A New Silicon Mediated Rearrangement of Epoxides

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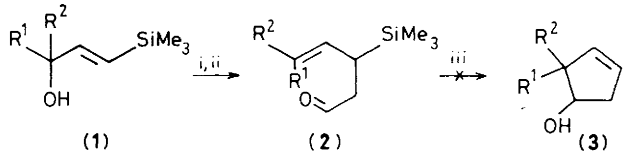
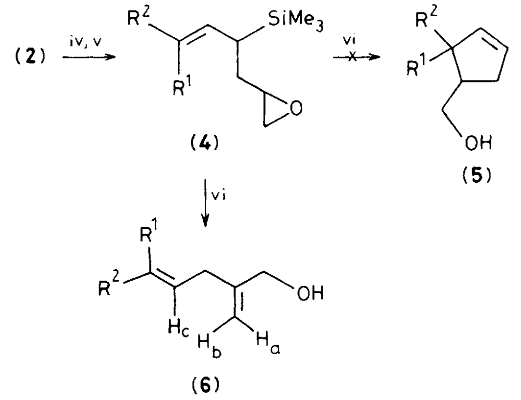
Epoxides (**4**) rearrange when treated with stannic chloride in dry dichloromethane giving allylic alcohols (**6**).

Silicon mediated cyclisations are now powerful tools in the synthetic chemist's armoury,[1,2] and we were attracted by the possibility of using the Claisen rearrangement to generate a precursor for variously substituted five-membered rings (**3**) (Scheme 1). As in our hands, all attempted cyclisations failed, we decided to employ epoxides (**4**) to study the desired cyclisations (Scheme 2).

Epoxides (**4**) were formed in good yield from (**2**) using



Scheme 1. *Reagents:* i, $Hg(OAc)_2$–$EtOCH{=}CH_2$; ii, heat; iii, Lewis acid.

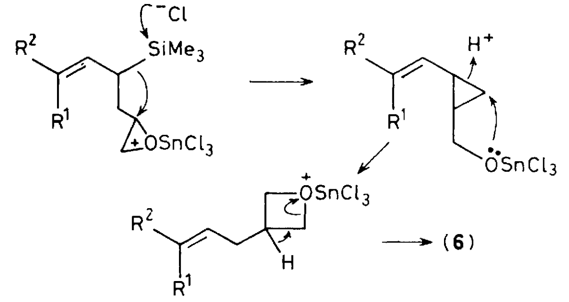


		Yield (%)
a;	$R^1 = R^2 = Me$	43
b;	$R^1, R^2 = [CH_2]_5$	45
c;	$R^1 = Me, R^2 = CH_2CH{=}CMe_2$	26[a]
d;	$R^1 = H, R^2 = Me$	38[a]
e;	$R^1 = H, R^2 = [CH_2]_4Me$	36[a]

[a] This yield refers to the *trans*-isomer.

Scheme 2. *Reagents:* iv, $PhSCH_2Li$–tetrahydrofuran; v, $Et_3O^+BF_4^-$; NaOH; vi, $SnCl_4$.

Johnson's method.[3] Treatment of (**4**) with stannic chloride in dichloromethane did not give (**5**) as expected, but the allylic alcohols (**6**) were obtained. Other Lewis acids failed to give this result.



Scheme 3

Thus, when stannic chloride (10 mol%) was added to a solution of (**4**) (1 mol. equiv.) in dichloromethane at 0 °C, a red colour was observed which faded on warming the mixture to room temperature. The reaction mixture was poured into saturated brine, extracted with ether and concentrated. Purification on silica gave (**6**).‡ We are now extending this reaction to other systems in order to understand its mechanism. One possibility is that a four-membered oxo-tin species is responsible for the formation of (**6**) (Scheme 3).

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References

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‡ All new compounds were characterised by n.m.r., i.r., and mass spectrometry. ^1H N.m.r. for (**6a**), δ 1.5 (1H, br.s, OH), 1.66 (3H, br.s, Me), 1.75 (3H, br.s, Me), 2.75 (2H, m, CH_2), 3.99 (2H, br.s, CH_2OH), 4.83 (1H, m, H_a), 4.96 (1H, m, H_b), and 5.18 (1H, m, H_c).