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Unexpected high oxidation of cyclohexane by Fe salts and dihydrogen peroxide in acetonitrile

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ABSTRACT

The reaction of cyclohexane (CyH) with 1.5 equivalent of dihydrogen peroxide (30% aqueous solution) in the presence of 1 mol% of an iron(II) or iron(III) salt (without added ligand), at 50 °C in acetonitrile, produces cyclohexanol (Cy–OH) and cyclohexanone (Cy=O) in high yields (up to 87% of CyH is converted to Cy–OH + Cy=O). Remarkably, CyH is totally converted within 2 h in the presence of Fe(ClO₄)₂ as catalyst under argon, producing 45% of Cy–OH and 42% of Cy=O. The addition of a tridentate Schiff-base ligand, namely 2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**), leads to a clear increase of the selectivity towards Cy–OH + Cy=O, which are obtained with an overall yield of 93% (and even 100% selectivity to Cy–OH and Cy=O) in the case of the [Fe(ClO₄)₃/**dapb**] catalytic system.

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1. Introduction

The oxidation of cyclohexane (CyH) into cyclohexanone (Cy=O) and cyclohexanol (Cy–OH) is of great industrial importance. Over one billion tonnes of Cy=O and Cy–OH are produced each year worldwide, which are mostly used in the manufacture of Nylon-6 and Nylon-6,6 [1]. In the industrially applied process, cobalt naphthenate is used to initiate the radical oxidation of cyclohexane using molecular oxygen from the air and heating the solution to 160 °C at a pressure of 15 bar. However, after 40 min, only 4% of CyH is converted to oxidized products and with 80% selectivity towards Cy=O and Cy–OH [2].

An ideal procedure for the oxidation of CyH would be one that yields only Cy=O and Cy–OH with 100% conversion of CyH using either O₂ or H₂O₂ as the oxidant, in an environmentally benign solvent, carried out at room temperature (RT) and pressure, and uses a highly active and recyclable catalyst [3].

Nature has provided a hint as to the type of catalyst that can be employed in the oxidation of CyH because certain bacteria produce methane monooxygenase, an enzyme with a dinuclear iron site

capable of oxidizing methane to methanol under mild conditions [4]. Many current studies are dedicated to using biomimetic, non-heme iron catalysts for the oxidation of alkanes [5–12]. The selective catalytic oxidation of CyH is an ongoing challenge, since activation of the C–H bond is quite difficult at room temperature and pressure, and the ideal reaction conditions have yet to be achieved [13].

As early as 1876, Fenton found that iron(II) salts in an acidic aqueous solution using dihydrogen peroxide as oxidant is capable of oxidizing alkanes [14,15]. Many mechanisms have been proposed for this reaction, most involving reactive radicals such as OH• or OOH• and others involving reactive, high-valent iron species (so-called iron(IV)- and iron(V)-oxido species); although, it is believed that the various mechanisms compete in different ways depending on the reaction conditions [16]. A major problem with Fenton chemistry is that it does not oxidize alkanes selectively [7]. The late Sir Derek Barton has introduced a system, called the Gif family, for the selective oxygenation of CyH (Cy=O: Cy–OH ratio up to 19:1), which operates at room temperature and uses atmospheric dioxygen or dihydrogen peroxide as oxidant, an iron salt as catalyst and with pyridine (buffered with acetic acid) as the solvent [17–19].

The search for a catalytic system that oxidizes CyH selectively and efficiently is ongoing. Britovsek et al. [20] have noted that multidentate ligands containing nitrogen (preferably pyridine) donors with a *cis* orientation of two labile co-ligands are desirable criteria in catalyst design. Recently, Tang et al. [21] have reported very promising results, where 99% conversion of CyH to Cy=O and Cy–OH (one:ol ratio of 1.00) within 12 h

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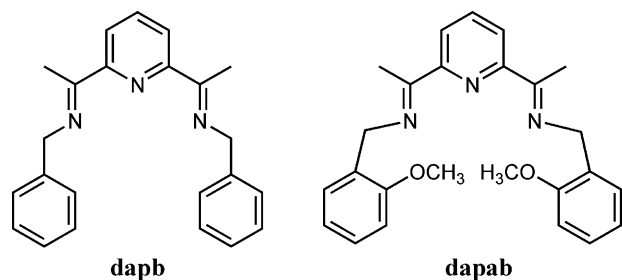


Fig. 1. Structures of the ligands 2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**) and 2,6-bis[1-(2-methylanisolylimino)ethyl]pyridine (**dapab**) [21].

using iron(II) tetrafluoridoborate with the ligand 2,6-bis[1-(2-methylanisolylimino)ethyl]pyridine (**dapab**; Fig. 1) as the catalytic precursors with acetonitrile as the solvent at 50 °C using H₂O₂ as the oxidant (catalyst:substrate:oxidant ratio of 1:100:150) [21].

This system has now been further analyzed by introducing modifications to the ligand in order to better understand its selectivity and to possibly improve the reaction rate. The results herein described, show that using 2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**) increases the selectivity of the oxidation of CyH under the same reaction conditions used by Tang et al. [21], as compared to using the free iron salt in acetonitrile as the catalyst precursor. Most surprisingly, even the Fe(II)/Fe(III) salts with only acetonitrile solvent as ligand, show already high activity.

2. Results and discussion

2.1. Synthesis of the ligand

2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**)

The tridentate ligand 2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**; Fig. 1) has been prepared by condensation of benzyl amine with 2,6-diacetylpyridine (see Section 4). The reaction of two equivalents of the primary amine with one equivalent of 2,6-diacetylpyridine under argon in methanol at room temperature produces the Schiff base **dapb** with a yield of 53%. The condensation reaction is carried out in the presence of a catalytic amount of formic acid, as described in the literature [22]. It has been found that water significantly hinders the reaction as the ligand is obtained only with a poor yield of 21% in the presence of atmospheric water vapour.

2.2. Iron catalyzed oxidation reactions

Catalytic oxidation reactions of CyH have been carried out at 50 °C in acetonitrile, a solvent for which often good results have been indicated in the literature [23,24]. All oxidation reactions give a two-phase solution, and upon the addition of H₂O₂ (for all except the deeply purple coloured **dapb** with iron-salt precursor solutions), the solution immediately changes from yellow to a darker yellow/brown. A control has been run under the standard conditions with no iron catalyst and no CyH oxidation has occurred after

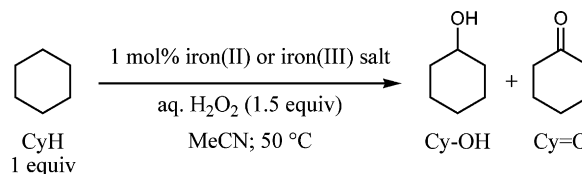


Fig. 2. Iron-catalyzed oxidation of alkanes with H₂O₂.

6.3 h. This result already indicates that an iron species must play a major role in the catalytic oxidation of CyH.

The ligand **dapb** has been tested with four different iron(II) and iron(III) salts, using a Fe:substrate:H₂O₂ ratio of 1:100:150 (Fig. 2). After our results had been obtained using [**dapb**-Fe^{II/III}] catalysts on the oxidation of CyH, an investigation of the catalytic species has been pursued by removing one starting material at a time, so as to observe the effect of each precursor. From this investigation, it has been found that the four tested iron salts [i.e. Fe(BF₄)₂, Fe(CIO₄)₂, Fe(CIO₄)₃ and FeCl₃] all do catalyze the oxidation of CyH in acetonitrile under the reaction conditions listed, even without the **dapb** ligand.

2.2.1. Iron(II) tetrafluoridoborate

In earlier studies, the related ligand 2,6-bis[1-(2-methylanisolylimino)ethyl]pyridine (**dapab**) has been tested as catalyst precursor with Fe(BF₄)₂ [21]. Therefore, **dapb** (Fig. 1) has been first used in combination with Fe(BF₄)₂ for comparison. The oxidation reaction of cyclohexane (CyH) catalyzed by Fe(BF₄)₂ and **dapb** in a 1:1 ratio was found to be completed after a reaction time of 23 h (Table 1, entry 1). 32% of cyclohexanol (Cy–OH) and 42% of cyclohexanone (Cy=O) are produced (based on CyH), together with 6% of cyclohexylhydroperoxide (Cy–OOH). The detection of Cy–OOH suggests that at least one major reaction mechanism of the oxidation involves a Haber-Weiss, free-radical pathway [5,25]. The reaction is not very selective, because also 19% of by-products are obtained (which have not been further analyzed). In contrast, when the ligand bearing two methoxy substituents at the *ortho* position of the phenyl rings, namely **dapab** (Fig. 1) is used, no by-products are generated and 100% conversion of CyH is reached after a reaction time of 12 h (see results described by Tang et al. [21]). It thus appears that the methoxy groups play an important role in the formation of more selective and active catalytic species, as suggested by Tang et al. [21]. Moreover, **dapb** has been found to gradually decompose during the course of the catalytic oxidation in a back reaction to 2,6-diacetylpyridine (diacpy), as confirmed by GC-MS analysis. Therefore, the catalytic activity of free Fe(BF₄)₂ has been examined (Table 1, entry 2). Surprisingly, the results are very similar to those obtained with the addition of **dapb**, albeit with more CyOOH formed (Table 1, entries 1 and 2). The ol:one ratio is different (compare 1.55–0.775 after 23 h), although in the first 2 h of each reaction the ol:one ratio is comparable. Such degradation of the ligand **dapab** has not been observed in the recently reported catalytic system [21]. In 1991, Fish et al. [26] reported the room-temperature oxidation of CyH to Cy–OH and Cy=O catalyzed by Fe(CIO₄)₃. The reaction

Table 1
Oxidation of cyclohexane (CyH) using Fe(BF₄)₂ as catalyst precursor in acetonitrile at 50 °C and the typical procedure described in Section 4

Entry	Catalyst	Time (h)	CyH conv. (%)	Major products	ol:one	% Desired prod.	% By-products
1	With ligand	23	100	Cy–OH (32); Cy=O (42); Cy–OOH (6)	0.77	81	19
2	No ligand	23	100	Cy–OH (29); Cy=O (19); Cy–OOH (34) ^a	1.55	81	19
3	No ligand, RT	2	13	Cy–OH (5); Cy=O (5); Cy–OOH (4)	0.94	13	<1

^a After addition of triphenylphosphane (PPh₃) to the reaction mixture to decompose Cy–OOH, the percentages of Cy–OH and Cy=O are 80% and 14%, respectively (corresponding to an ol:one ratio of 5.71).

Table 2Oxidation of cyclohexane (CyH) using Fe(ClO₄)₂ as catalyst precursor in acetonitrile at 50 °C and the typical procedure described in Section 4

Entry	Iron catalyst	Time (h)	CyH conv. (%)	Major products ^a	ol:one	% Desired prod.	% By-products
1	With ligand	19	100	Cy–OH (37); Cy=O (54)	0.68	91	9
2	No ligand	23	100	Cy–OH (27); Cy=O (60)	0.46	87	13
3	No ligand, acetone	19	100	Cy–OH (12); Cy=O (87)	0.14	99	<1
4	No ligand, argon	2	100	Cy–OH (45); Cy=O (42) ^b	1.1	87	13
5	With 2.5 equivalent ligand	19	100	Cy–OH (36); Cy=O (47)	0.77	83	17
6	With 2.5 equivalent diacpy	19	100	Cy–OH (23); Cy=O (69)	0.33	91	9
7	With 8 equivalent benzylamine	1	0	No reaction	–	–	–

^a 4–10% of Cy–OOH were detected during the course of the different oxidation reactions, but no Cy–OOH is remaining at the end of these reactions.^b No Cy–OOH was detected.

by Fish et al. was carried out with a catalyst:CyH:H₂O₂ ratio of 1:900:150 [26]. These experimental conditions (with the use of a large excess of CyH) resulted in the production of 20 mmol of Cy–OH per mmol of Fe(ClO₄)₃ and 3.9 mmol of Cy=O per mmol of iron (ol:one ratio of 5.13). In the present system, the conversions achieved correspond to as much as 39 mmol Cy–OH/mmol Fe and 19 mmol Cy=O/mmol Fe, using the same amount of H₂O₂. In addition, 34 mmol Cy–OOH/mmol Fe are produced, which can easily, and subsequently, be converted to Cy–OH and Cy=O (in the presence of PPh₃ [6], for instance). Indeed, after an excess PPh₃ has been added to a sample taken after 23 h, the Cy–OOH has been observed to decrease and eventually disappear, whereas the Cy–OH peak has increased substantially, as an ol:one ratio of 5.71 is then determined. Therefore, the present system appears to be significantly more efficient than the one described by Fish et al. [26] because higher turnover numbers are reached. Next, “free” Fe(BF₄)₂ has been tested as oxidation catalyst at room temperature (Table 1, entry 3). As expected, the oxidation rate is much lower and only 13% conversion of CyH is now achieved after a reaction time of 2 h, with an alcohol to ketone ratio of close to 1 (at 50 °C, the conversion after the same reaction time is about 75%).

2.2.2. Iron(II) perchlorate

Next, a different iron(II) salt bearing non-coordinating anions, namely Fe(ClO₄)₂, has been evaluated as catalyst precursor. The results are listed in Table 2. The oxidation reaction of cyclohexane (CyH) catalyzed by Fe(ClO₄)₂ and **dapb** in a 1:1 ratio yields 37% of Cy–OH and 54% of Cy=O (Table 2, entry 1). The catalytic result is comparable to the one obtained with Fe(BF₄)₂ (Table 1, entry 1), although iron(II) perchlorate leads to a slightly higher selectivity towards the formation of Cy–OH + Cy=O (91% instead of 81 for iron(II) tetrafluoroborate). Only traces of Cy–OOH are detected during the course of the oxidation reaction. Without added **dapb** ligand, similar conversions are achieved (see Table 2, entries 1 and 2). However, in contrast to Fe(BF₄)₂, now only traces of Cy–OOH are produced (see Table 1, entry 2 and Table 2, entry 2). As a result, the selectivity towards Cy–OH is much higher for Fe(ClO₄)₂ (the final ol:one ratio is 5.71 for Fe(ClO₄)₂, while it amounts to 0.46 in the case of Fe(BF₄)₂). The initial stages of the same reaction carried out in acetone, a good trap for OH• radicals [11,21], are much slower (2 h 37% CyH conversion, while 40% CyH conversion is reached after 5 min in acetonitrile), but also very selective (99%

selectivity towards Cy–OH and Cy=O), especially towards Cy=O (ol:one ratio 0.14 after 19 h). This result strongly suggests that a non-radical pathway is responsible for the selective oxidation reaction observed [12]. In addition, Cy–OOH is not detected. To corroborate this assumption, the [Fe(ClO₄)₂]-catalyzed oxidation of CyH has been performed under an argon atmosphere (Table 2, entry 4). Remarkably, total conversion of CyH is obtained already after 2 h, forming 87% of Cy–OH and Cy=O (ol:one ratio 1.1). No Cy–OOH has been detected in this case. Consequently, the proposed autooxidation pathway by Hermans et al. [27] is unlikely to be a major oxidation route of CyH using Fe(ClO₄)₂, as the autooxidation pathway of CyH involves cyclohexylperoxy radicals (CyOO•) that are generated from cyclohexyl radicals (Cy•) and dioxygen.

As observed with Fe(BF₄)₂, the ligand **dapb** is slowly decomposing during the reaction (the amount of 2,6-diacetylpyridine increases gradually in time, as determined by GC calibrated with pure 2,6-diacetylpyridine). Therefore, this ligand degradation has been investigated and reactions in the presence of excess ligand or in the presence of each ligand precursor have been carried out (Table 2, entries 5–7). Interestingly, when a 2.5:1 **dapb** to Fe(ClO₄)₂ ratio is used, the reaction does not begin until **dapb** is observed to extensively decompose to 2,6-diacetylpyridine (**diacpy**), and after 30 min, oxidation products are detected (Table 2, entry 5). After 19 h reaction time, 100% CyH conversion is reached with 83% selectivity toward Cy–OH and Cy=O (ol:one ratio of 0.77). Logically, **diacpy** has been tested subsequently as ligand (Table 2, entry 6). **Diacpy** with Fe(ClO₄)₂ in a 2.5:1 ratio is also catalytically active and selective in air, as only two by-products are formed after 19 h with 91% selectivity towards Cy–OH and Cy=O (ol:one ratio 0.33) and Cy–OOH is not detected. These results are comparable to those obtained with solely iron(II) perchlorate (Table 2, entries 2 and 6), thus suggesting that **diacpy** is not a ligand. Because benzylamine is the other side-product originating from **dapb** decomposition, this amine has been then added as a precursor along with Fe(ClO₄)₂ in a 8:1 ratio, and no reaction takes place, suggesting that it hinders the oxidation reaction of CyH (Table 2, entry 7), probably as the result of the formation of inactive [Fe(benzylamine)_x] species.

2.2.3. Iron(III) perchlorate and iron(III) chloride

The logical next step has been to use Fe(ClO₄)₃ as catalyst precursor, to find out whether or not the oxidation state of the starting iron salt has an influence on the catalytic efficiency. The results

Table 3Oxidation of cyclohexane (CyH) using Fe(ClO₄)₃ and FeCl₃ as catalyst precursor in acetonitrile at 50 °C and the typical procedure described in Section 4

Entry	Iron catalyst	Time (h)	CyH conv. (%)	Major products	ol:one	% Desired prod.	% By-products
1	With ligand	19	93	Cy–OH (35); Cy=O (58)	0.61	93	<1
2	No ligand	22	99	Cy–OH (25); Cy=O (55)	0.45	79	20
3	No ligand, RT	18	63	Cy–OH (31); Cy=O (13); Cy–OOH (14)	2.3	58	5
4	No ligand, RT, 3 × 0.33 equivalent H ₂ O ₂	71	64	Cy–OH (23); Cy=O (8); Cy–OOH (28)	2.9	59	5
5	No ligand, RT, 3 × 1 equivalent H ₂ O ₂	19	82	Cy–OH (16); Cy=O (11); Cy–OOH (42)	1.4	69	13
6	No ligand	22	100	Cy–OH (28); Cy=O (48); Cy–OOH (1)	0.59	78	22
7	No ligand, RT	19	55	Cy–OH (22); Cy=O (16); Cy–OOH (10)	1.4	48	6

of the oxidation tests on CyH using $\text{Fe}(\text{ClO}_4)_3$ are summarized in Table 3. The oxidation of CyH catalyzed by the $[\text{Fe}(\text{ClO}_4)_3/\text{dapb}]$ system, at 50°C in acetonitrile/water, produces selectively 93% of a mixture of Cy–OH and Cy=O, with a ol:one ratio of 0.61 (Table 3, entry 1). If the same reaction is performed without the addition of ligand **dapb**, CyH is totally converted after a reaction time of 22 h (Table 3, entry 2). However, the oxidation is less selective in this case, because 20% of by-products are obtained (including traces of Cy–OOH). Iron(II) perchlorate and iron(III) perchlorate give similar results (Table 2, entry 2 and Table 3, entry 2); therefore, the oxidation state of the starting iron salt most likely does not affect the catalytic efficiency. A few years ago, Shul'pin et al. [6] described the catalytic activity of $\text{Fe}(\text{ClO}_4)_3$ on the room-temperature oxidation of CyH in MeCN using H_2O_2 as the oxidant. These authors [6] reported the $[\text{Fe}(\text{ClO}_4)_3]$ -catalyzed oxidation of CyH to be inefficient, with turnover numbers (i.e. number of moles of products per 1 mol of the catalyst, TON) of 10 after a reaction time of 3 min. In the present case, a TON of 79 (Cy–OH + Cy=O) is achieved at 50°C (Table 3, entry 2) and 58 (Table 3, entry 3) at room temperature.

Next, the selectivity of the $\text{Fe}(\text{ClO}_4)_3$ -catalyzed reaction at room temperature has been investigated (Table 3, entry 3). As expected, the reaction is slower as only 63% of CyH is now converted to oxidation products. In addition, smaller amounts of by-products are generated (5% instead of 20%, see entries 2 and 3) and a significant quantity of cyclohexylhydroperoxide (Cy–OOH) is detected. In fact, Cy–OOH is known to decompose to Cy–OH and Cy=O over time [3]. Actually, this has been observed as well in the present study, by re-running the same samples in gas chromatography (GC) at a later date (~ 1 week after the sample was obtained). It has to be pointed out here that this decomposition of metastable Cy–OOH leads to a time-dependence from when the sample is taken to when it is analyzed by GC. Therefore, the percentages of Cy–OH and Cy=O were found to slightly vary depending on the time period between the sampling and the GC analysis.

The effect of the addition of H_2O_2 on the catalytic activity has been investigated to verify that the oxidant is not significantly decomposing during the catalytic oxidation reaction. Adding three times 0.33 equivalent of H_2O_2 to the oxidation reaction of cyclohexane using $\text{Fe}(\text{ClO}_4)_3$ at RT, using the otherwise typical reaction conditions, did not give any significant difference in the products (or the amounts) formed when the oxidant was added all at once. However, the rate of the reaction is much lower as the same CyH conversion is only reached after a reaction time of 71 h, instead of 18 h (Table 3, entries 3 and 4). It thus appears that dihydrogen peroxide remains stable during the course of the reaction. By adding one equivalent of H_2O_2 thrice (therefore, the total amount of H_2O_2 added is three times superior to the one of all other experiments) using otherwise the same conditions also yields the same products but at a much faster rate and with higher cyclohexane conversion.

The influence of the anion on the catalytic activity has been further studied by using FeCl_3 (Table 3, entries 6 and 7) instead of $\text{Fe}(\text{ClO}_4)_3$. At 50°C (Table 3, entry 6), total conversion of CyH is reached after 22 h with a selectivity towards Cy–OH + Cy=O of 78%. The results are comparable to those obtained with $\text{Fe}(\text{ClO}_4)_3$ (Table 3, entries 2 and 6), suggesting that the different counterions do not determine the catalytic cycles. This is confirmed by the reaction performed at room temperature (Table 3, entries 3 and 7), though the reaction with FeCl_3 is slightly slower.

The catalytic activity of FeCl_3 for the oxidation of CyH has been reported by Sawyer et al. [28,29] These authors used a $\text{FeCl}_3:\text{CyH}:\text{H}_2\text{O}_2$ ratio of 1:200:10 and the reaction was performed at room temperature [29]. In that case in acetonitrile, only 2.4% CyH is converted to Cy–OH and Cy–Cl (Cy–Cl stands for chlorocyclohexane), and 0.8% is converted to Cy=O, after a reaction time of 3 h. Based on H_2O_2 , the conversion of 3.2% CyH corresponds

to an efficiency of about 40%. More recently, Shul'pin et al. [6] have also shown that “free” FeCl_3 is capable of catalyzing the room temperature oxidation of CyH in acetonitrile, but with a low efficiency. In contrast to the two previous examples, the system herein presented does not involve a large excess of CyH. Moreover, the reactions reported in this study have been carried out at 50°C , while Sawyer and Shul'pin have performed the catalytic oxidations at room temperature. It thus appears that the present two experimental variations give rise to significant catalytic improvements. Indeed, all dihydrogen peroxide is consumed to convert the totality of CyH to oxidation products, resulting in 100% oxidation efficiency.

3. Concluding remarks

The oxidation of cyclohexane (CyH) using catalytic amounts of simple iron salts in acetonitrile (MeCN) under mild conditions, using H_2O_2 as the oxidant without controlling the pH, is reported, with $\text{Fe}(\text{ClO}_4)_2$ giving particularly promising results (100% CyH conversion within 24 h under all conditions tested at 50°C ; except when in the presence of eight equivalents of benzyl amine). CyH conversion occurs rapidly when under an argon atmosphere, and selectivity is enhanced when a radical trap is present, with $\text{Fe}(\text{ClO}_4)_2$ as the catalyst. No major influence of the counterion and the valency of the iron salt used on neither the rate of conversion nor the selectivity was found. When 2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**) is added as a catalytic precursor, selectivity tends to be enhanced, although decomposition of **dapb** occurs. It is concluded that two simultaneous and competing mechanisms are likely, i.e. a free radical pathway (involving HO^\bullet) and a non-radical pathway (presumably via a high-valent iron species), although the catalytic species is undetermined thus far.

4. Experimental

4.1. General remarks

Solvents and reagents were used as received. IR spectroscopy performed using a PerkinElmer FT-IR Spectrometer PARAGON 1000. C, H and N elemental analysis was performed using a PerkinElmer 2400 series II CHNS/O micro analyzer. MS was carried out on a ThermoFinnegan AQA ESI-MS. The thin layer chromatography (TLC) material used was Silica gel 60 F_{254} on an aluminium sheet.

4.2. Synthesis of 2,6-bis-[1-(benzylimino)ethyl]pyridine (**dapb**)

2,6-Diacetylpyridine (500 mg, 3.06 mmol) was dissolved in MeOH (6 mL) while being stirred. Benzyl amine was then added (657 mg, 6.13 mmol) and the system was flushed with argon to expel the water vapour in the air. Formic acid (four drops) [22] was added as a catalyst and the reaction was stoppered and stirred overnight. A yellow solution with a white precipitate formed which was collected by vacuum filtration and washed with an excess of methanol. Yield: 552 mg, 53%. Anal. Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_3$: C, 80.90%; H, 6.80%; N, 12.30%. Found: C, 80.58%; H, 6.12%; N, 11.90%. MS-EI⁺ (*m/z*) [*M*]⁺ 341.9 (Calcd. 341.5).

4.3. Typical oxidation procedure

The oxidation of CyH was carried out under air in a 50 mL two-necked round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser (when heated). Typically, the iron catalyst (0.02 mmol) was dissolved in MeCN (2 mL), to which CyH was then added (2.00 mmol). The oxidation reaction was initiated by the addition of 30% aqueous H_2O_2 (3.00 mmol) to give a total volume of

2.6 ± 0.1 mL. The reaction was then heated to 50 °C, and stabilized to within ±4 °C (monitored using a mercury thermometer) before the addition of H₂O₂. Samples of the reaction mixture were collected regularly according to the extraction procedure (see Section 4.4) in order to monitor the reaction by GC analysis.

In the case where the reaction was carried out under argon, the same equipment setup was used apart from a septum sealing the neck not connected to the reflux condenser and after temperature stabilization, a hollow tube needle used to bubble argon into the reaction mixture for 10 min prior to the addition of H₂O₂ and continued throughout the reaction.

When H₂O₂ is added in three steps, the oxidant is added and after 5 min, a sample is extracted. Then, the next portion of oxidant is added and the procedure is repeated until all three H₂O₂ additions have been carried out and samples obtained.

4.4. GC analysis

The oxidation of CyH was stopped by removing the catalyst from the substrate by extraction using distilled H₂O and diethyl ether. Typically, three drops of distilled H₂O was added to three drops of the reaction sample to be analyzed in a 1.5 mL short thread vial, which was then filled for 3/4 with diethyl ether. The vial was then capped using a septum containing, screw top lid and vigorously shaken. The diethyl ether layer contained all of the oxidized products and was colourless whereas the bottom aqueous layer contained the iron complexes formed. The colour of the aqueous layer varied, depending on the catalytic precursors used.

GC analysis was carried out using a Hewlett-Packard 5890 Series GC (CP-Sil-5 CB WCOT Fused Silica capillary column, 50 m × 0.25 mm inside diameter (i.d.), 0.25 μm film thickness) with dihydrogen carrier gas. The oven temperature was increased stepwise according to the following protocol: the temperature was held at 50 °C for 2 min, raised to 250 °C at a rate of 10 °C/min, where it was held for 3 min. Standard injections were 3 μL collected from the diethyl ether layer. The products of most of the samples analyzed were determined by comparison with the commercially available compounds whereas the non-commercial available products were determined by GC-MS analysis.

The chromatogram obtained from the above GC (with specified protocol) did not separate Cy=O from Cy–OH, and so the samples were also analyzed using a Varian Star 3400 CX Series GC (CP-WAX58 (FFAP)–CB WCOT Fused Silica capillary column, 25 m × 0.32 mm i.d., 1.2 μm film thickness) with dihydrogen carrier gas. The following oven temperature protocol was used: the temperature was held at 50 °C for 1 min, raised to 225 °C at a rate of 10 °C/min, where it was held for 10 min. Standard injections were 2 μL collected from the diethyl ether layer. The retention times of Cy=O and Cy–OH were found to be 7.13 and 8.52 min, respectively, as determined by comparison with the commercially available compounds. The Varian Star 3400 CX Series GC was used to determine the ol:one ratio, and so the percentage of Cy–OH and Cy=O can be determined:

The percentages of Cy–OH and Cy=O were determined as follows: the Hewlett-Packard 5890 Series GC gave a single peak corresponding to both Cy–OH and Cy=O;

$$\text{Cy-OH} + \text{Cy=O} = \text{X}$$

The Varian Star gave a ratio of Cy–OH to Cy=O:

$$\text{Cy-OH/Cy=O} = \text{Y}$$

Then the percent Cy–OH and Cy=O can be found from;

$$\text{Cy-OH} = \text{X} \times \text{Y} \times (1 + \text{Y})^{-1}$$

$$\text{Cy=O} = \text{X} \times (1 + \text{Y})^{-1}$$

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