Silyl enol ether cation radicals in solution: nucleophile assisted Si–O bond cleavage

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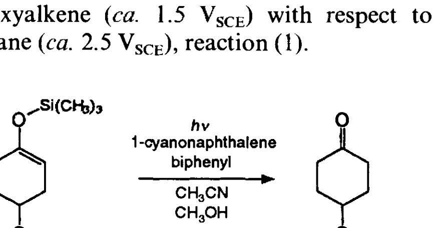
The sterically hindered silyl enol ethers **1**–**3** have been synthesised and the structure of the sterically most congested representative, *i.e.* **2**, has been elucidated by X-ray analysis. The corresponding cation radicals $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$ have been generated in solution through electrochemical and chemical electron transfer. The one-electron oxidation with 2 equivalents of $[Fe(phen)_3](PF_6)_3$ furnished in all three cases 3-mesityl-4,6,7-trimethyl-2-phenylbenzofuran **4** in high yield. In cyclic voltammetry experiments the kinetics of the Si–O bond cleavage in the silyl enol ether cation radicals in dichloromethane and acetonitrile have been determined in the presence of various nucleophiles (methanol, 2-methylpropan-2-ol, pyridine and 2-bromopyridine). From the data, a nucleophile assisted Si–O bond cleavage mechanism has been inferred.

Introduction

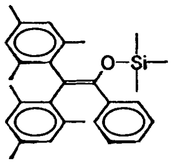
The last decade has witnessed an increasing acceptance within the organic community to consider electron transfer oxidation,[1] one of the conceptually simplest elemental reactions in chemistry, for selective catalytic[2] and stoichiometric transformations.[3] In this context, the chemistry of silyl enol ether cation radicals has received particular attention recently, since they constitute important intermediates in the α-umpolung of ketones and aldehydes,[4] in synthetically useful cyclisations[5] and dimerisations[6] and in redox-triggered protection group chemistry.[7] In addition, various other α-substitution reactions of silyl enol ethers,[3] *e.g.* in the presence of cerium(IV) ammonium nitrate, silver oxide or tetranitromethane, may proceed *via* an electron transfer induced mechanism.[8] For all the cited transformations above the bond cleavage of $RX^{\cdot+}$ into fragments $R^{\cdot}$ and X^+ or R^+ and $X^{\cdot}$, the so called catiomesolytic cleavage,[9] is a process of paramount importance since it limits directly the lifetime of the odd-electron species.

A great deal of effort has been devoted to the protection of carbonyl groups and selective deblocking strategies, due to the widespread occurrence of ketones and aldehydes in organic transformations.[10] In this context, an elegant demonstration of the potential of catiomesolytic cleavage reactions was provided by Gassman,[7] who demonstrated that silyl enol ethers can be deprotected selectively to the parent carbonyl compounds *via* the corresponding silyl enol ether cation radicals, even in the presence of a silyl alkyl ether group. This transformation is successful because of the decisively lower oxidation potential of a siloxyalkene (*ca.* 1.5 V_{SCE}) with respect to that of a siloxyalkane (*ca.* 2.5 V_{SCE}), reaction (1).



(1)

To achieve maximum efficiency and selectivity in the deprotection step the rate of the mesolytic Si–O bond cleavage should be as fast as possible. Unfortunately, there is a general lack of rate data and of mechanistic details concerning mesolytic fragmentation reactions, including kinetic data for the cleavage of silyl enol ether cation radicals, which renders reliable predictions almost impossible. Hence, we decided to investigate the one-electron oxidation of silyl enol ethers **1**–**3**. Due to the steric hindrance about the β-carbon exerted by the aryl groups, side reactions of the cation radicals, in particular dimerisation and attack by nucleophiles, are completely excluded, which should allow selective study of the Si–O bond cleavage.



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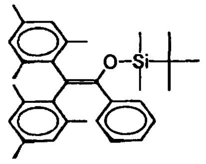

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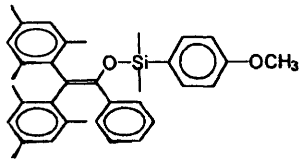

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Results

Synthesis

The silyl enol ethers were synthesised by a modification of the method of Cazeau *et al.*[11] starting from 2,2-dimesityl-1-phenylethenol and the appropriate silyl chlorides (for **1** and **3**) or silyl trifluoromethanesulfonate (for **2**), respectively. All three products were crystallised from acetonitrile to afford colourless rhombic crystals. The yields were 60%, 31% and 42% for **1**, **2** and **3**, respectively.

X-Ray structure

The crystal structure of silyl enol ether **2** exhibits the same three-blade propeller conformation as the parent enol, the 2,2-dimesityl-1-phenylethenol (Fig. 1).[12] All three aryl groups are appreciably twisted from planarity with the double bond, although not in a symmetrical fashion, leading to an effective shielding of C(2) prohibiting any attack at this position.

Table 1 Selected data for the structure of **2**

Bond distances (Å)		Bond angles (°)		Torsional angles (°)	
C(1)–C(2)	1.345(3)	O–C(1)–C(2)	122.6(2)	Si–O–C(1)–C(2)	71.33(0.24)
C(1)–O	1.372(2)	C(1)–C(2)–C(31)	121.1(2)	C(1)–C(2)–C(31)–C(32)	58.50(0.25)
O–Si	1.658(1)	C(2)–C(1)–C(21)	125.5(2)	O–C(1)–C(2)–C(31)	7.10(0.27)
		C(1)–C(2)–C(41)	120.4(2)	C(21)–C(1)–C(2)–C(41)	12.55(0.28)

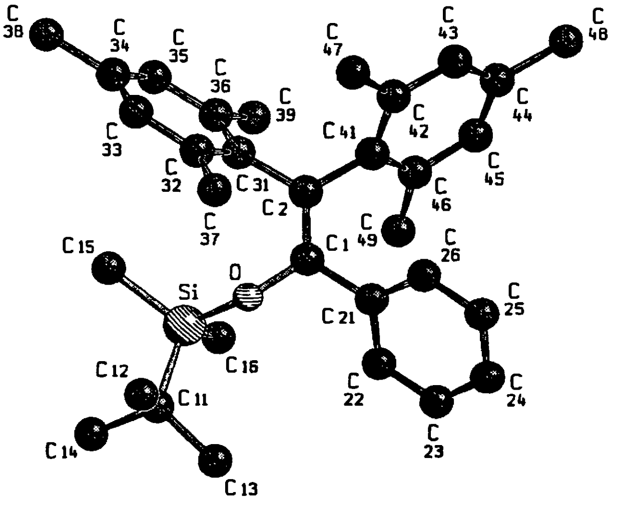


Fig. 1 Schakal plot of silyl enol ether **2** as determined by X-ray structure analysis

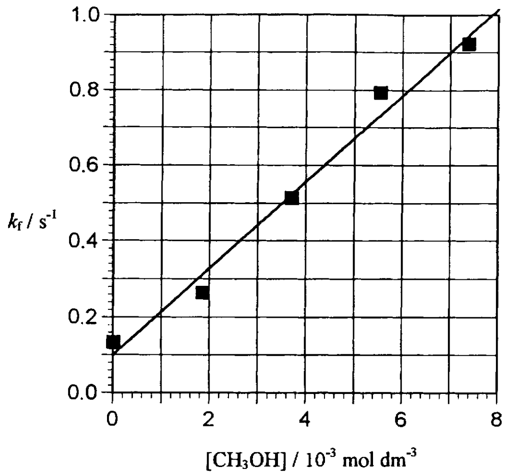
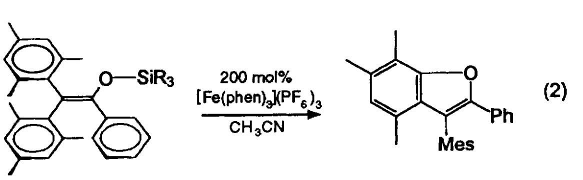


Fig. 2 Plot of pseudo-first-order rate constants *versus* concentration of methanol for system **2** in dichloromethane

In comparison with the 2,2-dimesityl-1-phenylethenol the O–C(1)–C(2) and the C(1)–C(2)–C(31) angles are increased by 2° and 3°, respectively, and the C(2)–C(1)–C(21) angle is decreased by nearly 4°, witnessing a significantly enlarged buttressing effect of the large trialkylsiloxy substituent onto the phenyl and the *Z*-mesityl groups in comparison with the enol. In line with the steric compression the C(1)=C(2) double bond is twisted from planarity as documented by the torsional angles C(21)–C(1)–C(2)–C(41) = 12.55° and O–C(1)–C(2)–C(31) = 7.10°.

Chemical oxidation

In all three cases the one-electron oxidation of silyl enol ethers **1**, **2** and **3** with [Fe(phen)$_3$](PF$_6$)$_3$ (phen = 1,10-phenanthroline) (**FePhen**, $E_{\frac{1}{2}}$ = 0.70 V *vs.* ferrocene/ferrocenium), reaction (2), afforded as the sole product 3-mesityl-4,6,7-trimethyl-2-phenylbenzofuran **4** in high yields.



(2)

1-3

4

78 - 93 %

Cyclic voltammetry with scan rates of 20–500 mV s^{-1}

To probe the stability and reactivity of $1^{\cdot+}$, $2^{\cdot+}$ and $3^{\cdot+}$ we have recorded the cyclic voltammograms (CVs) of the silyl enol ethers. The CVs exhibited in all three cases irreversible anodic waves in acetonitrile indicating a fast chemical step following the electrochemical oxidation. Characteristically, with all model compounds a decrease of $i_{pa}v^{-\frac{1}{2}}$ with increasing v was observed (i_{pa}: anodic current, v: sweep rate) indicative of an ECE-mechanism. The anodic peak potentials (E_{pa} *vs.* ferrocene/ferrocenium at 100 mV s^{-1}) are 0.65 V for the trimethylsilyl enol ether **1**, 0.73 V for the *tert*-butyldimethylsilyl enol ether **2**, and 0.68 V for the 4-methoxyphenyl(dimethyl)silyl enol ether **3**, respectively. These peak potentials are only marginally higher than that of 2,2-dimesityl-1-phenylethenol which has recently been measured as 0.61 V.[13] All silyl enol ether oxidation waves were followed by a second, anodically shifted wave at $E_{\frac{1}{2}}$ = 0.87 V (500 mV s^{-1}) which exhibited a nearly reversible behaviour which is characteristic of a common product being formed in the oxidation of **1**–**3**.

In dichloromethane as well the anodic waves for **1** and **3** proved to be irreversible whereas, however, the CV of the *tert*-butyldimethylsilyl enol ether **2** exhibited an almost reversible wave at 0.67 V (100 mV s^{-1}) indicating that this cation radical is much more persistent than $1^{\cdot+}$ and $3^{\cdot+}$. For $2^{\cdot+}$ the rate of fragmentation in dichloromethane was determined as k_f = 1.3×10^{-1} s^{-1} at room temperature using a working curve for an ECEC-mechanism following the analysis according to Nicholson and Shain.[14] Furthermore, cyclic voltammetry experiments with **2** in the presence of nucleophiles have been performed, which indicated that the reduction wave decreased with increasing concentration of the added nucleophile. As the pseudo-first-order rate constants, determined as described above, depended linearly on the nucleophile concentration, the second-order rate constants could readily be calculated. All these data are listed in Table 2. As exemplified for the case of methanol in Fig. 2, the slope of the plot of the pseudo-first-order rate constants *versus* the concentration of the nucleophile gave the second-order rate constant.

Fast scan CV experiments

Higher scan rates diminish the timescale of the cyclic voltammetry experiment so that one-electron reduction of short lived cation radicals may compete with the follow-up reaction. Thus,

Table 2 Pseudo-first-order rate constants for silyl enol ether $2^{\cdot+}$ in dichloromethane as a function of added nucleophile and the corresponding second-order rate constants

Nucleophile	Concentration of nucleophile/ 10^{-3} mol dm^{-3}	Pseudo-first-order rate constants k_f/s^{-1}	Second-order rate constant $k_f/10^2$ dm^3 mol^{-1} s^{-1}
Without nucleophile	—	0.13	
Pyridine	1.44	0.22	3.7
	2.47	0.68	
	3.09	1.31	
2-Bromopyridine	2.56	0.27	1.1
	4.10	0.39	
	5.64	0.75	
Methanol	1.85	0.26	1.1
	3.70	0.51	
	5.53	0.79	
	7.38	0.92	
2-Methylpropan-2-ol	3.95	0.21	0.15
	9.22	0.27	
	14.50	0.31	
	23.73	0.35	
	29.78	0.79	

Table 3 Rate constants k_f for the follow-up reaction of the silyl enol ether cation radicals at room temperature

	k_f/s^{-1}		
Solvent	$1^{\cdot+}$	$2^{\cdot+}$	$3^{\cdot+}$
Acetonitrile	$> 10^4$	6.0×10^2	$> 10^4$
Dichloromethane	1.3×10^2	1.3×10^{-1}	9.4×10^1

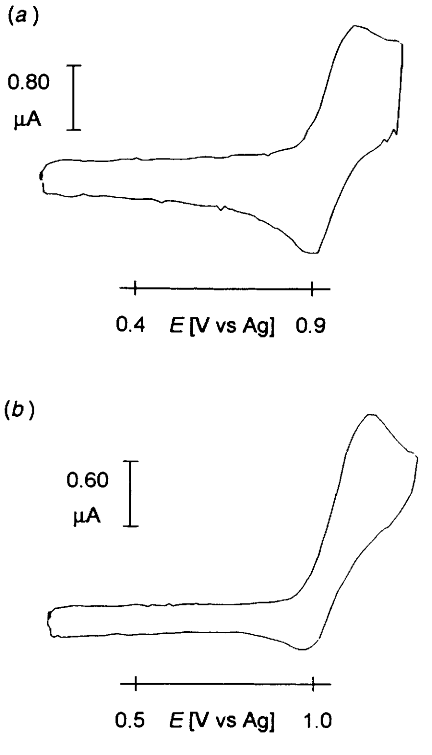


Fig. 3 Cyclic voltammetric waves of **3** at 1000 V s^{-1} in CH_2Cl_2 (*a*) without nucleophile and (*b*) containing 1.2×10^{-2} mol dm^{-3} methanol at room temperature

in dichloromethane the CVs of systems **1** and **3** become more and more reversible beyond 50 V s^{-1} whereas in acetonitrile for these systems still only irreversible waves are observed. Hence, reversible oxidation potentials *vs.* ferrocene/ferrocenium at a scan rate of 2000 V s^{-1} could be determined for **1** ($E_{\frac{1}{2}}$ = 0.68 V) and **2** ($E_{\frac{1}{2}}$ = 0.69 V) in dichloromethane. In contrast, the bulkier *tert*-butyldimethylsilyl enol ether **2** exhibits a reversible wave in acetonitrile at scan rates >300 V s^{-1}. Following the same kinetic analysis as described above, the pseudo-first-order rate constants k_f for the follow-up reaction for systems **1–3** were measured in two solvents (see Table 3, Fig. 3).

As in the case of $2^{\cdot+}$, the pseudo-first-order rate constants of the chemical follow-up reaction k_f of $1^{\cdot+}$ and of $3^{\cdot+}$ in the presence of nucleophiles were determined in dichloromethane resulting in a linear increase of the rate constants with the nucleophile concentration as shown in Tables 4 and 5. From the slopes of the appropriate correlations, the second-order rate constants were evaluated. Silyl enol ether cation radical $1^{\cdot+}$ gives $k_f = 8.7 \times 10^5$ dm^3 mol^{-1} s^{-1} and 2.1×10^5 dm^3 mol^{-1} s^{-1} for methanol and 2-methylpropan-2-ol, respectively, whereas k_f for $3^{\cdot+}$ in the presence of methanol is 1.1×10^5 dm^3 mol^{-1} s^{-1}.

Discussion

Selectivity of Si–O bond cleavage in silyl enol ether cation radicals

A concise picture of the Si–O bond fragmentation in silyl enol ether cation radicals is now provided by our electrochemical and chemical oxidation results. The one-electron oxidation of silyl enol ether **1–3** with **FePhen** yields as the only product 3-mesityl-4,6,7-trimethyl-2-phenylbenzofuran **4** in good yields which is also the product of the one-electron oxidation of 2,2-dimesityl-1-phenylethenol.[15] As **4** displays a reversible wave at $E_{\frac{1}{2}}$ = 0.87 V, the second anodic wave in the CVs of the silyl enol ethers at exactly the same half-wave potential can be definitely ascribed to the oxidation of the benzofuran already formed in the timescale of the cyclic voltammetry experiment.

The experimental results of the one-electron oxidation chemistry of **1–3** can be summarized as follows. (*i*) As a stable

Table 4 Pseudo-first-order rate constants for silyl enol ether $1^{\cdot +}$ in dichloromethane as a function of added nucleophile and the corresponding second-order rate constants

Nucleophile	Concentration of nucleophile/ 10^{-3} mol dm^{-3}	Pseudo-first order rate constants k_f/s^{-1}	Second order rate constant $k_f/10^5$ dm^3 mol^{-1} s^{-1}
Without nucleophile	—	1.3×10^2	
Methanol	6.2	6.7×10^3	8.7
	12.3	1.2×10^4	
	18.5	1.6×10^4	
	36.9	3.3×10^4	
2-Methylpropan-2-ol	6.2	2.4×10^3	2.1
	12.4	3.0×10^3	
	18.5	4.9×10^3	
	37.6	8.3×10^3	

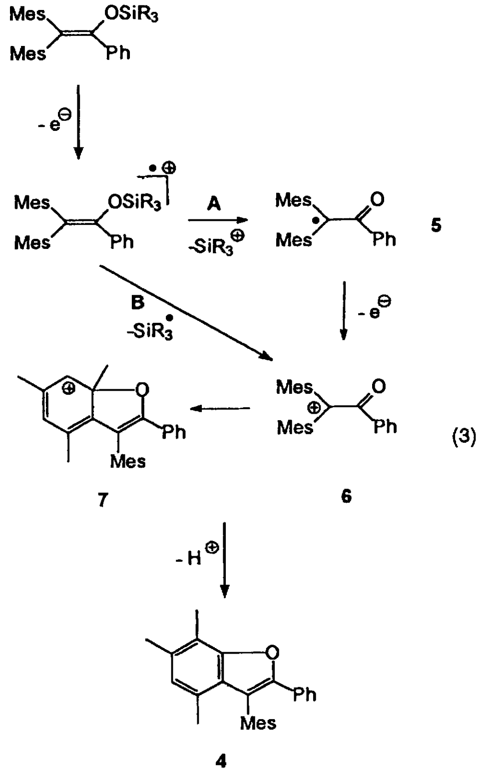
Table 5 Pseudo-first order rate constants for silyl enol ether $3^{\cdot +}$ in dichloromethane as a function of added methanol with a second-order rate constant $k_f = 1.1 \times 10^5$ dm^3 mol^{-1} s^{-1} derived thereof

Concentration of methanol/ 10^{-3} mol dm^{-3}	Pseudo-first-order rate constants k_f/s^{-1}
Without methanol	9.4×10^1
6.2	3.7×10^2
12.3	8.0×10^2
21.5	2.0×10^3
30.8	2.5×10^3
36.9	2.9×10^3
46.1	4.9×10^3
58.4	6.9×10^3
70.7	7.4×10^3

product the benzofuran **4** is obtained in both the chemical oxidation and cyclic voltammetry experiment. (*ii*) $i_{pa}v^{-\frac{1}{2}}$ Decreases with increasing sweep rate. (*iii*) i_{pc}/i_{pa} Approximates 1 with increasing sweep rate. Importantly, the latter two criteria do not allow the differentiation between an EC$_{irr}$- or ECE-mechanism, hence it is not possible by using the Nicholson–Shain [14] criteria to differentiate between the two modes of bond cleavage, **A** and **B** [reaction (3)]. From formation of the benzofuran **4** it can be inferred that the benzoyl(dimesityl)-methyl cation **6** is involved because it is known to undergo cyclisation to the benzofuran,[13] but again this does not allow us to distinguish between the two fragmentation selectivities **A** and **B**.

However, there are two strong arguments for selective Si–O bond cleavage according to mechanism **A**: (*i*) in line with mechanism **B**, which was recently established for the O–CO bond fragmentation in enol acetates,[16] we would only expect a moderate rate increase (a factor of 10–20) when switching from dichloromethane to acetonitrile, but an acceleration of $> 10^3$ was found; (*ii*) fragmentation according to **B** should not result in a nucleophile assisted bond cleavage.[16] In addition, the PET oxidations of simple silyl enol ethers [5,7] clearly indicate that α-carbonyl radicals are the direct cleavage products, since only these can afford the carbonyl products after back electron transfer or hydrogen atom abstraction.

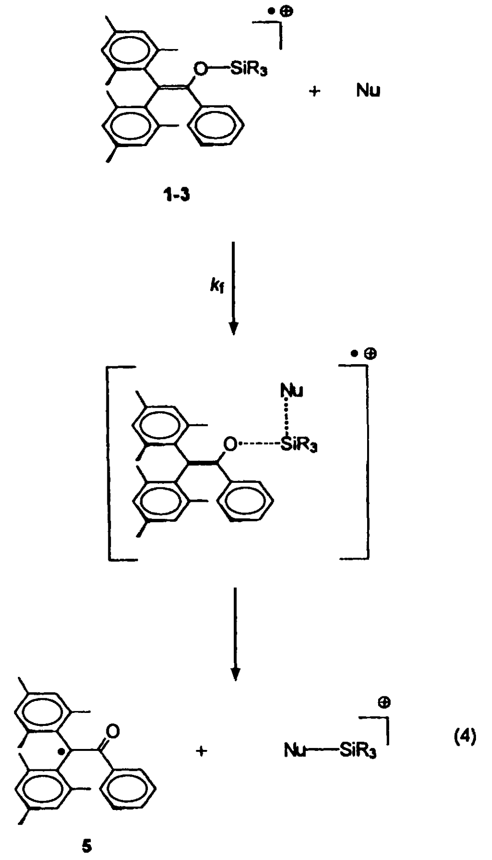
Hence, the silyl enol ether cation radicals $1^{\cdot +}$–$3^{\cdot +}$ fragment into the benzoyl(dimesityl)methyl radical **5** and the appropriate silylium ion which is expected to be associated with the solvent.[17] The α-carbonyl radical **5** is immediately oxidized further because its oxidation potential is significantly lower than those of the silyl enol ethers **1**–**3** [E_{pa} (**5**) = 0.24 V [13] *vs.* E_{pa} = 0.65–0.73 V]. After a Nazarov-type cyclisation of the resulting α-carbonyl cation **6** the cyclohexadienyl cation **7** is formed which subsequently undergoes [1,2]-methyl-shift and deprotonation to yield the benzofuran **4**. Thus, the mechanism analogous to that of the one-electron oxidation chemistry of 2,2-dimesityl-1-phenylethenol.



Kinetics of Si–O bond cleavage in silyl enol ether cation radicals

The kinetic results provide a strong case for a nucleophile assisted Si–O bond cleavage mechanism, consonant with observations provided in a seminal paper by Dinnocenzo *et al.* on the photoinduced electron transfer fragmentation of alkylsilanes.[18] Therein, and in following papers it was demonstrated that benzyltrialkylsilane cation radicals underwent C–Si bond cleavage assisted by several nucleophilic addends as supported by a whole battery of mechanistic tests.[19] In agreement with their mechanistic hypothesis we find that the fragmentation rate constant in our systems increased: (*i*) when switching from dichloromethane to acetonitrile; (*ii*) the stronger the nucleophile, *e.g.* methanol *vs.* pyridine; (*iii*) the less hindered the nucleophile, *e.g.* 2-methylpropan-2-ol *vs.* methanol; and (*iv*) the smaller the alkyl groups at the silyl functionality, *e.g.* *tert*-

butyldimethylsilyl *vs.* trimethylsilyl. Hence, as a whole these results can only be rationalised by postulating an attack of the nucleophile onto the silyl group in the rate determining step of Si–O bond dissociation [reaction (4)]. Indeed, the rate constants in Tables 2–5 convincingly document the importance of steric hindrance at the silyl atom, whereas mesomeric effects, *e.g.* in $3^{\cdot +}$, only play a minor role, in agreement with kinetic results for hydride transfer from hydrosilanes.[20]



As silyl enol ethers have recently found use as enol equivalents in one-electron oxidation functionalisations,[4] it is interesting to compare the O–Si cleavage in $1^{\cdot +}$–$3^{\cdot +}$ with the O–H cleavage in the corresponding enol cation radical. Recently, the kinetics of the deprotonation of the 2,2-dimesityl-1-phenylethenol cation radical in dichloromethane at room temperature have been determined[21] providing $k_f = 2 \times 10^4$ s^{-1} which is more rapid than the O–Si cleavage reaction in $1^{\cdot +}$–$3^{\cdot +}$ by a factor of 10^2 to 10^5 (see Table 3). Hence, only by the proper choice of the alkyl groups at the Si atom may silyl enol ethers react as enol substitutes. On the other hand, variation of R at the silyl atom allows one to slow down O–Si bond cleavage in a controlled manner if one wishes the silyl enol ether cation radical to react prior to bond fragmentation with π-nucleophiles for example, a strategy already used in synthetically interesting cyclisation reactions.[5]

As oxidation potentials of enols are still rare, it may be very convenient to approximate them through the oxidation potentials of silyl enol ethers, as demonstrated through the comparison of $E_{\frac{1}{2}}$ **1** = 0.68 V *vs.* $E_{\frac{1}{2}}$ (2,2-dimesityl-1-phenylethenol) = 0.67 V, both measured in dichloromethane at high scan rates.

In summary, we have for the first time presented experimental evidence that the oxidative Si–O bond cleavage in silyl enol ethers is assisted by nucleophiles. It is shown that the silyl enol ether cation radicals $1^{\cdot +}$–$3^{\cdot +}$ react analogously to the parent enol cation radical with the silylium ion displacing the proton.

Experimental

General aspects

Acetonitrile was purchased from Riedel-de-Haen (Chromasolv) and distilled from CaH_2. Dichloromethane was purchased from Roth (Rotipuran) and distilled from P_4O_{10}. Tetrabutylammonium hexafluorophosphate was purchased from Fluka. 2,2-Dimesityl-1-phenylethenol was prepared as described in the literature.[12] For the cyclic voltammetry measurements in the range of 20–500 mV s^{-1} a potentiostat 362 from Princeton Applied Research and an XY-recorder 7004 B from Hewlett-Packard were used. The fast scan cyclic voltammetry experiments were performed with a digitising oscilloscope HP 54510 A, a function generator HP 3314 A, both Hewlett-Packard, and a potentiostat developed by Professor Amatore, Paris.[22] The mass spectra were determined using a MAT90, Finnigan, at 70 eV. The NMR spectra were measured on a Bruker model AC 250 NMR spectrometer, the IR spectra on a spectrometer 1605 FT-IR, Perkin-Elmer, using KBr plates. Elemental analyses were performed at the Institute for Inorganic Chemistry, University of Würzburg. Melting points were determined on a Büchi SMP-20 apparatus and are uncorrected.

2,2-Dimesityl-1-phenyl-1-(trimethylsiloxy)ethene 1

2,2-Dimesityl-1-phenylethenol (1.00 g, 2.8 mmol) and NEt_3 (0.39 g, 3.9 mmol) were dissolved in a mixture of anhydrous acetonitrile (10 cm^3) and anhydrous dichloromethane (6 cm^3). The reaction mixture was stirred for 10 min, then NaI (0.55 g, 3.7 mmol) and $Si(CH_3)_3Cl$ (0.40 g, 3.7 mmol) were added. After heating to reflux for 3 days the mixture was diluted with dichloromethane (10 cm^3), cooled to 0 °C and washed with cold saturated aqueous $NaHCO_3$ (20 cm^3). The organic layer was dried over Na_2SO_4 and filtered. The solvent was evaporated and the residue was crystallised twice from acetonitrile to yield rhombic, colourless crystals of the title compound (0.72 g, 60%), mp 143–144 °C (Found: C, 81.9; H, 8.6. $C_{29}H_{36}OSi$ requires: C, 81.25; H, 8.46%); *m/z* (EI) 73, 179, 219, 323, 413, 428 (M^+); δ_H($CDCl_3$; 250 MHz) 7.27–7.07 (5 H, m, Ph-H), 6.82 (2 H, s, mesityl-H), 6.65 (2 H, s, mesityl-H), 2.29 (6 H, s, mesityl-CH_3), 2.20 (6 H, s, mesityl-CH_3), 1.96 (6 H, s, mesityl-CH_3), −0.01 [9 H, s, $Si(CH_3)_3$]; ν_{max}/cm^{-1} 2940 (C–H), 2900 (C–H), 1610 (C=C), 1590, 1445, 1255, 1090, 860, 700.

1-(*tert*-Butyldimethylsiloxy)-2,2-dimesityl-1-phenylethene 2

To a solution of 2,2-dimesityl-1-phenylethenol (1.42 g, 4.0 mmol) in anhydrous CH_2Cl_2 (10 cm^3) was added NEt_3 (0.60 g, 5.0 mmol) first and then *tert*-butyldimethylsilyl trifluoromethanesulfonate (1.16 g, 4.4 mmol) after stirring for 2 min. The mixture was heated to reflux for 42 h and then diluted with CH_2Cl_2 (10 cm^3) cooled to 0 °C and washed with cold saturated aqueous $NaHCO_3$ (20 cm^3). The organic layer was separated and dried over Na_2SO_4. The solvent was almost completely evaporated, and diethyl ether (5 cm^3) was added to dissolve the residue. After removing a red precipitate the solvent was evaporated again and the product was crystallised from CH_3CN to yield rhombic, colourless crystals of the title compound (0.59 g, 31%), mp 112–113 °C (Found: C, 81.8; H, 9.1. $C_{32}H_{42}OSi$ requires: C, 81.64; H, 8.99%); *m/z* (EI) 73, 177, 207, 413, 470 (M^+); δ_H($CDCl_3$; 250 MHz) 7.32–7.30 (2 H, m, Ph-H), 7.15–7.09 (3 H, m, Ph-H), 6.80 (2 H, s, mesityl-H), 6.63 (2 H, s, mesityl-H), 2.26 (6 H, s, mesityl-CH_3), 2.19 (6 H, s, mesityl-CH_3), 2.00 (6 H, s, mesityl-CH_3), 0.92 (9 H, s, Bu^t), −0.23 [6 H, s, $Si(CH_3)_2$]; ν_{max}/cm^{-1} 2910 (C–H), 2840 (C–H), 1610 (C=C), 1595, 1475, 1255, 1160, 840, 790.

Table 6 One-electron oxidation of silyl enol ethers **1**–**3** with **FePhen**

Starting material		**FePhen**	Yield of
Comp.	Quantity (mmol)	(mmol)	**4** (%)[a]
1	0.040	0.080	78
2	0.045	0.090	93
3	0.045	0.090	82

[a] Yields determined by using *m*-nitroacetophenone as an internal NMR reference.

1-[4-Methoxyphenyl(dimethyl)siloxy]-2,2-dimethyl-1-phenylethene 3

To a solution of 2,2-dimesityl-1-phenylethenol (0.52 g, 1.5 mmol) in anhydrous acetonitrile (5 cm^3) and dry dichloromethane (3 cm^3) was added NEt_3 (0.18 g, 1.8 mmol). The solution was stirred for 10 min and then NaI (0.27 g, 1.8 mmol) and 4-methoxyphenyl(dimethyl)silyl chloride[23] (0.36 g, 1.8 mmol) were added. The reaction mixture was heated to reflux for 3 days. After cooling to room temperature the solvent was evaporated and the product was purified by column chromatography (neutral alumina, 4:1 hexane–diethyl ether, R_f = 0.71) to yield a colourless oil which solidified on standing. After crystallisation from acetonitrile colourless needles of the title compound were obtained, mp 124–125 °C (Found: C, 80.45; H, 7.6. $C_{35}H_{40}O_2Si$ requires: C, 80.72; H, 7.74%); *m*/*z* (EI) 135, 165, 323, 412, 520 (M^+); δ_H($CDCl_3$; 250 MHz) 7.38 (2 H, d, *J* 8.0, anisyl-H), 7.16–6.98 (5 H, m, Ph-H), 6.85 (2 H, d, *J* 8.0, anisyl-H), 6.73 (2 H, s, mesityl-H), 6.60 (2 H, s, mesityl-H), 3.82 (3 H, s, OCH_3), 2.25 (6 H, s, mesityl-CH_3), 2.15 (6 H, s, mesityl-CH_3), 1.84 (6 H, s, mesityl-CH_3), 0.15 [6 H, s, $Si(CH_3)_2$]; ν_{max}/cm^{-1} 2928 (C–H), 2856 (C–H), 1610 (C=C), 1599, 1474, 1252, 1081, 830, 780.

One-electron oxidation of silyl enol ethers 1, 2 and 3

Under nitrogen two test tubes were loaded with silyl enol ether (100 mol%) and $[Fe(phen)_3](PF_6)_3$ (200 mol%), respectively. 1.5 cm^3 and 2.5 cm^3 of anhydrous acetonitrile were added to the oxidant and to the silyl enol ether, respectively. Then the silyl enol ether solution was transferred through a syringe to the blue oxidant solution with the colour changing to red immediately. The resulting reaction mixture was then stirred at room temperature for 14 h. The reaction was quenched with aqueous $NaHCO_3$ and the mixture was extracted with dichloromethane. Product analysis was performed by using ^{1}H NMR spectroscopy. The yields of benzofuran **4** are given in Table 6. δ_H($CDCl_3$; 250 MHz) 7.55–7.48 (2 H, m, Ph-H), 7.30–7.17 (3 H, m, Ph-H), 6.98 (2 H, s, mesityl-H), 6.76 (1 H, s, 5-H), 2.54 (3 H, s, 7-CH_3), 2.40, 2.39 (two s, each 3 H, 4- and 6-CH_3), 2.02 (6 H, s, mesityl-*o*-CH_3), 1.89 (3 H, s, mesityl-*p*-CH_3). For complete characterisation see ref. 15.

Cyclic voltammetry

The cyclic voltammetry measurements were performed in a homemade electrochemical cell using a platinum disk (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a silver wire as reference electrode. All potentials were eventually referenced to internal ferrocene. The potential measurements (0.1 V s^{-1} in acetonitrile) and kinetic analysis were performed on a 1 × 10^{-3} mol dm^{-3} solution of the substrate with tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) as the supporting electrolyte. Fast Scan CV in the range of 10–15 000 V s^{-1} was performed with platinum or gold ultramicroelectrodes[24] of 25 or 10 μm diameter applying a substrate concentration of 1 × 10^{-2} mol dm^{-3}.

Kinetic measurements

Rate constants were determined by comparing the experimental i_{pa}/i_{pc} ratios to ones obtained by digital simulation[25] varying k_f, assuming an $E_1C_1E_2C_2$ mechanism including the disproportionation $\mathbf{1}^{\cdot+}$ ($\mathbf{2}^{\cdot+}$, $\mathbf{3}^{\cdot+}$) + **5** ⟶ **1** (**2**, **3**) + **6** as an additional C-step (C_3). The following data were used in the simulation: $E_1 = 0.68$ V, $E_2 = 0.24$ V, $k(C_{1,forw}) = 0.1$–2000 s^{-1}, $k(C_{1,back}) = 10^{-4}$ s^{-1}, $k(C_{2,forw}) = 10^6$ s^{-1}, $k(C_{2,back}) = 10^{-4}$ s^{-1}, k $(C_{3,forw}) = 10^6$ s^{-1}, $k(C_{3,back}) = 0.045$ s^{-1}, $k^0{}_{hetero} = 0.1$ cm s^{-1}. As starting and switching potential we chose 0.4 and 0.9 V, respectively.

The second-order rate constants were obtained from the correlation of the pseudo-first-order rate constants k_f *versus* the concentration of added nucleophile. The error range for all rate determination did not exeed 10%.

Crystal data

$C_{32}H_{42}OSi$, M = 470.8. Monoclinic, a = 15.583(4) Å, b = 9.6480(4) Å, c = 19.677(4) Å, β = 101.82(1)°, V = 2896 Å^3, space group $P2_1/c$ (No. 14), Z = 4, D_c = 1.080 g cm^{-3}, white rhombic crystals. Crystal size: 0.36 × 0.18 × 0.16 mm.

Data collection and processing. Enraf Nonius CAD4 diffractometer, ω–2θ-scan mode using Cu-Kα (λ = 1.541 84 Å) radiation with a graphite monochromator; 5966 reflections measured, 5808 unique, giving 4175 with $I > 2\sigma(I)$.

Structure analysis and refinement. The structure was solved by direct methods and difference Fourier techniques and was refined using full-matrix least-squares refinement. The applied weighting scheme was $\omega(F) = 1/\sigma^2(F)$. All non-H-atoms were refined with anisotropic thermal parameters. H-atoms were found in the difference Fourier map and refined isotropically. Extinction correction was applied (a = 1.1568 × 10^{-6}). The refinement converged at R = 0.045 and R_w = 0.042. All calculations were done with the program system MolEN[26] on a VAXstation 3100 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

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† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1995, Issue 1.

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