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CARBONIUM ION REARRANGEMENTS CONTROLLED BY THE PRESENCE OF A SILYL GROUP[1]

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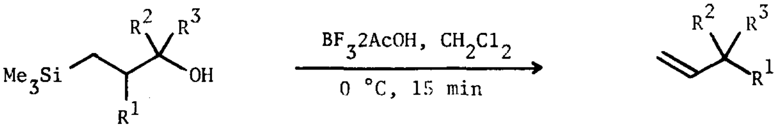
Summary: Tertiary alcohols with a γ-silyl group (**3**) generally undergo a simple carbonium ion rearrangement in acid giving a single alkene product (**4**) with loss of the silyl group.

We reported earlier several examples of carbonium ion rearrangements of the general type (**1** → **2**) in which the migrating group R has been a diphenylphosphinoyl group,[2] a phenylthio group,[3] and, in the norbornyl series, an alkyl group.[4] In each case, the rearrangement was encouraged and the outcome controlled by the presence of the silyl group, but these reactions were all rather special cases. We now report results for tertiary alcohols in general.

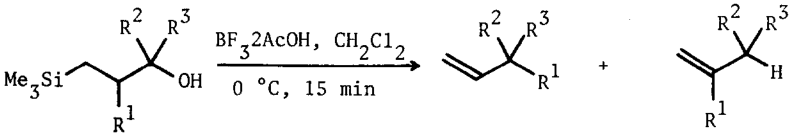
(**1**)

(**2**)

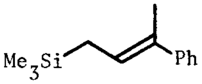


(**3a**)	$R^1 = H$, $R^2 = R^3 = Me$	(**4a**)	100% (n.m.r.)
(**3b**)	$R^1 = H$, $R^2 = Me$, $R^3 = Ph$	(**4b**)	72%[14]
(**3c**)	$R^1 = Ph$, $R^2 = R^3 = Me$	(**4c**)	85%
(**3d**)	$R^1 = Ph$, $R^2 = Me$, $R^3 = Et$	(**4d**)	83%
(**3e**)	$R^1 = Ph$, $R^2 = Me$, $R^3 = Ph$	(**4e**)	82%
(**3f**)	$R^1 = Ph$, $R^2 = Me$, $R^3 = CH{=}CH_2$	(**4f**)	77%
(**3g**)	$R^1 = Ph$, $R^2 = Me$, $R^3 = Bu^t$	(**4g**)	0%[15]

The results with the tertiary alcohols (**3a-3g**) show that hydride shift, for which there is precedent,[5] and phenyl shift are fairly well-behaved reactions. Alkyl shift is a little more complicated in that hydride shift competes with it (**3h-3m**): when the migrating group R^1 is methyl (**3h**), or when the migration terminus has *two* aryl groups (**3i**), hydride shift is the major reaction, but when R^1 is a larger alkyl group (**3j** and **3k**) alkyl shift is the major reaction, except that with a t-butyl group (**3m**) fragmentation takes place, and migration of the t-butyl group is only a minor pathway.

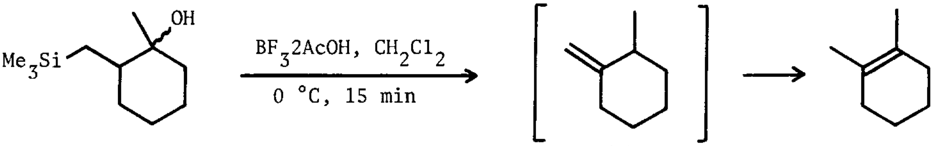


(**3h**) R^1 = Me, R^2 = Me, R^3 = Ph (**4h**) 11% (**5h**) 71%[16]
(**3i**) R^1 = Et, R^2 = R^3 = Ph (**5i**) 79%
(**3j**) R^1 = Et, R^2 = Me, R^3 = Ph (**4j**) 60% (**5j**) 15%[16]
(**3k**) R^1 = Pr^i, R^2 = Me, R^3 = Ph (**4k**) 87%
(**3m**) R^1 = Bu^t, R^2 = Me, R^3 = Ph (**4m**) 30% +

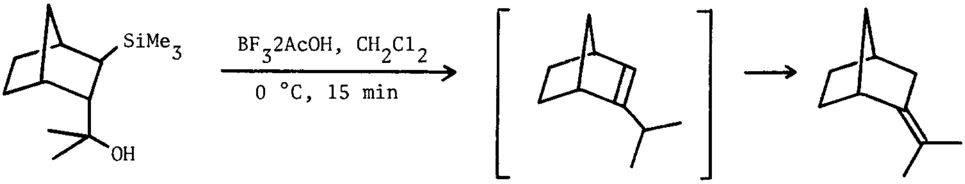


(**6**) 70% (n.m.r.)

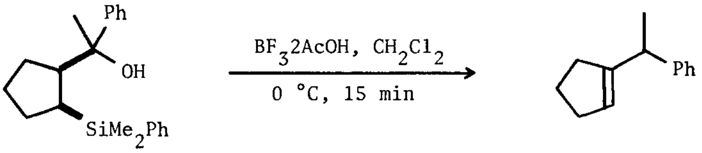
When the alkyl group was a ring residue (**7**, **9**, and **11**), only hydride shift occurred. This was true for both stereoisomers of **7**, and, in the case of both **7** and **9**, the first-formed products were isomerised, understandably enough, under the reaction conditions. An attempt at a



(**7**) (**8**) 100% (n.m.r.)



(**9**) (**10**) 76%

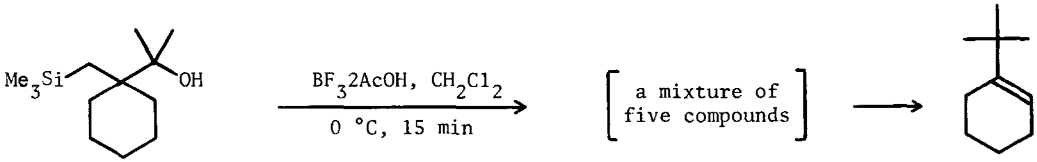


(**11**) 80%

ring-expansion reaction in which hydride shift could not compete (as it did with **9** and **11**) was unsuccessful: the alcohol (**12**) gave initially a mixture of five products, and longer treatment with acid gave only 1-t-butylcyclohexene. Finally we examined two cases with substituents on C-3: one

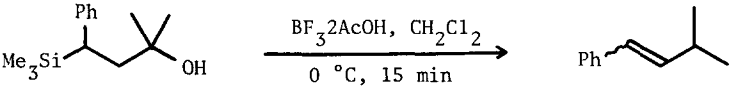
(**13**) was uneventful, the other (**14**) proceeded beyond the first-formed alkene (**15**) to give the indane (**16**).

The pattern of our results bears a very close resemblance to the corresponding pinacol rearrangments. Thus, hydride and phenyl shifts are well known,[6] hydride migrates faster than alkyl when the alkyl group is methyl[7,8] or when the migration terminus has two aryl groups,[9] and larger alkyl groups migrate faster than hydride,[7] except when they are ring residues.[10]



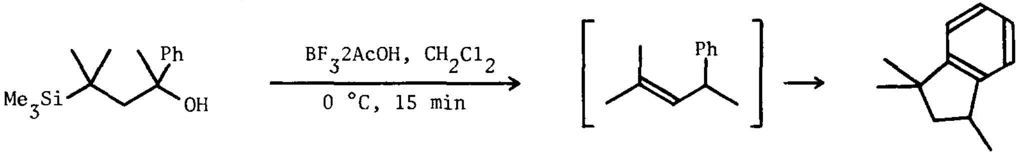
(**12**)

72%



(**13**)

88%



(**14**)

(**15**)

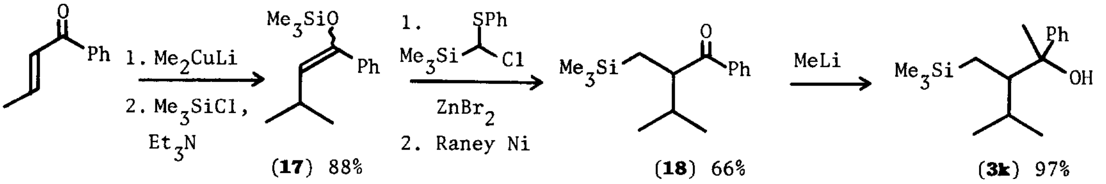
(**16**) 82%

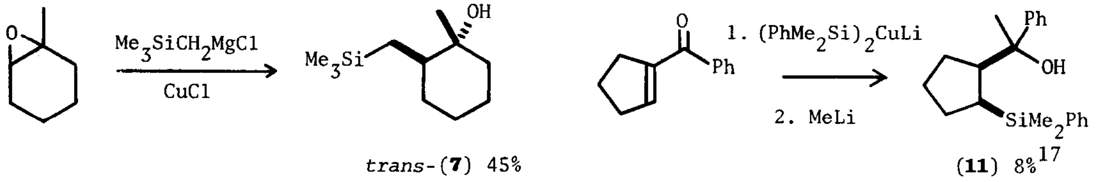
The γ-silyl alcohols used in this work were synthesised in several different ways. One example of each is illustrated in the synthetic scheme on the next page, where it is clear that a wide variety of structures can be assembled with comparative ease. Particularly noteworthy is the use of Paterson's phenylthioalkylation-desulphurisation reaction[11] for the introduction of the trimethylsilylmethyl group (**17** → **18**) α to ketone or ester.[12]

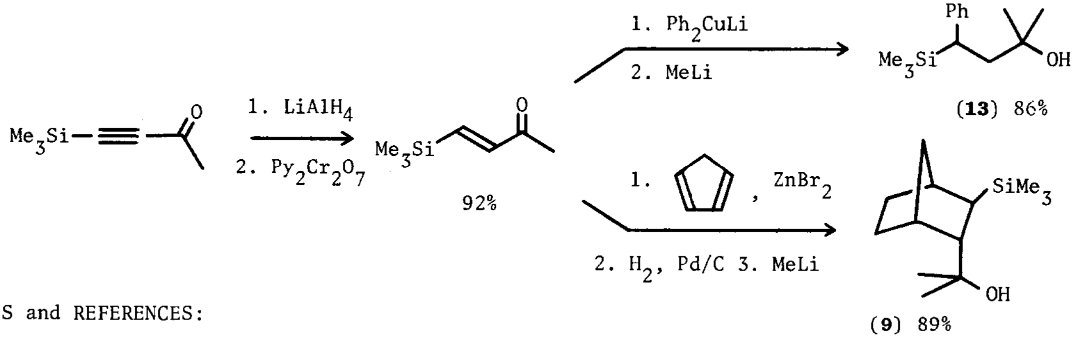
In no case did we observe any cyclopropane products during the rearrangement reactions, although they have been observed in related reactions.[5,13] Other things being equal, it seems that when C-1 is primary, cyclopropanes are the usual products,[13] when C-1 is secondary, there is competition between cyclopropane formation and rearrangement,[5] and when C-1 is tertiary, judging by the present work, rearrangement is the usual pathway.

In summary, the silicon-controlled carbonium ion rearrangement is a fairly well-behaved process, with a reasonably predictable outcome. It is cleaner, on the whole, than the corresponding pinacol rearrangement, because the aldehydes or ketones produced in that reaction are usually unstable to the reaction conditions, whereas the alkene products of the silicon-controlled rearrangement are stable when they are mono- or 1,2-disubstituted. The γ-silyl alcohols are easily prepared and the final products are notable in that several of them have quaternary carbons. We are investigating the possibility of arresting the reaction at the stage of the first-formed products in those cases (**5h**, **5j**, **8**, and **10**) where it is a 1,1-disubstituted alkene and does not survive the conditions used to initiate the rearrangement.

THE SYNTHESIS OF γ-SILYL ALCOHOLS:







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11. I. Paterson and I. Fleming, *Tetrahedron Lett.*, 993, 995, and 2179 (1979).
12. We thank Dr. Paterson for first showing that phenylthiotrimethylsilylmethylation worked.
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14. Under the usual conditions, a minor product (25%) was the allylsilane (**6**), but by treating this product with $BF_3$2AcOH at 70 °C for 5 min, it underwent protodesilylation to give more of the alkene (**4b**), so that the overall yield (isolated) was a respectable 72%.
15. In this case, a methyl shift from the t-butyl group preceeded any phenyl shift, and fragmentation followed the methyl shift, so that the products were styrene and 2,3-dimethyl-2-butene.
16. In this case, the product actually observed was the result of subsequent isomerisation to the more substituted alkene, 2-(methyl or ethyl)-3-phenyl-2-butene. The products were not separated, but the ^{1}H-n.m.r. spectra were easily interpreted, and the ratios of products were measured by g.l.c.
17. The major product of this reaction was the *trimethyl*silyl analogue of **11**; the phenyl group had been displaced by the neighbouring alkoxide, and this in its turn had been displaced by a second equivalent of methyl-lithium. Phenylsilanes in general do not react with methyl-lithium in this way. This reaction can be avoided by using only one equivalent of methyl-lithium.

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