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Ring Expansion by Siloxy-Cope Rearrangement

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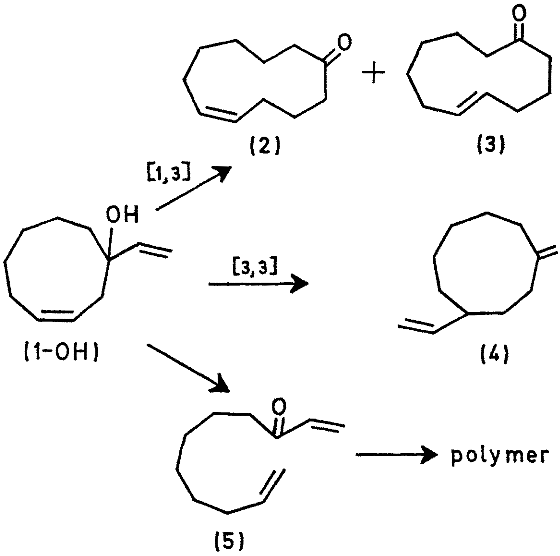
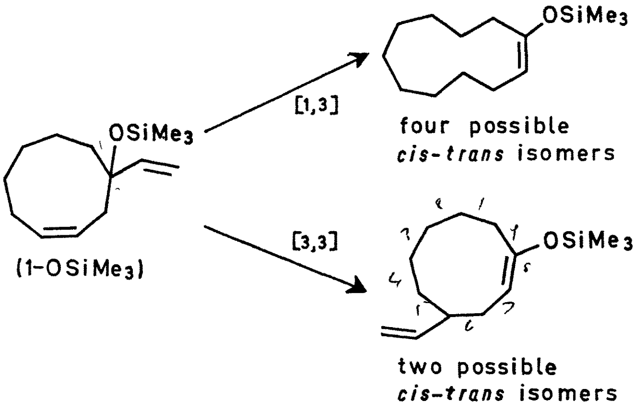
Summary A high-yield, two-carbon ring expansion leading to δε-unsaturated ketones has been developed.

THE oxy-Cope rearrangement can be used as a two-carbon ring expansion leading to δε-unsaturated ketones.[1,2] For example, *cis*-1-vinylcyclonon-3-en-1-ol, (**1**-OH), gives *cis*-5-cycloundecenone, (**2**), as the major isolable product (see Table).[2] The yields are low, however, because approximately 60% of the products are polymeric. This apparently results from polymerization of (**5**) which is formed by β-hydroxy-olefin cleavage.[3]



We have discovered a high-yield variation, herein referred to as the siloxy-Cope rearrangement, in which trimethylsiloxy-derivatives are used to prevent the undesired cleavage reaction. Thus, (**1**-OSiMe$_3$) rearranged thermally by [1,3] and [3,3] sigmatropic shifts to give six trimethylsiloxy enol ethers which were hydrolysed in high overall yield to the ketones (**2**), (**3**), and (**4**) (see Table). No appreciable β-hydroxy-olefin cleavage product or polymer was formed. The trimethylsiloxy-derivative is especially well suited for the present purpose since it is easily prepared† in high yield and does not undergo other side reactions. In contrast, the methoxy-derivative, (**1**-OMe), gave only retro-ene reaction.



The selectivity of the siloxy-Cope case is less than that of the oxy-Cope rearrangement, *i.e.* more *trans*-isomer (**3**) and [3,3] shift product are formed from (**1**-OSiMe$_3$) than from **1**(-OH). This is not due to lower selectivity of initial

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† A mixture of one part alcohol, two parts Tri-Sil (Pierce Chemical Co.) and four parts dimethyl sulphoxide was used.

product formation from (**1**-OSiMe$_3$) (see 20 min result) but is due to interconversion of the products. The reaction mixture at 12 h appears to represent an equilibrium between the trimethylsiloxy-derivatives of (**1**), (**2**), (**3**), and (**4**). This is not the case with (**1**-OH) since the ketones (**2**), (**3**), and (**4**) do not interconvert under the reaction conditions.‡

Formation of both *cis*- and *trans*-products suggests a biradical intermediate in which rotation in the allylic radical competes with re-closure. The question is not yet settled, however, since sequential concerted reactions could also give this result.

Products[a] *from pyrolysis of* cis-1-*vinylcyclonon-3-en-1-ol*, (**1**-OH) *and* cis-1-*trimethylsiloxy-1-vinylcyclonon-3-ene*, (**1**-OSiMe$_3$)

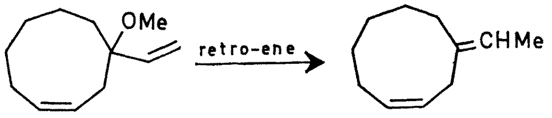
					Products[c]			
Compd.	Conditions[b]	(**1**-OH)	(**2**)	(**3**)	(**4**)	(**5**)	Olefins	Yield[d]
(**1**-OH	290° 2·5 h	13	49	10	5	10	13	23%
(**1**-OSiMe$_3$)	286° 20 min	89	7	1	1	—	2	
	286° 12 h	6	53	29	10	—	2	76%
	286° 20 h	9	46	29	10	—	6	73%

[a] Products shown for (**1**-OSiMe$_3$) are after hydrolysis.

[b] Pyrex ampoules, gas phase, *ca.* 100 mg of substrate in a 60 ml ampoule.

[c] The figures represent percentages of volatile materials as determined by g.l.c.

[d] Yields were determined by using an internal g.l.c. standard and represent the yield of ring-expanded products (**2**) and (**3**) from (**1**-OH) or (**1**-OSiMe$_3$).



(1-OMe)

The use of the siloxy-group to prevent β-hydroxy-olefin cleavage is not limited to the ring expansion shown here but is generally applicable. For example, the siloxy variation should be quite useful for acyclic systems where cleavage competes with [3,3] oxy-Cope rearrangement.[5]

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‡ Analyses and spectral data of the rearranged ketones are consistent with the structures shown.

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