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OXY-COPE REARRANGEMENTS OF MEDIUM-SIZED RINGS

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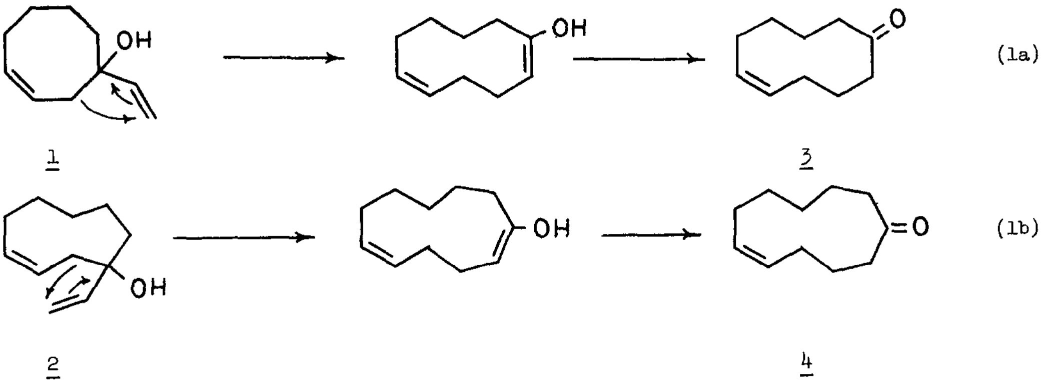
The oxy-Cope rearrangement[1] represents a possible synthetic pathway to certain specifically substituted medium and large ring compounds. The present paper concerns the use of this rearrangement as a two carbon ring expansion which results in δ,ϵ-unsaturated medium-sized ring ketones (eq. 1).



(1a)

1 **3**

(1b)

2 **4**

cis-1-vinyl-3-cycloocten-1-ol[2], **1**, and *cis*-1-vinyl-3-cyclononen-1-ol, **2**, were prepared from *cis*-3-cycloocten-1-ol[3] and *cis*-3-cyclononen-1-ol respectively by oxidation to the ketone followed by reaction with vinyl Grignard. *cis*-3-cyclononen-1-ol was synthesized from *cis*-2-cycloocten-1-ol[4] by the one carbon ring expansion method outlined by Winstein et. al.[5]

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When heated in the gas phase, both 1 and 2 have been found to undergo [1,3] sigmatropic rearrangement (eq. 1)[6] yielding cis-5-cyclodecenone, 3, and cis-5-cycloundecenone,[7] 4, respectively, (see Table I).

TABLE I

Pyrolysis Products from cis-1-vinyl-3-cycloocten-1-ol, 1, and cis-1-vinyl-3-cyclononen-1-ol, 2

Compd	Conditions[a]		Product Percentages[b]			
	temp	time	[1,3] Shift Products	β-Hydroxy olefin Cleavage	Other Isometric Products	Hydro-carbon Products
1	355°,	40 min	16[c]	7	5[d]	15
2	290°,	2.5 hr.	21	4	6	5

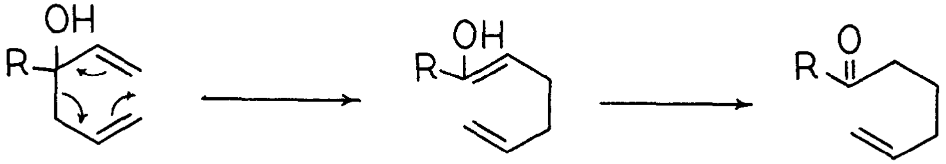
[a] Pyrex ampoules

[b] Actually isolated or calculated using gas chromatography with an internal standard.

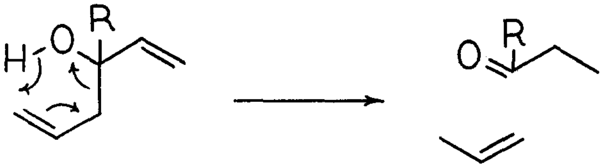
[c] The 16% yield includes several fused ring ketones which result from further rearrangement of 3.

[d] Mainly an unknown alcohol

This is somewhat unusual in that only 7-vinyl-7-hydroxy-norbornene has been reported to rearrange in a similar way.[1] Most other 3-hydroxy-1,5-hexadiene systems[1,8-10] rearrange predominantly by a [3,3] sigmatropic shift (eq. 2) or by β-hydroxyolefin cleavage (eq.3) and give no products resulting from a [1,3] shift.[6] β-Hydroxyolefin cleavage products, 1,9-decadien-3-one and 1,10-undecadien-3-one, are formed from 1 and 2 but products resulting from [3,3] shift have not been observed; however, they may have been formed and subsequently polymerized.[9]



(2)



(3)

Thermodynamically, all three rearrangement processes appear favorable *viz.*, ΔΔH for [1,3] or [3,3] shifts to the enols were estimated[11] to be -4 kcal/mol and ΔΔH for cleavage was estimated[11] to be -1 kcal/mol. Presumably the [3,3] shift and β-hydroxy-olefin cleavage pathways normally predominate because the transition states for these concerted reactions are usually very favorable. For 1 and 2, these transition states are less favorable since they require the vinyl or hydroxyl group to lie over the crowded center of the medium-sized ring. This is especially unfavorable for the vinyl group which probably accounts for the lack of [3,3] rearrangement products. A [1,3] sigmatropic shift with inversion is an allowed process[12] and this transition state appears possible for 1 and 2 but the conditions necessary for reaction suggest a non-concerted pathway which can now compete because the other rearrangements are less favorable.

Further work on these and related systems is in progress.

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