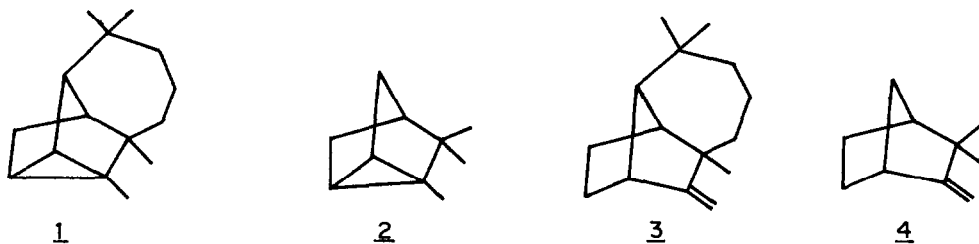


METHYLCYCLOPROPANE-HALOGEN REACTION: FACILE HOMOALLYLIC
FUNCTIONALIZATION IN LONGIFOLENE/CAMPHENE
VIA LONGICYCLENE/CYCLENE^{1,2}

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IN CONTINUATION of our studies on the electrophilic reactions³ of the methylcyclopropane moiety in isoprenoid substrates-longicyclene 1 / cyclene 2, we have investigated the reaction with halogens (Br₂, ICl) in an attempt to achieve facile homoallylic functionalization in longifolene 3 / camphene 4. The generation of some otherwise inaccessible and synthetically-useful⁴ halides



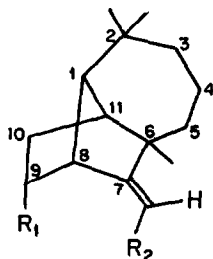
based on the bicyclic olefins 3 / 4 is described in this communication.

The product outcome of the bromine-longicyclene reaction was dictated by the solvent used. In ether, there was hardly any homoallylic bromination (< 10%) and (E)- ω -bromolongifolene 5^{3a} was the major product (75%). On the other hand, formation of the homoallylic/vinylic bromination product - 9-bromo- ω -bromolongifolene 7^{3a} in 35%⁵ yield with equimolar amount of the reagent in pyridine was rendered near quantitative (97%) when two moles of bromine was used.

Although ICl failed to react with longicyclene 1 in pyridine, the ICl-C₅H₅N complex (m.p. 136°) in AcOH effectively transformed 1 into 9-iodo-longifolene 8 (73%)⁶: C₁₅H₂₃I (M⁺ 330); PMR(CCl₄): 1.03, 0.93, 0.93 ppm (tertiary Me singlets); 3.68, 3.77 ppm (1H, dd, J = 9 Hz, -CH₂CHI₂-); 4.70, 4.98 ppm (1H singlets, exo-methylene). IR(smear): 1650, 895 cm⁻¹.

Chromatographic resolution (silica gel/IIa) of the bromination product

of cyclene 2 in pyridine yielded the homoallylic/vinylic dibromo compound 9 ^{3a}

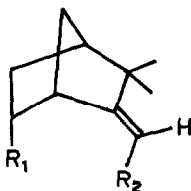


5: R₁ = H, R₂ = Br

6: R₁ = Br, R₂ = H

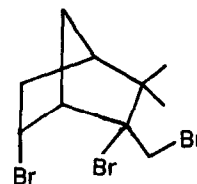
7: R₁ = R₂ = Br

8: R₁ = I, R₂ = H



9: R₁ = R₂ = Br

11: R₁ = I, R₂ = H



10

in major amount (61%). The minor compound was characterized as the tribromo compound 10 (m.p. 100°, 32%; precursor for 9): C₁₀H₁₅Br₃ (M⁺ - HBr 290, 292); PMR(CCl₄): 1.05, 1.42 ppm (tertiary Me singlets); 3.80 ppm (2H, q, J = 12 Hz, -CH₂Br); 4.12, 4.20 ppm (1H, dd, J = 7 Hz, -CH₂CHBr-CH₂-).

ICl-pyridine complex in AcOH transformed cyclene 2 into a mixture of products from which the homoallylic iodo compound 11 was isolated (silica gel/IIa) in a reduced yield (42%)⁶ as compared to the related sesquiterpene case 8. Compound 11: C₁₀H₁₅I (M⁺ 262); PMR (CCl₄): 1.02, 1.07 ppm (tertiary Me singlets); 3.73, 3.80 ppm (1H, dd, J = 8 Hz, -CH₂CHI-CH₂-); 4.67, 4.93 ppm (1H singlets, =CH₂). IR(smear): 1650, 895 cm⁻¹.

The stereoelectronically-controlled mode of cleavage of cyclopropane in longicyclene 1 by strongly electrophilic halogen (pyridine perbromide/ICl-pyridine complex) generates almost exclusively the longifolene skeleton functionalized at C-9; with bromine as reagent further reaction also invariably takes place to furnish the homoallylic/vinylic dibromo compound 7.

Satisfactory elemental analyses were obtained for the compounds described above.

REFERENCES AND NOTES

- 1 Communication No. ~~2805~~, National Chemical Laboratory, Poona.
- 2 Newer Aspects of Longifolene-XII.
- 3 a) S.N.Suryawanshi and U.R.Nayak, Tetrahedron Letters 3595 (1977).
b) S.N.Suryawanshi and U.R.Nayak, Tetrahedron Letters 2619 (1977).
c) S.N.Suryawanshi and U.R.Nayak, Tetrahedron Letters 465 (1978).
- 4 The synthetic potential of compds. 7 and 8 will be described subsequently.
- 5 10-15% of the monobromide 6 was also formed; the hydrocarbon was identified as essentially unchanged longicyclene.
- 6 The balance consisted of a mixture of two acetates.

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