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A New Method of Generating Anionic σ-Complexes by the Reaction of 7-Silanorbornadiene with Alkali

Mikhail P. Egorov, Anton M. Gal'minas and Oleg M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328

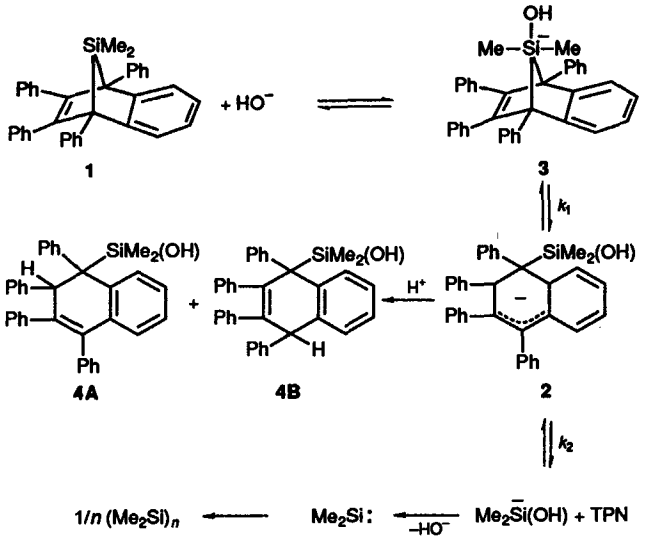
The reaction of 7-silanorbornadiene **1** with dry KOH results in the formation of the long-lived anionic σ-complex **2**.

It is well known, that Meisenheimer-type anionic σ-complexes play a key role as intermediates in aromatic nucleophilic substitution.[1–3] Such complexes can be prepared by reversible reactions between aromatic substrates, containing strong electron-withdrawing substituents, and nucleophiles.[1–3] Thus, the first anionic σ-complexes, containing E—C(sp^3) bonds (E = Si, Ge, Sn), were prepared by the reaction of R_3E^- anions with 1,3,5-trinitrobenzene.[3,4]

We now wish to report a new method for the generation of anionic σ-complexes, involving irreversible nucleophilic cleavage of an endocyclic Si—C bond in a strained heterocycle, 7,7-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorborna-2,5-diene **1**. The addition of dry KOH powder to a benzene solution of **1** in the presence of 18-crown-6 is accompanied by the appearance of a deep colour. The colour disappears either when **1** is completely decomposed, with the formation of 1,2,3,4-tetraphenylnaphthalene (TPN) and oligomers $(Me_2Si)_n$, or when the mixture comes into contact with air or a protonic agent (water or alcohol).

The UV spectrum of this coloured species (λ_{max_1} 590 nm, λ_{max_2} 440 nm, λ_{max_3} 330 nm, $\epsilon_1:\epsilon_2:\epsilon_3 = 2:1:2$) is similar to that of the anionic σ-complexes of 1-X-2,4-dinitrophenylnaphthalenes (λ_{max} 520, 330–360 nm)[5,6] and differs completely from the UV spectrum of the anion-radical of $(TPN)^-$ (λ_{max} 570 nm). The latter was obtained by the reaction of TPN with sodium [tetrahydrofuran (THF), 20°C]. Moreover, the coloured solution shows no EPR spectrum, so one can exclude a radical nature for the coloured intermediate. These data testify to the structure of the intermediate as that of anionic σ-complex **2**, which is formed as a result of heterolytic cleavage of the endocyclic Si—C bond in **1**. Nucleophilic cleavage of Si—C bonds in open-chain systems has been extensively studied by Eaborn *et al.*[7–9] The formation of carbanions as possible intermediates in these reactions has often been suggested and in at least one case such a carbanion has been detected by its UV spectrum.[9]

Anionic σ-complex **2** may be formed either directly or *via* pentacoordinated intermediate **3**, arising at the first stage of the reaction between **1** and OH^- ion (Scheme 1). The formation of such a hypercoordinated species during reactions between organosilicon compounds and nucleophiles is now well established.[10–13] σ-Complex **2** dissociates to TPN and, probably, $Me_2Si(OH)^-$. The latter undergoes α-elimination with the formation of Me_2Si [giving $(Me_2Si)_n$] and OH^-.



Scheme 1

It should be noted that σ-complexes of TPN cannot be generated by the usual method involving attack of a nucleophile (MeO^-, HO^-, $MeCOCH_2^-$, *etc.*) on TPN.

The reaction of **1a** with aqueous KOH proceeds without the appearance of any colour and gives the corresponding silanols **4** as a mixture of isomers **4A** and **4B** (1:2.5) in high yields. It seems that, in this case, trapping of **2** with water is faster than its dissociation, although a concerted pathway for this reaction certainly cannot be completely excluded. The silanols **4** were isolated and characterized by their NMR, IR and MS spectra.†

† *Spectroscopic data* for silanols **4A,B**: ^{1}H NMR **4A** (C_6D_6) δ 0.65 (s, 3H, CH_3), 0.75 (s, 3H, CH_3), 2.0 (s, 1H, OH), 5.35 (1H, CH), 6.5–8.5 (24H, arom.); **4B** (C_6D_6) δ 0.6 (s, 3H, CH_3), 0.66 (s, 3H, CH_3), 2.0 (s, 1H, OH), 5.52 (s, 1H, CH), 6.5–8.5 (24H, arom.); MS **4A,B** (70 eV) *m/z* 507 (M^+), 506 $(M-H)^+$, 433 $(M-SiMe_2OH)^+$, 432 $(TPN)^+$, 356 $(TPN-Ph)^+$. IR ν_{OH}/cm^{-1} 3617, ρ_w(CH) 679 cm^{-1}.

Deuterolysis of **1a** under the same conditions results in deuterosilanols **5A,B**: IR ν_{OD}/cm^{-1} 2673, 2281 ρ_w 500 cm^{-1}; ^{1}H NMR **5A** (C_6D_6) δ 0.65 (s, 3H, CH_3), 0.75 (s, 3H, CH_3), 6.5–8.5 (24H, arom.); **5B** 0.60 (s, 3H, CH_3), 0.66 (s, 3H, CH_3), 6.5–8.5 (24H, arom.).

In contrast to 7-silanorbornadiene **1**, reaction of the corresponding 7-germanorbornadiene with either dry or aqueous KOH proceeds without detectable participation of the anionic intermediate and leads to the formation of TPN and oligomers $(Me_2Ge)_n$. Apparently, in this case the anionic σ-complex is more labile than **2** and its dissociation proceeds faster than protonation. Certainly we cannot exclude a concerted mechanism involving the breaking of endocyclic Ge—C bonds in the reaction of 7-germanorbornadiene with alkali.

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