Unusually Fast [1,3] Sigmatropic Shifts

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Summary Four medium-sized-ring 1-vinyl alcohols including one benzo-derivative are shown to undergo [1,3] sigmatropic shifts at room temperature under the influence of potassium hydride and hexamethylphosphoric triamide (HMPA) whereas thermal rearrangement of the trimethylsilyloxy derivatives requires *ca.* 300 °C.

Evans recently discovered[1] that the bicyclic oxy-Cope system (**1**) underwent a [3,3] sigmatropic rearrangement at an enormously enhanced rate when treated with potassium hydride in tetrahydrofuran (THF) or HMPA. Since [1,3] sigmatropic shifts have often been thought to be non-concerted it was not clear whether they could also show this rate enhancement. We now report the first [1,3] shifts of oxy-Cope systems occurring at room temperature.

In previous work we have shown[2] that systems like the nine-membered *cis*-(**2a**), and the ten-membered analogues *cis*-(**2b**) and *trans*-(**2b**) rearrange as the trimethylsilyl derivatives at *ca.* 280 °C to give three types of products [(**3**), (**4**), and (**5**)]. In each case the predominant rearrangement was a [1,3] sigmatropic shift resulting in a two-carbon ring expansion with retention of double bond stereochemistry (see Table).

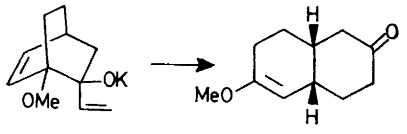
Table. Rearrangement product ratios for thermolysis of the trimethylsilyloxy derivatives near 280 °C compared to the potassium salt at room temperature in HMPA.

Compound	R	Time/ h[a]	Type of product[b] (**3**) : (**4**) : (**5**)	Yield/ %[c]
cis-(**2a**)	$SiMe_3$	2·3	73 : 15 : 12	90
cis-(**2a**)	K	2·75	55 : 34 : 11	62
cis-(**2b**)	$SiMe_3$	5·0	77 : 11 : 12	80
cis-(**2b**)	K	27·5	100 : 00 : 00	31
trans-(**2b**)	$SiMe_3$	0·6	5 : 85 : 10	80
trans-(**2b**)	K	3·0	00 : 88 : 12	67

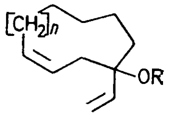
[a] Times for the $SiMe_3$ cases correspond to one half-life whereas those of the potassium salt are for 90—100% reaction. [b] For the HMPA cases, the ratios of volatile products were constant with time within the limits of error, *e.g.*, three experiments for *cis*-(**2a**) at 1·5 h gave a ratio of 3 : 4 : 5 of 54 ± 4 : 34 ± 2 : 12 ± 1, while at 5 h the ratio was 57 ± 6 : 29 ± 6 : 14 ± 1. [c] The yields were determined by g.l.c. with internal standard and are based on starting material consumed.

When *cis*-(**2a**), *cis*-(**2b**), and *trans*-(**2b**) are treated with potassium hydride in HMPA at room temperature, the [1,3] shift ring expansion again predominates. The ten-membered rings show no loss of double bond stereochemistry whereas *cis*-(**2a**) shows more loss than the thermolysis of the trimethylsilyloxy derivative. The [3,3] shift product (**5**) is formed to about the same extent in the thermolyses of *cis*-(**2a**) and *trans*-(**2b**) but is not formed in the case of *cis*-(**2b**). Unlike system (**1**), THF was much less effective as a solvent, *viz.*, *trans*-(**2b**) gave 34% conversion when refluxed for four days. The yields for the HMPA–KH route are less than the trimethylsilyl–thermal route for the cases cited in the Table. In other systems, the HMPA–KH method may prove more advantageous. For example, the benzo-system† (**6**) rearranges predominantly by the [1,3] shift under either set of conditions, but the yield for KH–HMPA (5·5 h, room temp.) is 56% whereas the trimethylsilyl route required 11 h at 350 °C and gives only a 28% yield. The reaction sequence involving (**6**) represents a new route into specifically substituted benzo-medium-sized ring systems which are generally difficult to prepare.

It is not certain whether the [1,3] shifts are concerted, *e.g.*, the ring system could break apart to give an allylic or benzylic anion which could then undergo internal Michael additions leading to the observed products.‡ Interestingly, the epimer of (**1**) which is geometrically precluded from reacting by a concerted [3,3] shift is reported not to rearrange as the potassium salt in refluxing THF[1] even though that system could have rearranged by a [1,3] shift.



(1)

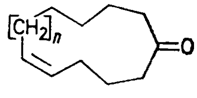


(2)

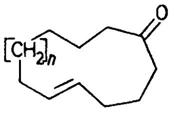
R = $SiMe_3$ or K

a; $n = 1$

b; $n = 2$



(3)



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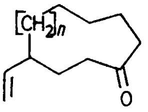
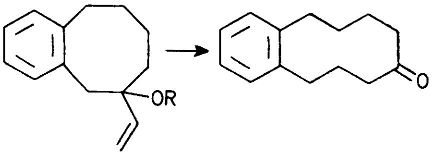


(5)



(6) (R = $SiMe_3$ or K)

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† The ketone precursor to (**6**) was prepared in 70% yield from benzosuberone using the Evans preparation of amino-alcohols (D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.*, 1974, **39**, 914) followed by Demjanow-Tiffeneau rearrangement (P. A. S. Smith and D. R. Baer, *Org. Reactions*, 1960, **11**, 157).

‡ 1-Vinylcyclodecanol and 1-vinylcyclononanol gave no detectable cyclododecanone or cycloundecanone when treated with KH–HMPA for 4 and 24 h respectively.

[1] D. A. Evans and A. M. Golab, *J. Amer. Chem. Soc.*, 1975 **97**, 4765.
[2] R. W. Thies, *J. Amer. Chem. Soc.*, 1972, **94**, 7074; R. W. Thies, and J. E. Billigmeier, *ibid.*, 1974, **96**, 200.