Oxidative Cleavage of Carbon–Silicon Bonds by Dioxygen: Catalysis by a Flavin–Dihydronicotinamide Redox System

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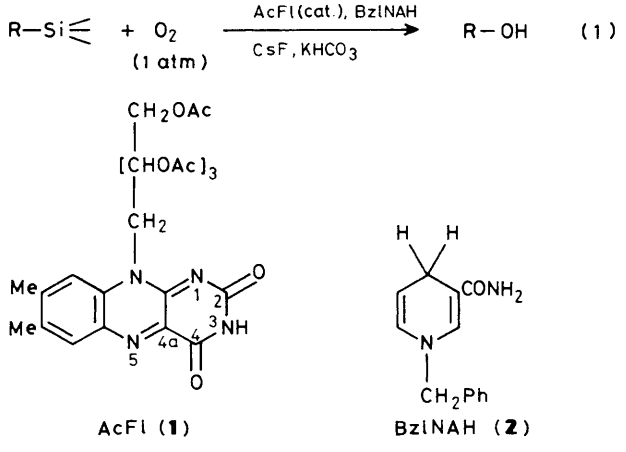
Carbon–silicon bonds in alkoxy- or fluoro-silanes readily undergo cleavage by dioxygen (molecular oxygen), catalysed by tetra-acetylriboflavin (5—10 mol %) in the presence of *N*-benzyl-1,4-dihydronicotinamide as reductant, together with fluoride ions as an essential additive.

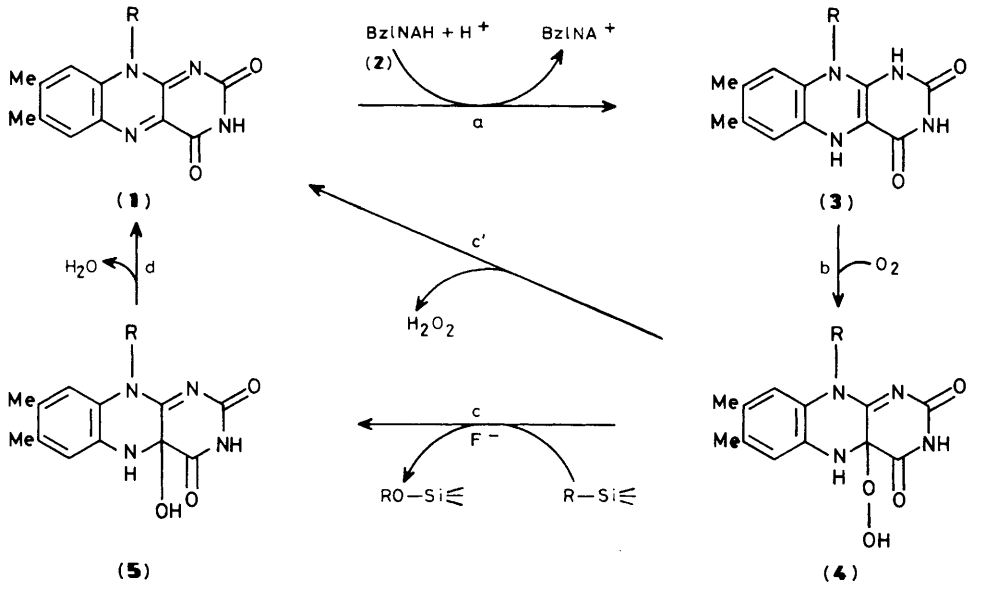
A high resistance to oxidizing agents and towards aerobic oxidation is an outstanding property of organosilicon compounds, which have found a wide range of uses in the silicone industry.[1] However, we have recently reported the oxidative cleavage of certain carbon–silicon bonds[2] by hydrogen peroxide[3] and by peroxy acids;[4] these new oxidations are finding a variety of synthetic uses.[5] We now report an efficient cleavage of carbon–silicon bonds by dioxygen (molecular oxygen), catalysed by tetra-acetylriboflavin (AcFl) (**1**), in the presence of *N*-benzyl-1,4-dihydronicotinamide(BzlNAH) (**2**) as reductant [equation (1)].

This represents the first application to organosilicon compounds of a biomimetic oxygenation system, based on enzymic flavin-dependent oxygen transfer, and analogous to the mono-oxygenases which catalyse epoxidation of alkenes, hydroxylation of hydroxybenzoates, oxygen transfer to sulphur and nitrogen compounds, and Baeyer–Villiger-type oxygenation of ketones.[6,7] It has been suggested that the key intermediates in these oxygenation reactions are 4a-hydroperoxyflavins (**4**), which tend to decompose to hydrogen peroxide and (**1**). The present oxygenation of carbon–silicon bonds may involve a similar catalytic cycle (Scheme 1). The organosilicon compounds may be oxidized by 4a-hydroperoxyflavin (**4**) (step c), or by H_2O_2 generated in step c′. These steps require at least one functional group on silicon, and the presence of fluoride ions, as in our previous oxidations with hydrogen peroxide or peroxy acids.[2–4] The primary products (alkoxysilanes) may be hydrolysed to the corresponding alcohols by water produced in the catalytic cycle.

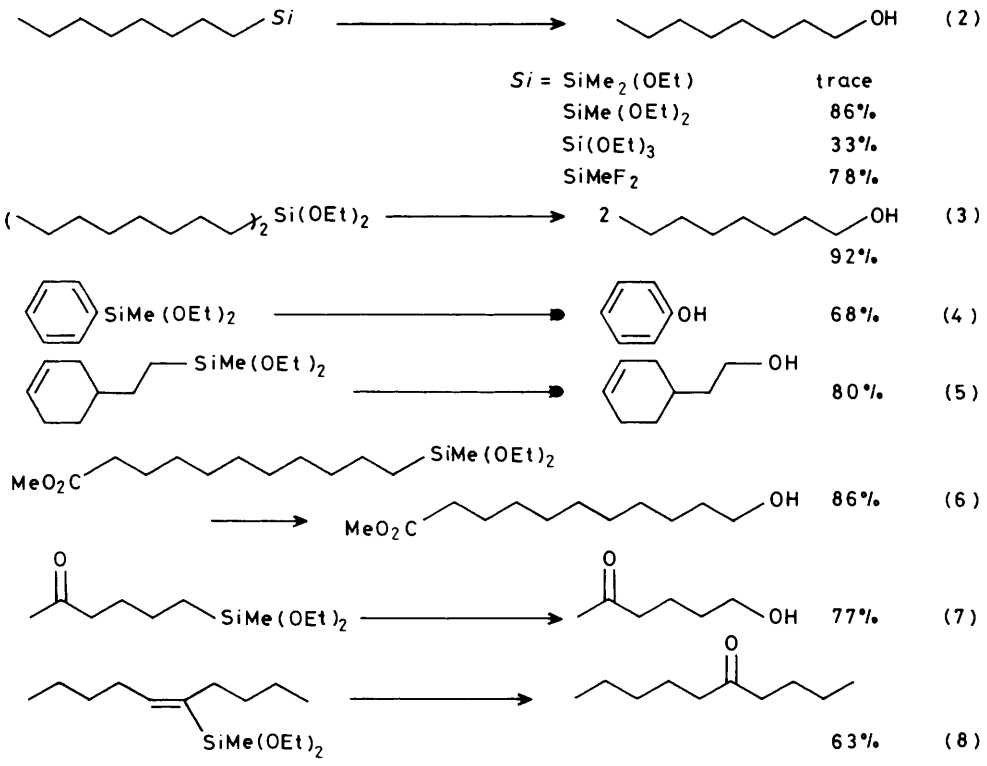
A typical experimental procedure is as follows. A mixture of diethoxy(methyl)(octyl)silane (1 mmol), $KHCO_3$ (1 mmol), CsF (6 mmol), AcFl (**1**)[8†] (0.1 mmol; 10 mol %), and BzlNAH (**2**)[9] (4 mmol; 2 equiv. per Si–C bond) in 1 : 1 dry tetrahydro-



† Acetylation of riboflavin was accelerated by addition of 4-dimethylaminopyridine as a catalyst.



Scheme 1



furan (THF)–dry ethanol (50 ml) (making a 2×10^{-2} M-solution) was stirred at 50 °C in the dark under 1 atm of dioxygen (balloon). After several hours, more BzlNAH (1 equiv.) was added, and the mixture was stirred for a total of 10—20 h. The starting silicon compound had then disappeared completely (g.l.c.). Solvents were evaporated off and the brown tarry residue was diluted with ether and filtered. The filtrate was evaporated and the residue subjected to column chromatography [silica gel; hexane–ethyl acetate (5 : 1)] to give pure octan-1-ol in 86% yield (of isolated material).

The oxidation was dependent upon several factors, as observed with (n-C_8H_{17})SiMe$(OEt)_2$ as model substrate; the yields (g.l.c.) of octanol given refer to the standard conditions, unless otherwise stated. (i) The amount of catalyst (**1**) may be reduced to 5 mol % (75% yield), but 1 mol % is not sufficient (<20% yield). (ii) The presence of fluoride ion (CsF, not KF) is essential (2 equiv., 62%; 1 equiv., 36%; 0.5 equiv., 9% yield). In the absence of CsF no oxidation occurs; starting material is unchanged. (iii) The oxidation may be achieved in air instead of pure dioxygen: 5 mol % of (**1**), 18 h, 64% yield.

(iv) The concentration of the substrate may also be important. With a 5×10^{-2} M-solution lower yields (55%) were obtained. This may be related to the total amount of dioxygen dissolved in the reaction mixture.‡ (v) The oxidation proceeds at lower temperatures, but slowly (at 25 °C for 3 h, 17%; for 23 h, 58% yield).

Results obtained under the standard conditions are summarized in equations (2)—(8). A dialkoxy silicon compound was more reactive than a monoalkoxy analogue [equation (2)]; the latter was recovered, but reacted in DMF[3,4] to form octan-1-ol in 66% yield after 15 h. A dialkyl silicon compound is converted into the alcohol [equation (3)]. A phenyl derivative gives phenol [equation (4)]. Several functional groups are unaffected by the oxidation. In particular, oxidative cleavage of carbon–silicon bonds leaves intact alkene and ketone functionalities [equations (5) and (7)], which might be expected to undergo epoxidation[7h] or Baeyer–Villiger oxidation.[7a] Alkensylsilanes thus can be oxidized to the corresponding ketones without formation of esters [equation (8)].

This simple oxidative cleavage of carbon–silicon bonds by dioxygen catalysed by a biomimetic redox system should be of synthetic and mechanistic interest. The present results might throw light on problems concerning the decomposition pathways of organosilicon compounds in the environment and their non-existence in nature.[11]

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‡ Solubility of O_2 (mol fraction): 5.635×10^{-4} at 323.15 K in EtOH; 8.16×10^{-4} at 298.15 K in THF.[10]