

A NEW SYNTHESIS OF ANGULARLY SUBSTITUTED OCTALINS VIA AN ANIONIC OXY-COPE
REARRANGEMENT⁴

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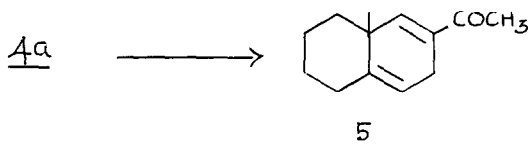
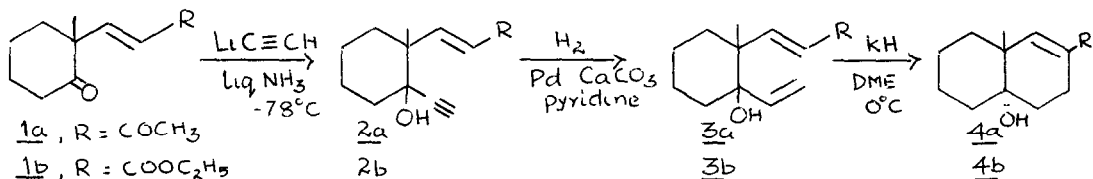
Abstract : The divinyl carbinols 3a and 3b furnished octalinols
4a and 4b respectively on treatment with base.

Anionic oxy-Cope rearrangements of 1,2-divinyl cycloalkan-1-ols have been reported¹ to yield ring enlarged products. Previous work from our laboratory² on base catalysed rearrangements of bicyclic systems incorporating an oxy-Cope moiety with an electron withdrawing carbonyl group at one of the terminal olefinic carbon atoms have also led to either ring enlargements only or ring enlargements and transannular reactions.

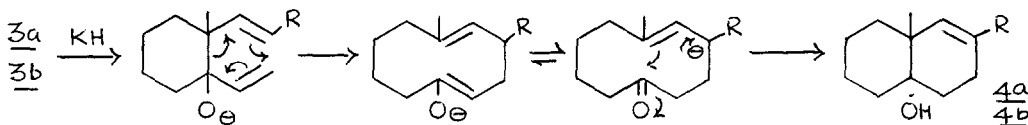
We report here a new synthesis of angularly substituted octalins, a ring system present in Vetivene type sesquiterpenes by base treatment of 1,2-divinyl cyclohexan-1-ols bearing a carbonyl group at an appropriate position.

Treatment of 2-methyl-2(3'-oxo-1'-butenyl)cyclohexanone 1a³ and 2-methyl-2(2'-carbethoxyvinyl)cyclohexanone 1b³ with lithium acetylide in liquid ammonia at -78°C afforded the ethynyl carbinols 2a and 2b respectively in 80% yield. While 2a was obtained as a colourless crystalline solid⁵ (m.p.65-66°C) 2b was obtained as a viscous liquid⁵. Partial hydrogenation of the carbinols 2a and 2b in pyridine in the presence of Pd/CaCO₃ gave the vinyl carbinols 3a and 3b respectively as light yellow viscous liquids⁵ in excellent yields. No attempt has been made to assign the stereochemistry for the vinyl groups in 3a and 3b. It is presumed that the two vinyl groups are cis to each other in view of the ease with which 3a and 3b undergo the rearrangement. Treatment of 3a and 3b with potassium hydride in 1,2-dimethoxyethane at 0°C for an hour followed by work up and chromatography over silica gel (benzene-ethylacetate) afforded 4a and 4b respectively as light yellow viscous liquids⁵ in 50% yield.

The structure of 4a was further confirmed by its smooth dehydration in boiling 10% ethanolic sulfuric acid to give 5 in 80% yield. The unique feature of



the transformation of 3a and 3b to the octalinols 4a and 4b respectively is the bond formation between the terminal olefinic carbon atoms without any apparent skeletal rearrangement. However, the reaction must undoubtedly involve an anionic oxy-Cope rearrangement followed by a transannular aldol condensation as pictured below:



Work is in progress to extend this reaction for the synthesis of

γ -vetivene and ring-A nonaromatic steroids.

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References

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2. N.Raju, K.Rajagopalan and S.Swaminathan and J.N.Shoolery, Tetrahedron Letters, 21, 1577 (1980) and references cited therein.
3. K.Thangaraj, P.C.Srinivasan and S.Swaminathan, Synthesis, 0000 (1982).
4. Part XIII. Part XII see P.Geetha, C.A.M.A.Huq, K.Rajagopalan and S.Swaminathan, Tetrahedron Letters, 23, 569 (1982).
5. All new compounds were characterised by spectral data and elemental analysis.

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