The Formation of Ethers from *dl*-Citronellol in the Presence of Boron Trifluoride Etherate

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(Received June 23, 1975)

dl-Citronellol reacted with boron trifluoride etherate to give a mixture of a novel cyclic dicitronellyl ether (IX) and an acyclic dicitronellyl ether (X), along with eight minor products. Both major ethers were produced in equilibrium in the presence of the above reagent.

In previous papers it has been reported that a variety of ethers were obtained in reactions of boron trifluoride etherate with monoterpene alcohols, of allylic acyclic geraniol,[1] nerol,[2] and *l*-linalool,[2] of homoallylic cyclic *l*-isopulegol,[3] and of saturated bicyclic *d*-borneol[4] and *dl*-isoborneol.[4] The reactions may be regarded as the acid-catalyzed intermolecular dehydration of these alcohols and/or their isomers. In one case,[2] there was observed further cyclization of the ether, the primary product. In the present work, a study of an analogous acid-catalyzed reaction of *dl*-citronellol (I), in which one double bond is at the ζ-position for the hydroxyl group is reported. Some of the results have previously been reported.[5]

Results and Discussion

The reaction conditions and the product distributions in the present study are summarized in Table 1. In each run, the reaction mixture was roughly divided into two fractions by setting up the boundary at the boiling point of 130 °C in distillation under reduced pressure (3.5 mmHg).

Characterization of Monoterpene Products. Each low-boiling fraction was submitted to column chromatography with silica gel. The hydrocarbon portion thus obtained was small in all runs, and the analysis employing glc comparisons with authentic samples and a combined glc-mass spectrometric technique revealed this part to be a mixture of four compounds, namely, α-terpinene (II), dipentene (III), 2,4(8)-*p*-methadiene (IV), and terpinolene (V). The alcoholic portion was also found to be a mixture of the reactant and three other alcohols, the latter being identified as isopulegol (VI), menthol (VII),[6] and tetrahydrogeraniol (VIII) mainly from spectral data. VIII was the major product. The yields of these alcohols slightly increased with an increase in the amount of boron trifluoride etherate.

Characterization of Dimerized Products. Thin layer and gas chromatography of the high-boiling fractions indicated the production of two dimerized compounds in Experiments 1 and 2, and of three compounds in Experiment 3. Isolation and characterization of these compounds are as follows:

2,2,6,10,10,14-Hexamethyl-1,9-dioxacyclohexadecane (IX): The least polar compound in the column chromatography of the high-boiling fraction was isolated as colorless needles, mp 61—62 °C. Its molecular formula was determined to be $C_{20}H_{40}O_2$ corresponding to a dimerized molecule of the reactant from mass spectra analysis and using the method of Rast. Despite the hydrogen deficient formula, this compound was not hydrogenated over an Adams catalyst in acetic acid. It may be of particular significance that a singlet at δ 1.10 for twelve hydrogens and a doublet at δ 0.85 for six hydrogens with J=6 Hz were observed in the NMR spectrum. The former was assigned to two *gem*-dimethyl groups located on a tertiary carbon and the latter to two secondary methyls. In addition, a triplet at δ 3.28 for four hydrogens with J=6 Hz was assigned to two methylene groups adjacent to the oxygen atoms. In the IR spectrum there was no indication of the presence of a hydroxyl group, but a characteristic absorption band was observed at 1085 cm^{-1} for the ether linkage. These spectroscopic results strongly suggest a highly symmetric structure for this dimeric ether. Thus, the compound was determined to be 2,2,6,10,10,14-hexamethyl-1,9-dioxacyclohexadecane (IX). Additional evidence was obtained from the fact that the reaction of this ether with hydroiodic acid afforded tetra- and di-hydrogeranyl iodides which were prepared independently.

3,7,7,11,15-Pentamethyl-8-oxa-14-hexadecen-1-ol (X): The moderately polar compound eluted by column

Table 1. Reaction of citronellol with boron trifluoride etherate

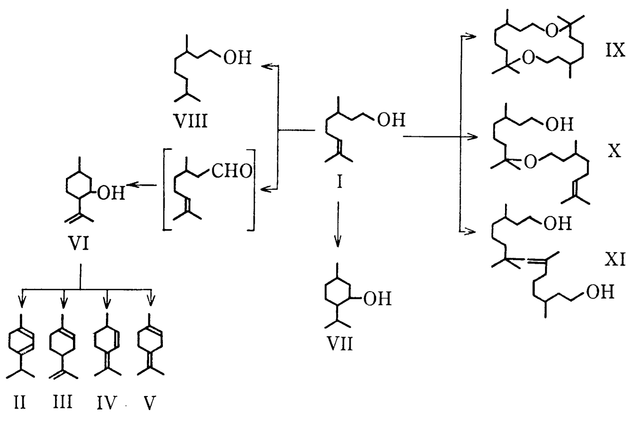
	Reaction condition				Reaction product[a)] (%)											
Experiment No.	Citronellol (I)	BF$_3$·Et$_2$O	React. temp.	React. period	Low-boiling fraction (monoterpene)								High-boiling fraction (dimer)			Residue (polymer)
						Hydrocarbons				Alcohols						
	(g)	(ml)	(°C)	(hr)	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	
1	10	1	20	72	66.0	trace				0.1	0.1	0.8	32.0	1.0	—	—
2	10	2	20	24	62.0	0.4				0.7	0.6	3.3	16.0	8.0	—	9.0
3	10	3	20	48	53.7	0.3				1.0	1.0	4.0	10.0	19.0	2.0	9.0

a) Percentages of reaction products were determined by glc on a column of Silicon SE-30 10% on Uniport B (60—80 mesh) at 200 °C.

chromatography of the high-boiling fraction was isolated as a colorless oil in all three runs. Although its molecular weight obtained by mass spectrometry was the same as that of IX, this oil absorbed one equivalent of hydrogen under catalytic reduction. Distinctive bands at 3350 cm^{-1} and 1070 cm^{-1} were present in the IR spectrum due to a primary hydroxyl group and the oil afforded monoacetate upon treatment with acetic anhydride in dry pyridine. Together with the NMR spectrum, this evidence indicates the oil to be 3,7,7,11,15-pentamethyl-8-oxa-14-hexadecen-1-ol (X). Reaction of the compound with phosphoryl chloride in dry pyridine converted it into an unsaturated ether ($C_{20}H_{38}O$), which was then hydrogenated. Further, the saturated ether was treated with hydroiodic acid giving the tetrahydrogeranyl iodide described above and 2,6-dimethyl-1-octene.[7)]

3,7,9,9,13-Pentamethyl-7-pentadecene-1,15-diol (XI): The most polar compound was isolated in a small amount as a colorless oil only from the high-boiling fraction of Experiment 3. This compound was also an isomer of the other two fractions. Taking account of both the spectral data obtained for this product and experiments analogous to those described above, this may be characterized as an unsaturated diol. For determining the position of the double bond, the compound was submitted to osmium tetroxide oxidation followed by silylation with a mixed reagent of hexamethyldisilazane and trimethylchlorosilane to be converted into trimethylsilyl ether. From precise analysis of the mass spectrum of the silyl ether, the unsaturated diol was characterized as 3,7,9,9,13-pentamethyl-7-pentadecene-1,15-diol, as is shown in detail in the Experimental Section.

Reaction Sequence. As given in Table 1, three monoterpene alcohols and four hydrocarbons were found in the low-boiling fraction of the product. Of the monoterpene alcohols, tetrahydrogeraniol (VIII) was the major product in all three runs. Isopulegol (VI) was assumed to be produced by way of citronellal as a possible intermediate, since this cyclization took place with ease under similar conditions. Although citronellal could not be detected in the present study, VIII and citronellal should be produced by disproportionation of citronellol (I). Another alcohol, menthol (VII), was formed probably by cyclization of the reactant (I), in a manner similar to that described in an earlier report.[6)] Since the four hydrocarbons were all cyclic diolefins, their precursor should be a cyclic unsaturated alcohol if acid-catalyzed dehydration follows. Isopulegol (VI), mentioned above, may be the most probable precursor in this reaction. These processes are summarized in Scheme 1.



Scheme 1.

Table 2. Conversion of cyclic (IX) and acyclic (X) ethers in the presence of boron trifluoride etherate

Composition after the treatment	Starting compound	
	Cyclic diether (IX)	Acyclic ether (X)
IX	86%	42%
X	11	33
XI	1	20
Others	2	5

In the present study, IX and X were the main products. The former, cyclic diether, was predominant when one ml of boron trifluoride etherate was used for ten grams of I, whereas the latter, its isomeric acyclic ether, was preferentially produced when three ml of the reagent was applied. Under the same conditions, IX, could be converted into X in an 11% yield and X was transformed into IX and XI in 42% and 20% yields respectively, as shown in Table 2. Thus, these compounds were in equilibrium under the reaction conditions. The distribution of these dimerized products was estimated by glc analysis where ten grams of citronellol (I) was treated with various amounts of boron trifluoride etherate. The results are given in Fig. 1. It is clearly shown that the distribution is markedly influenced by the molar ratio of the acidic reagent to I.

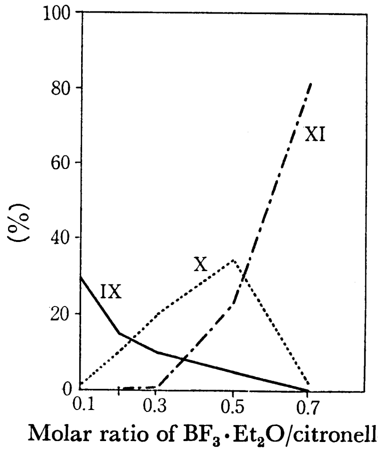


Fig. 1. Dependence of three dimerized species on the concentration of $BF_3 \cdot Et_2O$.
Citronellol each 10 g, no solvent, room temperature, 48 hr.

The formation of the cyclic diether (IX) in the presence of boron trifluoride etherate may be interesting in view of the natural occurrence of large membered cyclic compounds.

Experimental

Apparatus. The glc was carried out using a Hitachi-063, equipped with an FID detector, a stainless-steel separating column (3 mm × 3 m) packed with Carbowax 6000 (10%) on Diasolid (60—80 mesh), DEGS (10%) on Shimalite W (60—80 mesh), and Silicon SE-30 (10%) on Uniport B (60—80 mesh); the flow rate of nitrogen, the carrier gas, 20 ml/min. The mass spectra were obtained using a combined apparatus, Shimadzu-LKB 9000 glc and mass spectrometer: a glass separating tube (3 mm × 3 m) packed with Carbowax 20 M (10%) on Diasolid (60—80 mesh); temperature program, 5 °C/min from 50 °C to 120 °C; ionization energy, 70 eV; ion accelerating voltage, 3500 V; ionization chamber temperature, 200 °C. The NMR spectra were measured in a $CDCl_3$ solution using a 60 MHz spectrometer, Hitachi R-20, with TMS as an internal reference.

Materials. Commercial citronellol was used, after being purified through repeated fractionations. Bp 109 °C/4 mmHg, d_4^{25} 0.8530, n_D^{25} 1.4539, $[\alpha]_D^{25}$ ±0° ($CHCl_3$). A single peak was observed in glc in each case for separating columns of Carbowax 6000, Silicon SE-30, and DEGS, and the IR and NMR spectra coincided with those of authentic samples.

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

Reaction of Citronellol with $BF_3 \cdot Et_2O$. To 10 g of citronellol 1, 2, or 3 ml of $BF_3 \cdot Et_2O$ was added drop by drop, the mixture being allowed to stand for 72, 24, and 48 hr at room temperature (*ca.* 20 °C). The mixture, after having been shaken with a saturated aqueous solution of sodium carbonate to decompose the excess of $BF_3 \cdot Et_2O$, was washed with water, dried over anhydrous sodium sulfate, and fractionated into low-boiling (bp 55—130 °C/3.5 mmHg) and high-boiling (bp 130 °C/3.5 mmHg) fractions under reduced pressure.

Characterization of Monoterpene Compounds. Each low-boiling fraction from Experiments 1—3 was eluted over a silica gel column with hexane and then with a mixture of ethyl acetate and hexane (v/v 15: 85) for separation into hydrocarbons and alcohols.

Hydrocarbons: Gas chromatographic analysis of each hydrocarbon portion was carried out on a separating column packed with Carbowax 6000 by comparison with authentic samples. The mass spectra of these compounds were obtained using the combined glc-mass spectrometer. Thus, II, III, IV, and V were identified.

Alcohols: The alcohol portions showed three peaks in the glc on a DEGS-packed column in addition to the reactant peak. The gas chromatographic analysis of the portion was carried out using authentic samples, and also each compound was isolated by preparative glc for determining the IR and NMR spectra. The compounds were thus identified as VI, VII, and VIII.

Characterization of Dimerized Compounds. The high-boiling fractions from Experiments 1 and 2 were shown to consist of two compounds (R_f 0.7 and 0.6; t_R 5.3 and 6.3) from tlc with a mixed solvent of ethyl acetate and hexane (v/v 15: 85) and from glc on a Silicon SE-30-packed separating column at 200 °C. The high-boiling fraction from Experiment 3 contained three compounds (R_f 0.7, 0.6, and 0.2; t_R 5.3, 6.3, and 10.5). Each fraction was chromatographed over a silica gel column with hexane and then with mixtures of hexane and ethyl acetate increasing in the concentration of ethyl acetate stepwise from 2% to 14%, each compound being isolated.

2,2,6,10,14-Hexamethyl-1,9-dioxacyclohexadecane (IX). The compound with R_f 0.7 and t_R 5.3 was isolated by elution chromatography as white needles, mp 61—62 °C. Mass: *m/e* 41 (36%), 43 (29), 55 (57), 69 (65), 81 (29), 83 (base, C_6H_{11}), 95 (21), 109 (18), 123 (21), 138 (25, $M^+-C_{10}H_{22}O_2$), 140 (50, $M^+-C_{10}H_{20}O_2$), 157 (25, $C_{10}H_{21}O$), 199 (11, $M^+-C_7H_{13}O$), 297 (11, M^+-CH_3), 312 (2, M^+, $C_{20}H_{40}O_2$). IR (CCl_4, cm^{-1}): 1380 and 1362 ($CH_3-\overset{|}{\underset{|}{C}}-CH_3$), 1085 (C–O–C). NMR ($CDCl_3$, ppm): 0.85 (6H, d, J=6 Hz, $C\underline{H}_3-\overset{|}{C}H-$), 1.10 (12H, s, $(C\underline{H}_3)_2-C-O-$), 3.28 (4H, t, J=6 Hz, $-O-C\underline{H}_2-CH_2-$).

Found: C, 76.72; H, 13.01%; mol wt (Rast), 317. Calcd for $C_{20}H_{40}O_2$: C, 76.86; H, 12.90%; mol wt, 312.5.

Ether Bond Cleavage of IX: Compound IX (100 mg) was heated with hydroiodic acid (d=1.7, 0.2 ml) under reflux for 10 min. The mixture, after having been poured into water (30 ml), was extracted with ether. After the organic layer was washed with a 10% aqueous solution of sodium bicarbonate and with water and dried over sodium sulfate, evaporation of the solvent gave a colorless oil in a 90% yield, showing two peaks at t_R 9.8 and 10.8 in glc on a Silicon SE-30-packed column. The oil was separated by elution chromatography over a silica gel column with hexane as an eluent.

Identification of Tetrahydrogeranyl Iodide: The compound with t_R 9.8 was a colorless oil, the yield of which was 75% of the ether-cleaved products. n_D^{20} 1.4748. The mass, IR, and NMR spectra were respectively superimposable on those of tetrahydrogeranyl iodide prepared as described below.

Identification of Dihydrogeranyl Iodide: The compound with t_R 10.8 of the ether-cleaved products was also a colorless oil, the yield of which was 25% of the ether-cleaved products. n_D^{20} 1.4978. The mass, IR, and NMR spectra were respectively coincident with those of dihydrogeranyl iodide which was prepared as described below.

Synthesis of Tetrahydrogeranyl Iodide. Tetrahydrogeraniol (2.5 g) was heated with a mixture of red phosphorus (0.15 g) and resublimed iodide (1.3 g) with stirring at 150 °C for 7 hr. The reaction product was taken up into ether. The solution was filtered, and the filtrate was washed successively with water, a 5% aqueous sodium hydroxide solution and water and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave tetrahydrogeranyl iodide as a colorless oil in a 77% yield, which was further purified by elution chromatography over a silica gel column with hexane. n_D^{20} 1.4749. Mass: *m/e* 39 (45%), 41 (70), 43 (base), 55 (14), 57 (85), 71 (53), 85 (14), 99 (13), 127 (5, I^+), 141 (12, $C_{10}H_{21}$), 268 (2, M^+, $C_{10}H_{21}I$). IR (CCl_4, cm^{-1}): 1386, 1381, 1368, 1208, 1178. NMR ($CDCl_3$, ppm): 0.87 (9H, d, J=6 Hz, $C\underline{H}_3-\overset{|}{C}H-C\underline{H}_3$, $C\underline{H}_3-\overset{|}{C}H-$), 1.26 (8H, br.s, $-C\underline{H}_2-$), 3.21 (2H, t, J=6 Hz, $-CH_2-C\underline{H}_2-I$).

Synthesis of Dihydrogeranyl Iodide. A mixture of dihydrogeraniol (2.0 g), red phosphorus (0.1 g) and resublimed iodide (1.0 g) was heated at 150 °C for 3 hr. The mixture was treated similarly as in the case of the preparation of tetrahydrogeranyl iodide to give dihydrogeranyl iodide as a colorless oil in a 58% yield. n_D^{18} 1.4973. Mass: *m/e* 41 (67%), 55 (80), 69 (base), 83 (60), 95 (5), 97 (10), 109 (4), 127 (4, I^+), 139 (5, $C_{10}H_{19}$), 266 (3, M^+, $C_{10}H_{19}I$). IR (CCl_4, cm^{-1}): 1660, 1181, 830. NMR ($CDCl_3$, ppm): 0.87 (3H, d, J=6 Hz, $C\underline{H}_3-\overset{|}{C}H-$), 1.60 and 1.67 (each 3H, br.s, $C\underline{H}_3-\overset{|}{C}=CH-$), 3.22 (2H, t, J=6 Hz, $-CH_2-C\underline{H}_2-I$), 5.06 (1H, m, $-\overset{|}{C}=C\underline{H}-$).

3,7,7,11,15-Pentamethyl-8-oxa-14-hexadecen-1-ol (X). The compound with R_f 0.6 and t_R 6.3 of the high-boiling fraction was isolated as a colorless viscous oil by the above-mentioned elution chromatography. n_D^{27} 1.4601. Mass: *m/e* 41 (28%), 43 (20), 55 (42), 67 (10), 69 (90), 81 (33), 83 (base), 95 (15), 109 (6), 123 (16, C_9H_{15}), 138 (12), 139 (15, $C_{10}H_{19}$), 156 (13, $C_{10}H_{20}O$), 197 (23, $M^+-C_7H_{15}O$), 297 (2, M^+-CH_3), 312

(3, M^+, $C_{20}H_{40}O_2$). IR (CCl_4, cm^{-1}): 3350, 1070 ($-OH$), 1080 ($C-O-C$), 1650, 830 ($-\overset{|}{C}=CH-$), 1380, 1363 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$). NMR ($CDCl_3$, ppm): 0.85 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 1.10 (6H, s, $(C\underline{H}_3)_2-\overset{|}{C}-O-$), 1.60, 1.68 (each 3H, br.s, $C\underline{H}_3-\overset{|}{C}=CH-$), 3.30 (2H, t, $J=6$ Hz, $-\underset{|}{\overset{|}{C}}-O-C\underline{H}_2-CH_2-$), 3.64 (2H, t, $J=6$ Hz, $-CH_2-C\underline{H}_2-OH$), 1.90 (1H, br.s, $-O\underline{H}$), 5.05 (1H, m, $-C\underline{H}=\overset{|}{C}-$).

Catalytic Hydrogenation of X: Compound X (300 mg) was hydrogenated over platinum oxide (30 mg) in acetic acid (7 ml) to take up one molar equivalent of hydrogen. The mixture was treated according to the usual procedure, dihydro X being obtained as a colorless oil in a good yield. Mass: *m/e* 41 (77%), 43 (base), 55 (77), 57(65), 69 (52), 83 (21), 85 (26), 87 (11), 141 (10), 199 (13), 314 (trace, M^+,$C_{20}H_{42}O$). IR (CCl_4, cm^{-1}): 3370, 1075 ($-OH$), 1070($C-O-C$), 1380, 1368 ($CH_3-\overset{|}{C}H-CH_3$ and $CH_3-\underset{|}{\overset{|}{C}}-CH_3$). NMR ($CDCl_3$, ppm): 0.85 (12H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$ and $C\underline{H}_3-\underset{|}{\overset{|}{C}}-C\underline{H}_3$), 1.10 (6H, s, $(C\underline{H}_3)_2\overset{|}{C}-O-$), 2.00 (1H, br.s, $-O\underline{H}$), 3.30 (2H, t, $J=6$ Hz, $-O-C\underline{H}_2-CH_2-$), 3.65 (2H, t, $J=6$ Hz, $-CH_2-C\underline{H}_2-OH$).

Acetylation of X: Acetic anhydride (1 ml) was added to a solution of X (500 mg) in dry pyridine (1 ml) and the mixture was allowed to stand overnight at room temperature. The mixture, after having been poured into water, was extracted with ether, and evaporation of the solvent gave monoacetate as an oily substance in a good yield. IR (CCl_4, cm^{-1}): 1745, 1245 (CH_3COO-), 1080 ($C-O-C$), 1382, 1370 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$). NMR ($CDCl_3$, ppm): 0.88 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 1.10 (6H, s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-C\underline{H}_3$), 1.60, 1.68 (each 3H, br.s, $C\underline{H}_3-\overset{|}{C}=CH-$), 2.02 (3H, s, $C\underline{H}_3COO-$), 4.05 (2H, t, $J=6$ Hz, $CH_3-COO-C\underline{H}_2-CH_2-$), 5.05 (1H, m, $-C\underline{H}=\overset{|}{C}-$).

Dehydration of X: A solution of phosphoryl chloride (0.2 ml) in dry pyridine (1 ml) was added to a solution of X (500 mg) in the same solvent under cooling at −5 °C, and the mixture was allowed to stand at the same temperature for 24 hr. The mixture, after having been poured into a 10% ice-cooled aqueous solution of sodium bicarbonate, was taken up into ether. Evaporation of the solvent gave a dehydrated compound (X-A) as an oily substance in a good yield. IR (CCl_4, cm^{-1}): 1650, 890 ($CH_2=\overset{|}{C}-$), 1670, 830 ($-CH=\overset{|}{C}-$), 1080 ($C-O-C$), 1385, 1369 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$). NMR ($CDCl_3$, ppm): 0.88 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 1.12 (6H, s, $(C\underline{H}_3)_2=\overset{|}{C}-O-$), 1.60, 1.68 (3H and 6H, each br.s, $-\overset{C\underline{H}_3}{\overset{|}{C}}=\underset{H}{\underset{|}{C}}-$ and $-\overset{\underline{H}_3C}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-$), 3.30 (2H, t, $J=6$ Hz, $-O-C\underline{H}_2-CH_2-$), 4.70 (2H, br.s, $C\underline{H}_2=\overset{|}{C}-$), 5.10 (1H, m, $-C\underline{H}=\overset{|}{C}-$).

Catalytic Hydrogenation of Dehydrated Product X-A: Catalytic hydrogenation of the dehydrated product (X-A, 400 mg) over platinum oxide (40 mg) in acetic acid (6 ml) took up two molar equivalents of hydrogen to give a tetrahydroproduct (X-B) as an oily substance in a good yield. Mass: *m/e* 39 (20%), 41 (85), 43 (95), 55 (91), 57 (base), 69 (98), 81 (72), 83 (44), 85(54), 97 (22), 140 (6), 141 (21), 173 (27), 199 (50, $M^+-C_7H_{15}$), 265 (3, $M^+-CH_3-H_2O$), 280 (2, M^+-H_2O), 298 (trace, M^+, $C_{20}H_{42}O$). IR (CCl_4, cm^{-1}): 1382, 1365, 1082. NMR ($CDCl_3$, ppm): 0.85 (12H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-C\underline{H}_3$ and $C\underline{H}_3-\overset{|}{C}H-$), 1.08 (6H, s, $(C\underline{H}_3)_2\overset{|}{C}-O-$), 3.25 (2H, t, $J=6$ Hz, $-O-C\underline{H}_2-CH_2-$).

Ether Bond Cleavage of the Tetrahydro-Compound X-B: X-B (300 mg) was heated with hydroiodic acid ($d=1.7$, 0.4 ml) under reflux for 10 min, and the reaction product was chromatographed over silica gel with hexane to give two compounds with t_R 7.6 and 9.8 in good yields.

Identification of 2,6-Dimethyl-1-octene: The compound with t_R 7.6 of the ether-cleaved products was obtained as a colorless oil in a relative yield of 30%. Mass: *m/e* 41 (36%), 43 (50), 55 (59), 57 (75), 69 (base), 83 (80), 95 (29), 97 (43), 111 (42), 126 (25), 140 (41, M^+, $C_{10}H_{20}$). The mass spectrum of this compound was in good agreement with that of 2,6-dimethyl-1-octene.[7]

Identification of Tetrahydrogeranyl Iodide: The compound with t_R 9.8 of the ether-cleaved products was obtained as a colorless oil in a relative yield of 70%. The mass, IR, and NMR spectra were respectively superimposable on those of the synthetic samples of tetrahydrogeranyl iodide mentioned above.

3,7,9,9,13-Pentamethyl-7-pentadecene-1,15-diol (XI). The most polar compound (R_f 0.20 and t_R 10.5) of the high-boiling fraction separated in Experiment 3 was isolated in elution chromatography as a colorless oil. n_D^{28} 1.4770. Mass: *m/e* 41 (base), 43 (86%), 55 (68), 57 (56), 59 (10), 67 (25), 69 (71), 70 (40), 71 (41), 81 (22), 83 (20), 95 (18), 112 (11), 123 (8), 138 (4), 156 (3), 269 (2, $M^+-C_3H_7$), 297 (2, M^+-CH_3), 312 (1, M^+, $C_{20}H_{40}0_2$). IR (CCl_4, cm^{-1}): 3350, 1065, 1020 ($-OH$), 1388, 1371 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$), 1650, 860 ($-CH=\overset{|}{C}-$). NMR ($CDCl_3$, ppm): 1.63 (3H, br.s, $C\underline{H}_3-\overset{|}{C}=CH-$), 0.85 (6H, s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-C\underline{H}_3$), 0.90 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 3.59 (4H, t, $J=6$ Hz, $-CH_2-C\underline{H}_2-OH$), 3.80 (2H, br.s, $-O\underline{H}$), 5.09 (1H, m, $-C\underline{H}=\overset{|}{C}-$).

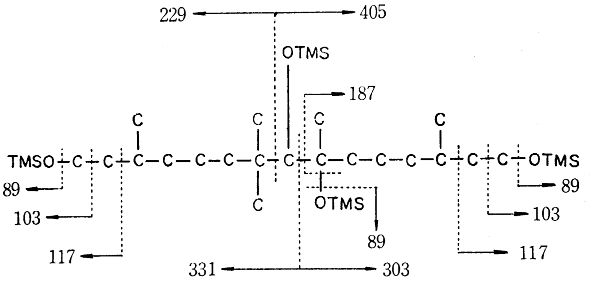
Found: C, 76.67; H, 13.04%; mol wt (Rast), 310. Calcd for $C_{20}H_{40}O_2$: C, 76.86; H, 12.90%; mol wt, 312.5.

Acetylation of XI: XI (100 mg) was treated with acetic anhydride (0.7 ml) in dry pyridine (1.0 ml) at room temperature according to the manner indicated above to give a diacetate as an oily substance in a good yield. IR (CCl_4, cm^{-1}): 1389, 1371 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$), 1740, 1250 ($CH_3COO-$), 1650, 855 ($-CH=\overset{|}{C}-$). NMR ($CDCl_3$, ppm): 0.82 (6H, s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-C\underline{H}_3$), 0.90 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 2.02 (6H, s, $C\underline{H}_3-COO-$), 4.09 (4H, t, $J=6$ Hz, $-CH_2-C\underline{H}_2-COOCH_3$), 5.05 (1H, m, $-\overset{|}{C}=C\underline{H}-$).

Catalytic Hydrogenation of XI: XI (500 mg) was hydrogenated over platinum oxide (50 mg) in acetic acid (7 ml), and took up one molar equivalent of hydrogen to give a dihydroderivative as a colorless oil in a good yield. Mass: *m/e* 41 (68%), 43 (base), 55 (64), 56 (44), 57 (52), 59 (8), 67 (36), 69 (56), 70 (32), 71 (36), 77 (8), 81 (40), 83 (20), 95 (28), 112 (12), 121 (6), 123 (12), 141 (21), 199 (18), 296 (2, M^+-H_2O), 314 (trace, M^+, $C_{20}H_{42}O_2$). IR (CCl_4, cm^{-1}): 3350, 1065, 1020 ($-OH$), 1388, 1371 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$). NMR ($CDCl_3$, ppm): 0.85 (6H, s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-C\underline{H}_3$), 0.90 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 3.14 (2H, br.s, $-O\underline{H}$), 3.65 (4H, t, $J=6$ Hz, $-CH_2-C\underline{H}_2-OH$).

Oxidation of XI: A solution of osmium tetroxide (500 mg) in 4 ml of dry benzene was added to a solution of XI (500 mg) in a mixture of dry benzene (5 ml) and dry pyridine (0.5 ml) and the mixture was allowed to stand at room temperature for 6 days. After benzene had been distilled out from the mixture, the residual portion was diluted with ethanol (10 ml), then the solution was refluxed with a 10% aqueous sodium sulfite solution (10 ml) for 2 hr. Brown precipitates thus formed were filtered off, and the filtrate was extracted with chloroform to give a glycol as a colorless oil in a 90% yield. IR (CCl_4, cm^{-1}): 3400, 1160, 1070 ($-OH$). NMR ($CDCl_3$, ppm): 0.90 (6H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$), 0.99 (6H, s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-C\underline{H}_3$), 1.25 (3H, s, $C\underline{H}_3-\underset{|}{\overset{|}{C}}-OH$), 2.84 (4H, br.s, $-O\underline{H}$), 3.40 (1H, m, $-\underset{|}{\overset{|}{C}}-C\underline{H}-OH$), 3.65 (4H, t, $J=6$ Hz, $-CH_2-C\underline{H}_2-OH$).

Trimethylsilylation of the Glycol: Hexamethyldisilazane (0.1 ml) and trimethylchlorosilane (0.05 ml) were successively added to a solution of the above glycol (3 mg) in dry pyridine (0.5 ml), and the mixture was heated at 65 °C for 7 min. The mixture was treated according to a usual procedure to give trimethylsilyl ether as an oily substance. Mass: *m/e* 69 (45%), 71 (25), 73 (40), 75 (45), 81 (50), 83 (95), 89 (10), 95 (67), 103 (48), 117 (27), 123 (30), 129 (62), 131 (60), 139 (40), 147 (45), 171 (55), 187 (45), 218 (50), 229 (26), 242 (10), 288 (base), 303 (18), 316 (15), 331 (12), 405 (2), 456 (16), 545 (5). This spectrum was reasonably explained by following fragmentation.



Conversion of Cyclic Diether (IX) and Acyclic Ether (X) by $BF_3 \cdot Et_2O$. A solution of IX (100 mg) in dry ether (1 ml) was mixed with 0.02 ml of $BF_3 \cdot Et_2O$ and the mixture was allowed to stand at room temperature for 48 hr. After the excess catalyst had been decomposed by the addition of a small amount of water, the separated oily layer was analyzed by glc with the Silicon SE-30 separation column. The conversion of acyclic ether was similarly examined. The results are given in Table 2.

The author wishes to express sincere gratitude to Professor Shûichi Hayashi of Hiroshima University for kind and continuous guidance in the course of this work, and also to Assistant Professor Mitsuru Nakayama of Hiroshima University for valuablesuggestions.

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