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NOVEL MIGRATION OF METHYL GROUP OF 6,10,10-TRIMETHYL-4-OXOTRICYCLO-$[4.4.0.0^{1,3}]$DECANE WITH BORON TRIFLUORIDE IN ACETIC ACID-ACETIC ANHYDRIDE

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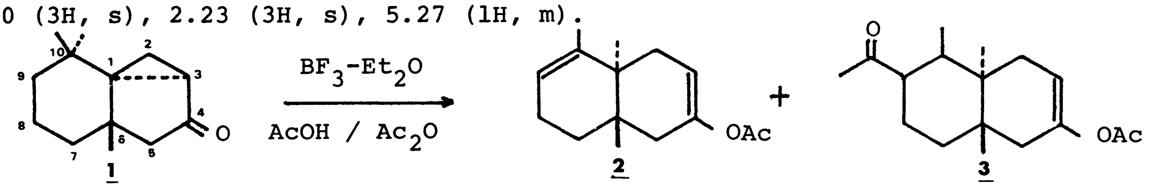
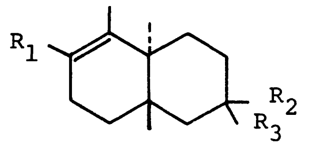
6,10,10-Trimethyl-4-oxotricyclo$[4.4.0.0^{1,3}]$decane (1) undergoes migration of one of the gem-dimethyl group on treatment with boron trifluoride in acetic acid-acetic anhydride giving the acetates (2) and (3).

Although acid-catalyzed angular methyl migration on the substituted octalin[1)] and its related compounds[2a-e)] has been documented, the gem-methyl migration product has little known in literature.[3)] Interest in these reactions prompted us to investigate acid-catalyzed cleavage of 6,10,10-trimethyl-4-oxotricyclo $[4.4.0.0^{1,3}]$decane (1), derived from thujopsene.[4)] We now found that one of the gem-dimethyl attached to the ketone (1) migrated to the angular position at the C-1 carbon.

A solution of BF_3-Et_2O (1 ml, 8 mmol) was slowly added at room temperature to a solution of (1) (1.92 g, 10 mmol) in 20 ml of AcOH-Ac_2O (1:1). The mixture was heated at 50 °C for 2 h, decomposed with cold water, extracted with ether, and concentrated. The residue was chromatographed (SiO_2) to give 49.2 % of the compound (2), a colorless oil; IR (neat)ν 1755 cm^{-1} (>C=O); NMR ($CDCl_3$)δ 0.98 (3H, s), 1.03 (3H, s), 1.65 (3H, d, J=1.5 Hz), 2.10 (3H, s), 5.28 (2H, m) and 10.2 % yield of the compound (3), a colorless oil; IR (neat)ν 1755 (>C=O), 1687 cm^{-1} (α,β-unsaturated ketone); NMR ($CDCl_3$)δ 0.98 (3H, s), 1.08 (3H, s), 1.78 (3H, s), 2.10 (3H, s), 2.23 (3H, s), 5.27 (1H, m).



When the reaction was carried out at 100 °C, only the compound (3) was obtained in 41.3 % yield. This result reveals that the compound (2) would be a precursor of the compound (3). Hydrolysis of 2 and 3 with alcoholic KOH at room temperature afforded 4 in quantitative yields, colorless crystals; mp 78-79 °C; MS m/e 192 (M^+); IR (KBr)ν 1718 cm^{-1} (>C=O); NMR ($CDCl_3$)δ 0.92 (3H, s), 1.38 (3H, s), 1.68 (3H, d, J=1.5 Hz), 5.27 (1H, m) and acetyl octalone (5); mp 59-61 °C; MS m/e 234 (M^+); IR (KBr)ν 1718 (C=O), 1683 cm^{-1} (α,β-unsaturated ketone); NMR ($CDCl_3$)δ 0.96 (3H, s), 1.32 (3H, s), 1.78 (3H, s), 2.25 (3H, s). The structure of 2 is deduced from its spectral data as well as chemical evidence. Wolff-Kishner reduction of 4 gave octalin (6), colorless crystal, in 76.8 %; mp 48-51.5 °C; IR (KBr)ν 1635 cm^{-1} (C=C); NMR (CDCl$_3$)δ 0.95 (3H, s), 1.08 (3H, s), 1.56 (3H, d, J=1.5 Hz), 5.15 (1H, m), whose spectral data were identical with those of reported.$^{5)}$



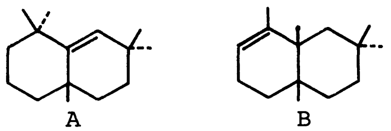
4. R$_1$=H, R$_2$=R$_3$=O
5. R$_1$=Ac, R$_2$=R$_3$=O
6. R$_1$=R$_2$=R$_3$=H
7. R$_1$=Ac, R$_2$=H, R$_3$=OH
8. R$_1$=COOH, R$_2$=H, R$_3$=OH
9. R$_1$=COOH, R$_2$=R$_3$=O

The structure of 3 was also confirmed by following chemical evidence. Catalytic reduction of the acetyl ketone (5) with Raney nickel catalyst (W-1) in ethanol at 50-55 °C yielded an alcohol (7) in 92 % yield; IR (neat) ν 3455 (-OH), 1698 (>C=O), 1617 cm^{-1} (C=C); NMR (CDCl$_3$)δ 1.07 (3H, s), 1.20 (3H, s), 1.78 (3H, s), 2.25 (3H, s), 4.17 (1H, m). Haloform reaction of 7 (5 % aq. KOCl, 80 % dioxane, KOH, at room temperature) gave a carboxylic acid (8) in 66 % and subsequent oxidation of 8 with Jones reagent afforded (9) in 69 % yield; mp 208-211 °C; IR (KBr)ν 1713 (C=O), 1675 cm^{-1} (α,β-unsaturated carboxylic acid); NMR (CDCl$_3$)δ 0.93 (3H, s), 1.33 (3H, s), 2.07 (3H, s). Decarboxylation of 9 at 245-250 °C for 15 min gave the octalone (4). Thus, acetyl octalone (5) could be converted into the octalone (4) through four steps.

Acknowledgment; The authors wish to express their gratitude to Takasago Perfumery Co., Ltd., for the donation of crude thujopsene.

References and Notes

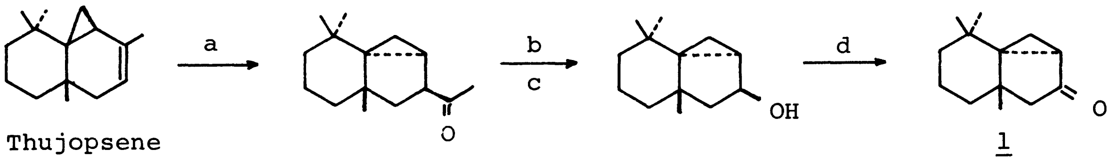
1) A. R. Hochstetler reported that acid-catalyzed isomerization of a substituted octalin (A) afforded product (B) in 9 % yield; J. Org. Chem., 39, 1400 (1974).



A B

2) a) S. Nagahama, Bull. Chem. Soc. Jpn., 33, 1467 (1960); b) W. G. Dauben and L. E. Friedrich, Tetrahedron Lett., 1967, 1735; c) W. G. Dauben and E. I. Aoyagi, Tetrahedron, 26, 1249 (1970); d) S. Ito, M. Yatagai and K. Endo, Tetrahedron Lett., 1971, 1149; e) D. Caine and S. L. Graham, ibid., 1976, 2521.
3) J. A. Marshall and A. R. Hochstetler, J. Chem. Soc., Chem. Commun., 1967, 732.

4) The compound (1) was synthesized according to the following scheme.*



a: Tl(OAc)$_3$/AcOH, b: MCPBA/CH$_2$Cl$_2$, c: KOH/EtOH, d: Jones reagent

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5) R. E. Ireland, M. I. Dawson, C. J. Kowalski, C. A. Lipinski, D. R. Marshall, J. W. Tilley, J. Bordner and B. L. Trus, J. Org. Chem., 40, 973 (1975).

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