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CARBON SILICON BOND CLEAVAGE IN THE OXIDATION OF BENZYLIC SILANES BY CERIUM(IV) AMMONIUM NITRATE

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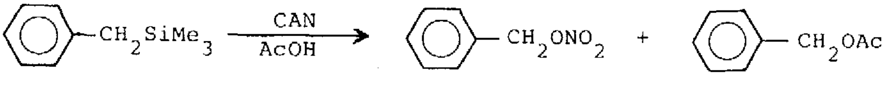
Summary: Benzyltrimethylsilanes react with cerium(IV) ammonium nitrate in AcOH to give products of C-Si cleavage (benzyl nitrate and acetate), under very mild conditions and in quantitative yields. The reaction rate is very sensitive to the nature of the ring substituents ($\rho = -5.4$), which clearly suggests the operation of one electron transfer mechanism.

The C-Si bond is generally considered to be fairly resistant to oxidative cleavage[1]. However, recent reports clearly indicate that this statement does not apply to one electron oxidations. Accordingly, C-Si bond cleavage has been shown to occur, under mild conditions, in electrochemical and photosensitized oxidations of allyl- and benzyltrimethylsilanes[2].

In all these reactions, one electron transfer mechanism appears reasonable: the formation of a radical cation has been suggested, which undergoes fast C-Si bond rupture.

In this note we wish to report that efficient C-Si bond breaking also takes place, under very mild conditions, when benzyltrimethylsilanes react with cerium(IV) ammonium nitrate (CAN) in acetic acid. The electron transfer nature of this reaction is clearly supported by a kinetic investigation.

When CAN (4 mmol) and benzyltrimethylsilane (2 mmol) react in AcOH (100 ml), under nitrogen a mixture (3:1) of benzyl nitrate and acetate is formed (eq. 1) with an overall yield (75%, after 5h at room temperature and 95%, after 15 min at 60°C) which is practically quantitative with respect to the CAN and the substrate consumed. The stoichiometry of the reaction is that expected, that is two moles of CAN are needed to oxidize one mole of substrate.



(1)

The reaction appeared very suitable for a kinetic investigation which was carried out, for a number of ring substituted benzyltrimethylsilanes, by following the disappearance of CAN spectrophotometrically at 420 nm. Using an excess of substrate clean first order plots were obtained up to 70% of reaction. No retarding effect of added Ce(III) was observed; in fact the reaction rate increased slightly in the presence of Ce(III) nitrate. The second order rate constants, calculated as usual, are reported in the Table.

Table. Kinetic Data for the Reaction of Ring Substituted Benzyltrimethylsilanes with CAN in Acetic Acid, at 25°C[a].

Ring Substituent	$k, M^{-1}s^{-1}$
$p\text{-}CH_3$	2.1×10^{-1}
H	2.6×10^{-3} [b]
p-Cl	3.7×10^{-3}
m-Cl	6.8×10^{-5}
$m\text{-}CF_3$	3.9×10^{-6}

[a] The concentration of CAN was always 3×10^{-3}M, that of substrate ranged from 3×10^{-2} to 3×10^{-1}M; AcOH was purged with nitrogen. [b] k is 3.4×10^{-3} $M^{-1}s^{-1}$ when the reaction is carried in the presence of $Ce(NO_3)_3$, 1.8×10^{-3}M.

The kinetic data clearly show that the reaction rate is strongly influenced by the nature of the ring substituent. When these data are plotted against the substituent σ^+ values a ρ value of -5.4 is calculated (r = 0.981). This high and negative ρ value clearly supports the operation of an electron transfer mechanism (Scheme), where the benzyl radical formed from the aryltrimethylsilane radical cation (presumably via reaction with AcOH) reacts with CAN to give the products mostly by an oxidative ligand transfer, as already observed in the CAN-promoted oxidations of alkylaromatics[3]. The absence of a retarding effect of Ce(III)

$$ArCH_2SiMe_3 + Ce^{IV}ONO_2 \longrightarrow ArCH_2SiMe_3\rceil^{+\cdot} + Ce^{III}ONO_2$$

$$ArCH_2SiMe_3\rceil^{+\cdot} + AcOH \longrightarrow ArCH_2^{\cdot} + AcOSiMe_3 + H^+$$

$$ArCH_2^{\cdot} + Ce^{IV}ONO_2 \xrightarrow{AcOH} ArCH_2ONO_2 + ArCH_2OAc$$

Scheme

suggests a rate determining formation of the radical cation.

In line with the electron transfer mechanism is the observation that the reaction of benzyltrimethylsilane with CAN is much faster than that of toluene. Thus, *no reaction* between toluene and CAN takes place under the conditions used in the present work. Even mesitylene reacts with CAN.in AcOH at a rate which is still much lower (100 times) than that of benzyltrimethylsilane[4]! A significantly different reactivity of toluene and benzyltrimethylsilane has also been qualitatively noted in the photoreaction of these substrates sensitized by iminium salts[5], a reaction suggested to occur by an electron transfer mechanism.

This difference can reasonably be attributed to the lower oxidation potentials of benzyltrimethylsilanes with respect to those of the corresponding methylbenzenes (i.e. benzyltrimethylsilane and toluene have E_p values, *vs.* SCE, which are 1.84[6] and 2.25 V[7], respectively). Interestingly, in this respect, the reactivity of benzyltrimethylsilane nicely fits the log k/E_p plot for the CAN-induced reaction of methylbenzenes (Figure), which clearly indicates that the abstraction of an electron from the aromatic ring plays the major role in the side-chain oxidation of both methylbenzenes and benzylsilanes.

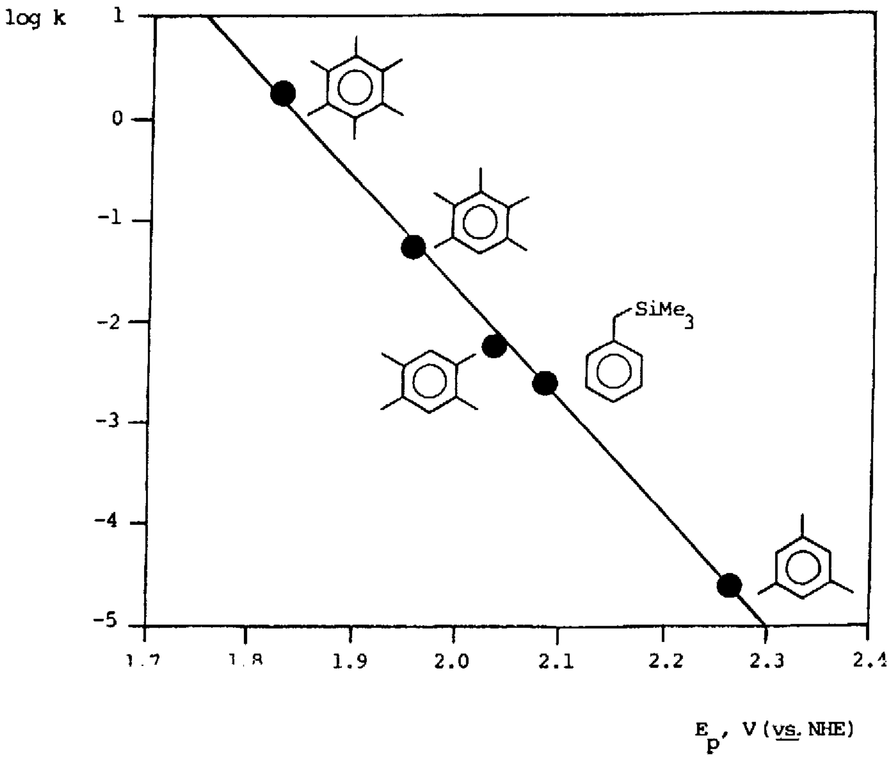


Figure. Plot of reactivity against E_p values data for the oxidation of polymethylbenzenes and benzyltrimethylsilane with CAN in AcOH. Data from ref. 4 and 8.

It has been suggested that the relatively low E_p values for benzylic silanes depend up on the strong hyperconjugative interaction between the σ C-Si bond and the π aromatic system[9]. This interaction weakens the C-Si bond, so that the cleavage of this bond is kinetically most favored decomposition mode of the benzylsilane radical cation.

Finally, it has recently been observed that when benzylic silanes react with free radical species, only a hydrogen atom transfer reaction from the methylene group occurs, and the C-Si bond remains intact[10]. We therefore suggest that the reactions of benzylic silanes may represent a mechanistic criterion allowing discrimination between electron tarnsfer and hydrogen atom transfer mechanisms in oxidation reactions, a distinction which nowadays is of very great importance, in view of the increasing interest in electron transfer reactions in organic chemistry[11].

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References and Notes

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