Pergamon

Tetrahedron, Vol. 53, No. 2, pp. 487-510, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)00996-9

The Selective Functionalization of Saturated Hydrocarbons. Part 37.[†] Utilization of a New Oxidant: Bis(trimethylsilyl) peroxide.[††]

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Abstract: The selective oxidation of alkanes to ketones using $Fe^{III}(PA)_3$ and $Fe^{III}(PA)_2Cl_2,Pyr_2H$ is performed with bis(trimethylsilyl) peroxide by a non radical mechanism. The Fe^{III}-Fe^{V} manifold is responsible for the oxidation process. Without a suitable chelating ligand (PA), only formation of oxygen was observed. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Although considered relatively unreactive because of their saturated bonds, alkanes are not chemically inert. In the number of the reaction of alkanes, oxidation takes a great place. Most of the oxidation reactions are free radical in nature and produce a variety of products without high selectivity. In biological systems a broad range of selective oxidations of hydrocarbon substrates by dioxygen are catalyzed by metalloenzymes.[1,2] Among these metalloenzymes, the most extensively studied remain Cytochrome P-450 (heme-iron enzyme), [3] which catalyzes the transfer of one oxygen atom from dioxygen into a wide variety of substrates, and methane monooxygenase (MMO) (non-heme-iron enzyme) [4] which converts methane to methanol. In 1983, faced with the challenge to design an oxidation system for saturated hydrocarbons having economic relevance, we started a new chapter in this field that would be known as Gif chemistry.[5] The first system Gif^{IV}, which oxidized selectively alkanes to ketones with a superior yield to those reported for comparable model systems, used Fe^{II}, O_2 and Zn^0 in pyridine-acetic acid. The unusual selectivity observed, selective secondary substitution, was explained by a non radical way and by the formation of an active species such as $Fe^V{=}O$. Later, the Fe^{II}-superoxide system was supplemented by the Fe^{III}-H_2O_2 system.[6] A σ Fe-C bond species was postulated as an intermediate in these systems and an alkyl hydroperoxide was fully characterized (when the reaction was carried out in pyridine-acetic acid).[7,8] Recent studies allowed us to distinguish two different manifolds in Gif

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[†] Part 36: Barton, D. H. R. and Chavasiri, W. Submitted for publication.

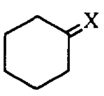
[††] This paper is dedicated with appreciation and admiration to Prof. Nelson J. Leonard on the occasion of his eightieth birthday.

systems.[9] The Fe^{II}-Fe^{IV} manifold, which permits the selective functionalization by ionic trapping (chloride, azide, and others), involves a carbon radical by fragmentation of the Fe^{IV}-C bond. And, the Fe^{III}-Fe^{V} manifold, responsible for selective ketonization, does not produce any radicals. Accurate titration for Fe^{II} and Fe^{III} made an important contribution.[10] Further, we were able to explain the formation of alkyl trapping when the reaction was carried out with the Fe^{III}-H_2O_2 system in presence of radical traps such as 2-methyl-1,4-naphthoquinone,[11] diphenyl diselenide[12] and Tempo.[13] In all these cases the Fe^{II}-Fe^{IV} manifold was involved in the reaction. The presence of a suitable chelating ligand such as picolinic acid (PA) was found to be essential in order to obtain a reaction with the hydrocarbon. Also, the ligand environment of the catalyst in solution of the Fe^{III}-H_2O_2 system was clarified using ^{13}C NMR spectroscopy.[14] The presence of a μ-peroxo-dimer was proposed.

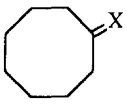
During the search for a new oxidant for Gif chemistry, bis(trimethylsilyl) peroxide[15] appeared to be suitable for the activation of saturated hydrocarbons. Different preparative methods are known in literature,[16,17] and this oxidant shows a reasonable thermal stability. Also, it can be handled in the pure state and distilled.[18] The bis(trimethylsilyl) peroxide, which is a masked form of 100% hydrogen peroxide, was used as a synthon for OH^+ for electrophilic hydroxylation,[19] a source of Me_3SiO^+ for electrophilic oxidation,[20] and a versatile oxidant for alcohols,[21] phosphines[15,22], phosphites[23] and sulfides.[15,24] When transformed into bis(trimethylsilyl) monoperoxysulfate, bis(trimethylsilyl) peroxide became a useful oxidant for the Baeyer-Villiger oxidation.[25] Only a few examples of oxidation of hydrocarbons were found in the literature.[26] In this work, we report the utilization of bis(trimethylsilyl) peroxide as oxidant in Gif systems.

RESULTS AND DISCUSSION

Utilization of $Fe^{III}(PA)_3$

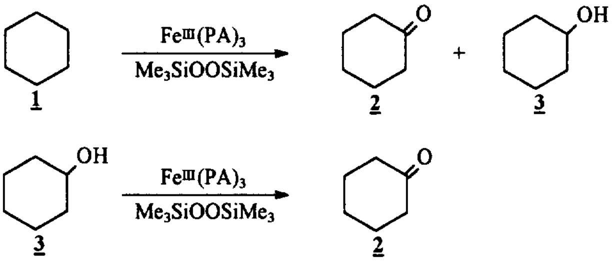


1 X=H_2
2 X=O
3 X=OH,H
4 X=-*2*-pyridine,H
5 X=-*4*-pyridine,H
6 X=Cl,H
7 X=Br,H



8 X=H_2
9 X=O
10 X=OH,H
11 X=Cl,H
12 X=Br,H

The first quality required of an oxidant in Gif systems is the ability to activate a saturated hydrocarbon in the presence of an iron catalyst. The oxidation of cyclohexane 1 using $Fe^{III}(PA)_3$ as catalyst and bis(trimethylsilyl) peroxide as oxidant in pyridine showed similar results to those obtained with hydrogen peroxide. Cyclohexanone 2 was the major product with a small amount of cyclohexanol 3 as it is shown in the **Table 1** (entry 1). The reaction is catalytic but an increase of $Fe^{III}(PA)_3$ from 0.1 to 0.3 mmol did not influence very much the efficiency (51 to 67 %). The addition of acetic acid-d4 decreased slightly the formation of the oxidation products (entry 2), so we decided not to add this acid in further experiments. In contrast to the usual Gif systems ($Fe^{II}/Zn/O_2$ or Fe^{III}/H_2O_2), alcohol could also be efficiently transformed into the corresponding ketone (entry 3) as it is described in **Scheme 1**.



Scheme 1: Oxidation of cyclohexane 1 and cyclohexanol 3 with the $Fe^{III}(PA)_3$ system.

A series of blank experiments served to establish that each component is essential for a successful reaction. Also in absence of a suitable carboxylic acid such as picolinic acid, only traces of oxidation products were detected but with a rapid formation of oxygen.

Table 1: Oxidation of cyclohexane 1 and cyclohexanol 3 with the $Fe^{III}(PA)_3$-$Me_3SiOOSiMe_3$ system.

Entry	Substrate	Products (mmol)		Eff. (%)
		R=O 2	R-OH 3	
1	1 20 mmol	0.73	0.19	37
2	1 20 mmol + 1.5 mmol of CD_3CO_2D	0.64	0.13	31
3	3 20 mmol	2.38	16.25	48
4	1 10 mmol	0.60	0.30	36
	20 mmol	0.86	0.42	51
	30 mmol	1.01	0.50	64
5	3 10 mmol	1.47	8.14	29
	20 mmol	2.38	16.25	48
	30 mmol	2.43	26.70	49

These reactions were carried out with 0.5 mmol of $Fe^{III}(PA)_3$ and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine (dried over KOH under reflux) at RT, overnight, under air. PA refers to picolinic acid, RT to room temperature, Eff. to efficiency which was calculated assuming that 2 mmol of $Me_3SiOOSiMe_3$ were used to produce 1 mmol of ketone or alcohol when the substrate is hydrocarbon. When alcohol is the substrate, only 1 mmol of peroxide was used.

A study of the rate of oxidation of the cyclohexane 1 revealed that the half-life, which is 3h at room temperature, decreased to 1h30 when the reaction was carried out at 50°C. Also the efficiency rose from 43% to 59% when the temperature was increased.

The half-life for the conversion of cyclohexanol 3 into cyclohexanone 2 was also 3h at room temperature.

Keeping the concentration of Fe^{III} and of oxidant constant, we observed that the efficiency increased with the concentration of substrate (entries 4 and 5). When 30 mmol of cyclohexane were used, the efficiency reached 64% (entry 4). On the other hand, the selectivity was not very high (ratio one/ol = 2) compared to that observed in entries 1 and 2 (ratio one/ol = 3.8 and 4.9). Using the alcohol 3 as substrate (entry 5), the efficiency increased when the amount introduced went from 10 mmol to 20 mmol. We can see that the oxidation of alkane and alcohol by this system presents some similarities. This suggests that the same active species is responsible for the activation of the substrate. Also, when the reaction was carried out with a small amount of cyclohexane (10 mmol) compared to pyridine (90 mmol), using 2 mmol of $Fe^{III}(PA)_3$ and 2 mmol of oxidant, the efficiency observed with $Me_3SiOOSiMe_3$ was 33%. When H_2O_2 was used as oxidant, the efficiency was only 10%.

In order to verify the hypothesis of a common intermediate and to see if the alcohol was not an intermediate in the oxidation of alkane to ketone, a series of competitive reactions was carried out as is shown in **Table 2**. It had been verified that cyclooctane 8 was oxidized to cyclooctanone 9 and cyclooctanol 10 as for cyclohexane 1 (**Table 1**).

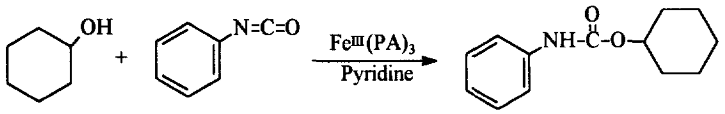
Table 2: Competitive oxidation with different alkanes and alcohols.

Entry	Substrates	Products (mmol)			
		R=O 2	R-OH 3	R=O 9	R-OH 10
1	1 10 mmol + 8 10 mmol	0.25	traces	0.67	0.09
2	3 10 mmol + 10 10 mmol	0.44	9.92	1.12	9.46
3	3 10 mmol + 8 10 mmol	0.66	9.84	0.02	0.04
4	1 10 mmol + 10 10 mmol	traces	n.d.	1.30	8.15
5	3 1 mmol + 8 20 mmol	0.10	0.50	0.97	0.19
6	1 20 mmol + 10 1mmol	0.66	traces	0.28	0.45

These reactions were carried out with 0.3 mmol of $Fe^{III}(PA)_3$ and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine (dried over KOH under reflux) at RT, overnight, under argon. n. d. refers to not detected.

The oxidation of substrates in C_8 was more than two times faster than the oxidation of substrates in C_6 (entries 1 and 2). The entries 3 and 4 showed that when using equal quantities of alcohol and alkane, the oxidation of alcohol is faster. Also, when an excess of hydrocarbon was used, the concentration of C-H bond increased and the formation of the corresponding ketone was detected.(entries 5 and 6). It is clear that the ketone is not formed by only oxidation of the alcohol and that there is an intermediate that gives both ketone and alcohol.

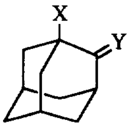
Thus, in the entry 2, it was shown that the cyclooctanol was oxidized faster than cyclohexanol. The fact that in the entry 6 the cyclooctanol was only partially oxidized and the cyclohexane transformed in 0.66 mmol of cyclohexanone showed that the alcohol can not be an intermediate of the oxidation of hydrocarbon. If it was the case, the cyclooctanol should be totally transformed in cyclooctanone. It might be argued that the alcohol could be bonded to the iron. To verify this, different work-up procedures were carried out using oxalic acid, *tert*-butanol or sodium sulfide, compounds known to displace any ligand bonded to iron. In that case, we should see an increase of the quantity of alcohol which was not seen. Also, the addition of phenylisocyanate 13 in the reaction did not reveal the presence of the adduct 14 corresponding to the addition of alcohol on the isocyanate 13. A blank experiment showed that when we carried out a reaction with 5 mmol of cyclohexanol, 5 mmol of phenylisocyanate in presence of $Fe^{III}(PA)_3$ in pyridine, 2.16 mmol of the adduct 14 was formed (**Scheme 2**).



3 13 14

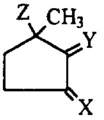
Scheme 2

In the study of Gif Chemistry, the regioselectivity observed during the oxidation of adamantane[27] and the determination of the Kinetic Isotope Effect[28] received careful attention. When 8 mmol of adamantane 15 were oxidized by $Me_3SiOOSiMe_3$ (4 mmol) under air, adamantanone 16 (0.22 mmol) and 1-adamantanol 20 (0.22 mmol) were the major products, accompanied by 2-adamantanol 17 (0.08 mmol) and a mixture of the *tert*-adamantyl pyridine in *2-* and *4-* position 21 et 22 (0.04 mmol for both compounds). Adamantane was recovered (7.13 mmol) giving a good mass balance (97 %).The secondary / tertiary product ratio, C_2/C_3, gave a value of 1.02. This value is similar to those found in the previous Gif systems,[29] and differs from the value of 0.28 found in the case of a radical reaction in pyridine [9a] and 0.15 for other radicals selectivities found in the literature[30,31]



15 X=H, Y=H_2
16 X=H, Y=O
17 X=H, Y=OH,H
18 X=H, Y=Cl,H
19 X=H, Y=Br,H

20 X=OH, Y=H_2
21 X=-*2*-pyridine, Y=H_2
22 X=-*4*-pyridine, Y=H_2
23 X=Cl, Y=H_2
24 X=Br, Y=H_2

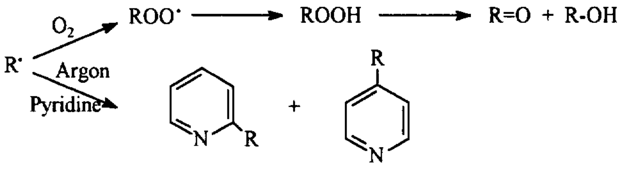


25 X=Y=H_2, Z=H
26 X=O, Y=H_2, Z=H
27 X=OH,H, Y=H_2, Z=H
28 X=H_2, Y=O, Z=H
29 X=H_2,Y=OH,H, Z=H
30 X=Y=H_2, Z=OH

The utilization of methylcyclopentane **25** as substrate gave a selectivity with a ratio C_2/C_3 of 12.3. The 3-methylcyclopentanone **26** was the major product formed (0.20 mmol) followed by the 2-methylcyclopentanone **28** (0.09 mmol) and 2-methylcyclopentanol **29** with the 3-methylcyclopentanol **27** (0.11 mmol for both). Only 0.035 mmol of tertiary alcohol **30** were detected. A value of 11 was found for the Gif^{IV} system and around 15 for the Gif-Orsay system using electrochemistry.[32]

The Kinetic Isotope Effect[33] value found for this system was $k_H/k_D = 3$, not far removed from those found with the other Gif systems.[28]

The presence of a radical intermediate was excluded since all these values were not in accordance with radical selectivity. Also, no pyridine coupled products were found in this system (except in the particular case of the tertiary position of adamantane) and it is known that pyridine reacts easily with carbon centered radicals.[9a,34] In order to bring more evidences against radical intermediates, we carried out the oxidation reaction under different atmospheres (argon, air and oxygen). If a carbon radical was the precursor of the reaction, the oxidation products should be increased under oxygen and decreased under an argon atmosphere (pyridine coupled products should be detected instead) (**Scheme 3**).



Scheme 3

The results are presented in **Table 3**. Between the reaction carried out under argon and under air, no difference was observed and no pyridine coupled products were detected under argon. Under oxygen, only a small increase of the oxidation products was detected. We concluded that the oxygen of the oxidation products did not come from the molecular oxygen, but from the peroxide. It is also clear that no carbon centered radicals were present during the oxidation of a hydrocarbon by the system Fe^{III}-$Me_3SiOOSiMe_3$.

Table 3: Effect of oxygen on the oxidation of cyclohexane **1**.

Entry	Conditions	Products (mmol)		
		R=O **2**	R-OH **3**	Eff. (%)
1	Air	0.58	0.14	29
2	Argon	0.59	0.18	31
3	Oxygen	0.73	0.23	38

These reactions were carried out with 20 mmol of cyclohexane 1, 0.3 mmol of $Fe^{III}(PA)_3$ and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine (dried over KOH under reflux) at RT, overnight.

At this stage of the study, several aspects such as the product distribution, the chemoselectivity and the regioselectivity of this new system were very similar to Gif Chemistry and more precisely to the Fe^{III}-H_2O_2 system. Another characteristic of Gif Chemistry, is the ability to oxidize saturated hydrocarbons even in presence of more easily oxidizable compounds such as diphenyl sulfide **31**.[35] It was concluded that no radical can be involved in this reaction, but an original species such as $Fe^{V}=O$.[36] We decided to add some diphenyl sulfide in our reaction to see if this unusual chemoselectivity occurred also in the $Me_3SiOOSiMe_3$ system. It is known in the literature that bis(trimethylsilyl) peroxide can easily oxidize sulfide to sulfoxide[15b,24] but not under the conditions here used (**Table 4**, entry 1).

Table 4: Oxidation of diphenyl sulfide **31**.

Entry	Conditions	Products (mmol)					Mb	Eff.
		PhSPh **31**	PhSOPh **32**	$PhSO_2Ph$ **33**	R=O **2**	R-OH **3**	(%)	(%)
1	A, **1** 0 mmol	4.88	0.04	n.d;	---	---	98	< 1
2	B, **1** 10 mmol	---	---	---	0.58	0.14	---	29
3	C, **1** 10 mmol	4.91	0.66	0.05	0.51	0.15	110	38
4	C, **1** 0 mmol	3.94	0.45	0.04	---	---	90	10

Except as specified, these reactions were carried out with 0.3 mmol of $Fe^{III}(PA)_3$ and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine (dried over KOH under reflux) at RT, overnight, under air. (A) without Fe. (B) without diphenyl sulfide. (C) with 5 mmol of diphenyl sulfide. Mb refers to mass balance.

The other results from the **Table 4** show the same paradox encountered in other Gif systems. In the entry 2, a standard reaction was carried out. In the entry 3, the addition of diphenyl sulfide **31** did not make any change to the hydrocarbon oxidation. An equal quantity of diphenyl sulfoxide **32** was detected with a small amount of diphenyl sulfone **33**. Without hydrocarbon, the formation of sulfoxide **32** and sulfone **33** was not increased (entry 4). This indicates that the active species responsible for the activation of hydrocarbon is not the same as the one responsible for the oxidation of the sulfide.

Since the beginning of this study, we were concerned that $Me_3SiOOSiMe_3$ might be hydrolyzed if some precautions to avoid moisture in the reaction were not taken. The pyridine was normally dried over KOH. The effect of added water was examinated. Surprisingly, the efficiency of the reaction decreased slowly only after the addition of 10 mmol of H_2O (**Figure 1**). Also, the addition of a small amount of water (1 or 5 mmol) increased slightly the formation of the ketone 2 and alcohol 3. Adding the right amount of water (3 mmol of H_2O/5 mmol of $Me_3SiOOSiMe_3$), the half-life of the reaction decreased from 3h to 1h.

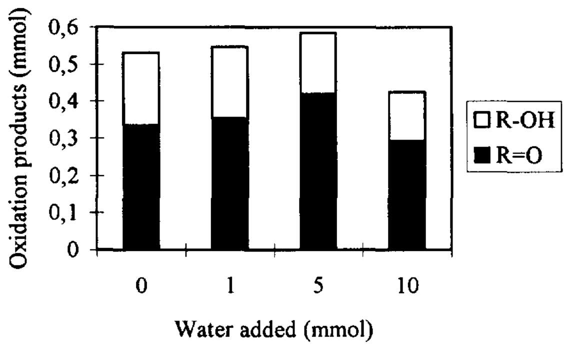
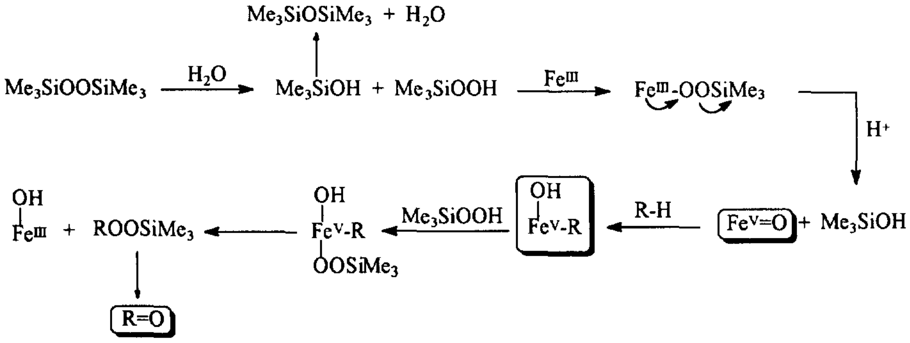


Figure 1: Variation of the amount of ketone 2 and alcohol 3 formed in the presence of different amounts of water.

Conditions: cyclohexane 1 (40 mmol), $Fe^{III}(PA)_3$ (1 mmol) and $Me_3SiOOSiMe_3$ (1 mmol) in pyridine (45 ml) at RT, overnight, under argon.

The partial hydrolyzis of bis(trimethylsilyl) peroxide into trimethylsilyl hydroperoxide can be the explanation for this effect (**Scheme 4**).



Scheme 4: Proposed mechanism for hydrocarbon oxidation with the $Fe^{III}(PA)_3$-$Me_3SiOOSiMe_3$ system.

The hydroperoxide could react easily with Fe^{III} , followed by the formation of the oxenoid species $Fe^{V}=O$. The formation of trimethylsilanol, which dehydrates to hexamethyldisiloxane, is the driving force for the reaction. In order to verify this hypothesis, a ^{13}C NMR experiment of $Fe^{III}(PA)_3$ in pyridine-d^5 reacting with $Me_3SiOOSiMe_3$ was carried out. The appearance of $Me_3SiOSiMe_3$ signal corresponded with the decrease of the $Me_3SiOOSiMe_3$ signal.

At this point, we were interested in the efficiency of the reaction based on the oxidant. As we can see with the previous data already reported in this article, the efficiency of the reaction did not exceed 40%. No formation of oxygen was involved during the oxidation process and, by titration, all bis(trimethylsilyl) peroxide was consumed. In all these reactions, a small quantity of trimethylsilyloxycyclohexane was formed. Several blank experiments showed that the formation of this by-product came from a reaction between cyclohexanol and bis(trimethylsilyl) peroxide. Then, a series of experiments was realized to see if a relationship exists between the efficiency of the reaction and the quantity of peroxide added.

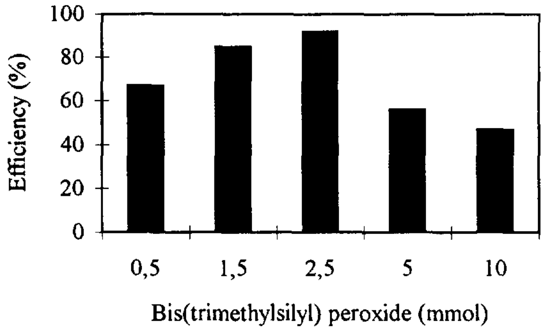


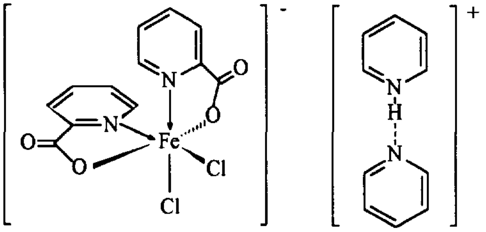
Figure 2: Variation of the efficiency using different amounts of bis(trimethylsilyl) peroxide
Conditions:cyclohexane **1** (40 mmol), $Fe^{III}(PA)_3$ (0.5 mmol) in pyridine (25 ml) at RT, overnight, under argon.

The results obtained by adding up to 20 equivalents (10 mmol) of $Me_3SiOOSiMe_3$ to the reaction are presented in **Figure 2**. It is clear that bis(trimethylsilyl) peroxide is decomposed when it is added in excess (5 and 10 mmol for 0.5 mmol of Fe^{III}), which explains the low efficiency observed in our previous experiments. However, using 2.5 mmol of peroxide or less gave a very good result with an efficiency reaching 92 %.

In the Fe^{III}-H_2O_2 system, when an argon stream was passed through the solution, surprisingly the formation of ketone was accompanied with the formation of alkyl chloride and Fe^{II}.[37] It is important to mention that in all other experiments starting with Fe^{III}-H_2O_2 without reducing agent, no chloride formation was detected. The presence of μ-peroxo-dimer losing dioxygen reversibly explains this result. In the case of $Fe^{III}(PA)_3$, LiCl and $Me_3SiOOSiMe_3$, only trace amount of chloride was seen (under air, the same amount was detected 1%). It is clear that it is not the same peroxo-dimer as in the $\mathrm{Fe^{III}(PA)_3}$-$\mathrm{Me_3SiOOSiMe_3}$ system (see **Scheme 4** above).

Utilization of the $\mathrm{Fe^{III}(PA)_2Cl_2}$, $\mathrm{Py_2H}$

In 1992, a single-iron complex **34** $\mathrm{Fe^{III}(PA)_2Cl_2}$, $\mathrm{(Py)_2H}$ was isolated from the reaction mixture ($\mathrm{Fe^{III}Cl_3}$, picolinic acid and cyclohexane in pyridine-acetic acid) and characterized by X-ray crystallography.[38] Because this complex came from a Gif reaction and its structure was known, we decided to use it instead of $\mathrm{Fe^{III}(PA)_3}$.



34

The oxidation of cyclohexane **1** using the complex **34** under the same conditions as those described in **Table 3** (entry 1) produced cyclohexanone **2** (0.80 mmol) and cyclohexanol **3** (0.13 mmol) without formation of oxygen. The efficiency was slightly higher (37%) in this case as is the selectivity (ratio one/ol = 6.2). The selectivity of the oxidation of adamantane **15** was defined using both oxidants $\mathrm{Me_3SiOOSiMe_3}$ (entry 1) and $\mathrm{H_2O_2}$ (entry 2) (**Table 5**).

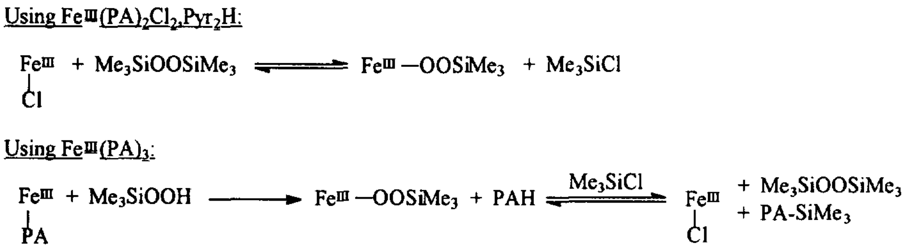
Table 5: Oxidation of adamantane **15**.

Entry	Oxidant	Products (mmol)								C_2/C_3	Mb
		R-H **15**	R=O **16**	R*s*-OH **17**	R*s*-Cl **18**	R*t*-OH **20**	R*t*-Cl **23**	R*t*-*2*-Pyr **21**	R*t*-*4*-Py **22**		(%)
1	$\mathrm{Me_3SiOOSiMe_3}$	6.88	0.26	0.07	0.02	0.24	0.04	0.10	0.06	0.80	96
2	$\mathrm{H_2O_2}$	7.14	0.25	0.06	0.03	0.14	0.04	0.13	0.08	0.87	98

These reactions were carried out with 8 mmol of adamantane **15**, 1 mmol of $\mathrm{Fe^{III}(PA)_2Cl_2,Pyr_2H}$ **34** and 4 mmol of $\mathrm{Me_3SiOOSiMe_3}$ in 30 ml of pyridine at 0°C to RT, under air overnight. The C_2/C_3 ratio is defined as an the total secondary products divided by the total tertiary products. Mb refers to mass balance.

The selectivity of the two systems is similar and presents a ratio C_2/C_3 different from those found in radical reactions,[9a,30,31] or when metalloporphyrins were the catalyst for oxidation.[39] Radicals have been detected only in the tertiary position with a competitive attack on oxygen and pyridine. No coupled product with pyridine were seen in the secondary position. Previously, it had been shown that both secondary and tertiary carbon radicals of adamantane react both with pyridine and oxygen.[40] Also, a Kinetic Isotope Effect of 2.48 was obtained for competitive oxidation of cyclohexane and its perdeutero analogue. This value is comparable to those found with several Gif systems (between 2.1 and 2.3) but not with the values for alkoxy or peroxy radicals.[41] It is obvious, as with $Fe^{III}(PA)_3$, that a non radical species is responsible for the activation of the hydrocarbon.

We saw in the previous paragraph that the addition of water could be the precursor of the formation of the intermediate trimethylsilyl hydroperoxide. In order to see if it was the same using the complex 34, a comparative study was made between a reaction carried out under dry conditions and one under standard conditions. If the presence of water influenced the oxidation, the efficiency should decrease when the reaction was carried out in a dry system. This was not the case, no difference was detected and the efficiency was 47 and 48% for the two experiments. The trimethylsilyl hydroperoxide is not the precursor of the oxidation of hydrocarbon with 34 as catalyst. However, the addition of Me_3SiCl in the solution before the addition of the peroxide inhibits the reaction and 60% of the peroxide remained. The same result was found when $Fe^{III}(PA)_3$ was used as catalyst. The formation of the trimethylsilyl derivative of the picolinic acid was seen by ^{13}C NMR and IR. An equilibrium (**Scheme 5**) is proposed to explain these results.



Using $Fe^{III}(PA)_2Cl_2,Pyr_2H$:

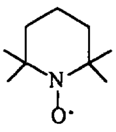
$$\underset{\mathrm{Cl}}{\mathrm{Fe^{III}}} + \mathrm{Me_3SiOOSiMe_3} \rightleftharpoons \mathrm{Fe^{III}{-}OOSiMe_3} + \mathrm{Me_3SiCl}$$

Using $Fe^{III}(PA)_3$:

$$\underset{\mathrm{PA}}{\mathrm{Fe^{III}}} + \mathrm{Me_3SiOOH} \longrightarrow \mathrm{Fe^{III}{-}OOSiMe_3} + \mathrm{PAH} \xrightleftharpoons{\mathrm{Me_3SiCl}} \underset{\mathrm{Cl}}{\mathrm{Fe^{III}}} \begin{array}{l} + \mathrm{Me_3SiOOSiMe_3} \\ + \mathrm{PA{-}SiMe_3} \end{array}$$

Scheme 5

We studied the influence of several radical traps in the system.



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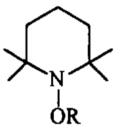


36 R= $c\text{-}C_6H_{11}$
41 R= CH_3

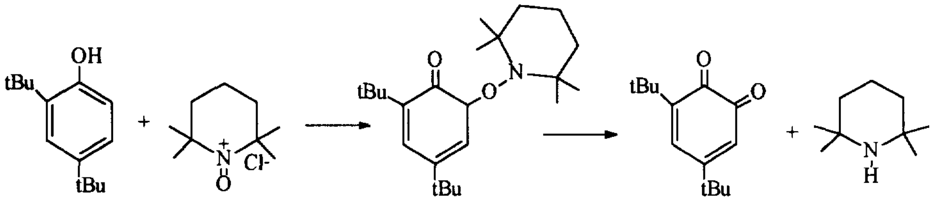
Tempo 35, which is a superior trap, was the first used. The reactions, which were carried out under air and under argon gave similar results and the formation of cyclohexanone and cyclohexanol were only partially replaced by the formation of cyclohexyl-Tempo 36 (**Table 6**). No cyclohexyl radical can be involved in this reaction. If it was the case, all the alkyl radical formed should be trapped by Tempo, which is a much better trap than oxygen. A careful study was already made showing that when a carbon radical was generated by photolysis from the corresponding Barton PTOC esters in presence of Tempo under oxygen, only alkyl-Tempo 36 was formed.[13]

Table 6: Effect of the Tempo 35 addition on cyclohexane 1 oxidation.

Entry	Conditions	Products (mmol)					
		R=O 2	R-OH 3	Tempo 35	cC_6H_{11}-Tempo 36	CH_3-Tempo 41	Mb in Tempo (%)
1	Air	0.51	n.d.	0.87	0.62	0.27	88
2	Argon	0.46	n.d.	0.86	0.77	0.30	97
3	Argon, A	---	---	0.73	---	0.48	66*

These reactions were carried out with 20 mmol of cyclohexane 1 , 0.5 mmol of Fe^{III}(PA)$_2$Cl$_2$,Pyr$_2$H 34, 2 mmol of Tempo 35 and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine at RT, overnight. (A) without hydrocarbon. * 0.115 of piperidine 39 was detected.

These results are also similar to those found during the study of Fe^{III}-H_2O_2.[13] The formation of some alkyl-radicals was explained by the oxidation of Tempo 35 by an Fe^{V} species to produce an oxoammonium salt 37 and an Fe^{IV} species. Fe^{IV} reacts rapidly with the hydrocarbon to form a Fe^{IV}-C bond which fragments into Fe^{III} and carbon radical.[13] To prove this hypothesis, the oxoammonium salt 37 was trapped by the 2,4-di-*tert*-butylphenol 38 to give the 2,2,6,6-tetramethylpiperidine 39 and the 3,5-di-*tert*-butyl *o*-benzoquinone 40 as it is illustrated in the **Scheme 6**.



38 37 40 39

Scheme 6: Mechanism of the 2,4-di-*tert*-butylphenol 38 oxidation by the oxoammonium salt 37.

The **Table 7** shows the results when 1 mmol of phenol 38 replaced the hydrocarbon. The quinone 40 and the piperidine 39 were detected. One other by-product, the methyl-Tempo 41 was detected in all the Tempo experiments. One can postulate that this compound was formed by β-scission of the trimethylsiloxy radical. This hypothesis is not convincing. First, if siloxy radicals were formed during the reaction, they should abstract the hydrogen of the hydrocarbon to produce carbon radicals as it is already described in literature.[42] Also, if radicals were in presence of the phenol 38, the formation of phenol radical should be followed by the formation of the *ortho-ortho* dimer.[43]

Table 7: Oxidation of 2,4-di-*tert*-butylphenol 38 the Fe^{III}- $Me_3SiOOSiMe_3$ system.

38	40	39	35	41	Mb in Tempo (%)	Mb in Phenol (%)
0.73	0.16	0.32	0.83	0.57	86	90

This reaction was carried out with 1 mmol of 2,4-di-*tert*-butylphenol 38, 0.5 mmol of $Fe^{III}(PA)_2Cl_2,Pyr_2H$ 34, 2 mmol of Tempo and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine, under argon at 0°C to RT, overnight. The solution was degassed before adding the peroxide. The amount of products are in mmol.

During a study of the photolysis of bis(trimethylsilyl) peroxide,[42] the formation of $Me_3SiO^{\cdot}$ was detected without formation of Me radical. Only higher bis(trialkylsilyl)peroxides, at low temperature, showed the presence of the corresponding alkyl radical. Thus, the β-scission would appear to be rather unlikely because the process would be strongly endothermic (DH° (C-Si) ca. 76 kcal mol^{-1}, DH° (π SiO) $\geq$ 38 kcal mol^{-1})[42]. In the case of the thermal decomposition of bis(trimethylsilyl) peroxide, the product of isomerization $Me_2(MeO)SiOSiMe_3$ was the major product obtained at 200°C, and Me radicals were detected only when the temperature was raised higher than 420°C.[44]

The preparation and the photolysis *in situ*[45] of the trimethylsilyl derivative of N-hydroxy-2-thiopyridone in presence of Tempo was carried in pyridine without obtaining any methyl-Tempo or 2-pyridyl methyl sulfide, but 12 % of 2,2'-dipyridyl disulfide was detected. When dimethyl-*tert*-butylsilyloxyl radicals were generated in the same conditions, 6 % of *tert*-butyl Tempo and 6 % of the 2,2'-dipyridyl disulfide were formed. Anyway, if some trimethylsiloxy radicals were involved in the hydrocarbon activation, it would be as a minor side reaction because all the results already proposed can not be explained by radical chemistry.

When diphenyl diselenide was used as a trap under argon, only traces of cyclohexylphenyl selenide were detected. The utilization of the oxidation power to oxidize diphenyldiselenide explains the absence of ketone and alcohol. This is expected in the Fe^{II}-Fe^{IV} manifold.[12]

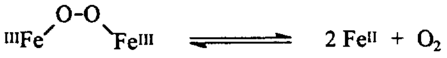
During the study using complex 34 and $Me_3SiOOSiMe_3$, no alkyl chloride was formed when the reaction was carried out under air (**Table 8**, entry 1). Adding LiCl did not lead to the formation of alkyl chloride. Passing argon through the solution gave an equal amount of cyclooctyl chloride 11 and cyclooctanone 9 formed simultaneously (entry 2). Except that no formation of Fe^{II} was detected by titration[10] in the $Me_3SiOOSiMe_3$ system, this result is similar to that when H_2O_2 was used.[37] This, can be explained by the greater stability of $Me_3SiOOSiMe_3$ in solution, which in excess, was able to oxidize Fe^{II}. A blank experiment showed that only two minutes were sufficient to oxidize Fe^{II} by $Me_3SiOOSiMe_3$, that makes the titration of Fe^{II} impossible in its presence.

Table 8: Effect of an argon stream on the distribution of products from the oxidation of cyclooctane 8.

Entry	Conditions	Products (mmol)				
		R-H 8	R=O 9	R-OH 10	R-Cl 11	Mb (%)
1	Air, 24h at 0°C to RT	74.52	1.24	0.11	n.d.	95
2	Argon stream, 5h at 0°C	77.65	0.48	0.08	0.49	98
	20h at 0°C	77.57	1.10	0.07	1.57	100
	24h at RT	80.5	1.13	0.07	1.68	104
3	Argon stream, 5h at 0°C	72.42	0.63	0.10	0.47	92
	O_2 stream, 20h at 0°C	71.12	1.39	0.12	0.47	92
	Air, 24h at RT	71.39	1.44	0.10	0.46	92

These reactions were carried out with 80 mmol of cyclooctane 8, 2 mmol of $Fe^{III}(PA)_2Cl_2{,}Pyr_2H$ 34, and 8 mmol of $Me_3SiOOSiMe_3$ in 60 ml of pyridine.

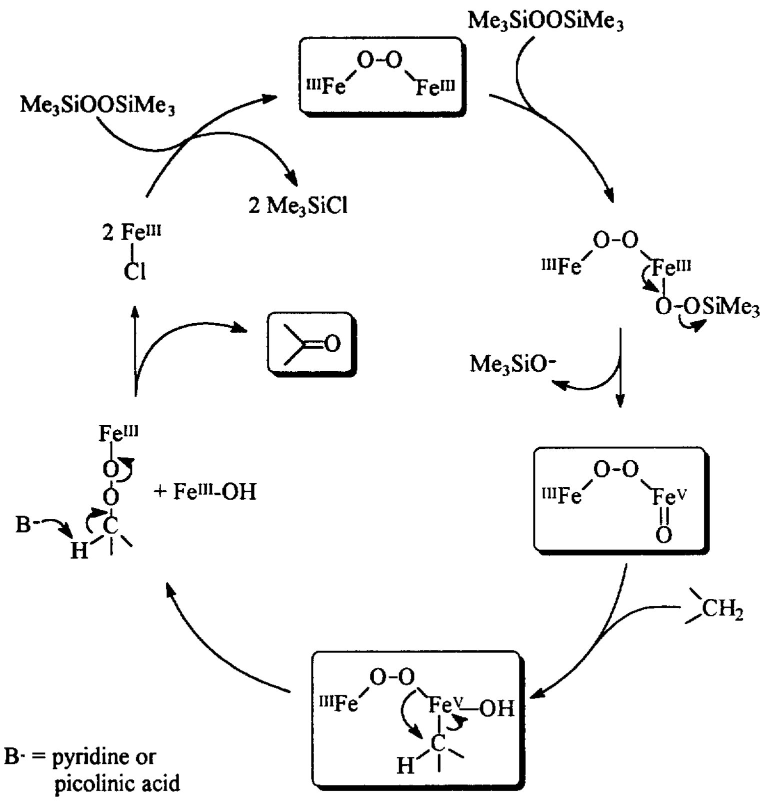
The sudden formation of chloride, which is normally the Fe^{II} reaction product was explained by the removal of oxygen from a μ-peroxo-dimer (**Scheme 7**).



$$^{III}Fe{-}O{-}O{-}Fe^{III} \rightleftharpoons 2\,Fe^{II} + O_2$$

Scheme 7

The entry 3 shows the displacement of the equilibrium with different conditions. The argon stream displaced the equilibrium on the right, forming alkyl chloride, as the oxygen replaced the equilibrium on the left reforming the μ-peroxo-dimer followed by the exclusive formation of the oxidation products. The example of cis-μ-1,2-peroxo diiron complex which is able to bind O_2 reversibly at ambient temperature was recently characterized by X-ray crystallography for the first time.[46] Several attempts were made to accumulate Fe^{II} in the absence of hydrocarbon using an argon stream without success; only 6% of Fe^{II} was detected.



$$Me_3SiCl + Me_3SiO^- \longrightarrow Me_3SiOSiMe_3 + Cl^-$$

Scheme 8: Proposed mechanism for hydrocarbon oxidation with $Fe^{III}(PA)_2Cl_2$,Pyr_2H-$Me_3SiOOSiMe_3$.

To summarize, we propose the catalytic cycle in **Scheme 8** to explain the results with the complex 34. It allows us to understand the non-radical nature of the reaction and the similarity found with the Fe^{III}-H_2O_2 system.[14] The fact that molecular oxygen is not involved in this reaction suggests that a second molecule of bis(trimethylsilyl) peroxide reacts with the μ-peroxo-dimer. The intermediate trimethylsilyl peroxy iron, after heterolytic fragmentation, gives the Fe^V oxenoid species. This species inserts itself in the C-H bond to produce the σ Fe-C bond. A ligand coupling between the alkyl and peroxyl moiety gives the alkyl peroxo iron which, with the help of a base, releases the oxidation products. The formation of hexamethyldisiloxane can be the driving of the reaction. When the reaction was followed kinetically by ^{29}Si NMR, we observed that the rapid formation of this compound corresponded to the disappearance of $Me_3SiOOSiMe_3$.

The presence of the right kind of carboxylic acid (picolinic acid in this article) is necessary to build the bridge before adding the oxidant. To simplify the scheme, we omitted the 2 picolinic acid ligated to the iron. To complete the coordination sphere, pyridine is proposed to be ligated also to the iron in the dimer formed from complex 34.

Utilization of Fe^{III}Cl$_3$

The importance of the carboxylic acid was already mentioned earlier in this paper. In accordance with the work done with hydrogen peroxide,[47] the absence of such a ligand inhibits almost all oxidation product formation (the efficiency was only 8.5%) (**Table 8**, entry 1). Instead, rapid oxygen formation was seen. Trying to understand how this formation occurred, we kept the amount of Fe^{III}Cl$_3$ constant and we increased the concentration of the oxidant from 1 to 4 mmol without hydrocarbon. As it is shown in the **Figure 3**, the formation of oxygen is almost quantitative and the half life for the formation of oxygen stays constant. If 2 equivalents of PA were added, no oxygen formation was seen.

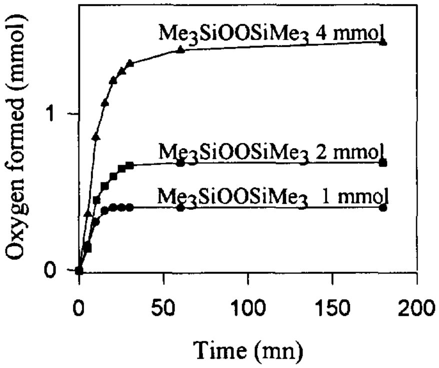
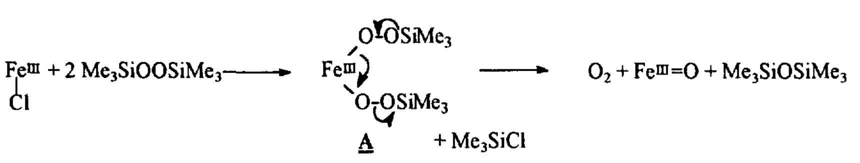


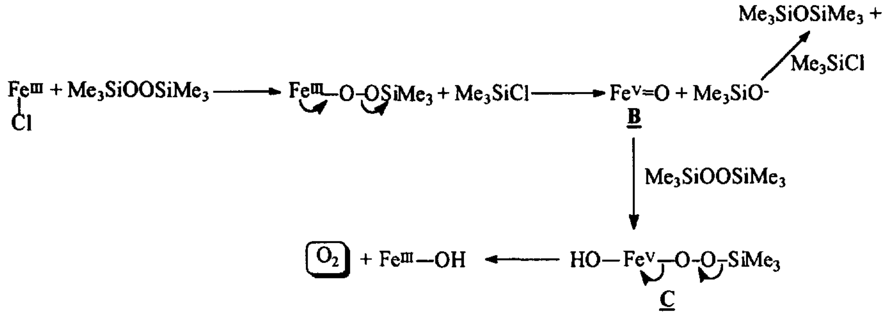
Figure 3: Kinetic analysis for the formation of oxygen with different amounts of $Me_3SiOOSiMe_3$.
Conditions: 1 mmol of Fe^{III}Cl$_3$ with $Me_3SiOOSiMe_3$ in Pyridine at 0°C to RT.

By these results, the mechanism involving the decomposition of the Fe^{III} ligated with two hydroperoxides A is dismissed (**Scheme 9**).



Scheme 9

In fact, if this was the case, the more peroxide added, the higher the concentration of the species containing the two hydroperoxides **A** should be. The half time of the reaction should be decreased which is not true.



Scheme 10: Proposed mechanism for the oxygen formation with the $Fe^{III}Cl_3$-$Me_3SiOOSiMe_3$.

The same characteristic was observed using H_2O_2,[47] allowing a proposition of the same kind of intermediate for this reaction (**Scheme 10**). The reaction of 1 mmol of $Fe^{III}Cl_3$ with 1 mmol of $Me_3SiOOSiMe_3$ in pyridine-d^5 was followed by ^{29}Si NMR. After 30 minutes, the signal corresponding to $Me_3SiOOSiMe_3$ disappeared completely and was replaced by the signal of the $Me_3SiOSiMe_3$ alone.

Now we know that the species formed with Fe^{III}-$Me_3SiOOSiMe_3$ is different depending on the presence or not of a carboxylate ligand. Also, we saw in earlier use, that diphenyl sulfide was oxidized to a minor extent with $Fe^{III}(PA)_3$-$Me_3SiOOSiMe_3$. The species formed preferred to oxidize the hydrocarbon instead. The effect of diphenyl sulfide was studied with $Fe^{III}Cl_3$ (**Table 9, entry 1**) to see if the new species formed was able to oxidize sulfide instead of making oxygen.

Table 9: Oxidation of diphenyl sufide 31 with the $Fe^{III}Cl_3$- $Me_3SiOOSiMe_3$.

Entry	Conditions	Products (mmol)					Mb in sulfide
		PhSPh 31	PhSOPh 32	$PhSO_2Ph$ 33	R=O 2	R-OH 3	(%)
1	A+ 1 20 mmol	---	---	---	0.187	n.d.	---
2	B+ 1 0 mmol	1.73	3.03	0.28	---	---	104
3	B+ 1 10 mmol	2.10	2.54	0.32	traces	n.d.	99

These reactions were carried out with 1 mmol of $Fe^{III}Cl_3$ and 5 mmol of $Me_3SiOOSiMe_3$ in 15 ml of pyridine (dried over KOH under reflux) at RT, overnight, under air. (A) without diphenyl sulfide 31. (B) with 5 mmol of diphenyl sulfide

Without hydrocarbon (entry 2), the sulfide **31** gave the sulfoxide **32** as major product and a small amount of sulfone **33** with a total yield of 66%. Adding 10 mmol of hydrocarbon **1** did not make a significant difference (entry 3) and, only traces of oxidation of hydrocarbon were detected.

The two Fe^{V} species showed in the **Scheme 10** could theoretically react with the sulfide **31**. But, if we assume that **B** and **C** can each deliver only one atom of oxygen to Ph_2S then the amount of sulfoxide and sulfone from **B** is 66% of theory with respect to oxidant whereas from **C** it is 132%. Since the mass balance is satisfactory, the oxidation products can not possibly come from a one oxygen atom transfer from **C**. This result is in accord with the theory postulated for the $Fe^{III}Cl_3$-H_2O_2 system.[47]

Other Fe^{III} complexes such as $Fe^{III}(fod)_3$, $Fe^{III}(2,2\ dipyridyl)_3Cl_3$ and $Fe^{III}(acac)_3$ were tested with the bis(trimethylsilyl) peroxide. The $Fe^{III}(fod)_3$, had the advantage to be soluble in a small amount of pyridine with cyclohexane (0.2 mmol of Fe^{III} with 50 mmol of cyclohexane in only 2 ml of pyridine). The efficiency of the reaction was around 37 % after 2 days but with a poor selectivity (one : ol < 2). Using $Fe^{III}(2,2\ dipyridyl)_3Cl_3$, the ketone was the only product formed but the reaction was slow and inefficient (12% after 2 days). Finally, the $Fe^{III}(acac)_3$, which was very soluble in a small amount of pyridine gave a slow reaction with this system. We considered that this reaction was radical in nature because 50% of the total of the products was the alkyl pyridine coupled products.

CONCLUSION

The utilization of bis(trimethylsilyl) peroxide and an Fe^{III} catalyst is able to oxidize saturated hydrocarbons to ketones as major products. Selectivity and chemioselectivity are similar to the Gif system. Radical intermediates are not present and an $Fe^{V}=O$ oxenoid species is proposed for the mechanistic pathway. Three different Fe^{III} catalysts were studied and presented different characteristics. $Fe^{III}(PA)_3$ is in a single iron state before and after the addition of the $Me_3SiOOSiMe_3$. It produces ketones and alcohols in relatively good yield. When $Fe^{III}(PA)_2Cl_2,Pyr_2H$ is used, the single iron species becomes a μ-peroxo-dimer in solution after the addition of the bis(trimethylsilyl) peroxide and the hydrocarbon. Ketone is still formed with a high selectivity. The absence of chelating ligands has a dramatic effect on the formation of oxidation products. Using a simple $Fe^{III}Cl_3$ salt, only a small amount of ketone and alcohol are produced and instead, a rapid oxygen formation is observed. The participation of an $Fe^{V}=0$ is again proposed for this catalase reaction.

EXPERIMENTAL

Unless otherwise stated, all chemicals were purchased from commercial sources and, after verification, used without further purification. ^{1}H and ^{13}C spectra were performed in deuterochloroform with tetrachloroethane as an internal standard on a Varian XL-200 spectrometer. ^{13}C and ^{29}Si NMR experiments were carried out at room temperature on a Varian XL-200 broad-band spectrometer. Chemical shifts are reported relative to TMS (δ = 0.00 ppm). UV-visible spectra were recorded on a Beckmann Du-7 spectrophotometer. Melting pts were measured using a Thomas-Hoover apparatus. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph using a DB-Wax or a DB-1 capillary column (15 meters long, film thickness 0.25 μm, J&W scientific). GC-MS analysis were carried out on a Hewlett-Packard 5890 series II gas chromatograph coupled to a Hewlett-Packard 5791 mass selective detector using a DB-5 column (30 meters long, film thickness 0.25 μm).

The pyridine was dried in two different ways as is stated in the text: under reflux over KOH or in the case of "dry conditions", under reflux over sodium.

Authentic samples (when not commercially available):

Bis(trimethylsilyl) peroxide was prepared according to a published procedure[17] and can be kept under argon at -18°C for months. As already remarked,[18] precautions have to be taken during its preparation.

The different salts used: $Fe^{III}(PA)_3$,[48] $Fe^{III}(PA)_2Cl_2$,PyrH 34[38] and the $Fe^{III}(fod)_3$[49] were prepared according to known procedures.

The authentic samples of the *2- and 4-cyclohexylpyridines* 4 and 5, *tert-2-and 4-adamantylpyridines* 21 and 22[50] were prepared by photolysis of the N-hydroxypyridine-2-thione derivatives[51] of the corresponding carboxylic acids[52] in pyridine-trifluoroacetic acid. *Cyclooctyl phenyl selenide* was synthesized also by photolysis of the N-hydroxypyridine-2-thione derivative of cyclooctyl carboxylic acid[52] in a solution of diphenyl diselenide in CH_2Cl_2. *Methyl Tempo* 41 and *tert*-butyldimethyl Tempo were prepared previously in the laboratory by the same method, using the the N-hydroxypyridine-2-thione derivative of the carboxylic acid and a solution of Tempo in CH_2Cl_2. The 2,2-dipyridyl disulfide was isolated from these reactions as a by-product. The *carbamic acid, phenyl cyclohexyl ester*[53] 14 was synthesized by addition of cyclohexanol 3 to phenyl isocyanate 13 with $AlCl_3$. *Cyclohexyloxy trimethylsilane*[54] was obtained by the reaction of cyclohexanol and trimethylsilylazide in THF. The oxoammonium salt, *2,2,6,6-tetramethyl-1-oxopiperidinium chloride*[55] 37 was prepared by bubbling Cl_2 gas into a solution of Tempo in CCl_4. The NMR data were in agreement with those already reported.[12]

Cyclohexyl Tempo 36:[8] Cyclohexyl Barton PTOC ester[51] (5 mmol) was added to a solution of Tempo (7 mmol) in CH_2Cl_2 at 0°C under argon. The solution was irradiated at room temperature until the total

consumption of the Barton PTOC ester. The solvent was removed by evaporation and the residue was purified by column chromatography (silicagel, hexane 75/ether 25) affording 75% of a colorless oil.
^{1}H NMR ($CDCl_3$), δ (ppm): 3.6 (m, 1H), 2.2-1.2 (m, 16H), 1.1 (s, 12H); ^{13}C NMR ($CDCl_3$), δ (ppm): 81.7, 59.5, 40.1, 32.8, 25.8, 25.75, 24.9, 17.1.

General work-up procedure for the oxidation reaction:

An aliquot of the reaction mixture (1.0 ml) with a naphthalene solution in ether (1.0 ml) was washed with water and extracted with 10 ml of ether. The aqueous layer containing Fe salts was discarded. The organic layer was dried over $MgSO_4$. The products, including pyridine derivatives were quantified by gas chromatography from the organic layer.

General procedure for the reactions with Fe^{III}-$Me_3SiOOSiMe_3$:

The Fe^{III} complex (0.5 mmol) and cyclohexane (20 mmol) were dissolved in 15 ml of pyridine under air at room temperature. The reaction was initiated by the addition of 2 mmol of $Me_3SiOOSiMe_3$. The reaction mixture was stirred at room temperature overnight. The general work-up procedure (see above) was followed to quantify the products by gas chromatography.

General procedure for the reaction with Fe^{III}-$Me_3SiOOSiMe_3$ using a constant argon stream:

Fe^{III} complex (2 mmol) and cyclooctane (80 mmol) were dissolved in 60 ml of pyridine at room temperature. The solution was cooled at 0°C and the vessel was flushed with argon through the solution for 15 minutes. The reaction was initiated by the addition of 8 mmol of $Me_3SiOOSiMe_3$ and stirred at 0°C overnight under the stream of argon. After 20 h, the reaction was allowed to reach room temperature. General work-up procedure was followed to quantify the products by gas chromatography.

General procedure for the reactions with Fe^{III}-$Me_3SiOOSiMe_3$ in presence of 2,4-di-tert-butylphenol <u>38</u>:

2,4-Di-*tert*-butylphenol (1 mmol), Tempo (2 mmol) and $Fe^{III}(PA)_2Cl_2,Pyr_2H$ (0.5 mmol) were dissolved in pyridine (15 ml) and the reaction was deoxygenated and kept under argon. The $Me_3SiOOSiMe_3$ was added at room temperature stirred overnight under argon.

Quantification of the different products:

- An aliquot of the reaction mixture (1 ml) with a naphthalene solution in ether (1 ml) was washed with a NaOH solution (10%) saturated with NaCl and extracted two times with 5 ml of ethyl acetate. The combined organic layer were dry under $MgSO_4$ and Tempo, 2,4-di-tert-butylphenol and 2,2,6,6- tetramethyl piperidine were quantified by GC.

- The remaining solution was reduced by adding Zn (1 g) and AcOH (2 ml) under argon. After 30 mn, an other aliquot (1 ml) was taken and added to 2 ml of acetic anhydride. The aliquot was stirred under argon for 3h and worked up as described previously with a naphthalene solution (1 ml). The 3,5-di-*tert*-butyl-*o*-benzoquinone **40**, transformed into 1,2-diacetoxy-3,5-di-*tert*-butyl benzene,[13] was quantified by GC.

General procedure for the titration of peroxide remaining in solution:

An aliquot of the reaction mixture (1 ml) was added to a mixture of water (5 ml), acetic acid (5 ml) and KI (0.5g) under argon at room temperature. The reaction was stirred for 30 minutes and the I_2 formed was titrated with a $Na_2S_2O_3$ solution (40mM).Starch was used as indicator and produced a dark brown color until all the I_2 was consumed (the solution became colorless).

Measurement of the amount of O_2 evolved:

The reaction system was gastight and connected to a manometric burette filled with saturated brine solution which was saturated with air prior to use. The volume of oxygen gas evolved from the reaction was measured. During the readings, the pressure was always equilibrated using a separatory funnel by adjusting the brine levels to the same heights. Also, the appropriate temperature and atmospheric pressure were taken into account before each reading and considered in the calculation (22.4 ml corresponds to 1 mmol).

General procedure for generation of trialkylsiloxy radicals:[45]

N-hydroxy-2-thiopyridone (2 mmol) was dissolved in dried pyridine (10 ml) under argon. The solution was cooled ot 0°C and protected from the light. The trimethyl or tert-butyldimethylsilyl chloride was added and the reaction was stirred 60 minutes at room temperature (the formation of the Barton PTOC ether make the solution became yellow). Then, Tempo (3 mmol) was added and the reaction mixture was photolized for 1h at 0°C. General work-up procedure was followed to quantify the products by gas chromatography.

ACKNOWLEDGMENTS

We thank the Welch Foundation, the N.S.F. and the Schering-Plough Corporation for the support of this work.

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(*Received in USA* 21 *August* 1996; *revised* 10 *October* 1996; *accepted* 24 *October* 1996)