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The Esterification of Thujopsene with Bismuth(III) Sulfate in Carboxylic Acids

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Synopsis. The catalytic interaction of *cis*-(−)-thujopsene with a series of organic acids from acetic to octanoic in the presence of bismuth(III) sulfate afforded the corresponding esters in 20—34% yields, accompanied by skeletal rearrangement. The follow-up of the reaction, an investigation of the reaction conditions, and the effects of catalysts are described.

In organic acids, the autoxidation of some olefins occurs in the presence of bismuth(III) sulfate.[1] Valkanas[2] has recently found that the interaction of *d*-α-pinene with a series of organic acids from acetic to octanoic, over a wide range of olefin-to-acid ratios, yields esteric and rearrangement products. We have obtained some findings on the esterification of thujopsene **1** with a series of organic acids from acetic to octanoic in the presence of bismuth(III) sulfate. Thus, it may be seen that the esterification proceeds through a skeletal conversion to give a bicyclic ester as the major product, without any autoxidation reaction occurring.

The esterification of thujopsene was carried out using organic acid in a ratio of 20 parts of thujopsene to 0.25 parts of bismuth(III) sulfate at 70 °C for 40 h. The results are summarized in Tables 1 and 2, including the spectral data of the reaction products. The reactions all afforded the same reaction products, regardless of the carboxylic acid used. The amounts of esterification are shown to increase from 20 to 34% between acetic acid and valeric acid, and to decrease from 34 to 29% between valeric acid and octanoic acid. The structures of the esters were confirmed by means of the analytical and spectral data, and also by the fact that the hydrolysis of the esters afforded 2β-hydroxymethyl-2α,8,8,4aβ-tetramethyl-1(8a)-octalin (*cis*-neopentyl-type alcohol)[3] evenly, in disregard of the partial structures from carboxylic acids. The isomeric α-type neopentyl ester has already been reported by us.[4]

The rise-and-fall ratio of intermediates or products in the reaction path was observed by GLC (Fig.1): in a reaction time of 2 min, Peak **a** (thujopsene) is shown to isomerize into the other hydrocarbons of Peaks **b**, **c**, and **d**: in 15 min, Peak **a** decreases strikingly to give a hydrocarbon (Peak **c**) and Peak **e**: in 40 h, Peak **e** reaches a suitable amount and a new peak, **f**, appears. Peaks **c** and **f** were identified, by comparisons of the spectral (IR and NMR) data and the GLC retention times with those of authentic samples, as 1,4,11,11-tetramethylbicyclo[5.4.0]undeca-3,7-diene,[5] **3**, and 2,2,3,7-tetramethyltricyclo[5.2.2.0^{1,6}]undec-3-ene,[5] **4**, respectively.

Then, the suitable conditions of the esterification were determined by experiments using propionic acid. To obtain a high yield of the ester, the reaction must be carried out at the reaction temperature of 70 °C, for a reaction time of 40 h, and using carboxylic acid in a ratio of 20 parts of thujopsene to 0.25 parts of the

Table 1. Analytical data of the esters

	Ester	Yield %	Ester value Found(Calcd)	Found (Calcd) % C	H	IR (CCl_4) cm^{-1} $\nu_{C=O}$	ν_{C-O}
1	Acetic	20	16.24(16.28)	76.95(77.22)	10.51(10.67)	1740	1225
2	Propionic	24	20.45(20.50)	77.43(77.65)	10.66(10.86)	1738	1178
3	Butyric	28	24.24(24.31)	77.86(78.03)	10.92(11.03)	1738	1178
4	Valeric	34	27.72(27.78)	78.23(78.38)	11.05(11.18)	1737	1166
5	Hexanoic	31	30.85(30.94)	78.59(78.70)	11.17(11.32)	1737	1164
6	Heptanoic	30	33.75(33.83)	78.71(78.99)	11.36(11.45)	1737	1162
7	Octanoic	29	36.41(36.49)	79.08(79.25)	11.45(11.57)	1735	1160

Table 2. NMR spectra of the esters

Ester	ppm Value in chloroform-*d*
1	0.97(s, CH_3), 1.05(s, $2CH_3$), 1.16(s, CH_3), 2.03(s, $OCOCH_3$), 3.80(m, 2H), 5.07(s, 1H, olefinic)
2	0.98(s, CH_3), 1.04(s, $2CH_3$), 1.08(s, CH_3), 1.15(s, CH_3), 2.33(q, 2H), 3.80(q, 2H), 5.08(s, 1H, olefinic)
3	0.97(s, CH_3), 1.05(s, $3CH_3$), 1.15(s, CH_3), 2.28(t, 2H), 3.79(q, 2H), 5.08(s, 1H, olefinic)
4	0.98(s, CH_3), 1.04(s, $2CH_3$), 1.09(s, CH_3), 1.17(s, CH_3), 2.31(t, 2H), 3.80(q, 2H), 5.09(s, 1H, olefinic)
5	0.98(s, CH_3), 1.06(m, $3CH_3$), 1.16(s, CH_3), 2.30(t, 2H), 3.38(q, 2H), 5.09(s, 1H, olefinic)
6	0.98(s, CH_3), 1.04(d, $3CH_3$), 1.16(s, CH_3), 2.32(t, 2H), 3.80(q, 2H), 5.09(s, 1H, olefinic)
7	0.98(s, CH_3), 1.04(d, $3CH_3$), 1.15(s, CH_3), 2.30(t, 2H), 3.80(q, 2H), 5.08(s, 1H, olefinic)

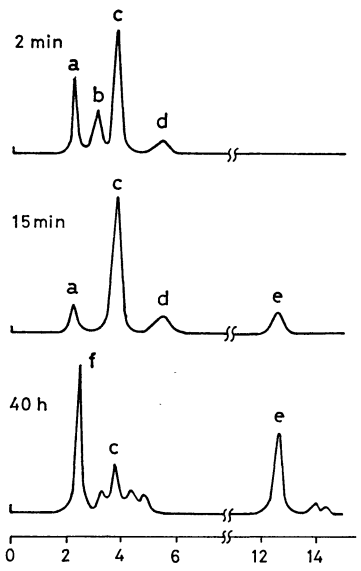
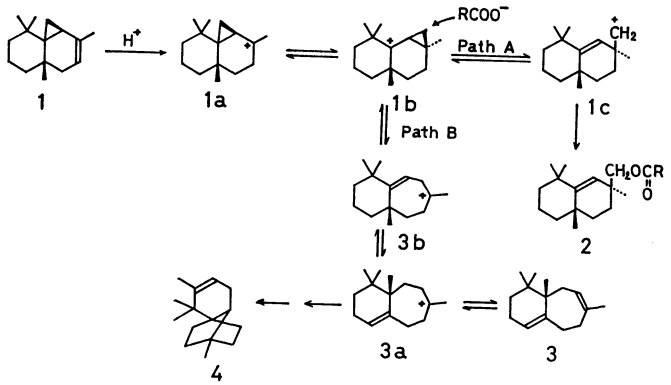


Fig. 1. Follow-up of the reaction path by GLC at the esterification of thujopsene using C_2H_5COOH and $Bi_2(SO_4)_3$.

catalyst.

In the presence of bismuth(III) sulfate, this esterification reaction proceeded most readily under mild conditions, accompanied by rearranged products of thujopsene. In this system, however, no ester or rearranged products could be found in a blank reaction at temperatures lower than 70 °C for 40 h or more. Also, tin(II) sulfate and antimony(III) sulfate showed a catalytic effect, affording the same products. In view of these results, and with reference to the reaction mechanisms using other reagents presented by Dauben and Friedrich[5] and by Hochstetler and Kitchens,[6] the esterification to give the β-type bicyclic ester as the major product, accompanied by the tricyclic hydrocarbon, **4**, may be explained as is shown in Scheme 1. By considering the results for the follow-up of the reaction shown in Fig. 1, the protonation of (−)-thujopsene leads to the **1b** cation the subsequent attack of the carboxylate anion as **1b** would lead to the bicyclic ester, **2**, *via* Path A. Path B would afford the tricyclic hydrocarbon, **4**, *via* the **3a** cation by the pathway reported by Dauben and Friedrich.[5]



Scheme 1.

Experimental

The spectra were recorded on a JEOL JNM-PMX 60 NMR spectrometer, using TMS as the internal standard, and a Shimadzu IR-400 IR spectrometer. The elemental analyses were performed by a Hitachi 026 CHN analyzer. The analytical GLC were performed on a Shimadzu GC-4B apparatus with a 1.5 m glass column packed with 15% OV-17, at 10 °C/min 150—250 °C. For the preparative GLC, a JEOL JGC-1100 apparatus was employed with 15% OV-17 at 240 °C.

The thujopsene used was purified by the careful distillation of Cedar H oil (Takasago Perfumery Co., Ltd.) through a concentric column; bp 120 °C/10 mmHg. The inorganic salts used for the catalyst and organic acids were commercial, extra-pure reagents.

Esterification of Thujopsene. A mixture of 3.07 g (15 mmol) of thujopsene, 0.3 mol of organic acid, and 2.65 g (3.75 mmol) of bismuth(III) sulfate was stirred in a thermostated bath at 70 °C for 40 h. After the organic acid had been removed under reduced pressure, the resulting residue was poured into a cold mixture of petroleum ether and 5% aqueous sodium hydroxide while standing. The petroleum layer was further washed with a sodium hydrogencarbonate solution and dried over anhydrous sodium sulfate, and then the solvent was removed. The residue was analyzed by GLC. The analytical sample was chromatographed on a silica gel column and further purified by preparative GLC to yield material of a 97—98% purity. The saponification value was determined using a 2-h boiling in a 90% aqueous ethanolic solution of 0.3 M potassium hydroxide.

Follow-up of the Reaction Path by GLC. A mixture of 1.54 g (7.5 mmol) of thujopsene, 11.1 g (0.15 mol) of propionic acid, and 1.33 g (1.88 mmol) of bismuth(III) sulfate was stirred at 70 °C in the manner described above. The reaction product was analyzed by GLC, using sample aliquots at appropriate time intervals after the reaction mixture had been worked-up as described above.

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