NOTES

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The Allylic Oxidation of Thujopsene

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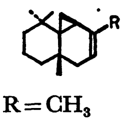
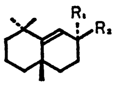
The allylic oxidation[1] of olefins to their acetate by mercuric acetate in acetic acid or other solvents occurs by means of an electrophilic addition. Brown[2] has shown that the oxymercuration-demercuration of olefins is an excellent method of obtaining alcohols. The procedure achieves the Markovnikov hydration of carbon-carbon double bonds without rearrangement, and it results in the preferential formation of *exo* hydroxyl derivatives.

Although several attempts to prepare a saturated alcohol by Brown's procedure have been unsuccessful with regard to thujopsene (**1**), we have obtained some findings on the reaction of thujopsene **1**, with mercuric acetate in acetic acid. Thus, it may be seen that, besides a skeletal conversion to give a bicyclic acetate (**4**), an allylic oxidation occurs at the methyl group, while these are no Markovnikov addition to **1**. Thus, **1** was first mercurated by heating it with mercuric acetate in acetic acid at 70°C for 3 hr; it was then demercurated by heating at 100—120°C for 3—4 hr. Glpc and tlc analyses of the reaction mixture showed two major products, (**2**) and (**3**), and a minor product, **4**. Samples of the three products were readily isolated from the mixture by means of preparative tlc.



1 : R = CH_3
2 : R = CH_2OAc
3 : R = CH_2OH



4 : $R_1 = CH_2OAc$, $R_2 = CH_3$
6 : $R_1 = CH_3$, $R_2 = CH_2Br$

The **2** product was a colorless liquid; its IR spectrum showed a presence of an acetoxyl group, while the NMR spectrum indicated the cyclopropane ring intact and the replacement of a methyl group by an acetoxymethyl group. The structure assigned to this product, **2**, was verified when the hydrolysis of **2** afforded thujopsenol (**5**).[3]

The **3** product, pale yellow crystals, was identified as thujopsenal by a direct comparison of its melting point and IR and NMR spectra with those of an authentic sample.

The minor product, **4**, a colorless liquid, was analyzed to be $C_{17}H_{28}O_2$. The NMR spectrum revealed the absence of any cyclopropane ring and the presence of an acetoxymethyl group. Because of the close resemblance of the NMR data to the related compound (**6**),[4] the structure of **4** was deduced to be as depicted.

Whenever the reaction carried out in an atmosphere of nitrogen or oxygen, the ratio of the yield of **3** to **2** was not affected. Although the reaction was attempted in various solvents (*e.g.*, in acetic acid-acetic anhydride, tetrahydrofuran-water, and acetic acid, acetone-water) the reaction products were almost always the same. The reaction in the presence of silver acetate[5] or hydroquinone does not seem to improve the yield.

Experimental

Materials and Methods. The thujopsene was obtained from Hiba (*Thujopsis dolabrata* Sieb. et Zucc.) oil. Thin-layer chromatography (tlc) and preparative tlc were performed on silica gel Merck G. The equipment used in this study was a Varian A-60 NMR spectrometer, a Shimadzu IR-27G grating IR spectrometer, a Shimadzu MPS-50 multipurpose UV spectrometer, and a Shimadzu UM-2 elemental-analyses apparatus.

Allylic Oxidation of Thujopsene. A solution of 5.8 g (28 mmol) of thujopsene in 10 m*l* of acetic acid was treated with a solution of 9.6 g (30 mmol) of mercuric acetate in 40 m*l* of acetic acid. The mixture was heated at 70°C for 3 hr. After the mercuration, the reaction temperature was elevated to 120°C, and then the solution was maintained at that temperature for 4 hr. The reaction mixture was cooled, treated with water, and extracted with ether. The ether solution was dried and evaporated, and the residue was distilled. After the removal of the unchanged hydrocarbon, these products, **2**, **3**, and **4**, were isolated by preparative tlc using a mixed solvent of *n*-hexane and ethyl acetate (9 : 1, by volume).

The sample of **2** (0.53 g, 14.4%) was a colorless liquid and showed the following spectral data: UV $\lambda_{\max}^{\text{EtOH}}$ 222 (ε 4509), $\lambda_{\max}^{\text{Hexane}}$ 221.5 mμ(ε 4488); IR (CCl_4) 1728 (C=O), 1227 (CH_3CO), 3011 cm^{-1} (cyclopropyl); NMR (CCl_4) 0.63 (s, 3, CH_3), 1.12 (s, 3, CH_3), 1.15 (s, 3, CH_3), 2.01 (s, 3,OC-OCH_3), 4.50 (s, 2 CH_3OAc), 5.25 ppm (m, 1, olefinic proton).

Found C, 77.68; H, 9.89%. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%.

The sample of **3** (0.34 g, 11.1%) consisted of pale yellow crystals; mp 75°C; IR (CCl_4) 1692 (C=O), 1649 cm^{-1} (C=C).

The sample of **4** (0.2 g, 5.4%) was a colorless liquid and showed the following spectral data: UV $\lambda_{\max}^{\text{EtOH}}$ 208 mμ. IR (CCl_4) 1730 (C=O), 1237 cm^{-1} (CH_3CO–), and NMR (CCl_4) 1.06 (d, 6, $2CH_3$), 1.14 (s, 3, CH_3), 1.20 (s, 3, CH_3),

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[3] O. Okuda, *Yakugaku Zasshi*, **73**, 1, 4, 6, and 9 (1953).

[4] M. Ito, K. Abe, H. Takeshita, and M. Yatagai, This Bulletin, **44**, 2168 (1971).

[5] S. Moon and B. H. Waxman, *J. Org. Chem.*, **34**, 1157 (1969).

2.05 (s, 3, $OCOCH_3$), 3.53 (1H, d, $J=12$ Hz), 3.95 (1H, d, $J=12$ Hz), 5.7 ppm (1H, singlet).

Found: C, 77.02; H, 10.48%. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67%.

Hydrolysis of Thujopsenyl Acetoate. The saponification of **2** with alcoholic potassium hydroxide for 20 min at 60°C led to the thujopsenol, **5**: mp 107—108°C; UV λ_{max}^{EtOH} 213 mμ(ε 4732), IR (KBr) 3350 (-OH), 3011 (cyclopropyl), 1674 cm^{-1} (C=C), and NMR (CCl_4) 0.65 (s, 3, CH_3), 1.15 (s, 6, $2CH_3$), 4.0 (m, 2, $-CH_2OH$), 5.41 ppm (m, 1, olefinic).

Found: C, 81.52; H, 10.81%. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98%.