

METHYL MIGRATION IN DEHYDROABIETIC ACID DERIVATIVE¹⁾

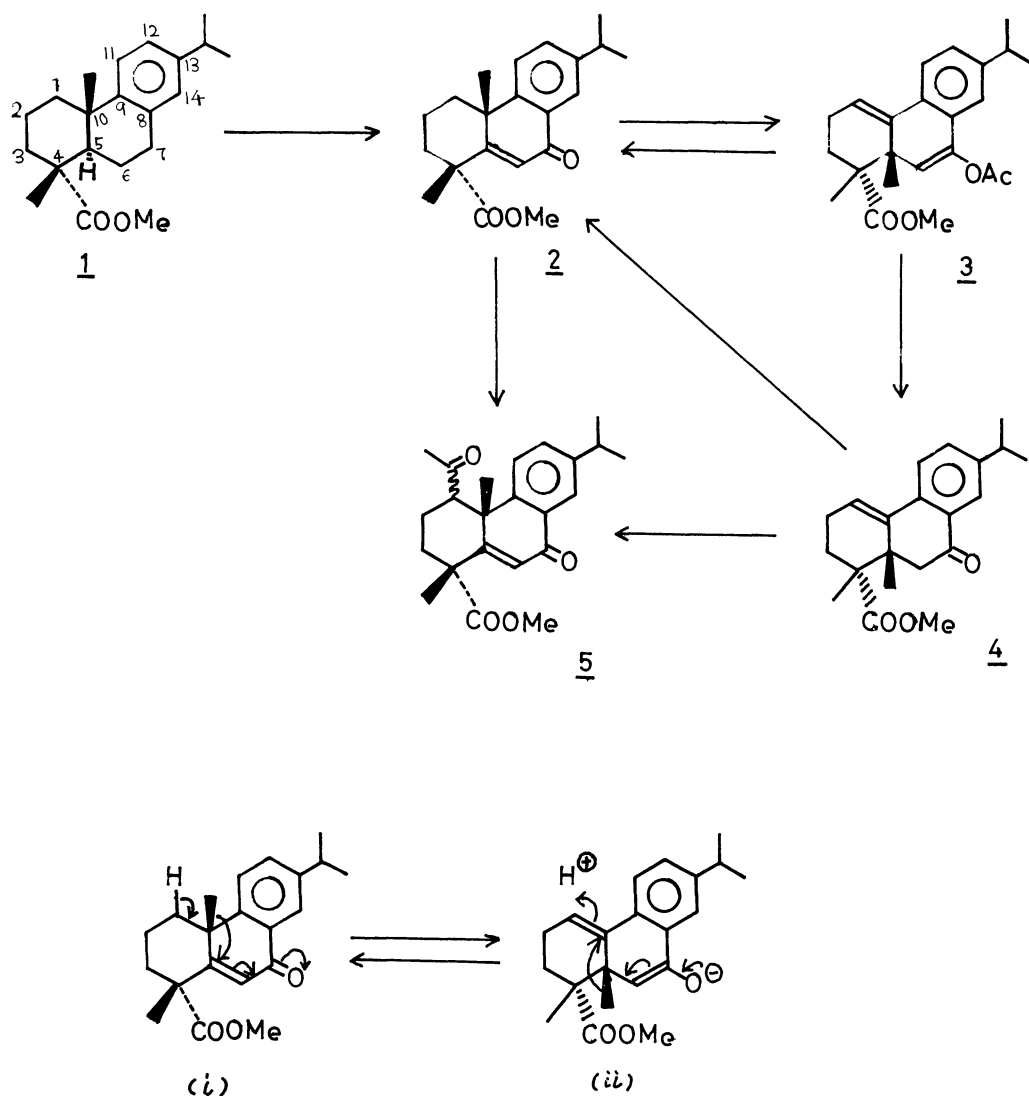
Akira TAHARA, Hiromitsu MIZUNO, and Tomihiko OHSAWA

Rikagaku Kenkyusho (The Institute of Physical and Chemical
Research), Wako-shi, Saitama

Benzonilidene compound (2) underwent rearrangement to 3 with 1,2-methyl migration and vice versa. Using the rearrangement, selective substitution at C-1 of dehydroabietic acid derivative was accomplished to give 5.

Benzonilidene compound (2)²⁾ derived from dehydroabietic acid (1), can be regarded as a kind of a dienone and 2 aroused our interest in its reactivity. We report herein that 1,2-methyl migration of 2 occurred under an acidic condition.

Under an acidic condition ($\text{Ac}_2\text{O}-\text{H}_2\text{SO}_4$, room temperature, 4 hr), 2 underwent rearrangement to enol acetate (3) (62% yield) accompanied with migration of C-10 methyl group to the C-5 position. Comparison of physical data of 3 [ir 1770, 1720, 1190; nmr 1.17, 1.25(C-4 and C-5 Me), 2.25(C-7 OCOMe), 5.68(C-6 H, s), 6.00(C-1 H, q, $J=1.8, 2.1$ Hz), 7.32(C-11 H, d, $J=7.2$ Hz), 6.95(C-12 H, q, $J=1.8, 7.2$ Hz), 6.76(C-14 H, d, $J=1.8$ Hz)] and 2 [ir 1730, 1655; nmr 1.51, 1.60(C-4 and C-10 Me), 5.91(C-6 H, s), 7.32(C-11 and C-12 H), 7.84(C-14 H, s; resonance at lower magnetic field than that of 3 by the anisotropic effect of 7-carbonyl group)] showed that enol acetate and trisubstituted olefin were newly observed in 3 instead of the dienone system in 2. Mild alkaline hydrolysis (KOH-EtOH, room temperature, 0.5 hr) of 3 gave 4 (80% yield) [ir 1730, 1684; nmr 1.15, 1.24(C-4 and C-5 Me), 6.26(C-1 H, q, $J=2.0, 2.0$ Hz), 7.43(C-11 H, d, $J=5.8$ Hz), 7.25(C-12 H, q, $J=0.9, 5.8$ Hz), 7.70(C-14 H, d, $J=0.9$ Hz; return to the higher magnetic field as in 2)]. These data are consistent with the fact that 4 is only different from 3 by structural alteration of 7-enol acetate to 7-carbonyl group. Location of the trisubstituted olefin in 4 (and therefore, 3) was evidently proved by intramolecular nuclear Overhauser effect (NOE, 100 MHz) between C-1 and C-11 hydrogen, which are sterical-



ly close. NOE on C-11 hydrogen (19.8% increase) and C-1 hydrogen (22.0% increase) was distinctly observed by the respective irradiation at C-1 and C-11 hydrogen. Thus, the newly appeared olefinic bond in 4 (and therefore, 3) should be located between C-1 and C-10. From these observations, 2 undergoes the Wagner-Meerwein type rearrangement (i \longrightarrow ii) rather than dienone-like one.

Furthermore, it is interesting to find that both compounds (3 and 4) easily reverted to the original compound 2 (quantitative yield) under a mild acidic condition (conc. H₂SO₄, room temperature, 2 hr). Regarding the mechanism of the reverse reaction (ii \longrightarrow i), a proton attacks the C-1 position during the progress.

Accordingly, if the electrophilic reagent is used in the absence of proton, selective substitution at C-1 should proceed. In fact, in aprotic medium ($\text{Ac}_2\text{O}-\text{BF}_3 \cdot \text{Et}_2\text{O}$, room temperature, 2 hr), acetyl group can be substituted at C-1 in 4 to give 5 (69% yield) [ir 1730, 1658; nmr 1.52, 1.71(C-4 and C-10 Me), 1.86(C-1 COMe), 3.64(C-1 H, m, width of half-height=10 Hz), 6.11(C-6 H, s), 7.13(C-11 H, d, $J=7.2$ Hz), 7.30(C-12 H, q, $J=7.2$, 1.8 Hz), 7.86(C-14 H, d, $J=1.8$ Hz)] with methyl migration. Also, this acetylation proceeded even in 2 to give 5, because 2 would react via methyl-rearranged compound.

This is the first successful selective substitution of the A-ring of dehydroabietic acid derivative (1 \longrightarrow 5). The reaction would make it possible to synthesize more interesting compound having substituent in A-ring from 1-abietic acid, the main component of pine rosin, which available on an industrial scale.

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References:

- 1) Ir(cm^{-1}) and nmr(δ)(60 MHz) spectra were measured in CCl_4 solution.
- 2) M. Ohta and L. Ohmori, Pharm. Bull.(Japan), 5, 96 (1957); E. Wenkert, R. W. T. Carney, and C. Kaneko, J. Am. Chem. Soc., 83, 4440 (1961).

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