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Side-Chain Oxidation of Benzyltrimethylsilanes by Iodosylbenzene in the Presence of Iron and Manganese Porphyrins

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Abstract: Benzyltrimethylsilanes react with iodosylbenzene in the presence of either iron(III) or manganese(III) tetrakis(pentafluorophenyl)porphyrin (TFPPM, with M = Fe, Mn) to give α-hydroxybenzyltrimethylsilanes, which are then rapidly converted into the corresponding benzaldehydes in the reaction medium. In these reactions the active species is the metal-oxo complex, TFPPM(V)=O, formed by iodosylbenzene and TFPPM. A relative reactivity study for a series of ring substituted benzyltrimethylsilanes has shown that when M = Fe, the reaction is quite selective ($\rho = -1.85$), with the *m*-MeO substituent exhibiting a much higher reactivity than expected. When M = Mn, a lower ρ value (-1.15) is observed and no anomalous reactivity is found with the *m*-MeO group. These result suggest that the side-chain hydroxylation of benzyltrimethylsilane by TFPPMn(V)=O occurs by the well known hydrogen atom transfer mechanism. For the corresponding reactions induced by TFPPFe(V)=O a coupled proton/electron transfer mechanism, which might involve the formation of a charge-transfer complex, seems more likely.

A wide variety of oxidative trasformation of organic substances can be performed using iron and manganese porphyrin catalysts, model systems of cytochrome P-450 monooxygenases[1]. Among these processes, hydroxylation of saturated carbon atoms has attracted the most attention for high selectivity and effectiveness.

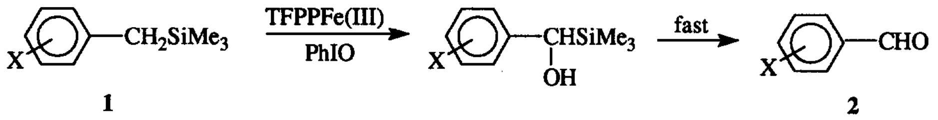
An intensive investigation of the oxidation mechanism of unactivated alkanes has led to the conclusion that the key step involves a hydrogen atom transfer (HAT) from the substrate to the metal-oxo complex, PM(V)=O formed by the interaction of the metalloporphyrin [PM(III)] with a suitable oxygen donor (i. e. iodosylbenzene)[1,2]. As shown in Scheme 1, a radical pair is obtained, which forms the hydroxylated product by an in cage oxygen rebound.More recent work has shown that, most probably the same mechanism also holds for the benzylic hydroxylation, a reaction involving more easily oxidizable compounds[3,4].

$$\mathrm{PM(III)} + \mathrm{PhIO} \longrightarrow \mathrm{PM(V){=}O} + \mathrm{PhI}$$

$$\mathrm{PM(V){=}O} + \mathrm{RH} \longrightarrow \mathrm{PM(IV)\text{-}OH} \,//\, \mathrm{R}^{\cdot} \longrightarrow \mathrm{PM(III)} + \mathrm{ROH}$$

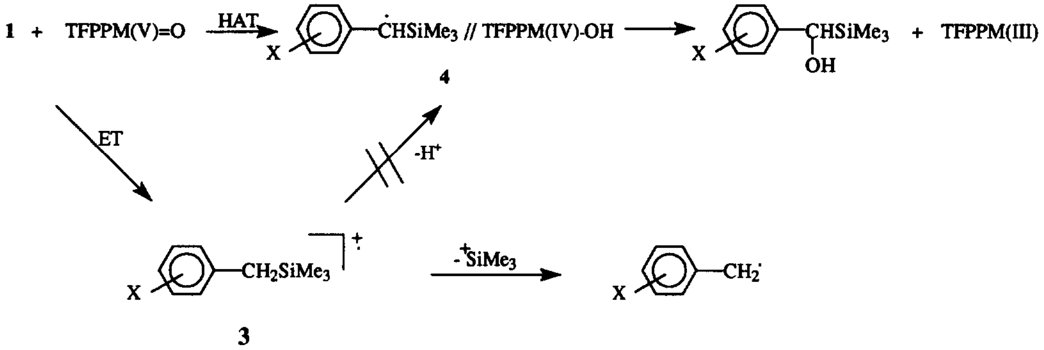
Scheme 1

We have recently investigated the oxidation of benzyltrimethylsilane and *p*-methoxybenzyltrimethylsilane in CH_2Cl_2 by iodosylbenzene, in the presence of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin iron(III) chloride [TFPPFe(III)][4]. In these reactions the corresponding benzaldehydes were obtained, but there is evidence that an α-hydroxybenzyltrimethylsilane is first formed, which is then readily converted into benzaldehyde under the reaction conditions (eq. 1, X = H, *p*-MeO).



(1)

For the side chain hydroxylation step, we have suggested a HAT mechanism (Scheme 2, M = Fe). An electron transfer (ET) mechanism, leading to the cation radical **3**, which is then deprotonated to give **4**, was considered unlikely in view of the overwhelming evidence indicating C-Si bond cleavage as the most favoured fragmentation path for a benzyltrimethylsilane radical cation[5].

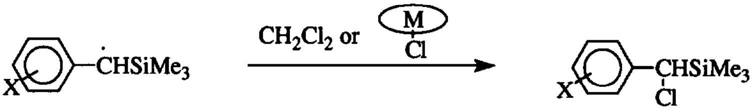


Scheme 2

To acquire more information on this point, which has an important bearing on the actual scope of the benzyltrimethyilsilane probe for the distinction between HAT and ET mechanisms[6], we have studied the effect of ring substituents on the rate of the side-chain oxidation of benzyltrimethylsilane induced by iodosylbenzene in the presence of TFPPFe(III), using the competitive method. For comparison purposes this study has also been partially extended to the corresponding reactions promoted by 5,10,15,20-tetrakis(pentafluorophenyl)-porphyrin manganese(III) chloride [TFPPMn(III)].

RESULTS AND DISCUSSION

The reactions have been carried out in CH_2Cl_2 at 25 °C, using a 100 : 10 : 1 substrate : iodosylbenzene : metalloporphyrin molar ratio. In the reactions with TFPPFe(III) the corresponding benzaldehyde is the side-chain oxidation product observed when the substrate is **1** (X = H, *m*-OMe, *m*-Cl, *p*-Cl, *m*-CF_3, 3,5-Cl_2). With **1**(X = *p*-*t*-Bu, *p*-MeO) small amounts of the corresponding α-chlorobenzyltrimethylsilanes (**5**) are also found. Evidently with the latter two compounds some escape from the cage **4** has occurred and a fraction of α-trimethylsilylbenzyl radical has had the possibility to abstract a chlorine atom from the solvent CH_2Cl_2, or to undergo a ligand transfer with the metalloporphyrin chloride (Scheme 3, M = Fe). With **1**(X = *p*-MeO, *m*-MeO), nuclear hydroxylation was also observed.



5

Scheme 3

With TFPPMn(III), benzaldehyde and the chloroderivative **5** were always formed in comparable amounts. This result is expected since there is evidence that the in cage oxygen rebound is slower with manganese than with iron porphyrins[7]. In the former case, therefore, the extent of escape from cage of the α-trimethylsilylbenzyl radical (Scheme 3, M = Mn) is certainly larger than in the reactions with TFPPFe(III).

To show that the benzaldehyde can actually derive from a first formed α-hydroxybenzyltrimethylsilane, the latter compound has been synthesized and made to react under our reaction conditions. It has been found that the α-hydroxy derivative is rapidly converted into benzaldehyde, even in the presence of a large excess of benzyltrimethylsilane. On the other hand, the very high oxidizability of α-hydroxytetraalkylsilanes is well known[8].

The fate of silicon was qualitatively investigated using benzyldimethyloctylsilane as the substrate. Dimethyloctylsilanol was detected among the reaction products. The silanol might derive from the corresponding chloride during the work up procedure[9].

Relative reactivity data have been obtained by competitive experiments. A mixture of benzyltrimethylsilane and a ring substituted benzyltrimethylsilane (each substrate being in great excess with respect to the oxidant) has been made to react with iodosylbenzene and the metalloporphyrin. The relative reactivity of the two compounds has been determined by measuring (via GC) the molar ratio of the side-chain oxidation products (benzaldehydes or benzaldehydes plus the α-chlorosubstituted products) formed from each substrate. The results are collected in Table 1 [reactions with TFPPFe(III)] and 2 [reactions with TFPPMn(III)].

Table 1. Relative Reactivities in the Oxidation of Benzyltrimethylsilanes Promoted by TFPPFe(III)/PhIO in CH_2Cl_2 [TFPPFe(III) (5 μmol), PhIO (50 μmol) and substrate (0.25-1 mmol) in CH_2Cl_2 (3 cm^3)].

Substrate	Reactivity relative to $PhCH_2SiMe_3$[a]
p-OMe	38.0
m-OMe	6.80
p-*t*Bu	5.70
H	1.00
p-Cl	0.50
m-Cl	0.21
m-CF_3	0.19
3,5-Cl_2	0.09

[a] Ratio of the yields of aldehyde and (where formed) α-chlorobenzyltrimethylsilane measured by glc.

Table 2. Relative Reactivities in the Oxidation of Benzyltrimethylsilanes Promoted by TFPPMn(III)/PhIO in CH_2Cl_2 [TFPPMn(III) (5 μmol), PhIO (50 μmol) and substrate (0.25-0.5 mmol) in CH_2Cl_2 (3 cm^3)].

Substrate	Reactivity relative to $PhCH_2SiMe_3$[a]
p-OMe	8.20
p-tBu	2.45
H	1.00
m-OMe	1.09
m-Cl	0.38

[a] Ratio of the yields of aldehyde and α-chlorobenzyltrimethylsilane measured by glc.

When the relative reactivity values (k_X/k_H) for the reactions with TFPPFe(III) are plotted against the σ^+ values of the X substituents, a satisfactory Hammett correlation (Fig. 1, R = 0.987) is obtained provided the point for the *m*-MeO group is excluded from the plot. Accordingly, as shown in Fig. 1, **1**(X = *m*-MeO) exhibits a much larger reactivity (at least 10 times) than that expected on the basis of the σ^+ (or σ) value of the *m*-MeO group.

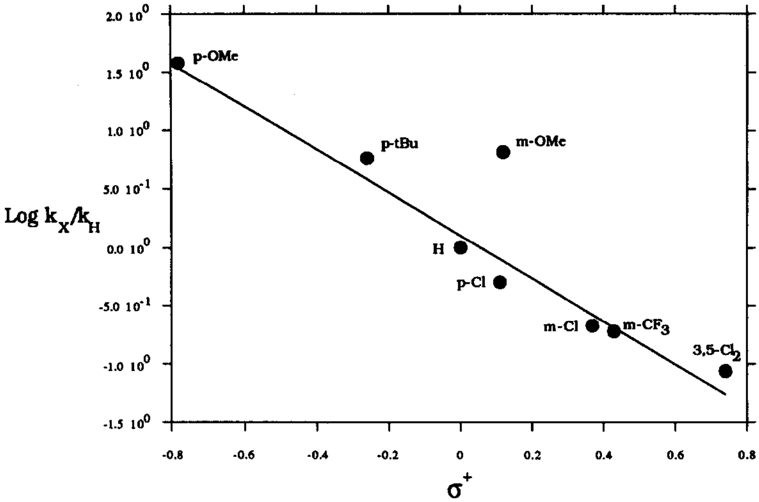


Fig 1. Hammett plot for the TFPPFe(III) catalysed oxidations of benzyltrimethylsilanes by iodosylbenzene. The point for the *m*-MeO group has not been included in the correlation (see text).

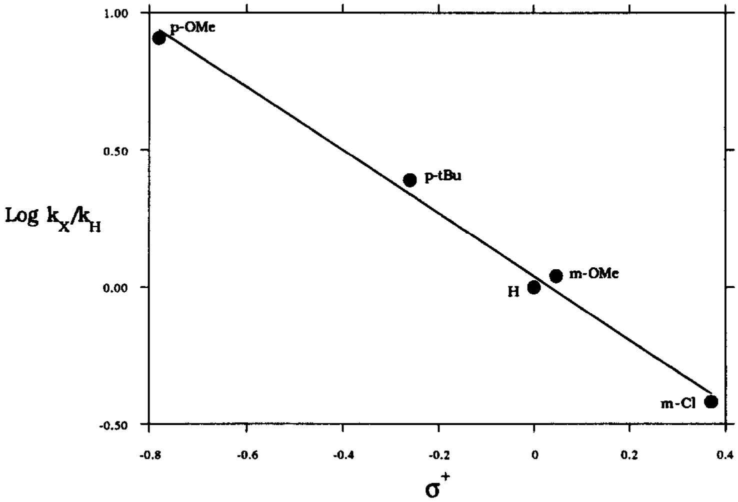
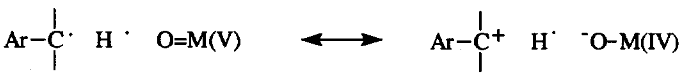


Fig. 2 Hammett plot for TFPPMn(III) catalysed oxidations of benzyltrimethylsilanes by iodosylbenzene.

From the correlation in Fig. 1 a ρ value of -1.84 is calculated and it is interesting to note that no improvement of the correlation is observed on replacing the single parameter Hammett equation with the dual parameter equation ($\log k_X/k_H = \rho\cdot\sigma_{\alpha\cdot} + \rho\sigma^{+}$) proposed by Arnold and his associates[10], as instead found by Lindsay Smith and coworkers for the case of oxidation of substituted toluenes by tetraphenylporphyrin iron(III) chloride in benzene[3].

With TFPPMn(III)/PhIO a satisfactory Hammett plot was also obtained (Fig. 2, R = 0.995), which has allowed us to calculate a ρ value of -1.15. Interestingly, in this reaction the *m*-MeO group does not exhibit any anomalous reactivity, as found before in the TFPPFe(III)/PhIO system, but nicely fits in with the correlation.

As already mentioned before, the benzylic oxidation by metalloporphyrins and iodosylbenzene is generally seen as a HAT process. However, the oxo-metal(V) porphyrin can exhibit substantial electrophilic behaviours with a transition state resonating between the structures **6** and **7**.



$$\mathrm{Ar{-}\overset{|}{\underset{|}{C}}\cdot\ \ H\ \cdot\ \ O{=}M(V)} \longleftrightarrow \mathrm{Ar{-}\overset{|}{\underset{|}{C}}{}^{+}\ \ H^{\cdot}\ \ {}^{-}O{-}M(IV)}$$

6 **7**

On this basis, the relatively large and negative ρ value observed for the reactions of TFPPFe(III) and benzyltrimethylsilanes might be justified by assuming a substantial contribution of structure **7** to the transition state of this process, due to an efficient stabilization of Fe(IV)-O$^-$ by the four pentafluorophenyl substituents in the porphyrin system.

However, this explanation does not account for the much higher (*ca* 10 times) than expected reactivity of the *m*-MeO group. In fact, in reactions occurring by a HAT mechanism, even though with significant polar character, the *m*-MeO group always exhibits a little rate retarding kinetic effect or no effect at all. Examples can be found in the side-chain bromination of toluenes by N-bromosuccinimide and in the benzylic hydrogen abstraction from cumenes and allylbenzenes by Br· and $Cl_3C\cdot$[11]. Clearly, in these cases, a MeO group in the *meta* position with respect to the side-chain can exert only a slight electron-withdrawing inductive effect, destabilizing the partial positive charge which develops in the transition state.

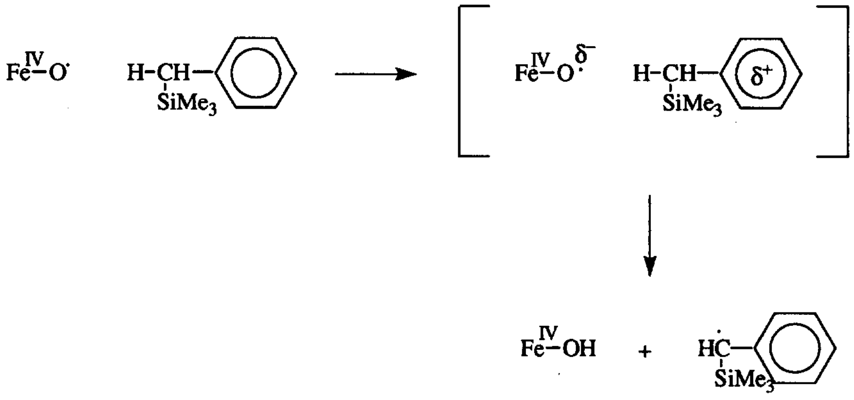
The large rate enhancing effect of the *m*-MeO group would seem more in line with an ET mechanism. Accordingly, a significant stabilization of the radical cation intermediate is provided by the MeO group, even though it is *meta* to the side-chain. *m*-Methoxytoluene has a much lower oxidation potential than toluene ($\Delta E^{o} \sim 0.6$ V)[12] and, more significantly, **1**(X = *m*-MeO) has been found to be much more reactive (*ca* 80 times) than **1**(X = H) in the oxidation with potassium 12-tungstocobalt(III)ate, Co(III)W, a reaction certainly occurring by an ET mechanism[13].

However, an ET mechanism seems unlikely on the basis of the following grounds. First, the occurrence of such a mechanism should imply that the benzyltrimethylsilane cation radical is exclusively deprotonated to give the α-trimethylsilylbenzyl radical, without undergoing any C-Si bond cleavage, which is instead, as already mentioned, the by far preferred decomposition path for this species. Even if some competition between deprotonation and C-Si bond rupture cannot be excluded, expecially in a medium which cannot provide any nucleophilic assistance to the breaking of the C-Si bond[14], it does not seem sound to suggest that *only* the former reaction is observed under our reaction conditions.

Second,the reaction selectivity appears to be too small for an ET mechanism. In the oxidation of benzyltrimethylsilanes by cerium(IV) ammonium nitrate, a bona fide ET reaction, a much larger ρ value (-5.4) has been measured[5a] than the one observed in the present work. On the same line is the observation that the rate enhancing effect of the *m*-MeO group is much larger in the ET reaction with Co(III)W than in the oxidations catalyzed by TFPPFe(III).

Finally, in the light of the good correlation of Fig. 1, the validity of the ET mechanism should be extended to include substrates like **1**(X = 3,5 Cl_2) and **1**(X = *m*-CF_3), which seems unlikely in view of the high oxidation potential [an E^o value of *ca* 2.3 V vs NHE can be extimated for **1**(X = *m*-CF_3)][15] of these substrates.

A reasonable suggestion which can account for the effect of the *m*-MeO group without invoking the formation of a radical cation intermediate is that the transfer of hydrogen takes place inside a charge-transfer complex formed by the iron complex and the benzyltrimethylsilane as illustrated in Scheme 4.



Scheme 4

In this charge-transfer complex a partial positive charge resides on the aromatic ring and therefore some stabilization by a ring methoxy group is expected, whatever its position with respect to the side-chain. The hydrogen transfer step takes on to a certain degree the nature of a proton transfer and this suggestion is somewhat equivalent to say that the reaction involves a concerted electron/proton transfer. In other words, the C-H bond cleavage is suggested to lag behind the transfer of an electron from the aromatic ring to Fe(V)=O, so that the transition state of the process resembles an aromatic cation radical, even though this species is not formed as a reaction intermediate.

Concerted electron/proton transfer paths have been given serious consideration in recent years to account for the behaviors of several processes which are difficult to rationalize on the basis of either an HAT or an ET mechanism[16]. The theoretical implications of this hypothesis have also been discussed[16b,c].

Probably, in the case in study, the occurrence of a concerted electron/proton transfer mechanism can be induced by the good oxidizing power of TFPPFe(V)=O combined with the electron releasing effect of the CH_2SiMe_3 group which increase the oxidizability of the aromatic system. As we move from TFPPFe(III)/PhIO to TFPPMn(III)/PhIO, the oxidizing power of the metal-oxo complex (which is accordingly better described as an oxy-radical complex Mn^{IV}-O·) certainly decreases and therefore it is not surprising that with the manganese porphyrins the reactivity data can be interpreted on the basis of a HAT mechanism, with the *m*-methoxy group exhibiting the reactivity predicted by its σ value.

EXPERIMENTAL

Methods. Gas cromatographic analyses were performed on a Varian Vista 6000 gas-cromatograph coupled with a Hewlett-Packard Model 3390A reporting integrator. Nitrogen was used as carrier gas with FID detection. GC column used for analyses was a 25mX0.32mm fused silica CPSil OV1701 capillary column. GC-MS analyses were performed on a HP 5890 GC equipped with a 15mX0.2mm silica capillary column coated with methyl silicone gum and coupled with a HP 5970 MSD. UV/Vis spectra were recorded on a HP 8452 spectrophotometer.

Materials. The solvent CH_2Cl_2 was distilled from P_2O_5 and degassed with argon before use. Iodosylbenzene was prepared by hydrolysis of the corresponding diacetate (Aldrich) with aqueous sodium hydroxide[17]. 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin iron(III) chloride was purchased from Aldrich. 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin manganese(III) chloride was prepared by DMF metallation procedure of the corresponding porphyrin ligand [5,10,15,20-tetrakis(pentafluorophenyl)porphyrin from Aldrich] and characterized by its visible spectra[18].

Benzyltrimethylsilane (Fluka) required further purification and was distilled under reduced pressure (p.e. 75 °C at 20 mmHg). Ring substituted benzyltrimethylsilanes and benzyldimethyloctylsilane have been prepared by Grignard reaction of the appropriate benzylmagnesium chloride with trimethylchlorosilane and dimethyloctylchlorosilane (Aldrich) in anhydrous THF as described in the literature[19]. The α-chlorobenzyltrimethylsilanes were obtained by treatment of the corresponding bromides (obtained by side chain bromination of the corresponding benzyltrimethylsilanes with NBS in CCl_4[20]) with tetrabutylammonium chloride in refluxing CH_3CN. α-hydroxybenzyltrimethylsilane was obtained by hydrolysis of α-Br-benzyltrimethylsilane in refluxing H_2O:acetone (10:1). Benzaldehyde, *p*-methoxy, *p*-chloro, *m*-chloro, *m*-methoxy benzaldehydes were commercially available. *p*-*t*-Butyl, *m*-trifluoromethyl and 3,5-dichloro benzaldehydes were prepared from the corresponding alcohol (Aldrich) by oxidation with pyridinium chlorochromate in CH_2Cl_2.

Oxidation Procedure. All reactions were run under an argon atmosphere in 10ml Schlenk flasks at room temperature. In the standard procedure for the oxidations, iodosylbenzene (50 μmol) was added to a stirred solution of catalyst (5 μmol) and substrate (500 μmol) in CH_2Cl_2 (3 cm^3). After 3 h reaction mixtures were treated with aqueous Na_2SO_3, an internal standard was added and then the organic phase was analyzed by GLC or GC/MS. The identity of the products was verified by comparison with authentic specimens and by GC/MS. No product formation was observed in the absence of either iodosylbenzene or the catalyst. Benzaldehydes were the almost exclusive (traces of phenyltrimethylsilyl ketone were also noted) side-chain oxidation products in the oxidation catalyzed by TFPPFe(III) [the yields referred to the oxidant were: 1.3 % for **1**(X = *m*-Cl), 1.8% for **1**(X = *p*-Cl), 2.4% for **1**(X = H), 4.8% for **1**(X = *p*-*t*-Bu) and 12.5 % for **1**(X = *p*-OMe)]. Nuclear hydroxylation products were observed with **1**(X = *p*-OMe) (7 %) and **1**(X = *m*-OMe) (5 %). Small amount of α-chlorobenzyltrimethylsilanes **3** were observed in the oxidation of **1**(X = *p*-OMe) (1.2 %) and of **1**(X = *p*-*t*Bu) (2.5 %).

In the reactions promoted by TFPPMn(III), benzaldehydes [the yields referred to the oxidant were: 0.7 % for **1**(X = *m*-OMe), 4.6% for **1**(X = *m*-Cl), 9.3% for **1**(X = H) and 15.6 % for **1**(X = *p*-OMe)] were always accompanied by substantial amounts of the corresponding α-chlorobenzyltrimethylsilanes [the yields referred to the oxidant were: 0.5 % for **1**(X = *m*-OMe), 2.9% for **1**(X = H), 3.1% for **1**(X = *m*-OMe) and 10.8 % for **1**(X = *p*-OMe)]. Nuclear hydroxylation products were observed in the oxidation of **1**(X = *m*-OMe) (7.6 %).

Oxidation of α-hydroxybenzyltrimethylsilane. A mixture of *p*-*t*-butil-benzyltrimethylsilane (500 μmol) and α-hydroxybenzyltrimethylsilane (10 μmol) was oxidized following the standard procedure mixing the oxidant to a stirred solution of the catalyst (both TFPPFe(III) and TFPPMn(III) were used) and of the two substrates. After 1 h the reaction mixture was treated with aqueous Na_2SO_3 and the organic phase analyzed by GLC and GC/MS. *All* of the α-hydroxybenzyltrimethylsilane had reacted, almost being converted into benzaldehyde (extremely small amounts of phenyltrimethylsilyl ketone were also observed).

Oxidation of benzyldimethyloctylsilane. In the oxidation of benzyldimethyloctylsilane iodosylbenzene (50 μmol) was added to a stirred solution of TFPPFe(III) (5 μmol) and of the substrate (500 μmol) in CH_2Cl_2 (3 cm^3) following the standard procedure. The organic phase was analyzed by GLC and GC/MS and two products were detected: benzaldehyde and dimethyloctylsilanol. The latter compound was also observed treating a solution of dimethyloctylchlorosilane in CH_2Cl_2 with aqueous Na_2SO_3 (according to the standard reaction procedure).

Competitive oxidation. In the standard procedure for competitive oxidation, iodosylbenzene (50 μmol) was added to a stirred solution of catalyst (5 μmol) and of two substrates: ring substituted benzyltrimethylsilane, **1**-X, (250-1000 μmol) and benzyltrimethylsilane, **1**-H, (375-1000 μmol) in CH_2Cl_2 (3 cm^3). The reactivity ratio (k_X/k_H) was obtained by measuring, *via* GLC using an internal standard,the molar ratio of the side-chain oxidation products (benzaldehydes and, where formed, α-chlorobenzyltrimethylsilanes) formed from the two substrates. The values were corrected for differences in the initial concentrations of the two substrates according to the equation:

$$k_X/k_H = \frac{\text{mmol } \mathbf{2}\text{-X} + \text{mmol } \mathbf{3}\text{-X}}{\text{mmol } \mathbf{2}\text{-H} + \text{mmol } \mathbf{3}\text{-H}} \times \frac{[\mathbf{1},\text{H}]}{[\mathbf{1},\text{X}]}$$

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