Silicon in Synthesis. Unusual Transformations of 4-Hydroxybutenylsilanes

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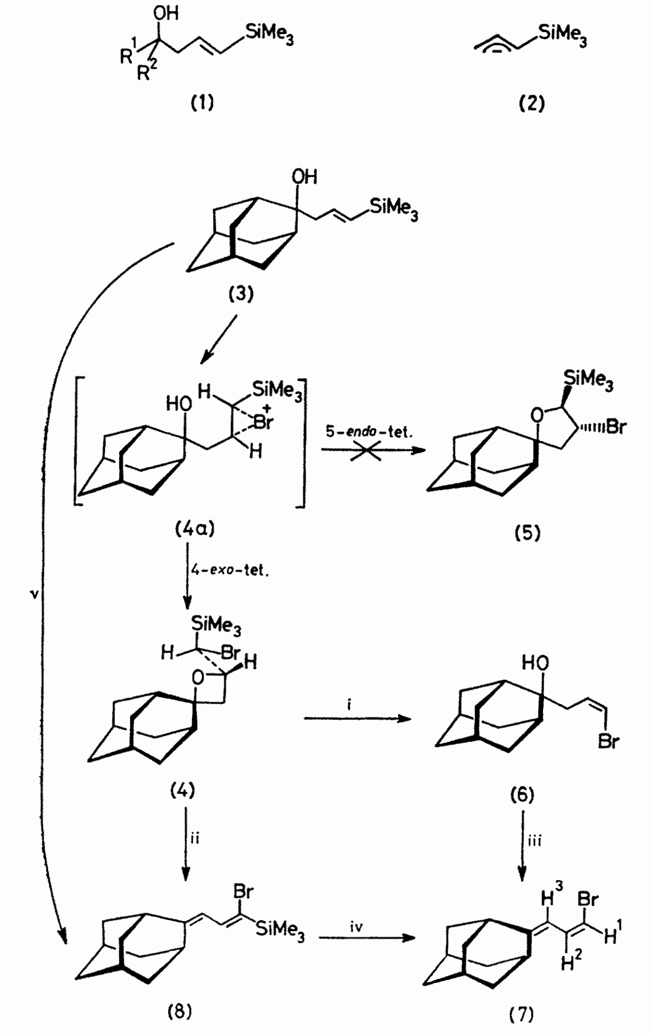
Summary The adduct (**3**) formed from adamantan-2-one and allyltrimethylsilyl anion (**2**) is converted by *N*-bromosuccinimide into the spiro-oxetan (**4**), which undergoes a number of elimination reactions to give (**6**), (**7**), and (**8**).

The 4-hydroxybutenylsilanes (**1**) have recently become available from the reaction of the allyltrimethylsilyl anion (**2**) with aldehydes and ketones.[1] Here we describe unexpected reactions of 4-hydroxybutenylsilanes with electrophilic bromine that lead to interesting new structural types. These experiments illustrate that the so-called β-effect, an underlying principle of much organosilicon chemistry,[2] cannot always be taken to be a firm generalization.[3]

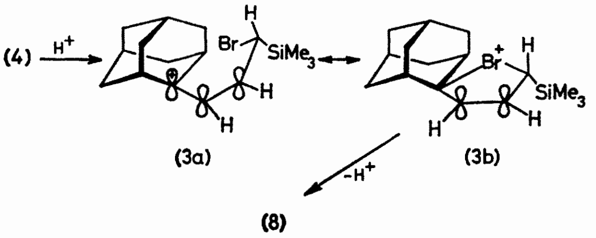
The adduct (**3**) formed from adamantan-2-one and the anion (**2**), m.p. 70—75 °C, was treated with *N*-bromosuccinimide (NBS) in tetrahydrofuran (THF) at 0 °C. A single compound, the oxetan (**4**), was formed in 80% yield. The structure of (**4**), δ 4·59 (1H, q, J 7·8 Hz), 3·37 (1H, d, J 7·8 Hz), 2·37—1·81 (4H, m), 1·66 (12H, s), and 0·14 (9H, s), was established by subsequent chemical transformations. A plausible and expected alternative structure for (**4**) is (**5**). These structures (**4**) and (**5**) correspond to

4-*exo*-tet and 5-*endo*-tet opening of the bromonium ion intermediate (**4a**), respectively, the former being the favoured and observed course (Scheme 1).[4]



SCHEME 1. i, KF.2H$_2$O–Me$_2$SO, 40—45 °C; ii, H$^+$, 40 °C; iii, SOCl$_2$–pyridine; iv, KF.2H$_2$O–Me$_2$SO; v, NBS–THF, reflux.

Treatment of (**4**) with potassium fluoride dihydrate in Me$_2$SO at 40—45 °C gave the *cis*-vinyl bromide (**6**), m.p. 117—119 °C (68%). This *trans*-elimination confirms the structure of (**4**). Dehydration of (**6**) with SOCl$_2$–pyridine gave the bromodiene (**7**), $J_{1,2}$ 10·8, $J_{2,3}$ 6·96, and $J_{1,3}$ −1·21 Hz. If the oxetan (**4**) is warmed to 40 °C in the presence of a trace of mineral acid, it is cleanly converted into the trimethylsilylbromodiene (**8**). Direct treatment of (**3**) with *N*-bromosuccinimide in THF at reflux gave (**8**) (80%), m.p. 92—97 °C. The structure of (**8**) was established by treatment with potassium fluoride dihydrate–Me$_2$SO to give the bromodiene (**7**), 90% (Scheme 1).[5] The unexpected and unprecedented conversion of (**4**) into (**8**) requires rationalization since it would have been predicted that the trimethylsilyl group would be lost to give (**7**), directly. The initial product (**4**), from the addition of Br$^+$ to (**3**) is the kinetic product (1,2-addition); heating this adduct in the presence of acid can lead to the thermodynamic adduct *via* the bromonium ion (**3b**). Stereospecific formation of (**4**), and subsequently conversion *via* (**3b**) into (**8**) is completely stereospecific; the 1,4-bromonium ion (**3b**)[6] has the proton in the same plane as the π-system, whereas the trimethylsilyl group is orthogonal to the π-system. Because of these stereoelectronic considerations, the intermediate (**3b**) undergoes proton loss rather than loss of the trimethylsilyl group, leading to (**8**) (Scheme 2).[1,7]



SCHEME 2

The reactions described in this paper show that 4-hydroxyvinylsilanes are useful precursors to a range of unusual compounds (**4**), (**6**), (**7**), and (**8**), and further illustrate the geometrical requirements of cations β to silicon. All new compounds were fully characterized by ^{1}H and ^{13}C n.m.r., i.r., and mass spectral and microanalytical data.

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