One-electron Oxidation of 2,2-Dimethyl-2-silaindane by Potassium 12-Tungstocobaltate(III). Lack of Evidence for Stereoelectronic Effects on the Cleavage of a β-Carbon–Silicon Bond in an Aromatic Cation Radical

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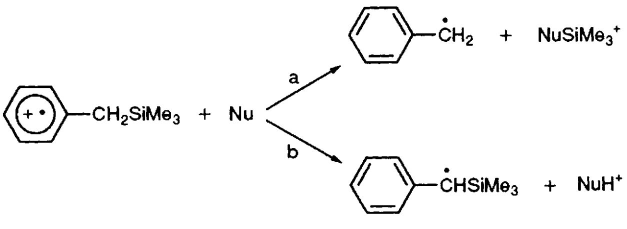
The one-electron transfer oxidation of 2,2-dimethyl-2-silaindane by $K_5Co^{III}W_{12}O_{40}$ leads, in a slow step, to a radical cation which then undergoes fast C–Si bond cleavage, thus indicating that the rate of this cleavage is not significantly affected by the orientation of the C–Si bond with respect to the aromatic system.

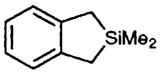
It is well known that conformational factors can influence the cleavage rate of a C–H or C–C β bond in an aromatic radical cation. In particular, the cleavage is strongly favoured if the bond and the aromatic π system are collinear (stereoelectronic effect). When this alignment is not possible, the rate of bond cleavage is significantly decreased and in many instances no cleavage is observed.[1] We now report that, in contrast, when the cleavage involves a β C–Si bond, there is no evidence for the operation of stereoelectronic effects.

Benzyltrimethylsilane radical cations undergo rapid cleavage of the C–Si bond (Scheme 1, path a) at a rate that greatly exceeds that of the reaction involving the cleavage of the β C–H bond (path b), which accordingly is generally never observed.[2] In these substrates the cleavage of the C–Si bond should also be favoured by conformational factors, since the most important conformation of benzyltrimethylsilane is the one with the C–Si bond aligned with the π system.

To assess if and to what extent stereoelectronic effects may influence the C–Si bond cleavage we have carried out a product and kinetic study of the oxidation of 2,2-dimethyl-2-silaindane **1** with $K_5Co^{III}W_{12}O_{40}$, abbreviated as $Co^{III}W$ (a *bona fide* one-ectron transfer oxidant[3]), in $AcOH-H_2O$. Unlike in benzyltrimethylsilane, in **1** the C–Si bond cannot be collinear with the π system, but is forced to be almost coplanar with it, as shown by the nearly complete suppression of any hyperconjugation between this bond and the π orbitals.[4] In contrast, the β C–H bonds are collinear with the π orbitals, and therefore perfectly suited for the cleavage. Thus in $\mathbf{1}^{\cdot+}$ stereoelectronic effects might reverse the usual reactivity order of the C–Si and C–H bond cleavage, or at least make the latter competitive with the former.



Scheme 1 Nu = nucleophile



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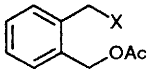

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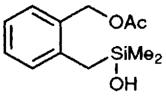

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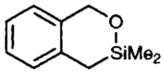

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Compound **1** reacts with an excess of $Co^{III}W$ in $AcOH-H_2O$ at 55 °C with almost 100% conversion into the monoacetate **2** (X = OH) and the diacetate **2** (X = OAc) of benzene-1,2-dimethanol.† Compounds **3** and **4** (the latter presumably deriving from the former) are probably formed first, and are then converted into **2** by further reaction with $Co^{III}W$. It was not possible, however, to isolate **3** and **4** in a high state of purity since they interconvert, and, in addition undergo extensive decomposition during column chromatography. Thus, their structure has been assigned on the basis of spectroscopic data.

There is no doubt that **3** and **4** as well as **2** derive from C–Si bond cleavage in $\mathbf{1}^{\cdot+}$. No C–H bond cleavage has taken place, since 1-acetoxy- and 1-hydroxy-2,2-dimethylsilaindane have not been detected. Further oxidation of these products, involving C–Si bond cleavage, can be excluded as well, since it would have led to benzaldehyde derivatives, which were not observed. Thus, in spite of the unfavourable stereoelectronic factor, $\mathbf{1}^{\cdot+}$ behaves like the benzyltrimethylsilane cation radical, undergoing cleavage of the C–Si bond as the most favoured reaction pathway.‡

A kinetic study at 55 °C in $AcOH-H_2O$ (70:30), with concentrations of the substrate 30–60 times higher than those (1–5 × 10^{-4} mol l^{-1}) of $Co^{III}W$,§ shows that the oxidations follow regular second-order kinetics, first order in **1** and first order in $Co^{III}W$. The value of the second-order rate constant (k_{obs} = 1.1 × 10^{-2} l mol^{-1} s^{-1}) is practically unaffected (k_{obs} = 1.0 × 10^{-2} l mol^{-1} s^{-1}) by added $Co^{II}W$ (5 × 10^{-4} mol l^{-1}), whereas the rate is significantly decreased by added salts [k_{obs} = 1.5 × 10^{-3} l mol^{-1} s^{-1}) with AcONa (0.1 mol l^{-1}) and 2.5 × 10^{-3} l mol^{-1} s^{-1} with $NaClO_4$ (0.1 mol l^{-1})].

The kinetic pattern is exactly the same than that observed in the corresponding oxidations of benzyltrimethylsilanes.[5] Therefore, the reaction of **1** with $Co^{III}W$ can be described by the mechanism in Scheme 2, with the rate determined in the

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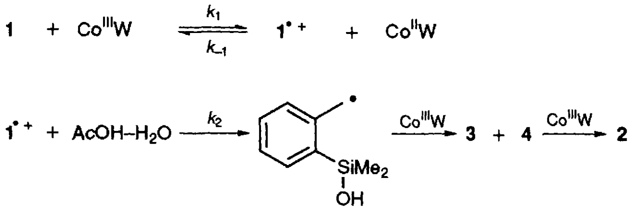
† The reaction of **1** (0.5 mmol) with an excess of $Co^{III}W$ (3 mmol, three times the amount required by 1:2 stoichiometry) at 55 °C in $AcOH-H_2O$ (7:3) under argon leads, after 24 h, to a mixture of **2** (X = OH) and **2** (X = OAc) (0.8:1) identified by comparison with authentic specimens. The conversion is almost 100%. However, the reaction of 2.3 mmol of **1** with 4.4 mmol of $Co^{III}W$ gives two products, identified as **3** and **4** by ^1H NMR spectroscopy and GC–MS analysis. **3**: ^1H NMR ($CDCl_3$): δ 7.35–7.05 (m, ArH), 5.13 (s, CH_2OAc), 2.22 (s, CH_2SiOH), 2.09 (s, OCOMe), 1.23 (s, SiOH) and 0.14 (s, CH_2SiMe_2); MS *m/z* 178 (M^+ − AcOH), 163, 133, 104, 75 [$(CH_3)_2SiOH)^+$] and 43 (CH_3CO^+). **4**: ^1H NMR ($CDCl_3$): δ 7.40–7.00 (m, ArH), 4.81 (s, CH_2O), 2.06 (s, CH_2Si) and 0.16 (s, $SiMe_2$); MS *m/z* 178 (M^+), 163, 133 and 104.

‡ Interestingly, C–Si bond cleavage of **1** remains the almost exclusive reaction pathway when the reaction is carried out under much more basic conditions (AcOK, 0.4 mol l^{-1}), which should favour the base-catalysed deprotonation progress.[3]

§ Kinetic studies were carried out at 55 °C by rapid addition of a $Co^{III}W$ solution (25–100 μl, 3 × 10^{-2} mol l^{-1}) to a solution of **1** (1.6 × 10^{-3} mol l^{-1}) in $AcOH-H_2O$ (7:3) and following the disappearance of $Co^{III}W$ spectrophotometrically at 390 nm.[5]



Scheme 2

electron-transfer step. It follows that not only is the cleavage of the C–Si bond the exclusive reaction route of **1**$^{•+}$, but it is also a very fast process ($k_2 > k_{-1}$), as found in the oxidation of benzyltrimethylsilanes.

Summing up, we have been unable to detect any substantial difference, both in the product type and in the kinetic pattern, between the one-electron oxidation of **1** by Co^{III}W and the corresponding reaction of benzyltrimethylsilanes in AcOH–H_2O. It can be concluded, therefore that, at least under these reaction conditions, stereoelectronic effects play a very minor role with respect to the cleavage of a β C–Si bond in an aromatic cation radical. A possible suggestion is that the C–Si bond cleavage is intrinsically such a rapid process (presumably owing to the strong energy of the Si–O bond which forms when the nucleophile, AcOH–H_2O, attacks **1**$^{•+}$ at silicon) that its rate remains very high, even when conformational factors do not allow the bond and the aromatic π system to be collinear.

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