

# Radical chemistry of *tert*-butyl hydroperoxide (TBHP). Part 2. Studies of the Fe<sup>II</sup>–TBHP mechanism

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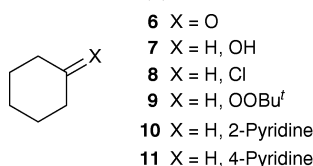
By maintaining the iron catalyst in the ferrous [iron(II)] state, the oxidation chemistry of TBHP was dominated by the *tert*-butoxyl radical. Saturated hydrocarbons were readily oxidized.

**La chimie radicalaire de l'hydroperoxyde de *tert*-butyle (TBHP). Partie 2. Etudes mécanistiques du système Fe<sup>II</sup>–TBHP.** En maintenant le fer à l'état d'oxydation II, la chimie de TBHP est dominée par la présence de radicaux *tert*-butoxylés. Les hydrocarbures saturés sont facilement oxydés.

In our preceding paper<sup>1</sup> on the radical chemistry of TBHP, we showed how the reactions could be simplified by maintaining the ferric [iron(III)] state of the iron throughout the reaction by addition of the appropriate oxidizing agent. In this second paper we keep the iron in the ferrous [iron(II)] state by addition of a suitable reductant. Again, there is a major simplification of the chemistry. As discussed in Part 1,<sup>1</sup> we showed that if the iron was maintained as Fe<sup>III</sup>, then the chemistry observed was that of the *tert*-butylperoxyl radical. Similarly, as in Part 1, Scheme 1 suggests that if the iron is kept as Fe<sup>II</sup>, then the key reaction will be: Fe<sup>II</sup> + Bu<sup>t</sup>OOH + H<sup>+</sup> → Fe<sup>III</sup> + Bu<sup>t</sup>O<sup>•</sup> + H<sub>2</sub>O. In this sequel, we present the evidence for this conclusion.

Saturated hydrocarbons are noted for their kinetic inertia towards oxygen at room temperature. Nevertheless, the subject is of major interest to bioorganic, bioinorganic and organic synthetic chemists.<sup>2,3</sup> In many respects, TBHP is more useful than H<sub>2</sub>O<sub>2</sub> because its efficiency as an oxidant is not wasted in a catalase-type decomposition to give oxygen.<sup>4</sup>

Hydrogen sulfide reduces Fe<sup>III</sup> to Fe<sup>II</sup> and, in Gif chemistry, permits the Fe<sup>II</sup>–Fe<sup>IV</sup> manifold to be studied.<sup>5</sup> Some other reductants that have served well for this purpose are stannous [tin(II)] chloride, vanadium(II) chloride and vanadium(III)



**Scheme 1** Fe<sup>II</sup>-catalyzed oxidation of cyclohexane

chloride. They reduce any Fe<sup>III</sup> to Fe<sup>II</sup> very rapidly. Since the Fe<sup>II</sup> oxidation chemistry is always very fast also, the relatively slow reduction of TBHP to *tert*-butanol by these reducing agents does not interfere in the oxidation chemistry being studied.

In Table 1, some typical results (formulae numbering as in the preceding paper) are presented for the reaction of TBHP with various reducing agents in the presence of cyclohexane. Vanadium di- and tri-chlorides (entries 1 and 2) react with TBHP to generate *tert*-butoxyl radicals. These afford cyclohexyl pyridines in significant yield with only traces of chloride formation. Stannous chloride (entry 3) reduces TBHP, but without formation of *tert*-butoxyl radicals. As expected, FeCl<sub>2</sub> itself (entry 4) gives *tert*-butoxyl radicals. The major reaction is the fast formation of cyclohexyl chloride (from the efficient R<sup>•</sup> + FeCl<sub>3</sub> reaction). Vanadium trichloride and FeCl<sub>2</sub> together (entry 5) give a similar result.

The formation of *tert*-butoxyl radicals from TBHP by the action of VCl<sub>2</sub> and VCl<sub>3</sub> is interesting. This complicates the interpretation of the Fe<sup>II</sup> experiments. However, both VCl<sub>2</sub> and VCl<sub>3</sub> instantly reduced Fe<sup>III</sup> to Fe<sup>II</sup> in the absence of TBHP.

In Tables 2 to 6, the effect of the addition of a reducing agent on the Fe<sup>III</sup>–TBHP and Fe<sup>II</sup>–TBHP oxidations of cyclohexane is reported. In all of these tables, the effect of hydrogen sulfide, stannous chloride or vanadium chloride is to increase markedly the concentration of cyclohexyl radical giving mainly chloride.

In Table 2, entry 1, the *tert*-butylperoxyl radicals that are initially formed couple together to furnish<sup>6</sup> oxygen and *tert*-butoxyl radicals. The latter are responsible for the abstraction

**Table 1** Competition between Fe<sup>II</sup>-catalyzed functionalization of cyclohexane and transformation of TBHP by reducing agents in the presence of cyclohexane<sup>a</sup>

Entry	Conditions	Time/min	8	10	11	8 + 10 + 11 <sup>c</sup>
1	VCl <sub>2</sub> alone	4	0.02	0.32	0.14	0.48
2	VCl <sub>3</sub> alone	1	0.02	0.21	0.10	0.33
3	SnCl <sub>2</sub> alone	4	n.d. <sup>b</sup>	0.005	n.d.	tr. <sup>c</sup>
4	FeCl <sub>2</sub> alone	1	0.43	0.04	0.02	0.49
5	VCl <sub>3</sub> + FeCl <sub>2</sub>	4	0.35	0.03	0.01	0.39

<sup>a</sup> C<sub>6</sub>H<sub>12</sub> (20 mmol); TBHP (1 mmol); LiCl (10 mmol); pyridine (15 mL); FeCl<sub>2</sub> (1 mmol, when present); VCl<sub>3</sub> or VCl<sub>2</sub> (5 mmol, when present); SnCl<sub>2</sub> (3 mmol, when present); RT under argon. All reactions were complete in 4 min, but were followed for 1 h. All data in mmol. <sup>b</sup> n.d. = not detected. <sup>c</sup> tr. = trace.

**Table 2** Influence of stannous chloride on the Fe<sup>III</sup>-catalyzed functionalization of cyclohexane<sup>a</sup>

Entry	6	7	8
1	0.61	0.12	0.13
2a	0.92	0.13	1.15
2b	1.24	0.13	0.28

<sup>a</sup> FeCl<sub>3</sub> · 6H<sub>2</sub>O (1 mmol); TBHP (10 mmol); C<sub>6</sub>H<sub>12</sub> (20 mmol); pyridine (30 mL); RT under air. Entry 1: reaction for 9 h. Entry 2a: same reaction mixture as in entry 1 but results are given after having added 6 mmol of SnCl<sub>2</sub> at *t* = 9 h and stirring overnight. Entry 2b: same as entry 2a without SnCl<sub>2</sub> (commensurate with entry 1 stirred overnight). Total reaction time ≈ 24 h. The pyridine coupling products **10** and **11** are detected only in trace amounts. All data in mmol.

of hydrogen to furnish cyclohexyl radicals. These then react with oxygen to furnish the ketone **6** and the alcohol **7**. A minor amount of chloride **8** is formed from the reaction of the radical with FeCl<sub>3</sub>. In entry 2a, the reaction was run for 9 h, as in entry 1. Then 6 mmol of SnCl<sub>2</sub> was added. At this point of the experiment, the iron is reduced to Fe<sup>II</sup> and TBHP is therefore decomposed into *tert*-butoxyl radicals (and no longer into *tert*-butylperoxyl radicals). Thus, this increases the concentration of *tert*-butoxyl radicals (Fe<sup>II</sup> chemistry is fast: the half-life is only several minutes) and suppresses the formation of oxygen. Therefore, there is a small increase in ketone and a major increase in chloride formation from the cyclohexyl radicals. Entry 2b is the blank experiment without reductant.

In Table 3, the slow reaction of Fe<sup>III</sup>-TBHP is again observed. After 2.5 h, one of three different reductants that convert Fe<sup>III</sup> to Fe<sup>II</sup> was added and then left for 22 h. Vanadium tri- and di-chlorides are efficient reductants and give major amounts of chloride (entries 2a and 2b). In entry 2c, stannous dichloride was less efficient, but we must note that this entry is different (6 mmol of reductant) from 2a in Table 2. The blank experiment in Table 3 (entry 2d) agreed with the blank experiment in Table 2.

In Table 4, the effect of tin chloride on an experiment starting with FeCl<sub>2</sub> was studied. Again, the reductant had a major effect on the formation of chloride from the cyclohexyl radicals.

Another reagent that reduces Fe<sup>III</sup> to Fe<sup>II</sup> is hydrogen sulfide. This can be demonstrated by simple titration for Fe<sup>II</sup>. Table 5 (entry 1) shows how a limited amount of hydrogen sulfide gives only limited amounts of oxidation products, but produces a major amount of chloride from radical chemistry.

In a further comparison of reducing agents (Table 6) using FeCl<sub>2</sub>, the major effect of Fe<sup>II</sup> on chloride production was quite clear. In each case the *tert*-butoxyl radicals give major amounts of chloride.

**Table 3** Comparison between several reducing agents towards the Fe<sup>III</sup>-catalyzed functionalization of cyclohexane<sup>a</sup>

Entry	Reductant	6	7	8
1	—	0.10	0.04	n.d. <sup>b</sup>
2a	VCl <sub>3</sub>	0.21	n.d.	2.89
2b	VCl <sub>2</sub>	0.25	n.d.	2.32
2c	SnCl <sub>2</sub>	0.28	0.08	0.49
2d	none	0.81	0.09	0.22

<sup>a</sup> FeCl<sub>3</sub> · 6H<sub>2</sub>O (1 mmol); TBHP (10 mmol); C<sub>6</sub>H<sub>12</sub> (20 mmol); pyridine (30); VCl<sub>3</sub> or VCl<sub>2</sub> (5 mmol, when present); SnCl<sub>2</sub> (3 mmol, when present); RT under air. Entry 1: reaction for 2.5 h. Entry 2: same reaction mixture as in entry 1 but results are given after having added *x* mmol of a reductant at *t* = 2.5 h and stirring overnight. Total reaction time ≈ 22.5 h. The pyridine coupling products **10** and **11** are detected only in trace amounts. All data in mmol. <sup>b</sup> n.d. = not detected.

In Tables 2 to 6, TBHP was added in one portion at the beginning of the experiment. Under these circumstances, the *tert*-butoxyl radicals have the chance to react with TBHP to give *tert*-butylperoxy radicals, which eventually react by the alkylperoxyl bimolecular self-reaction.<sup>6</sup> In Table 7, two different ways of adding TBHP are compared. The portionwise

**Table 4** Influence of stannous chloride on the Fe<sup>II</sup>-catalyzed functionalization of cyclohexane<sup>a</sup>

Entry	6	7	8
1	0.14	n.d.	2.27
2	0.75	0.13	0.50

<sup>a</sup> FeCl<sub>2</sub> · 4H<sub>2</sub>O (1 mmol); TBHP (10 mmol); C<sub>6</sub>H<sub>12</sub> (20 mmol); pyridine (30); RT under air; reaction time 10 h. Entry 1: addition of SnCl<sub>2</sub> (3 mmol). Entry 2: blank experiment without SnCl<sub>2</sub>. The pyridine coupling products **10** and **11** are detected only in trace amounts. All data in mmol. <sup>b</sup> n.d. = not detected.

**Table 5** Influence of hydrogen sulfide on the Fe<sup>II</sup>-catalyzed functionalization of cyclohexane<sup>a</sup>

Entry	TBHP						
	6	7	8	left	Bu'OH	(Bu'O) <sub>2</sub>	MB <sub>TBHP</sub> <sup>b</sup> /%
1	tr. <sup>c</sup>	n.d. <sup>d</sup>	1.85	n.d.	8.12	n.d.	82
2	0.87	n.d.	0.38	5	3.83	0.11	90

<sup>a</sup> FeCl<sub>2</sub> · 4H<sub>2</sub>O (1 mmol); TBHP (10 mmol); C<sub>6</sub>H<sub>12</sub> (20 mmol); pyridine (30 mL); LiCl (15 mmol); RT under air; reaction time 24 h. Entry 1: addition of H<sub>2</sub>S (5 mmol). Entry 2: blank experiment without H<sub>2</sub>S. The pyridine coupling products **10** and **11** are detected only in trace amounts. All data in mmol. <sup>b</sup> Mass balance with respect to TBHP. <sup>c</sup> tr. = trace amount. <sup>d</sup> n.d. = not detected.

**Table 6** Comparison of several reducing agents toward the Fe<sup>II</sup>-catalyzed functionalization of cyclohexane<sup>a</sup>

Entry	Reductant	6	7	8	10	11
1	VCl <sub>3</sub>	0.05	n.d. <sup>b</sup>	1.90	0.09	0.02
2	VCl <sub>2</sub>	0.13	n.d.	1.90	0.08	0.03
3	SnCl <sub>2</sub>	0.10	0.03	0.76	n.d.	n.d.
4	none	0.45	0.08	0.32	0.04	0.02

<sup>a</sup> FeCl<sub>2</sub> · 4H<sub>2</sub>O (1 mmol); TBHP (5 mmol); C<sub>6</sub>H<sub>12</sub> (20 mmol); pyridine (30); VCl<sub>3</sub> or VCl<sub>2</sub> (2 mmol, when present); SnCl<sub>2</sub> (1.2 mmol, when present); RT under argon; reaction time 8 h. Reducing agent (when present) was added at the beginning of the experiment. All data in mmol. <sup>b</sup> n.d. = not detected.

**Table 7** Influence on the product distribution of the way of adding TBHP during the Fe<sup>II</sup>-catalyzed oxidation of cyclohexane **1**<sup>a</sup>

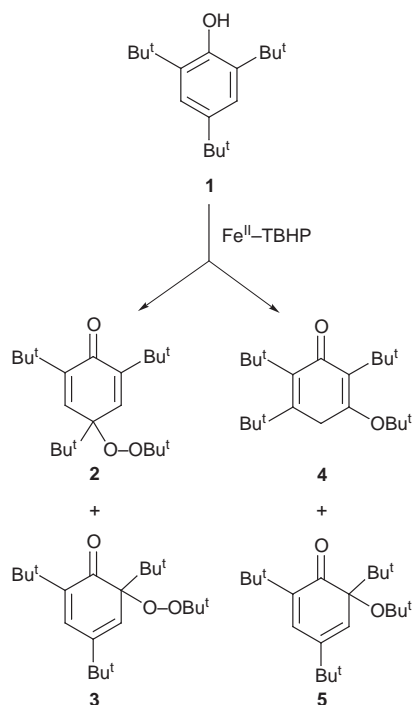
Entry	6	7	8	10	11
1	0.47	0.09	0.51	0.02	tr. <sup>b</sup>
2	0.39	0.06	1.27	0.06	0.04

<sup>a</sup> FeCl<sub>2</sub> (1 mmol); TBHP (5 mmol); C<sub>6</sub>H<sub>12</sub> (20 mmol); pyridine (15 mL); RT under air; reaction time 7.5 h. Entry 1: TBHP added all at once. Entry 2: TBHP added portionwise over 15 min. All data in mmol. <sup>b</sup> tr. = trace amount.

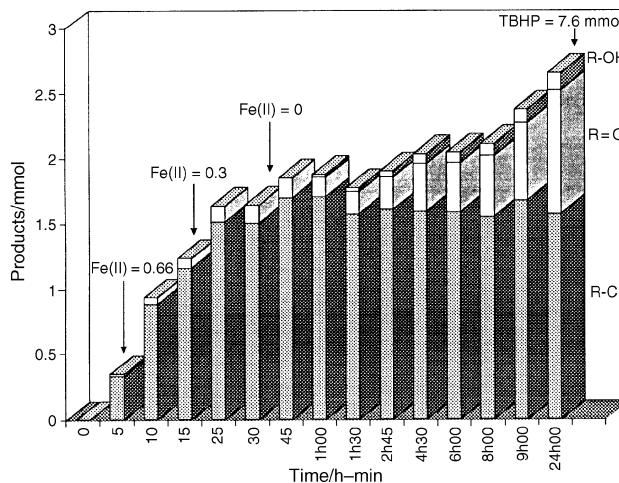
addition was about two times as efficient as the single addition at the beginning of the experiment.

In Table 8, the results of the addition of a reducing agent on the oxidation of 2,4,6-tri-*tert*-butylphenol are summarized. Although TBHP is added slowly by means of a syringe pump, the *tert*-butoxyl radicals react with TBHP to give *tert*-butylperoxyl radicals [eqn. (3) in Scheme 1 of ref. 1]; this explains why, keeping the iron as Fe<sup>II</sup>, we still detect the adducts **2** and **3** (Scheme 2). However, Table 8 clearly shows that the presence of the reducing agent increases the ratio (4 + 5)/(2 + 3); this confirms eqn. (2) of Scheme 1 in the preceding paper.<sup>1</sup>

Finally, by means of a syringe pump for the addition of TBHP and the use of tin chloride, it was possible to obtain very high yields of cyclohexyl chloride. The reaction was followed kinetically with concomitant titration of Fe<sup>II</sup> in order to study carefully the product distribution as a function of the oxidation state of the iron. The results are presented in Fig. 1. When the iron is in the Fe<sup>II</sup> oxidation state, cyclohexyl chloride is the main product (half-life:  $t_{1/2} \approx 10$  min). Some ketone and coupling products with pyridine are only detected in minor amounts. As has already been mentioned in a previous communication,<sup>8</sup> as soon as Fe<sup>II</sup> is oxidized to Fe<sup>III</sup>, a marked change in the product distribution occurs: chloride formation almost stops and is replaced by the formation of ketone and



**Scheme 2** Fe<sup>II</sup>-catalyzed oxidation of 2,4,6-tri-*tert*-butylphenol



**Fig. 1** Kinetic study of the Fe<sup>II</sup> + TBHP-catalyzed functionalization of cyclohexane. FeCl<sub>2</sub> (1.5 mmol); TBHP (10 mmol added slowly with a syringe pump over 15 min); C<sub>6</sub>H<sub>12</sub> (20 mmol); SnCl<sub>2</sub> (0.3 mmol); pyridine (30 mL); RT under air. The pyridine coupling products **10** and **11** are detected only in trace amounts.

alcohol. The ketone and the alcohol minor product are formed by dimerisation of the *tert*-butylperoxyl radical with formation of oxygen, the *tert*-butoxyl radical and a minor amount of di-*tert*-butyl peroxide. A blank experiment showed that the Fe<sup>II</sup> or Fe<sup>III</sup> plus TBHP systems slowly oxidize cyclohexyl chloride into cyclohexanone; this explains why the amount of chloride slightly decreases with time.

In conclusion, a system composed of FeCl<sub>2</sub> and *tert*-butyl hydroperoxide in a mixture of an alkane and pyridine readily afforded alkyl chloride as the major product. The addition of a reducing agent preserved the Fe<sup>II</sup> in solution and allowed more efficient transformations. When Fe<sup>II</sup> is converted to Fe<sup>III</sup>, a dramatic change in the product distribution is observed and ketone and alcohol are formed, as opposed to alkyl chloride.

The Fe<sup>II</sup>-TBHP system involves *tert*-butoxyl radicals that result from the homolytic decomposition of Fe<sup>II</sup>-O-O-Bu<sup>t</sup>. These oxygen-centered radicals are able to abstract hydrogen from the substrate to generate carbon-centered radicals.

The results presented in this and the preceding paper show that the presence of a higher valence state of iron other than Fe<sup>III</sup> is not required for this *tert*-butyl hydroperoxide chemistry. This, of course, does not mean that with different ligands on the iron higher valence states might not be involved.<sup>9</sup>

## Experimental

Gas chromatographic analysis was performed on a Hewlett-Packard 5890 series II instrument, equipped with a flame ionization detector with N<sub>2</sub> as a carrier gas and a Hewlett

**Table 8** Influence of a reductant on the oxidation of 2,4,6-tri-*tert*-butylphenol **1**<sup>a</sup>

Entry	x <sup>b</sup>	y <sup>c</sup>	z <sup>d</sup>	Reductant	Time/min	1 left	2	3	4	5	MB <sub>1</sub> <sup>e</sup> /%	Ratio (4 + 5)/(2 + 3)
1a	5.3	10	0	—	15	1.00	2.76	1.03	0.56	0.41	108	0.26
1b	5.3	10	15	H <sub>2</sub> S	15	2.76	1.08	0.40	0.77	0.51	104	0.86
2a	5.3	5	0	—	15	2.64	1.10	0.37	0.87	0.63	106	1.02
2b	5.3	5	2	VCl <sub>3</sub>	15	4.34	0.33	0.12	0.50	0.35	106	1.89
2c	5.3	5	2	VCl <sub>2</sub>	15	3.77	0.35	0.13	0.54	0.41	98	1.98
3a	5	5	0	—	90	1.49	1.28	0.45	1.14	0.88	105	1.17
3b	5	5	2	VCl <sub>3</sub>	90	2.28	0.50	0.18	0.98	0.67	92	2.43

<sup>a</sup> FeCl<sub>2</sub> · 4H<sub>2</sub>O (1 mmol); pyridine (15 mL); RT under air. The pyridine coupling products **10** and **11** are detected only in trace amounts. All quantities are in mmol except as noted. <sup>b</sup> Mmol of **1**. <sup>c</sup> Mmol of TBHP (added by means of a syringe pump: 5 mmol over 15 min). <sup>d</sup> Mmol of reductant. <sup>e</sup> Mass balance with respect to **1**.

Packard 3396 A integrator. The column used was a DB-Wax (30 m long, 0.25  $\mu$ m film thickness, 0.32 mm i.d.) from J&W Scientific.

Unless otherwise stated, all solvents and chemicals were purchased from commercial sources and used, after verification, without further purification. TBHP was used as a 90% aqueous solution, after checking its purity by iodometric titration.

### General procedures

**Reactions with 1.** To a solution of **1** ( $x$  mmol) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (1 mmol) in pyridine (15 mL) was slowly added TBHP ( $y$  mmol), by means of a syringe pump, with stirring at room temperature. At the end of the reaction, the reaction was quenched with a 20% aqueous solution of sulfuric acid. The aqueous phase was extracted three times with diethyl ether. The combined organic layers were washed with a saturated solution of sodium bicarbonate, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Quantification was carried out by  $^1\text{H}$  NMR using 1,1,2,2-tetrachloroethane as an internal standard.

**Reactions with  $\text{Fe}^{\text{II}}$ -TBHP.** To a solution of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (1 mmol) and cyclohexane (20 mmol) in pyridine (30 mL) was added TBHP (10 mmol) with stirring at room temperature. After 24 h, an aliquot (1 mL) of the reaction mixture was added to a saturated solution of aqueous sodium bicarbonate (5 mL). The aqueous solution was extracted with diethyl ether (10 mL). The ethereal solution was dried over  $\text{MgSO}_4$  and filtered. Naphthalene solution (1 mL, 0.08 M in diethyl ether) was added as an internal standard to the filtrate. The products were analyzed by gas chromatography.

**Titration of  $\text{Fe}^{\text{II}}$ .**<sup>10</sup> An aliquot of the reaction mixture (2 mL) was added to a 25% aqueous  $\text{H}_2\text{SO}_4$  solution (20 mL) at room temperature under an argon stream. After 5 min, the mixture was diluted to 250 mL with distilled water. Five milliliters of this solution was added to a mixture of  $(\text{NH}_4)_2\text{HPO}_4$  (10 mL at 10%) and water (15 mL). The pH of the solution was adjusted to 2.0–2.1 with an  $\text{H}_2\text{SO}_4$  solution (25%). The solution was transferred to a separating funnel and 4,7-diphenyl-1,10-phenanthroline solution in absolute ethanol (30 mL at 0.36 mM) was added. After shaking for a few seconds and allowing the solution to stand for several min, the solution was extracted with 10 mL of  $\text{CHCl}_3$ . The organic phase was transferred to a 25 mL volumetric flask and the solution was diluted to volume with absolute ethanol. The absorbance was measured in a 1 cm cell at 540 nm. The quantity of  $\text{Fe}^{\text{II}}$  was calculated as 1  $\mu\text{g}$  of  $\text{Fe}^{\text{II}}$  corresponding to an absorbance of 0.0156.

**Oxidation of cyclohexyl chloride.** To a solution of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1 mmol) and cyclohexyl chloride (20 mmol) in pyridine (30 mL) was added TBHP (10 mmol) with stirring at room temperature. After 24 h, the usual workup was carried out and the products were analyzed by gas chromatography. The disappearance of 32% and 25% of the cyclohexyl chloride for the  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  systems, respectively, was observed. Ketone and alcohol were formed instead.

**Use of  $\text{SnCl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{VCl}_2$  and  $\text{VCl}_3$  as reductants.** To a solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1 mmol) in pyridine (15 mL) was added  $z$  mmol of the reductant ( $z = 0.5$  for  $\text{SnCl}_2$  and  $z = 1$  for  $\text{VCl}_3$  and  $\text{VCl}_2$ ) with stirring under argon at room temperature. After 1 min, a titration of  $\text{Fe}^{\text{II}}$  was carried out (*vide supra*), which showed the presence of a quantitative amount of  $\text{Fe}^{\text{II}}$  (>80% in every case).

To a solution of  $\text{SnCl}_2$ ,  $\text{VCl}_3$  or  $\text{VCl}_2$  ( $z$  mmol) in pyridine (15 mL) was added TBHP (5 mmol) with stirring at room temperature. The disappearance of TBHP was followed with time by quantifying the resulting  $\text{Ph}_3\text{PO}$  by  $^1\text{H}$  NMR (*vide infra*) (the iodometric titration is not suitable in this particular case since the reductants interfere during the analysis by reducing the iodine). When  $z$  was equal to 5 mmol, the half-life of TBHP was only a few min.

**Quantification.** The NMR and GC quantifications have been performed according to the previously reported methods.<sup>1</sup> The determination of the residual oxidizing power was performed with triphenylphosphine (quantification of the resulting triphenylphosphine oxide) according to the following procedure. An aliquot of the reaction mixture (5 mL) was quenched with an excess of  $\text{Ph}_3\text{P}$  (typically 0.5 g). After 10 min at room temperature, the mixture was worked up with a 20% aqueous solution of sulfuric acid. The water layer was extracted three times with ether. The combined organic phases were washed with a saturated solution of sodium bicarbonate, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Quantification of the resulting  $\text{Ph}_3\text{PO}$  was carried out by  $^1\text{H}$  NMR using 1,1,2,2-tetrachloroethane as an internal standard.

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