BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (7), 2161—2162 (1979)

Structure of the Rearrangement Product of Dihydromayurone with Boron Trifluoride in Acetic Acid–Acetic Anhydride at 50 °C

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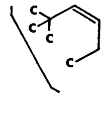
(Received November 24, 1978)

Synopsis. The structure of the second main product, 4-acetoxy-1,7,8-trimethyltricyclo[5.4.0.0^{4,8}]undec-9-ene, in the rearrangement reaction of dihydromayurone with boron trifluoride in acetic acid–acetic anhydride at 50 °C, and reaction mechanism is presented and discussed.

In a preceding communication,1) the formation of four kinds of corresponding acetates in the rearrangement reaction of dihydromayurone with boron trifluoride in acetic acid–acetic anhydride, has been described and related to the reaction temperature. The reaction at 50 °C afforded 7-acetoxy-2,2,3-trimethyltricyclo[5.2.2.0^{1,6}]undec-3-ene (**1**) in 45% yield. Chromatographic analysis of the reaction mixture over silica gel using benzene as the eluant gave compound **1**1) as a fast eluent in 45% yield, and an oily product (**2**) as slow eluent in 30% yield. The IR spectrum bands at 3060 and 1690 cm^{-1} disappeared indicating the presence of a cyclopropyl and carbonyl group, and the band at 1738 cm^{-1} indicated the presence of an ester group. The PMR spectrum contained signals at δ 1.95, 5.21, and 5.81 ppm, indicating the presence of one acetyl group and two vinyl protones. And the mass spectrum showed a molecular ion peak at *m/e* 248 (M$^+$), and fragment of this at *m/e* 206 (M−42). Thus, the structture of **2** has been assumed to be a isomeric acetate in which the cyclopropane ring was cleaved.

Hydrolysis of **2** with ethanolic potassium hydroxide gave the alcohol (**3**), the IR spectrum of which exibited a strong band at 3355 cm^{-1}, indicating the presence of a hydroxyl group. The PMR spectrum of one vinyl proton shows a doublet of doublets of doublets (J= 10.8, 2.5, and 2.5 Hz) at 5.18, and the other vinyl proton shows a doublet of doublets of doublets (J= 10.8, 5.0, and 3.5 Hz) at 5.78 ppm. Analysis was conducted by the decoupling technique. The C^{13}-NMR spectrum exibited the presence of C–O (δ 80.6 ppm (s)), and –CH=CH– (δ 127.8 (d) and 130.0 ppm (d)) linkages (Fig. 1).

Thus, the structure of **3** has been assigned to be a tertiary alcohol including the partial structure (**a**) and tricyclic compound. This partial structure was unambiguously substantiated by the following chemical evidences. Oxidation of **3** with osmium tetraoxide in ether afforded a diol (**5**) and subsequent oxidation of **5** with lead tetraacetate gave a dialdehyde (**6**). The PMR spectrum showed signals at δ 9.73 (t, 1, J=3.0 Hz) and 9.75 ppm (s, 1), indicating the presence of two formyl groups.



a

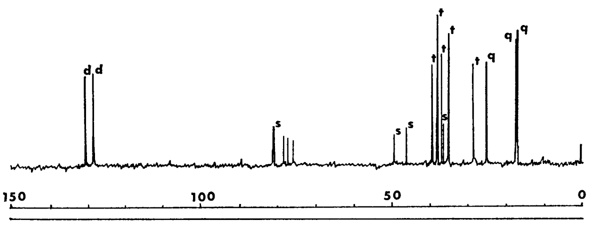
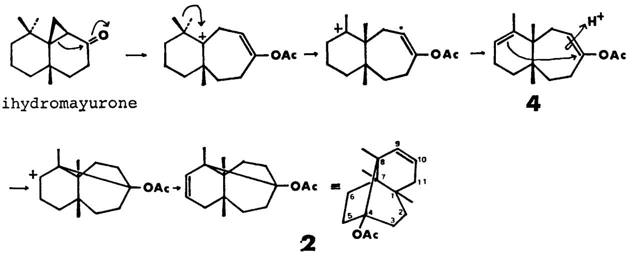
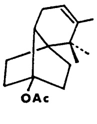


Fig. 1. C^{13}-NMR spectrum of compound **3**.

An attempt was made to obtain the acetate (**2**) from the acetate (**4**)1) under the above reaction conditions and the results indicate that **4** may be the precursor of **2**. The structure of **2** has been assumed to be 4-acetoxy-1,7,8-trimethyltricyclo[5.4.0.0^{4,8}] undec-9-ene on the basis of the above spectral data, the chemical evidence, and the reaction mechanism (Scheme 1).



Scheme 1.



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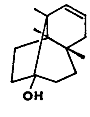

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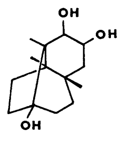

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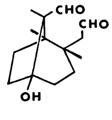

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Experimental

The melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The PMR spectra were recorded at 60 MHz and 100 MHz on a JEOL PMX-60 and a JEOL PS-100 spectrometer respectively, using Me$_4$Si as an internal standard. The C^{13}-NMR spectra were recorded on a JEOL FX-100 spectrometer, using Me$_4$Si as an internal standard. The IR spectra were determined on a Shimadzu IR-400 spectrometer. The elemental analyses were performed on a Hitachi 026 CHN analyzer.

Isomerization of Dihydromayurone. A mixture of dihydromayurone (2.06 g, 10 mmol), acetic acid (10 ml), acetic anhydride (10 ml), and boron trifluoride etherate (2 ml, 4.5 mmol) was heated at 50 °C for 2 h. The dark brown reaction mixture was poured into ice-water (20 ml) and extracted with ether. The extract was washed with aqueous $NaHCO_3$ solution, water, dried (Na_2SO_4), and evaporated to give an oily residue (2.87 g). The products were separated by column chromatography using silica gel. Elution with benzene gave **1** (1.11 g) and **2** (0.8 g) as colorless liquids, respectively. **2**: MS m/e 248 (M^+) and 206 (M−42); IR (neat) ν 1738 cm^{-1}; PMR ($CDCl_3$) δ 0.81 (s, 6, $2CH_3$), 1.01 (s, 3, CH_3), 1.95 (s, 3, CH_3), 5.21 (ddd, 1, J=10.8, 2.5, and 2.5 Hz), and 5.81 (ddd, 1, J=10.8, 5.0, and 3.5 Hz).

*Hydrolysis of **2**.* Compound **2** (1.24 g, 5 mmol) was hydrolyzed in alcohol (15 ml) with potassium hydroxide (560 mg, 10 mmol) at room temperature for 2 h. After the usual work-up a crude product (992 mg) was obtained. Recrystallization from hexane gave pure **3** (876 mg). **3**: Mp 145—148 °C; MS m/e 206 (M^+); IR (KBr) ν 3355 cm^{-1}; PMR ($CDCl_3$) δ 0.80 (s, 6, $2CH_3$), 1.02 (s, 3, CH_3), 5.18 (ddd, 1, J=10.8, 2.5, and 2.5 Hz), and 5.78 (ddd, 1, J=10.8, 5.0, and 3.5 Hz); C^{13}-NMR ($CDCl_3$) δ 17.0 (q), 17.2 (q), 24.9(q) 28.4(t), 34.6 (t), 35.7 (s), 36.3 (t), 37.4 (t), 39.3 (t), 45.9 (s), 49.0 (s), 80.6 (s), 127.8 (d), and 130.0 ppm (d). Found: C, 81.59; H, 10.66%. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75%.

*Oxidation of **3** with Osmium Tetraoxide.* To a stirred solution of **3** (782.8 mg, 3.8 mmol) in pyridine (2 ml) and ether (35 ml) was added dropwise a solution of osmium tetraoxide (1.0 g, 4.0 mmol) in ether (35 ml) under nitrogen at room temperature in 10 min. The mixture was subsequently stirred for 2 days. After the usual work-up a crude product (856 mg) was obtained. Recrystallization from ethyl acetate gave pure **5** (781 mg). **5**: Mp 210—212 °C; IR (KBr) ν 3350 cm^{-1}; PMR (DMSO-d_6) δ 0.72 (s, 3, CH_3), 0.97 (s, 3, CH_3), 1.05 (s, 3, CH_3), 3.57 (m, 1), and 4.61 (d, 1, J=6.0 Hz). Found: C, 70.42; H, 9.83%. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07%.

*Oxidation of **5** with Lead Tetraacetate.* To a stirred solution of **5** (141.2 mg, 0.6 mmol) in acetic acid (5 ml), kept at 15 °C, was added lead tetraacetate (285 mg, 0.65 mmol) in portions over 20 min. The mixture was stirred for 5 h at room temperature. The usual work-up gave a crude product (140 mg), which was chromatographed on a sillica-gel column. Elution with ethyl acetate and benzene (10:1) gave **6** (126 mg). Recrystallization from benzene gave pure **6** (105 mg) as colorless crystals. **6**: Mp 186—189 °C; IR (KBr) ν 3500, 2700, and 1703 cm^{-1}; PMR ($CDCl_3$) δ 1.02 (s, 3, CH_3), 1.10 (s, 3, CH_3), 1.15 (s, 3, CH_3), 9.73 (t, 1, -CHO, J=3.0 Hz), and 9.75 (s, 1, -CHO). Found: C, 71.08; H, 9.01%. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31%.

*Isomerization of **4**.* A mixture of **4** (248 mg, 1 mmol), acetic acid (1.5 ml), acetic anhydride (1.5 ml), and boron trifluoride etherate (0.2 ml, 0.45 mmol) was heated at 50 °C for 2 h. The usual work-up as reported above gave **2** (178.6 mg).

Reference

1) H. Sekizaki, M. Ito, and S. Inoue, *Chem. Lett.*, **1978**, 1191.