

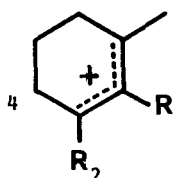
THE INITIATION OF CYCLISATION WITH 4-SUBSTITUTED CYCLOHEXENYL CATIONS

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Abstract: The diols (7) and (8) are cyclised to the dienes (10) and (11) with loss of the secondary hydroxyl group.†

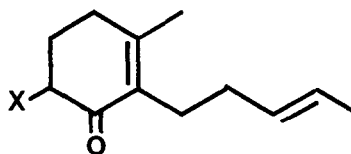
Trialkylated cycloalkenyl cations (1) have proved to be successful initiators of polyene cyclisation since their introduction by Johnson.¹ The work of Brunke² *et al* demonstrated that the unsymmetrical ion (2) is attacked by alkene preferentially at the methyl terminus, while we have shown³ the silyl cation (3) reacts only at the methyl terminus and that cyclisation is followed by *in situ* protodesilylation. The influence of substituents at C-4, in particular hydroxyl, has not been examined previously; we now wish to report our results pertinent to this problem.



1 ($R_2 = \text{Me}$)

2 ($R_2 = \text{Bu}^n$)

3 ($R_2 = \text{SiMe}_2\text{Ph}$)



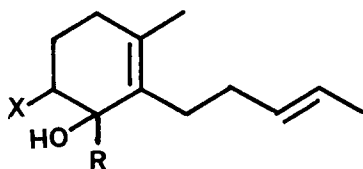
4 ($X = \text{H}$)

5 ($X = \text{OH}$)

6 ($X = \text{Cl}$)

†All compounds reported are racemic or achiral.

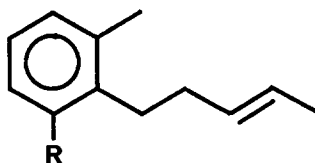
The cyclohexenone⁴ (4) was converted into the hydroxyl compound (5) as described previously⁵ and reacted with excess MeLi at 0° to give (7) (68%)⁶ and with BuⁿLi to form (8) (60%).⁶ Reaction of (7) with H.CO₂H-C-C₆H₁₂ at ambient temperature gave, after hydrolysis of the reaction mixture with 10MNaOH, two major products; the least polar (20%) was formulated as (10) [δ_{H} 7.0 (3H, m), 5.5 (2H, m), 2.29 (6H, s), 1.65 (3H, d)] while the other, C₁₃H₁₂O, (50%), showed λ_{max} 234nm; ν_{max} 3620cm⁻¹; δ_{H} 5.5 (2H, n), 3.77 (1H, m, J = 9, 9 and 6 Hz), 1.76 (3H, s), 1.01 (3H, d, J = 7 Hz), 0.84 (3H, s). Cyclisation of the butyl compound (8)



7 (X = OH, R = Me)

8 (X = OH, R = Buⁿ)

9 (X = Cl, R = H)



10 (R = Me)

11 (R = Buⁿ)

gave the hydrocarbon (11) (21%) and a compound, C₁₆H₂₆O (55%), whose u.v., i.r., and ¹H n.m.r. spectra were similar to those of the compound prepared from (7), except that the signal at δ_{H} 1.76 was absent and an *n*-butyl group was present. Extensive proton decoupling experiments established the part-structures shown in Figure 1 and, accepting that a *transoid*

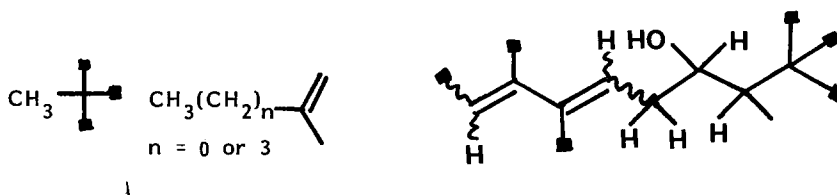
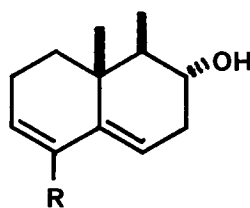
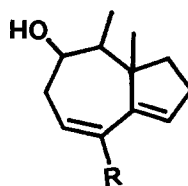


Figure 1



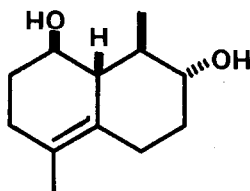
12 (R = Me)

13 (R = Buⁿ)

14

diene is present and rejecting anti-Bredt structures; this leads to the formulation of the cyclisation products as (12) and (13) or as (14) (R = Me or Buⁿ). We prefer (12) and (13) on the basis of mechanism as the formation of (14) would require extensive and unlikely rearrangements. In support of these formulations the alcohol (12) was oxidized (pyridinium chlorochromate) to a ketone, $\lambda_{\max}^{\text{EtOH}}$ 235nm; ν_{\max} 1715cm⁻¹; δ_{H} 5.62 (2H, m), 2.53 (1H, q, J = 7 Hz), 1.8 (3H, s), 1.03 (3H, d, J = 7 Hz), 0.76 (3H, s). On treatment with NaOEt λ_{\max} 235 changed to 298nm.

Reaction of (5) with CCl₄-Ph₃P gave the chloride (6) (79%), which reacted with MeLi to give a product which rapidly decomposed to the hydrocarbon (10). Reduction of (6) with NaBH₄ gave the chlorohydrin (9) (90%)⁶ which after cyclisation (H.CO₂H-C₆H₁₂) and hydrolysis gave



(15)

a diol, δ_{H} 4.0 (1H, m), 3.28 (1H, m), 1.63 (3H, s), 1.09 (3H, d), tentatively formulated as (15). Oxidation with pyridinium chlorochromate gave a dione, ν_{max} 1715cm^{-1} , δ_{H} 1.78 (3H, s), 1.09 (3H, d, $J = 6$ Hz).

These results indicate the difficulty of retaining a 3-substituent under these cyclisation conditions, but also suggest that such a substituent directs cyclisation to the terminus of the allyl cation remote from it.

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6. A mixture of *cis*- and *trans*-isomers is indicated by cap. g.l.c. Other compounds reported were homogenous by t.l.c. and/or cap. g.l.c., and all gave acceptable accurate mass measurements.

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