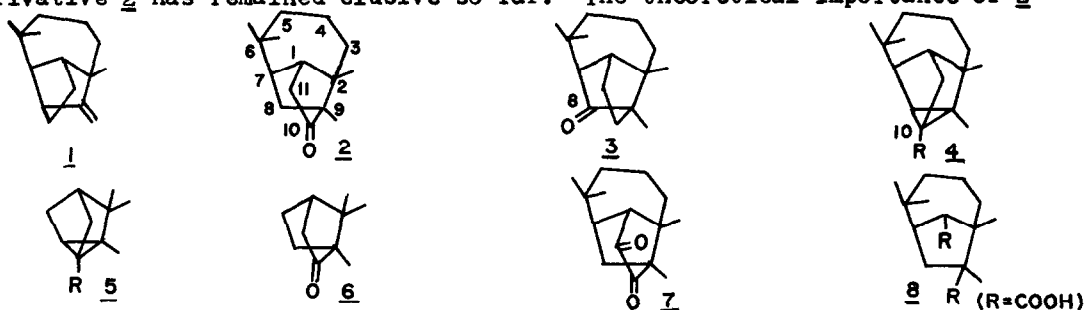


NOVEL LEAD TETRAACETATE OXIDATION OF LONGICYCLENE:
FORMATION AND REACTIONS OF THE ELUSIVE TRUE LONGICAMPHOR^{1,2}

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Notwithstanding the rich and bountiful chemistry of longifolene 1 unfolded during a long span of five decades and more, the 10-ketolongibornane derivative 2 has remained elusive so far. The theoretical importance of 2



stems from the fact that it constitutes the "true" longicamphor (active methylene intact) while the 8-keto longibornane 3, known for a long time as longicamphor, in the absence of $-\text{COCH}_2-$ moiety, should now be strictly designated pseudo-longicamphor. In a novel approach to achieve this strategic functionalization, the olefinic nature of the uniquely built-in methylcyclopropane moiety of a close relative of 1 viz. longicyclene³ 4 (R=H) has been exploited. This communication highlights the $\text{Pb}^{\text{IV}}/\text{OH}^-$ reaction on 4 (R=H) which generates the longicamphor 2 for the first time. The homoenol \rightarrow homoketone⁴ mechanistic pathway has also been established for the LTA/base transformation of longicyclene 4 (R=H)/cyclene 5 (R=H) to longicamphor 2 / camphor⁵ 6 by the actual isolation of the intermediate homoenol acetate in either case.

The product from Pb^{IV} oxidation of 4 (R=H) in AcOH (80°/6 hr), after base hydrolysis, followed by chromatography (SiO_2/IIa) furnished a pure ketone, $\text{C}_{15}\text{H}_{24}\text{O}$ (yield⁶: 75%; M^+ 220, base peak), the spectrochemical properties of which dictated structure 2 for it: IR (smear): 1745 and 1420 cm^{-1} ($\text{O}=\text{C}-\text{CH}_2-$ in a 5-ring); PMR (CCl_4): four tertiary methyl singlets at 0.83 (3H x 2), 0.87 and 1.02 δ (longibornane system). In sharp contrast to the extremely hindered pseudo-longicamphor 3, 2 was highly reactive: semicarbazone, m.p.

244°; 2,4-DNP, m.p. 118°. In conformity with the assigned structure 2, the ketone, on reduction (semicarbazone/KOBU^t) generated longibornane, identified by direct comparison. Finally, the ready response of the new ketone to two characteristic reactions of camphor clinched the structure 2 beyond any doubt: (a) 2 → longicamphorquinone 7 (yellow solid, m.p. 118°; SeO₂-AcOH) → longicamphoric acid 8 (m.p. 180°; alkaline H₂O₂) and (b) hydrazone of 2 → longicyclene 4 (R=H; yellow HgO).

The precursor for longicamphor 2, isolated from the LTA reaction before hydrolysis, has been characterized as 10-acetoxy longicyclene 4 (R=OAc): C₁₇H₂₆O₂ (M⁺ 262); IR (smear): 1750 and 1220 cm⁻¹; PMR (CCl₄): four tertiary methyl singlets at 0.93, 1.02 (3H x 2) and 1.05δ, 2.0δ (s, one -OCOCH₃). Homoketonization of the homoenol 4 (R=OH), arising from the substrate 4 (R=OAc) in alkaline medium, generates exclusively 2. In a comparative study, the formation of camphor in the oxidation of cyclene with LTA, has also been mechanistically rationalized in a similar fashion by isolating the parent tertiary acetate 5 (R=OAc; yield: 56%): C₁₂H₁₈O₂ (M⁺ 194); IR (smear): 1750 and 1235 cm⁻¹; PMR (CCl₄): three tertiary methyl singlets at 0.82, 0.98 and 1.02δ, 1.98δ (s, one -OCOCH₃).

Full details of this investigation, including the structures of other minor compounds isolated, will be published elsewhere.

REFERENCES AND NOTES

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- 6 Based on recovered longicyclene; without taking it into account the yield is ca 50%.