

Silicon in Synthesis. Unusual Transformations of 4-Hydroxybutenylsilanes

By ED EHLINGER and PHILIP MAGNUS*

(*Evans Chemistry Laboratory, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210*)

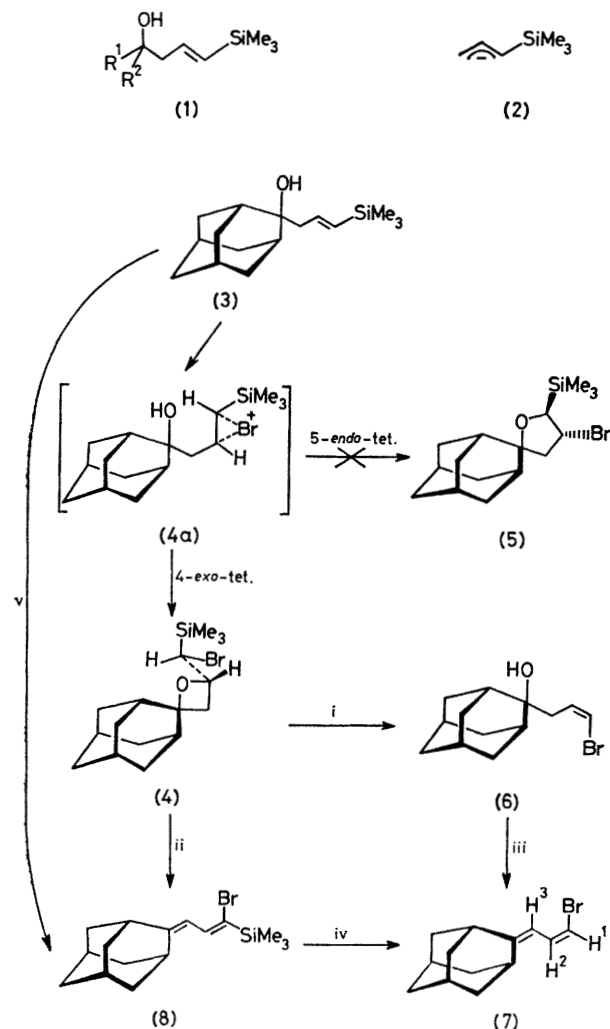
Summary The adduct (3) formed from adamantan-2-one and allyltrimethylsilyl anion (2) is converted by *N*-bromosuccinimide into the spiro-oxetan (4), which undergoes a number of elimination reactions to give (6), (7), and (8).

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

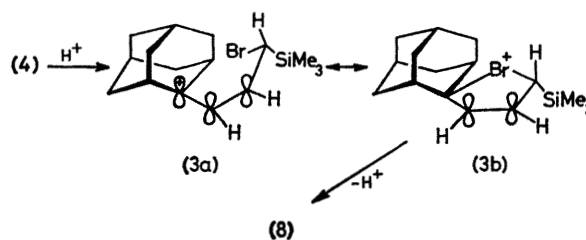
4-*exo*-tet and 5-*endo*-tet opening of the bromonium ion intermediate (4a), respectively, the former being the favoured and observed course (Scheme 1).⁴



SCHEME 1. i, $\text{KF} \cdot 2\text{H}_2\text{O} - \text{Me}_2\text{SO}$, 40–45 °C; ii, H^+ , 40 °C; iii, SOCl_2 -pyridine; iv, $\text{KF} \cdot 2\text{H}_2\text{O} - \text{Me}_2\text{SO}$; v, NBS-THF, reflux.

Treatment of (4) with potassium fluoride dihydrate in Me_2SO 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_2SO 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 ^1H and ^{13}C n.m.r., i.r., and mass spectral and microanalytical data.

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