

Homogeneous Catalysis

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Iron-Catalyzed Wacker-type Oxidation of Olefins at Room Temperature with 1,3-Diketones or Neocuproine as Ligands**

Florian Puls, Philipp Linke, Olga Kataeva, and Hans-Joachim Knölker*

Dedicated to Professor K. Peter C. Vollhardt on the occasion of his 75th birthday

Abstract: Herein, we describe a convenient and general method for the oxidation of olefins to ketones using either tris(dibenzoylmethanato)iron(III) [Fe(dbm)₃] or a combination of iron(II) chloride and neocuproine (2,9-dimethyl-1,10-phenanthroline) as catalysts and phenylsilane (PhSiH₃) as additive. All reactions proceed efficiently at room temperature using air as sole oxidant. This transformation has been applied to a variety of substrates, is operationally simple, proceeds under mild reaction conditions, and shows a high functional-group tolerance. The ketones are formed smoothly in up to 97% yield and with 100% regioselectivity, while the corresponding alcohols were observed as by-products. Labeling experiments showed that an incorporated hydrogen atom originates from the phenylsilane. The oxygen atom of the ketone as well as of the alcohol derives from the ambient atmosphere.

Introduction

A wide variety of transition metals are well-established as catalysts for a broad range of transformations in organic synthesis.^[1] In the past, mostly noble metals like platinum, rhodium, or palladium have been employed for this purpose. However, over the past few years, the development of sustainable methodologies based on earth-abundant first-row transition metals has gained much attention because of

the increasing demand for efficient and environmentally benign synthetic methods.^[2] In this context, iron occupies the center stage.^[3] Iron compounds offer several advantages as catalysts, including high abundance in the earth's crust, sustainability, low price, and high reactivity. Another driving force for the move from precious to abundant metal catalysis is the high toxicity of the noble metals.^[4,5] Iron exhibits a low toxicity and was involved in biological systems since early on in evolution.^[6]

Ketone moieties are found in a large number of biologically active compounds including drugs and natural products (Figure 1). Furthermore, ketones represent versatile intermediates in synthesis and crucial industrial building blocks.^[7]

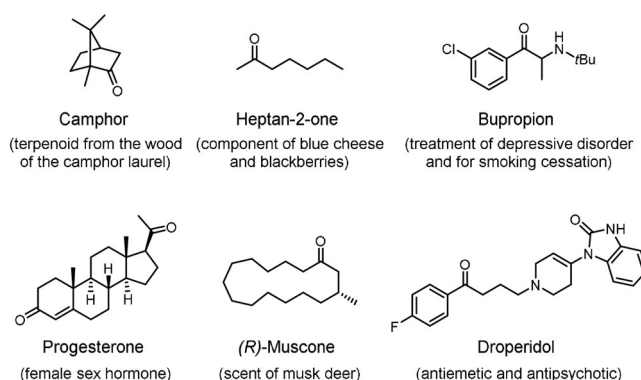


Figure 1. Selected biologically active and natural compounds with ketone moieties.

A common method for the synthesis of ketones is the palladium-catalyzed oxidation of alkene substrates, well known as the Wacker oxidation.^[8] Since its discovery in the late 1950s, this transformation has found a wide range of applications in natural product synthesis and in industry for the preparation of pharmaceuticals as well as commodity chemicals. Moreover, detailed mechanistic studies were reported.^[8] However, the Wacker process requires catalytic amounts of palladium and copper salts are used as reoxidant. This catalytic system is generally less efficient for the oxidation of internal alkenes and electron-deficient olefins. Despite recent progress to overcome these limitations,^[9] the search for inexpensive alternatives has led to the development of earth-abundant first-row transition-metal catalysis for this transformation with application of iron,^[10] cobalt,^[11] or nickel^[12] compounds as catalysts. Han et al. described a Wacker-type oxidation of alkenes to ketones in ethanol at 80 °C using iron(II) chloride as catalyst, polymethylhydrosiloxane

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Supporting information (synthesis of the iron complexes, complete characterization of all compounds, details of the optimization studies, copies of the NMR spectra (¹H, ¹³C + DEPT, ¹⁹F), Mössbauer spectroscopy of Fe(dbm)₃, and the mechanistic experiments) and the ORCID identification number(s) for the author(s) of this article can be found under:

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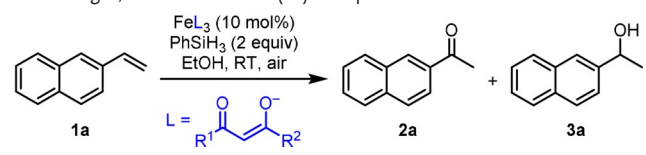
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(PMHS) as additive, and air as sole oxidant.^[10a] We described the conversion of olefins into ketones proceeding in ethanol at room temperature using iron(II)–hexadecafluorophthalocyanine as catalyst, triethylsilane as additive, and oxygen as sole oxidant.^[10b] In the course of our project directed towards the application of iron compounds as catalysts for operationally simple and convenient synthetic transformations,^[13] we have been searching to expand the toolkit for the iron-catalyzed Wacker-type oxidation. Herein, we describe the development of an efficient iron-catalyzed oxidation of alkenes to ketones at room temperature under air atmosphere using either readily available tris(dibenzoylmethanato)iron(III), or a combination of iron(II) chloride and neocuproine as catalysts and phenylsilane as reductive additive.

Results and Discussion

We used 2-vinylnaphthalene (**1a**) as model substrate and performed the oxidation under air in ethanol as solvent and with phenylsilane as additive. Because of their ready availability, we explored the application of 1,3-diketono iron(III) complexes as catalysts (10 mol%, Table 1).^[14] The acetylacetonate complex Fe(acac)₃ provided only low yields of 2-acetylnaphthalene (**2a**, Table 1, entry 1). Competing side reactions were radical dimerizations to either 1,3-di(naphth-2-yl)butane and 2,3-di(naphth-2-yl)butane,^[10b] or reduction of the olefin to 2-ethylnaphthalene.^[15] Then, we explored the effect of the ligand structure by testing a range of different 1,3-diketones as ligands at iron(III) (Table 1).

Table 1: Ligand optimization for the iron-catalyzed Wacker-type oxidation using 1,3-diketono iron(III) complexes.^[a]

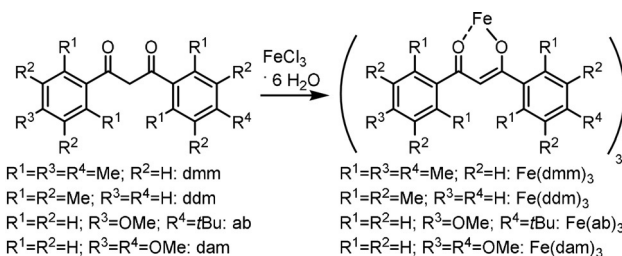


Entry	R ¹	R ²	t [h]	Yield 2a [%]	Yield 3a [%]
1	Me	Me	2	24	2
2	<i>i</i> Pr	<i>i</i> Pr	2	26	7
3	<i>t</i> Bu	<i>t</i> Bu	6	44	8
4 ^[b]	CF ₃	Me	24	1	0
5 ^[c]	CF ₃	CF ₃	24	6	0
6 ^[d]	CF ₃	Ph	24	5	0
7	Me	Ph	3.5	72	12
8	Ph	Ph	4.5	79	8
9 ^[e]	Ph	Ph	5.5	78	14
10 ^[e,f]	Ph	Ph	4.5	80	8
11 ^[g]	Ph	Ph	5	80	11

[a] Reaction conditions: **1a** (0.65 mmol), iron(III) catalyst (10 mol%), PhSiH₃ (2 equiv), EtOH (3 mL), room temperature, air; full conversion of starting material was indicated by TLC analysis; all yields given refer to isolated products. [b] 91 % of starting material was recovered. [c] 84 % of starting material was recovered. [d] 75 % of starting material was recovered. [e] With 3 mol% Fe(dbm)₃. [f] The reaction was carried out under O₂ (1 atm). [g] Reaction conditions: **1a** (6.5 mmol), Fe(dbm)₃ (3 mol%), PhSiH₃ (2 equiv), EtOH (30 mL), room temperature, air. Fe(dbm)₃ = tris(dibenzoylmethanato)iron(III).

With the more bulky diisobutyro- (dibm) or dipivaloylmethanato (dpm) ligands we obtained only slightly improved yields of **2a** along with the by-products resulting from radical dimerization (Table 1, entries 2 and 3). Alteration of the ligand electronics by using the electron-deficient trifluoroacetylacetonato (tfaa), hexafluoroacetylacetonato (hfaa), or 4,4,4-trifluoro-1-phenyl-1,3-butanedionato (tfba) ligands led to a sharp decrease of the yield for **2a** (Table 1, entries 4–6), presumably due to the increased Lewis acidity of the iron complexes and their lower potential to capture oxygen.^[16] Finally, iron(III) complexes containing ligands with one or two phenyl substituents like benzoylacetone (ba) or dibenzoylmethane (dbm) were employed for this reaction. With Fe(ba)₃ as catalyst, the yield of **2a** increased to 72 % (Table 1, entry 7) and application of tris(dibenzoylmethanato)iron(III) [Fe(dbm)₃] gave 79 % of **2a** along with 8 % of the corresponding alcohol **3a** (Table 1, entry 8). A reduction of the catalyst load from 10 to 3 mol% led to similar yields of **2a** (Table 1, entry 9). A pure oxygen atmosphere is not required as it led to no significant increase in product formation (Table 1, entry 10). We demonstrated that the catalyst Fe(dbm)₃ could be applied to a gram-scale synthesis. Thus, reaction of 6.5 mmol of **1a** afforded within 5 h 80 % of 2-acetylnaphthalene (**2a**) along with 11 % of the alcohol **3a** (Table 1, entry 11). Variation of the solvent, employment of hydrosilane additives other than PhSiH₃, or the addition of bases to the reaction gave either lower yields or no product (see Supporting Information, Tables S1–S3). Control experiments in the absence of either Fe(dbm)₃, or PhSiH₃, or air (by performing the reaction under an argon atmosphere) provided no product, thus emphasizing a crucial role for each of these components.

Next, we investigated the steric and electronic influence of substituents at the aryl moieties on the catalytic activity of the corresponding iron complex by introduction of methyl-, *tert*-butyl-, and methoxy groups (Scheme 1 and SI). Twofold Friedel–Crafts acylation of mesitylene or durene with malonyl dichloride led to the β-diketones dimesitylenecarbonylmethane (dmmH) or to didurenecarbonylmethane (ddmH).^[17] 4-(*tert*-Butyl)benzenecarbonyl]–[(4-methoxy)benzenecarbonyl]methane (avobenzene, abH) and di(4-methoxy)benzenecarbonylmethane (damH) are commercially



Scheme 1. Synthesis of aryl-substituted 1,3-diketono iron(III) complexes. For experimental details of the syntheses of Fe(dmm)₃, Fe(ddm)₃, Fe(ab)₃, and Fe(dam)₃, see SI. dmm = dimesitylenecarbonylmethanato, ddm = didurenecarbonylmethanato, ab = 4-(*tert*-butyl)benzenecarbonyl]–[(4-methoxy)benzenecarbonyl]methanato (avobenzonato); dam = di(4-methoxy)benzenecarbonylmethanato (dianisolecarbonylmethanato).

available. The corresponding iron complexes were prepared by mixing the appropriate 1,3-diketone ligand with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous ethanol at 60°C for 1 h (see SI for details). The structures for the complexes $\text{Fe}(\text{ba})_3$, $\text{Fe}(\text{dbm})_3$,^[18] $\text{Fe}(\text{dmm})_3$,^[19] $\text{Fe}(\text{ab})_3$,^[20] and $\text{Fe}(\text{ddm})_3$ were confirmed by X-ray analysis (Figures 2–4, Figure S1, and Figure S6).

Application of the substituted aryl 1,3-diketone iron(III) complexes as catalysts (5 mol%) in the Wacker-type oxidation of 2-vinylnaphthalene (**1a**) revealed significant differences of their catalytic activity (Table 2). Using $\text{Fe}(\text{dmm})_3$ and $\text{Fe}(\text{ddm})_3$, degradation of the catalyst during the reaction occurred (Table 2, entries 1 and 2). The avobenzene-derived iron(III) complex $\text{Fe}(\text{ab})_3$ showed a good performance as catalyst for the oxidation to **2a** and led to complete

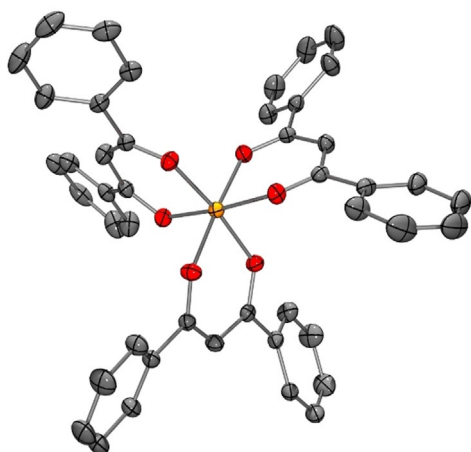


Figure 2. Molecular structure of tris(dibenzoylmethanato)iron(III) [$\text{Fe}(\text{dbm})_3$] in the crystal (thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity). Color code: C dark gray, O red, Fe orange.

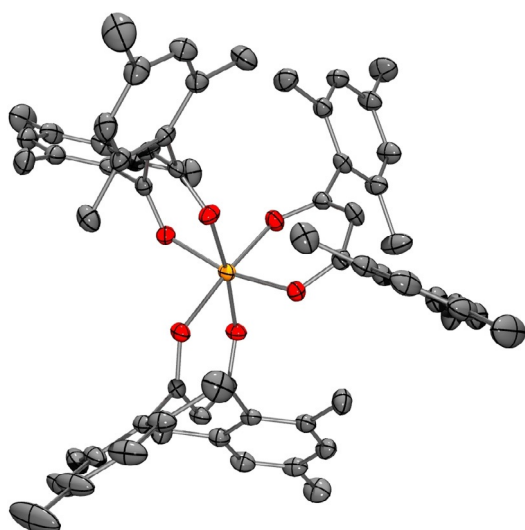


Figure 3. Molecular structure of tris(dimesitylenecarbonylmethanato)iron(III) [$\text{Fe}(\text{dmm})_3$] in the crystal (thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity). Color code: C dark gray, O red, Fe orange.

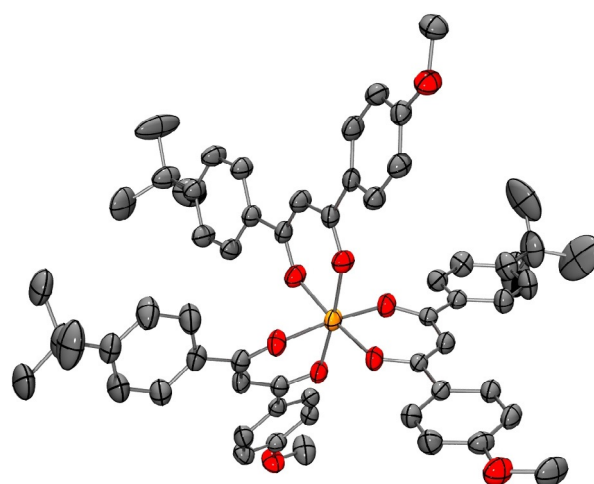
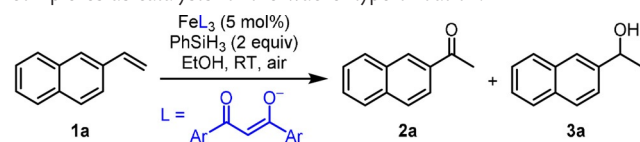


Figure 4. Molecular structure of tris{[4-(*tert*-butyl)benzenecarbonyl]-[4-methoxybenzenecarbonyl]methanato}iron(III) [$\text{Fe}(\text{ab})_3$] in the crystal (thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity). Color code: C dark gray, O red, Fe orange.

Table 2: Efficiency of substituted 1,3-diaryl-1,3-diketonato iron(III) complexes as catalysts for the Wacker-type oxidation.^[a]

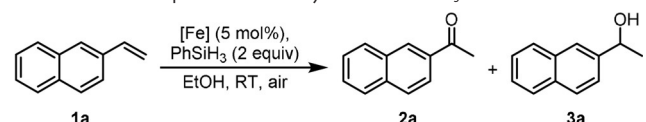


Entry	Iron(III) complex	<i>t</i> [h]	Reisolated 1a [%]	Yield 2a [%]	Yield 3a [%]
1	$\text{Fe}(\text{dmm})_3$	5.5	39	26	9
2	$\text{Fe}(\text{ddm})_3$	5.5	30	49	7
3 ^[b]	$\text{Fe}(\text{ab})_3$	3.5	–	70	10
4	$\text{Fe}(\text{dam})_3$	5.5	25	55	2

[a] Reaction conditions: **1a** (0.65 mmol), iron(III) catalyst (5 mol%), PhSiH_3 (2 equiv), EtOH (3 mL), room temperature, air; all yields given refer to isolated products. [b] Full conversion of starting material was verified by TLC analysis.

conversion of **1a** after only 3.5 h at slightly lower yields than obtained with $\text{Fe}(\text{dbm})_3$ (Table 2, entry 3). However, application of the more electron-rich complex $\text{Fe}(\text{dam})_3$ led to a decrease in the yield of **2a** as compared to the reaction using $\text{Fe}(\text{ab})_3$ (Table 2, entry 4).

In our previous report, we have shown that highly pure FeCl_2 (99.99%) in combination with Et_3SiH was not able to convert the alkene **1a** to the ketone **2a** at room temperature.^[10b] However, in preliminary experiments, we achieved a full conversion of **1a** even at room temperature after 4.5 h when PhSiH_3 was applied as additive. Therefore, we investigated the catalytic activity of a range of simple iron compounds in the Wacker-type oxidation of **1a** to **2a** at room temperature using PhSiH_3 as additive. 2-Vinylnaphthalene (**1a**) was treated with 5 mol% of an iron compound and 2 equiv of PhSiH_3 in ethanol under air (Table 3). Iron(II) or iron(III) chloride salts (Table 3, entries 1–3) and the readily available ionic liquid $[\text{bmim}][\text{FeCl}_4]$ ^[21] (Table 3, entry 10)

Table 3: Optimization for the iron-catalyzed Wacker-type oxidation using different iron compounds as catalysts with PhSiH₃ as additive.^[a]


Entry	Iron source	t [h]	Reisolated 1a [%]	Yield 2a [%]	Yield 3a [%]
1	FeCl ₂	4.5	–	69	13
2	FeCl ₂ ·4 H ₂ O	4.5	20	59	5
3	FeCl ₃	3.5	–	60	14
4	FeBr ₂	4.5	34	46	8
5	Fe(C ₂ O ₄)·2 H ₂ O	4.5	87	traces	0
6	FeF ₃	4.5	76	7	0
7	Fe(OAc) ₂	4.5	55	19	3
8	FeSO ₄ ·7 H ₂ O	4.5	66	2	0
9	[CpFe(CO) ₂] ₂	24	22	47	3
10	[bmim][FeCl ₄]	24	12	65	9
11 ^[b]	FeCl ₂	3.5	–	76	14
12 ^[c]	FeCl ₂	3	–	83	15

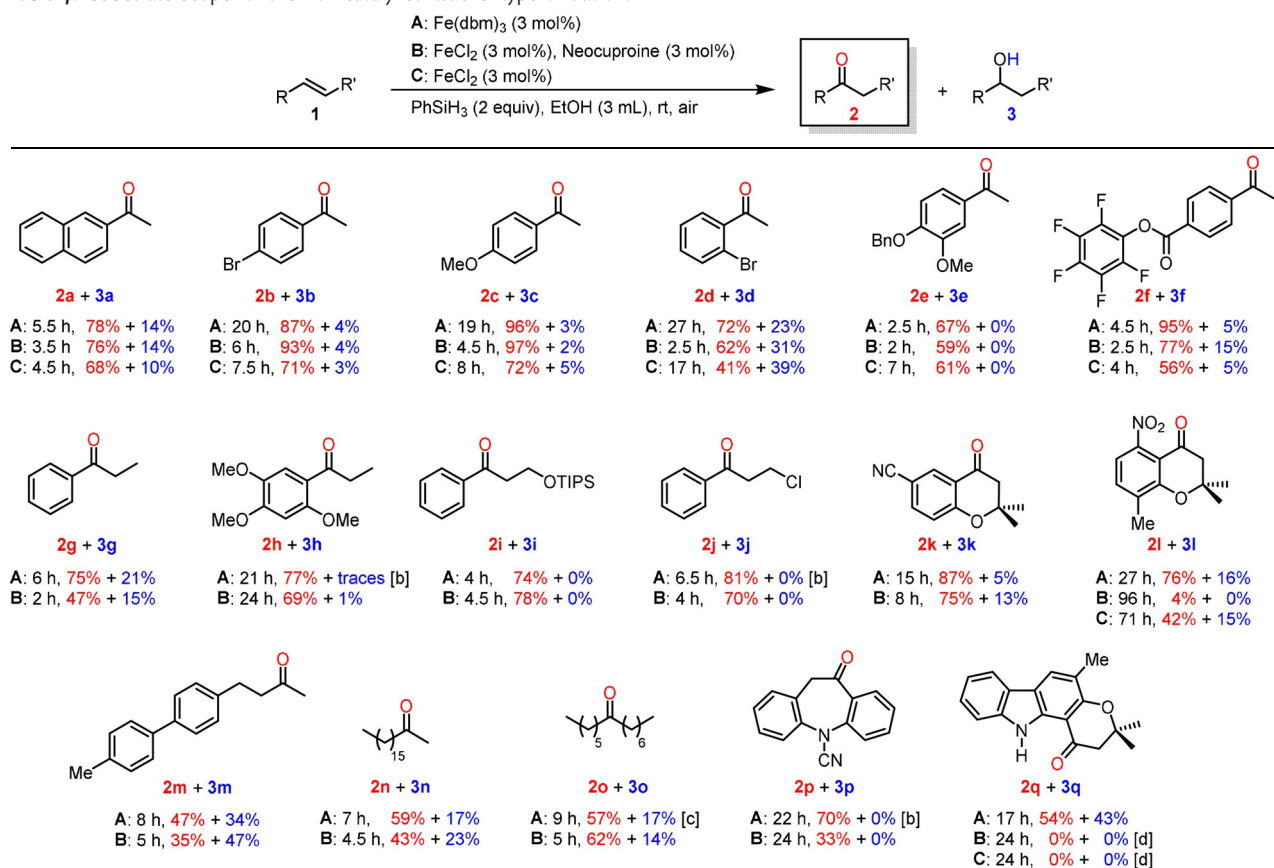
[a] Reaction conditions: **1a** (0.65 mmol), iron catalyst (5 mol %), PhSiH₃ (2 equiv), EtOH (3 mL), room temperature, air; all yields given refer to isolated products. [b] With FeCl₂ (3 mol %), and neocuproine (2,9-dimethyl-1,10-phenanthroline, 3 mol %). [c] Reaction conditions: **1a** (6.5 mmol), FeCl₂ (3 mol %), neocuproine (3 mol %), PhSiH₃ (2 equiv), EtOH (30 mL), room temperature, air. Bmim = 1-butyl-3-methylimidazolium, Cp = cyclopentadienyl.

gave moderate yields of **2a** in the range of 59–69 %, whereas other iron compounds were less efficient (Table 3, entries 4–9). In order to avoid the observed decomposition of substrate **1a**, we have studied a broad range of supporting ligands using FeCl₂ as catalyst and identified neocuproine (2,9-dimethyl-1,10-phenanthroline) as the best ligand to improve the catalytic performance (see SI, Table S4). A detailed optimization by variation of iron compounds, solvents, and hydrosilanes, and testing the presence of base additives (see SI, Tables S5–S8) led to the optimized reaction conditions, a combination of FeCl₂/neocuproine (3 mol % each) with phenylsilane (2 equiv) as additive in ethanol at room temperature, which provided **2a** in 76 % yield (Table 3, entry 11). This set of conditions appears to work even better on a larger scale. Starting with 1.0 g (6.5 mmol) of 2-vinylnaphthalene (**1a**), 2-acetylnaphthalene (**2a**) was obtained in 83 % yield (Table 3, entry 12).

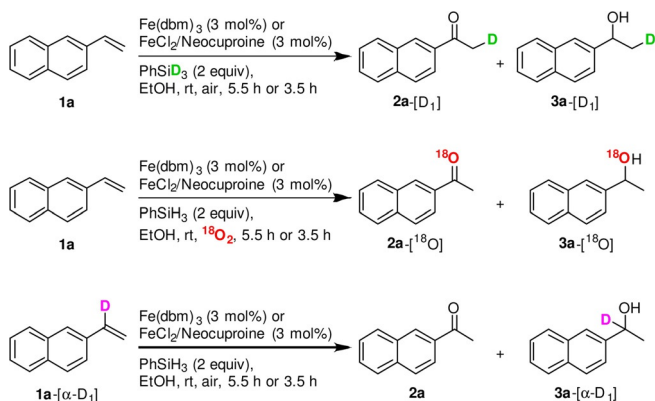
The substrate scope of the iron-catalyzed Wacker-type oxidation was investigated using the two sets of optimized reaction conditions described above with either 3 mol % of Fe(dbm)₃ (method A) or 3 mol % each of FeCl₂/neocuproine (method B) as catalyst systems in the presence of phenylsilane (2 equiv) in ethanol at room temperature under air (Table 4). In order to show the effect of the neocuproine ligand on the iron catalysis, some substrates have been converted using only 3 mol % of FeCl₂ as catalyst (method C). A range of terminal styrene derivatives (**1a–1f**) was efficiently transformed into the corresponding aryl methyl ketones **2a–2f** in yields of up to 97 % and with the alcohols **3a–3f** as the only by-products. The neocuproine ligand in method B generally leads to shorter reaction times and less decomposition of the substrate compared to method C using

only FeCl₂ as catalyst. Thus, the influence of neocuproine is ascribed to a ligand-accelerated catalysis.^[22] This assumption derives support from the fact that in contrast to the FeCl₂/neocuproine system, the preformed complex dichloro(2,9-dimethyl-1,10-phenanthroline-κN¹,κN¹⁰)iron(II), which has been characterized by X-ray analysis (Figure S8), does not catalyze the oxidation of **1a** (see SI). Non-terminal styrene derivatives (**1g–1j**) and chromenes (**1k** and **1l**) afforded regioselectively the corresponding benzylic ketones **2g–2l** in yields ranging from 74 to 87 %. The conversion of the naturally occurring phenylpropanoid α-asarone (**1h**) into the ketone **2h** proceeded faster with tris(benzoylacetonato)iron(III) [Fe(ba)₃] as catalyst. Surprisingly, reaction of cinnamyl chloride (**1j**) even after prolonged reaction times (48 h) and with a higher load of the catalyst Fe(dbm)₃ (10 mol %) gave a poor turnover of the starting material (35 % of **2j**, 49 % reisolated **1j**). However, using tris(benzoylacetonato)iron(III) (3 mol %) as catalyst provided the product **2j** in 81 % yield after 6.5 h with no alcohol **3j** as by-product. Aliphatic terminal or internal olefins (**1m–1o**) proved to be useful starting materials for the iron-catalyzed Wacker-type oxidation. Thus, using either method A or B afforded the corresponding ketones **2m–2o** in moderate yields (35–62 %) with an increased proportion of the alcohol by-products **3m–3o** (14–47 %). Octadecan-2-one (**2n**) is a natural product which has been isolated from various sources.^[23] Oxidation of the iminostilbene **1p** to the corresponding ketone **2p** proceeded very slowly with Fe(dbm)₃ as catalyst. With Fe(ba)₃ as catalyst (3 mol %), **2p** was obtained in 70 % yield. Compound **2p** is a direct synthetic precursor for the antiepileptic drug oxcarbazepine.^[24] Finally, we demonstrated the applicability of the present method for the synthesis of natural products. Oxidation of the pyrano[3,2-*a*]carbazole alkaloid girinimbine (**1q**)^[25] using Fe(dbm)₃ as catalyst (method A) provided the naturally occurring euchrestifoline (**2q**)^[26] in 54 % yield along with 43 % of the corresponding alcohol **3q**, whereas methods B and C failed in this case.

We have performed a series of mechanistic experiments in order to gain more information on the mechanism of the iron-catalyzed Wacker-type oxidation (see Supporting Information for details). All the mechanistic experiments described below have been accomplished with both sets of optimized reaction conditions, method A and method B. Using perdeuterated ethanol (EtOD-[D₅]) as solvent for the oxidation of **1a**, no deuterium was incorporated into the product. However, using PhSiD₃^[27] as reductive additive led to a deuterium incorporation of 97 % in the methyl groups of the ketone **2a** and in the alcohol **3a** (Scheme 2). No product was formed when the reaction was performed under argon. In order to support our assumption that the oxygen incorporated in the products **2a** and **3a** derives from the atmosphere, we have executed ¹⁸O-labeling experiments. In fact, running the experiments under an atmosphere of ¹⁸O₂, we detected an ¹⁸O-incorporation of 92 % into both products with method A and of 95 % with method B (see SI). This outcome unequivocally confirmed that the oxygen atoms incorporated into the ketone and into the alcohol both derive from the atmosphere. Using 2-vinylnaphthalene with a deuterium atom at the α-position (**1a**-[α-D₁], D-content 92 %) led exclusively to

Table 4: Substrate scope for the iron-catalyzed Wacker-type oxidation.^[a]

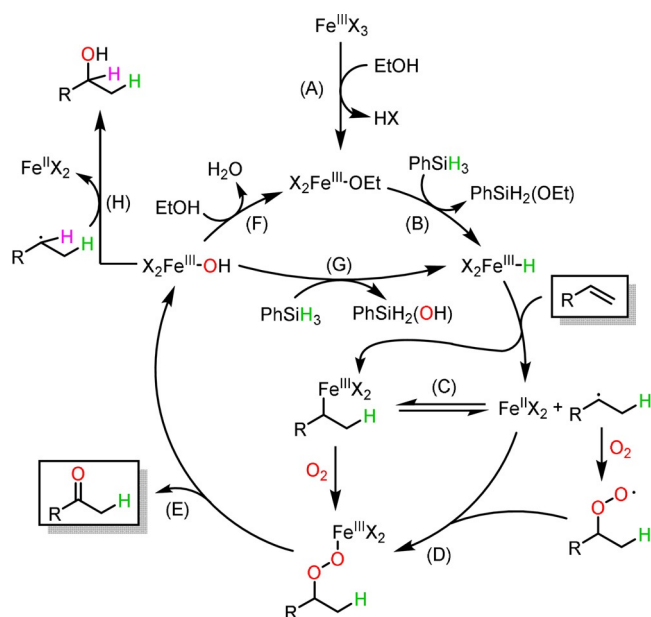
[a] For complete conversion of **1** (0.65 mmol), the progress of the reaction was monitored by TLC and GC–MS analysis of the reaction mixture. Yields given refer to isolated products (ketones **2a–2q**, alcohols **3a–3q**). [b] Tris(benzoylacetonato)iron(III) [Fe(ba)₃] (3 mol%) was used instead of Fe(dbm)₃. [c] NaOAc (6 mol%) was additionally added to accelerate the reaction (Table S8). [d] No conversion, starting material [girinimine (**1q**)] was quantitatively recovered. TIPS = triisopropylsilyl.

**Scheme 2.** Labeling experiments for the iron-catalyzed Wacker-type oxidation.

unlabeled ketone **2a** and labeled alcohol 1-deutero-1-(naphthalen-2-yl)ethanol (**3a**-[α -D₁]) with the same deuterium content (92%) at the benzylic position. Thus, we conclude that the alcohol **3a** is not formed via a subsequent iron-catalyzed reduction of the ketone **2a**. In line with this conclusion, reaction of the ketone **2a** with PhSiH₃ in the presence of either Fe(dbm)₃ or FeCl₂/neocuproine as catalysts

provided no alcohol **3a**. In contrast, our previous findings have shown that the iron-catalyzed Wacker-type oxidation of **1a** with iron(II)-hexadecafluorophthalocyanine as catalyst provided the alcohol **3a** at least to some extent via subsequent reduction of **2a**.^[10b] A radical mechanism is assumed for the iron-catalyzed Wacker-type oxidation based on the fact that no product was formed when the reaction was executed in the presence of TEMPO (2 equiv). Treatment of either 1-(naphthalen-2-yl)ethanol (**3a**) or the epoxide 2-(naphthalen-2-yl)oxirane under reaction conditions of either method A or method B did not afford the ketone **2a**. These results confirmed that neither a mechanism via hydration and subsequent dehydrogenation^[28] nor via epoxidation and subsequent Meinwald rearrangement^[29] is involved in the formation of ketone **2a**.

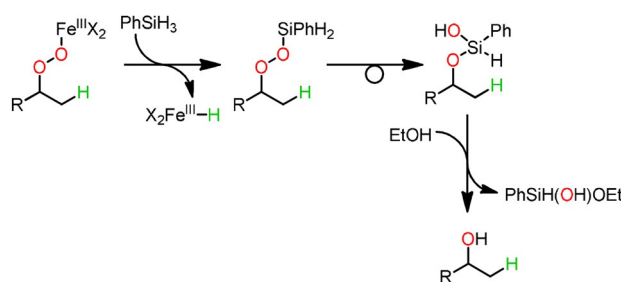
Based on the results of our mechanistic experiments and previous reports,^[10b,30] we propose the following catalytic cycle for the iron-catalyzed Wacker-type oxidation of olefins to ketones using the conditions described above (methods A–C, Scheme 3). Ligand exchange by ethanol and loss of a proton generate an iron(III) ethoxide complex FeX₂OEt (A). Subsequent reaction with PhSiH₃ leads to an iron(III) hydride complex along with PhSiH₂(OEt) (B).^[30a] Hydrogen atom transfer (HAT)^[31] with an olefin generates a carbon-



Scheme 3. Proposed mechanism for the iron-catalyzed Wacker-type oxidation of olefins to ketones using iron(III) compounds (method A–C).

centered radical and an iron(II) species which are in equilibrium with an iron(III)–alkyl complex (C). The latter can also be formed by insertion of the olefin into the iron(III) hydride complex (hydrometalation). Capturing of oxygen affords an iron(III)–peroxoalkyl complex (D). Finally, breaking of the O–O and C–H bonds provides the ketone (E)^[32] and an iron(III) hydroxide which either reacts with ethanol to regenerate the iron(III) ethoxide (F), or transmetalation with phenylsilane provides directly the iron(III) hydride species along with phenylsilanol as by-product (G). A hydroxyl radical transfer to the alkyl radical can form the alcohol as a by-product of this process (H).^[33]

Alternatively, a Mukaiyama hydration by metal exchange of the intermediate iron(III)–peroxoalkyl complex with hydrosilane could generate an iron(III) hydride and a silyl peroxoalkyl compound (Scheme 4).^[34] Rearrangement of the latter and reaction with ethanol would also lead to the alcohol.



Scheme 4. Proposed formation of the alcohol by-product via Mukaiyama hydration.

Conclusion

In summary, we have developed two protocols for the mild iron-catalyzed oxidation of olefins to ketones using phenylsilane (PhSiH₃) as reductive additive and either the readily available 1,3-diketono iron(III) complex tris(dibenzoylmethanato)iron(III) [Fe(dbm)₃] (or alternatively tris(benzoylacetonato)iron(III) [Fe(ba)₃]) or a combination of FeCl₂ and neocuproine as catalysts. Both protocols work at room temperature in ethanol as solvent and need only air as sole oxidant. Cyclic as well as acyclic styrenes and aliphatic alkenes are transformed into the corresponding ketones with good functional-group tolerance using one of the two optimized protocols. Labeling studies clearly identified the hydrosilane additive as the origin of the additional hydrogen atom at the terminal carbon atom and oxygen from the atmosphere as source for the oxo group. The method was shown to be useful for the synthesis of bioactive compounds and natural products.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: homogeneous catalysis · hydrosilanes · iron · ketones · olefins

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