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The Aromatization Observed on the Reaction of Terpinolene with Tetrahydrogeraniol in the Presence of Boron Trifluoride Etherate

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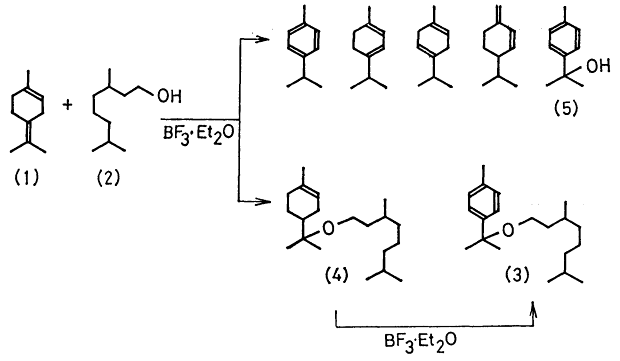
Synopsis. The reaction of terpinolene with tetrahydrogeraniol in the presence of boron trifluoride etherate gave an aromatic ether in addition to the corresponding aliphatic ether, along with *p*-cymene, *p*-cymen-8-ol, and the monoterpene hydrocarbons formed by double-bond migration. The aromatic ether was proved to form upon the treatment of the aliphatic ether with boron trifluoride etherate.

In connection with previous papers on the formation of ethers from monoterpene[1–6] and aliphatic[7,8] alcohols with boron trifluoride etherate, the effect of the same reagent on the addition reaction of tetrahydrogeraniol (**2**) to terpinolene (**1**) was examined.

In a typical experiment, equal portions (1.0 g) of terpinolene and tetrahydrogeraniol were mixed with boron trifluoride etherate (0.05 ml), after which the mixture was allowed to stand at room temperature for 5 days. The reaction mixture was then subjected to elution chromatography on silica gel, followed by preparative-GLC in Carbowax 6000, to give Compounds **3**, **4**, and **5** and also *p*-cymene. The structures of **3**, **4**, and **5** were characterized as 1-methyl-4-[1-(3,7-dimethyloctyloxy)-1-methylethyl]benzene, 1-methyl-4-[1-(3,7-dimethyloctyloxy)-1-methylethyl]-1-cyclohexene, and 1-methyl-4-(1-hydroxy-1-methylethyl)benzene (*p*-cymen-8-ol) respectively on the basis of their spectral data and chemical behavior.

Under mild conditions (Exp. No. 1, Table 1), the aromatic alcohol, **5**, *p*-cymene, and two ethers, **3** and **4**, were obtained as the major products. On the other hand, under vigorous conditions (Exp. No. 2), *p*-cymene was produced as the major product, together with small amounts of **3**, **4**, and **5** and three monoterpene hydrocarbons. Under these conditions, aromatic compounds were obtained as the main components. Furthermore, all the compounds were confirmed by GC/MS analysis. The aromatic ether, **3**, was also prepared albeit in a low yield, by treating the **4** ether with boron trifluoride etherate, as is shown in Table 2 and Scheme 1.



Scheme 1.

The results obtained in this paper are essentially comparable with those of previous works.[1,4–6] However, the formation of the aromatic compounds in considerable amounts is remarkable; this can be interpreted in terms of the participation of oxygen rather than disproportionation. In this connection, the obtaining of *p*-cymen-8-ol (**5**) is interesting; the mechanism of its formation is now under investigation.

Experimental

Apparatus. The IR spectra were taken in a CCl_4 solution, while the ^1H-NMR spectra were obtained in a CCl_4 solution, using TMS as the internal reference on a 60 MHz spectrometer. The mass spectra were measured by means of a Hitachi RMS-4 spectrometer under the following operating conditions: 80 eV, ionization-chamber voltage; 80 uA, total emission; 1800 eV, ion-accelerating voltage, and 200 °C, ionization-chamber temperature. The GLC was carried out on an FID-type apparatus in connection with a glass column (3 mm × 2 m) packed with OV-1 (2%) on Diasolid L (60—80 mesh) and DEGS (3%) on Shimalite W (60—80 mesh) under a 20 ml/min flow rate of a N_2 carrier.

Materials. Commercial **1** and **2** were used after repeated fractional distillations. Each of them showed a single peak in GLC with OV-1 and DEGS-packed columns, and the IR and ^1H-NMR spectra of these materials were coincident with those of authentic ones.

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

*Reaction of **1** with **2** in the Presence of $BF_3 \cdot Et_2O$.* To a mixture of **1** (1.0 g) and **2** (1.0 g), 0.05 ml or 0.15 ml of $BF_3 \cdot Et_2O$ was added, drop by drop. The mixture was then allowed to react at room temperature for 5 or 7 d respectively. The reaction mixture was shaken with a saturated aqueous solution of sodium carbonate to neutralize the remaining $BF_3 \cdot Et_2O$, washed with water, dried over anhydrous sodium sulfate, and separated through column chromatography on silica gel with a hexane–ethyl acetate mixture and through preparative-GLC with Carbowax 6000 (*cf.* Table 1).

*Characterization of **3**.* A colorless oil was obtained in a 10% yield. λ_{max}^{EtOH}: 272 nm (220), 264 (260), 256 (250), 251 (280), 217_{sh} (5320), 212 (5580); IR (CCl_4, cm^{-1}): 1511 (aromatic ring), 1385, 1379, 1360 ($CH_3\text{–}\overset{|}{C}H\text{–}CH_3$, $CH_3\text{–}\underset{|}{\overset{|}{C}}\text{–}CH_3$, $CH_3\text{–}\underset{|}{C}H\text{–}$), 1162, 1075 (C–O–C); ^1H-NMR (CCl_4): δ 0.88 (9H, d, $J=7$ Hz, $C\underline{H}_3\text{–}\overset{|}{C}H\text{–}C\underline{H}_3$, $C\underline{H}_3\text{–}\overset{|}{C}H\text{–}$), 1.23 (8H, bs, $\text{–}C\underline{H}_2\text{–}\times 4$), 1.53 (6H, s, $(C\underline{H}_3)_2\text{–}\overset{|}{C}\text{–O–}$), 1.66 (2H, bs, $\text{–}\overset{|}{C}\underline{H}\text{–}\times 2$), 2.38 (3H, s, $C\underline{H}_3$–Ar), 3.20 (2H, t, $J=7$ Hz, $\text{–O–}C\underline{H}_2\text{–}CH_2\text{–}$), 7.25 (4H, bs, aromatic proton); Mass (*m/e*): 290 (4%, M^+, $C_{20}H_{34}O$), 135 (15), 133 (58), 112 (30), 110 (22), 105 (21), 91 (21), 81 (19), 71 (49), 70 (35), 69 (50), 57 (67), 43 (base).

Table 1. Reaction conditions and reaction products

	Experiment No.	1	2
Reaction conditions	Terpinolene (g)	1.0	1.0
	Tetrahydrogeraniol (g)	1.0	1.0
	$BF_3 \cdot Et_2O$ (ml)	0.05	0.15
	React. period/d	5	7
	React. temp/°C	20	23
Reaction products (yield/%)[a]	α-Terpinene	7.7	2.0
	β-Phellandrene	3.0	2.8
	γ-Terpinene	1.2	5.6
	p-Cymene	21.8	76.4
	p-Cymen-8-ol (**5**)	37.6	0.6
	Aromatic ether **3**	10.1	8.6
	Aliphatic ether **4**	14.2	1.4
	Others	4.4	2.6

a) The ratios of the components were calculated by means of GLC from their relative peak areas.

Characterization of ***4.*** A colorless oil was obtained in a 14% yield. IR (CCl_4, cm^{-1}): 1680, 895 ($-CH=\overset{|}{C}-$), 1390, 1369 ($CH_3-\overset{|}{C}H-CH_3$, $CH_3-\underset{|}{\overset{|}{C}}-CH_3$), 1165, 1142, 1121, 1082 (C–O–C); ^1H-NMR ($CDCl_3$): δ 0.85 (9H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-$, $C\underline{H}_3-\overset{|}{C}H-C\underline{H}_3$), 1.10 (6H, s, $(C\underline{H}_3)_2-\overset{|}{C}-O-$), 1.67 (3H, s, $C\underline{H}_3-\overset{|}{C}=CH-$), 1.93 (4H, bs, $-C\underline{H}_2-\overset{|}{C}=\overset{|}{C}-\times 2$), 3.36 (2H, t, $J=7$ Hz, $-O-C\underline{H}_2-CH_2-$), 5.46 (1H, bs, $w/2=$ 8 Hz, $-C\underline{H}=\overset{|}{C}-$); Mass (*m/e*): 294 (2%, M^+, $C_{20}H_{38}O$), 199 (8), 141 (5, $C_{10}H_{21}$), 136 (15), 121 (5), 95 (9), 93 (10), 81 (12), 59 (8), 55 (21), 43 (base), 41 (55), 39 (14).

Catalytic Hydrogenation of ***4.*** Compound **4** (300 mg) was hydrogenated over platinum oxide (30 mg) in acetic acid (7 ml) to take up 1 mol-equivalent of hydrogen, thus giving the dihydro derivative of **4** as a colorless oil in a yield of 80%. IR (CCl_4, cm^{-1}): 1383, 1368 ($CH_3-\overset{|}{C}H-CH_3$. $CH_3-\underset{|}{\overset{|}{C}}-CH_3$), 1173, 1151, 1121, 1071 (C–O–C); ^1H-NMR ($CDCl_3$): δ 0.85 (12H, d, $J=6$ Hz, $C\underline{H}_3-\overset{|}{C}H-C\underline{H}_3$, $C\underline{H}_3-\overset{|}{C}H-\times 2$), 1.10 (6H, s, $(C\underline{H}_3)_2-\overset{|}{C}-O-$), 3.34 (2H, t, $J=7$ Hz, $-O-C\underline{H}_2-CH_2-$).

Preparation of Dihydro ***4.*** Tetrahydrogeranyl bromide (1.0 g) and sodium dihydro-α-terpineolate (1.0 g) were treated according to the Williamson procedure to give the dihydro derivative of **4** as a colorless oil in a yield of 15%.

Conversion of ***4*** *into* ***3*** *by* $BF_3 \cdot Et_2O$. The ether **4** (20 mg), was dissolved in dried ether (1 ml) and mixed with 0.04 ml of $BF_3 \cdot Et_2O$. After the mixture had then been allowed to stand at room temperature for 9 d, a small amount of water was added to the reaction mixture to decompose the excess reagent. The reaction mixture thus reacted was then analyzed by means of gas chromatography on the DEGS separation column to determine the compositions (*cf.* Table 2). Each compound was identified by comparing the retention times with those of authentic samples.

Table 2. Conversion of aliphatic ether **4** by $BF_3 \cdot Et_2O$ (%)

Unreacted ether	66.7
α-Terpinene	1.6
γ-Terpinene	1.4
p-Cymene	3.2
Tetrahydrogeraniol	14.5
Aromatic ether **3**	3.0
Others	9.6

The ratios of the components were calculated by means of GLC from their relative peak areas.

Characterization of ***5.*** Compound **5** was isolated as a colorless oil in a yield of 38%. λ_{max}^{EtOH}: 272 nm (330), 263 (390), 257 (310), 251 (210), 221_{sh} (6920), 216 (8080), 213 (8020); IR (CCl_4, cm^{-1}): 3599 (–OH), 1511 (aromatic ring), 1380, 1364 ($CH_3-\underset{|}{\overset{|}{C}}-CH_3$), 1168, 1112 (C–O–C); ^1H-NMR (CCl_4): δ 1.56 (6H, s, $(C\underline{H}_3)_2-\overset{|}{C}-O-$), 1.76 (1H, bs, $-O\underline{H}$, disappeared with D_2O), 2.36 (3H, s, $C\underline{H}_3-Ar$), 7.21 7.40 (each 2H, d, $J=8$ Hz, aromatic proton); Mass (*m/e*): 150 (20%, M^+, $C_{10}H_{14}O$), 135 (base), 133 (16), 91 (24), 43 (21). The spectra were in good agreement with those of 1-methyl-4-(1-hydroxy-1-methylethyl)benzene, the synthesis of which will be described in the following section.

Preparation of ***5.*** Methyl *p*-methylbenzoate (500 mg) in ether (20 ml) was refluxed with 5% methyllithium in ether (7 ml) for 6 h. The mixture was then treated according to the usual procedure to give 1-methyl-4-(1-hydroxy-1-methylethyl)benzene in a 70% yield.

GC/MS of Reaction Products. GC/MS analyses of reaction products were carried out using a glass column (3 mm × 2 m) packed with 3% OV-1 on Gas Chrom. Q under a 7 °C/min temperature program from 80 to 230 °C; 70 eV, ionization voltage; 3500 eV, ion-accelerating voltage; 290 °C, the ion-source temperature, and 270 °C, the separator temperature. Each compound was gas-chromatographically identical with the respective authentic sample.

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