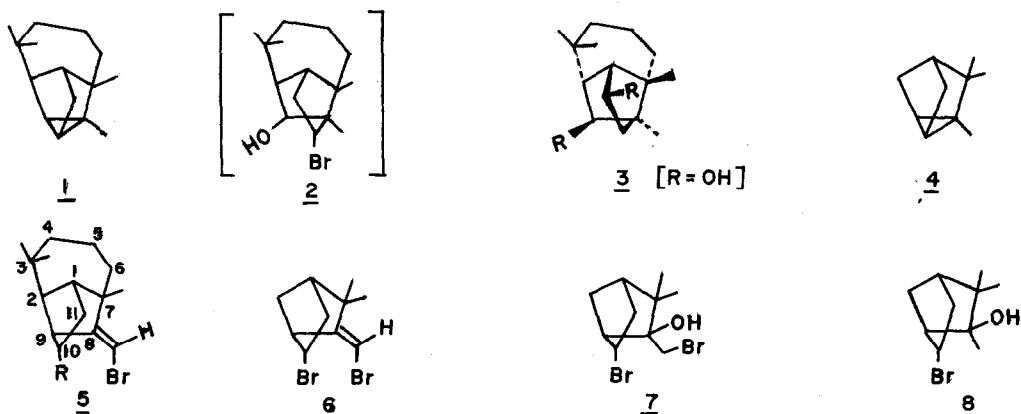


NOVEL HYPOBROMOUS ACID REACTION ON METHYLCYCLOPROPANE - A
DICHOTOMIC STUDY WITH LONGICYCLENE AND CYCLENE^{1,2}

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THE idea of HOBr-mediated cyclopropane ring-opening/functionalization was first mooted for the possible generation from longicyclene³ 1, a difunctional longibornane derivative of the type 2 - a viable synthon in the synthetic quest for culmorin⁴ 3 - the sesquiterpene diol mould metabolite from Fusarium culmorum. Experimental invalidation of this rather conceited



theoretical proposition notwithstanding, the action of HOBr on the methyl cyclopropane moiety in the sesquiterpene 1 provides an uniquely interesting study specially when compared with that of its monoterpene analog 4.

Chromatography (SiO_2/IIa) of the product from reaction of HOBr [NBS (2 mole eq.) - aq. dioxane- CaCO_3]⁵ on longicyclene gave no indication of any hydroxybromo derivative. Instead, the isolable major pure compound analysed for an oxygen-free dibromide, $\text{C}_{15}\text{H}_{22}\text{Br}_2$ (yield: ca 50%; M^+ 360, 362, 364) - clearly an unexpected but novel derivative whose structure has been spectroscopically rationalized as 10-bromo- ω -bromolongifolene 5 ($\text{R}=\text{Br}$): PMR (CCl_4): three tertiary Me singlets at 1.03 (3H x 2) and 1.07 δ , 3.33 (1H, br.s, $\text{HC}=\text{C}-\text{C}-\text{Br}$), 3.80 and 3.87 δ (1H, dd, $J = 8$ Hz, $\text{H}-\text{C}-\text{C}-\text{H}$, Br Br), 5.80 δ ⁶ (1H, s, $\text{>C}=\text{H}$). IR (smear): 3150, 1645, 785 and 765 cm^{-1} ($\text{>C}=\text{H}$). The formation of the

secondary/vinylic dibromide 5 (R=Br) in a HOBr reaction on the methylcyclopropane moiety in a substrate of the type 1 constitutes a unique transformation and must necessarily involve a multi-step mechanistic pathway (vide infra): HOBr additive-cleavage/dehydration/HOBr addition/dehydration.

In a comparative study the reaction of HOBr with cyclene 4 was considerably faster and proceeded to completion to furnish, on chromatography, three compounds: the unusual secondary/vinylic dibromide 6 (analogous to 5; 34%), its precursor, the bromo-bromohydrin 7 (10%) and the expected 1,3-hydroxybromide 8 (m.p. 80°; 30%). Validity of the structures assigned to these compounds is borne out by their spectral data. Compound 6: C₁₀H₁₄Br₂ (M⁺ 292, 294, 296); PMR (CCl₄): two tertiary Me singlets at 1.05 and 1.12 δ, 3.37 δ (1H, br.s, HC-C=C-Br), 3.83 and 3.90 δ (1H, dd, J = 8 Hz, -HC-CHBr-CH₂-), 5.80 δ (1H, s, >C<^{Br}_H); IR(smear): 3000, 1625, 800, 780 cm⁻¹ (>C<^{Br}_H). Compound 7: C₁₀H₁₆OBr₂ (M⁺-Br 231 and 233 and M⁺-Br-H₂O 213 and 215); PMR(CCl₄): two tertiary Me singlets at 0.92 and 1.05 δ, 3.53 δ (2H, q, J = 10 Hz, >C<^{OH}-CH₂Br), 4.0 δ (1H, br.m, -CH-CHBr-CH₂-); IR(smear): 3350, 770, 750 cm⁻¹. Compound 8: C₁₀H₁₇OBr (M⁺-Br 153); PMR (CCl₄): two ordinary Me singlets at 0.85 and 0.98 and one deshielded Me singlet at 1.20 δ (>C<^{OH}_{Me}), 4.10 δ (1H, br.m, -HC-CHBr-CH₂-); IR (nujol): 3150, 750 cm⁻¹.

Finally, it must be mentioned here that the unusual dibromo derivative 5 (R=Br) is formed only as a minor product (ca 10%) in the bromination (Et₂O/0°) of longicyclene 1 which generates the monobromide, ω-bromolongifolene 5 (R=H) in 75% yield.

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- 6 In the case of ω-bromolongifolene 5 (R=H) the vinylic proton appears as a singlet at 5.50 δ.