-11-dodecen-1-ol (**12**)*: As the second compound, a colorless oil was isolated. The molecular formula was determined to be $C_{15}H_{30}O_3$ (M^+ 258, Rast's 263). Mass *m/e* 31 (6%), 41 (32), 43 (13), 59 (6), 69 (base), 99 (20), 105 (12), 115 (7), 127 (5), 139 (6), 173 (5), 258 (1, M^+, $C_{15}H_{30}O_3$); IR (CCl_4) 3400, 1143 (-OH), 1075, 1025 (C-O-C), 3075, 1655, 900 (CH_2=C-), 1380, 1369 cm^{-1} (CH_3-CH-CH_3 and CH_3-C-CH_3); PMR (CCl_4) δ 1.13, 1.20 (each 6H, s, CH_3-C(O-)-CH_3×2), 1.65 (4H, t, J=6 Hz, -O-C(O-)-C**H**$_2$-CH_2-O- and -O-C(O-)-C**H**$_2$-CH_2-OH), 1.73 (3H, br s, **C**H_3-C=C-), 2.18 (2H, t, J=6 Hz, =C-C**H**$_2$-CH_2-), 2.50 (1H, br s, -OH), 3.38 (4H, t, J=6 Hz, -CH_2-C**H**$_2$-O-×2), 3.52 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-OH), 4.70 ppm (2H, br s, C**H**$_2$=C-).

*Acetyl Derivative of **12***: Colorless oil. IR (CCl_4) 1740, 1240, 1225 (CH_3COO-), 1075, 1030 (C-O-C), 3078, 1650, 889 cm^{-1} (CH_2=C-); PMR (CCl_4) δ 1.17, 1.21 (each 6H, s, $(CH_3)_2$-C(O-)-×2), 1.65 (4H, t, J=6 Hz, -O-C(O-)-C**H**$_2$-CH_2-O- and -O-C(O-)-C**H**$_2$-CH_2-OH), 1.75 (3H, br s, **C**H_3-C=C-), 2.00 (3H, s, **C**H_3COO-), 2.20 (2H, t, J=6 Hz, =C-C**H**$_2$-CH_2-), 3.40 (4H, t, J=6 Hz, -CH_2-C**H**$_2$-O-×2), 4.10 (2H, t, J=6 Hz, -CH_2-C**H**$_2$-$COOCH_3$), 4.70 ppm (2H, br s, C**H**$_2$=C-).

*Dihydro Derivative of **12***: Colorless oil. IR (CCl_4) 3500, 1145 (-OH), 1078 (C-O-C), 1386, 1370 cm^{-1} (CH_3-CH-CH_3 and CH_3-C-CH_3); PMR (CCl_4) δ 0.90 (6H, d, J= 6 Hz, **C**H_3-CH-C**H**$_3$), 1.22 (12H, s, $(CH_3)_2$-C(O-)-×2), 1.50 (2H, t, J=6 H, $(CH_3)_2$-CH-C**H**$_2$-CH_2-O-), 1.65 (4H, t, J=6 Hz, -O-C(O-)-C**H**$_2$-CH_2-O- and -O-C(O-)-C**H**$_2$-CH_2-OH), 2.30 (1H, br s, -O**H**), 3.41 (4H, t, J=6 Hz, -CH_2-C**H**$_2$-O-×2), 3.77 ppm (2H, t, J=6 Hz, -CH_2-C**H**$_2$-OH).

References

1) K. Nagai, *Chem. Pharm. Bull.*, **18**, 2123 (1970).
2) K. Nagai, *Bull. Chem. Soc. Jpn.*, **48**, 2317 (1975).
3) K. Nagai, *J. Soc. Hiroshima Univ., Ser. A*, **38**, 141 (1974).
4) K. Nagai, M. Nakayama, A. Matsuo, S. Eguchi, and S. Hayashi, *Bull. Chem. Soc. Jpn.*, **47**, 1193 (1974).
5) K. Nagai, *Bull. Chem. Soc. Jpn.*, **49**, 265 (1976).
6) W. M. Bandaranayake, L. Crombie, and D. A. Whiting *J. Chem. Soc., C*, **1971**, 811.