Oppenauer-type oxidation of secondary alcohols catalyzed by homogeneous water-soluble complexes¹

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Abstract: The catalytic system composed of $[Ir(COD)Cl]_2$, 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC), and sodium carbonate is highly efficient for the selective oxidation of benzylic, 1-heteroaromatic, aliphatic, and allylic secondary alcohols using catalyst:substrate ratios ranging from 0.4% to 2.5%. Sterically hindered allylic alcohols undergo selectively good conversions to the corresponding enones, while unhindered ones are completely isomerized to saturated ketones. Mercury tests indicate that the catalytic process is likely homogeneous. The mechanism proposed for this Oppenauer-type oxidation including the isomerization process is based on iridium-alkoxide species.

Key words: Oppenauer oxidation, water, catalysis, isomerization, secondary alcohols.

Résumé : Le système catalytique composé de $[Ir(COD)Cl]_2$, 2,2'-biquinoléine-4,4'-dicarboxylate de potassium (BQC), et du carbonate de sodium est très efficace pour l'oxydation sélective des alcools secondaires benzyliques, 1hétéroaromatiques, aliphatiques, et allyliques en cétones correspondantes en utilisant des quantités du catalyseur allant de 0,4 % à 2,5 %, par rapport aux substrats. Les alcools allyliques encombrés sont transformés, sélectivement, en énones correspondantes, alors que les alcools non-encombrés sont complètement isomérisés en cétones saturées. Les tests avec le mercure indiquent que le processus catalytique est, probablement, homogène. Le mécanisme proposé pour cette oxydation de type Oppenauer ainsi que pour l'isomérisation des alcools allyliques est basé sur la formation de l'espèce iridium-alkoxyde.

Mots clés : oxydation d'Oppenauer, eau, catalyse, isomérisation, alcools secondaires.

Introduction

The oxidation of alcohols to the corresponding aldehydes and ketones is one of the most fundamental and indispensable reactions in organic synthesis (1). For such transformations, the use of stoichiometric amounts of harmful inorganic oxidants, mainly chromium (VI) reagents, remains widespread (2). As a consequence for the increasing demand for efficient, cleaner, and environmentally friendly methods (3), numerous catalytic methods using small amounts of metallic derivatives and clean oxidants have been developed (4). Unfortunately, most of these catalytic transformations are accomplished in costly and toxic organic solvents. Furthermore, in the homogeneous processes, separation of the catalysts from the reaction products and their quantitative recovery in an active form are still the most important goals but practical problems remain. To overcome these disadvantages, aqueous organometallic catalysis has, recently, emerged

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as a very useful alternative technology (5). The water-soluble catalyst that operates and resides in water is, easily, separated from the reaction products by simple decantation. In addition, the products are not contaminated with traces of metal catalyst, and the use of organic solvents, such as benzene and chlorinated hydrocarbons is circumvented. Despite the obvious economical and ecological advantages of aqueous-phase catalysis, very few water-soluble catalysts have been reported for the oxidation of alcohols in water (6).

Oppenauer oxidation is an elegant and highly selective process for the oxidation of secondary alcohols to the corresponding ketones, with aluminum alkoxides (7). It can be carried out under mild conditions, and is compatible with many functional groups such as carbon–carbon double and triple bonds, halogens, amino groups, aldehydes, or sulphur atom-containing groups. The advantages of Oppenauer oxidation have led to the development of more efficient methods based on modified aluminum alkoxides (8) and the use of transition-metal complexes as catalysts (9).

In the past few years, we have developed different catalytic transformations in water including the hydration of nitriles to the corresponding amides catalyzed by $[Rh(COD)CI]_2-P(m-C_6H_4SO_3Na)_3$ (TPPTS) (10), organic solvent-free oxidation of alcohols with *tert*-butyl hydroperoxide catalyzed by water-soluble copper complexes (11), and transfer hydrogenation of aldehydes and ketones with isopropanol catalyzed by water-soluble rhodium complexes (12). In the present work, we describe the results for the hydrogen transfer oxidation (Oppenauer-type oxidation) of secondary alcohols with acetone, as the oxidant, catalyzed

by water-soluble iridium and rhodium complexes containing 2,2'-biquinoline-4,4'-dicarboxylic acid dipotassium salt (BQC) (eq. [1]). Some preliminary results have been published in a communication where we have reported the first example of a water-soluble transition-metal catalyst for Oppenauer-type oxidation of secondary alcohols with acetone (13).



Results and discussion

A number of catalytic systems based on different catalyst precursors and the water-soluble ligand $P(m-C_6H_4SO_3Na)_3$ (TPPTS) or BQC were tested for the oxidation of 1phenylethanol, which was chosen as the model substrate. The first experiments showed that the presence of the catalyst precursor, together with acetone and sodium carbonate is required to achieve oxidation of 1-phenylethanol. While RuCl₃•xH₂O and PdCl₂(PhCN)₂ exhibited no catalytic activity, [Rh(COD)Cl]₂ and [Ir(COD)Cl]₂ gave rise to active water-soluble systems (Table 1). The results in Table 1 indicate that the least active catalytic systems were provided by TPPTS (Table 1, entries 1 and 4). Nevertheless, we recently reported that [Rh(COD)Cl]2-TPPTS was found to be quite an effective catalyst for transfer hydrogenation of aldehydes and ketones with isopropanol, under basic conditions (12). Treatment of 1-phenylethanol (2.5 mmol) in the presence of Na₂CO₃ (2.5 mmol), with catalytic amounts of [Rh(COD)Cl]₂ (0.01 mmol) and BQC (0.15 mmol) in a deoxygenated mixture of water (10 mL) and acetone (5 mL) at 90 °C afforded, selectively, acetophenone in 15% yield after 2 h (Table 1, entry 2). Increasing the reaction time to 17 h lead to a 57% yield (Table 1, entry 3). Remarkably, when [Rh(COD)Cl]₂ was substituted for its iridium analog much more active catalyst was generated. Indeed, acetophenone was obtained in 82% and 98% yields, respectively, after 2 and 4 h (Table 1, entries 5 and 6). This catalytic system has been shown to be much less active than [Rh(COD)Cl]2-TPPTS for transfer hydrogenation of carbonyl groups with *i*-PrOH (12). In aqueous-phase catalysis, the most important aspects are product separation as well as catalyst recovery and recycling in further experiments. The durability of the [Ir(COD)Cl]2-BQC system was tested by carrying out three consecutive cycles with the same catalyst aqueous solution, carefully separated from the organic phase under a nitrogen atmosphere at the end of each run (Table 1, entries 6-8). Only a slight decrease in catalytic activity was observed among each of the three recycling experiments demonstrating the continuing viability of the catalyst. It is relevant to point out that no metallic iridium formation was observed after the reactions and the aqueous phases remained as clear-brown solutions, indicating that there was no decomposition of the catalyst. Analysis of the organic phases, which remained clear, by atomic absorption indi-

Table 1. Oxidation of 1-phenylethanol by acetone catalyzed with various catalytic systems.^a

	Catalyst		Time	Yield
Entry	precursor	Ligand	(h)	$(\%)^{b}$
1	[Rh(COD)Cl] ₂	TPPTS	2	7
2	[Rh(COD)Cl] ₂	BQC	2	15
3	[Rh(COD)Cl] ₂	BQC	17	57
4	[Ir(COD)Cl] ₂	TPPTS	2	9
5	[Ir(COD)Cl] ₂	BQC	2	82
6	[Ir(COD)Cl] ₂	BQC	4	98 ^c
7^d	[Ir(COD)Cl] ₂	BQC	4	82
8^e	[Ir(COD)Cl] ₂	BQC	4	68
9 ^f	[Ir(COD)Cl] ₂		4	5
10 ^g	[Ir(COD)Cl] ₂	BQ	4	4
11 ^h	[Ir(COD)Cl] ₂	BQ	4	39

^aReaction conditions: 1-phenylethanol (2.5 mmol), [M(COD)Cl]₂

(0.01 mmol), ligand (0.15 mmol), $\rm Na_2CO_3$ (2.5 mmol), water (10 mL), actone (5 mL), 90 °C, $\rm N_2.$

^bYields refer to isolated ketones.

^cFull conversion of the substrate was obtained.

^{*d*}Second cycle of entry 6.

^eThird cycle of entry 6.

^fReaction conditions: 1-phenylethanol (2.5 mmol), [Ir(COD)Cl]₂ (0.01 mmol), Na₂CO₃ (2.5 mmol), acetone (10 mL), 90 °C, N₂.

 g The reaction conditions are the same as in entry 9 except that BQ (0.15 mmol) was added to the mixture.

 h The reaction conditions are the same as in entry 10 except that water (10 mL) was added to the mixture.

cated that acetophenone was extracted without leaching of the catalyst. When the oxidation was performed with $[Ir(COD)Cl]_2$ alone or in combination with 2,2'-biquinoline (BQ) in acetone containing only 0.5% water very low yields were obtained (Table 1, entries 9 and 10). Addition of water (10 mL) increased the rate of oxidation and acetophenone was isolated in 39% yield (Table 1, entry 11). An analogous positive effect of water on the rate of this homogeneous Oppenauer-type oxidation has already been observed for RuCl₂(PPh₃)₃ (9*a*). These results, which demonstrate the superiority of aqueous-phase catalysis over the homogeneous one in this Oppenauer-type oxidation, are even more interesting since BQC is cheaper than BQ.³

To demonstrate the synthetic utility and to explore the scope and limitations of the [Ir(COD)Cl]2-BQC system, a range of different alcohols were subjected to oxidation by acetone in a series of batch autoclave experiments. A variety of benzylic secondary alcohols were smoothly and selectively oxidized in very high yields, with full conversions in some cases within 4 h (Table 2, entries 1-7). Under the same reaction conditions, 1-indanol led to 1-indanone with only a 53% yield. A better result was obtained by increasing the reaction time to 17 h (Table 2, entry 8). With a sterically encumbered alcohol, namely 2-methyl-1-phenyl-1-propanol, a 58% yield was achieved, while the substrate was sluggishly oxidized after 4 h (Table 2, entry 9). A special situation was observed in the case of 4-chromanol, which underwent, in addition to an oxidation of the benzylic alcohol, a hydrogenolysis of the ArO-CH₂ (Ar is the aromatic ring) bond

³BQC and BQ cost \$4166.70 and \$5854.12CAN per mol, respectively, from the Aldrich Chemical Co.

Run	Substrate	Time (h)	Product	Yield (%)
1	OH	4	O C	98 ^c
2	OH	4	° C	80
3	CH ₃ O	4	CH ₃ O	96 ^c
4	Br	4	Br	90
5	OH	4	O C	97 ^{<i>c</i>}
6	OH	4		96 ^c
7	OH	4	o C	90
8	OH	4 (17)	o C	53 (70)
9	OH C	4 (17)	° C	32 (58)
10	OH	4	O OH	99

Table 2. Oxidation of different benzylic alcohols by acetone using water-soluble $[Ir(COD)Cl]_2$ -BQC as the catalyst.^{*a*}

"Reaction conditions: substrate (2.5 mmol), [Ir(COD)Cl]₂ (0.01 mmol), BQC (0.15 mmol), Na₂CO₃ (2.5 mmol), water (10 mL), acetone (5 mL), 90 °C, N₂.

^bYields refer to isolated ketones.

^cFull conversion of the substrate was obtained.

leading to *ortho*-hydroxypropiophenone as the sole product (Table 2, entry 10). When the reaction was performed in the absence of acetone the same product was obtained and no 4-chromanone was detected. These results indicate that the production of *ortho*-hydroxypropiophenone from 4-chromanol is, probably due to an intramolecular transfer hydrogeno-lysis. The catalytic process is envisioned as a reaction between 4-chromanol and the water-soluble iridium system resulting in an iridium alkoxide complex, which, in turn, undergoes β -hydride elimination to produce a η^2 -ketone hydride species, where the 4-chromanone is still coordinated to the iridium. The transfer of iridium hydride to the methylene group of ArO-CH₂ of the coordinated 4-chromanone (intramolecular 1,3-hydride shift) leads to an iridium *ortho*-propionylphenoxide complex. Protonation with another 4-

chromanol molecule liberates *ortho*-hydroxypropiophenone and regenerates the iridium alkoxide species. The transfer of hydride to $ArO-CH_3$ did not occur in the case of 1-(4-methoxyphenyl)ethanol (Table 2, entry 3) since the methoxy group is located far from the metal hydride core.

To explore substrate scope further, we tested the efficiency of the $[Ir(COD)Cl]_2$ –BQC system to oxidize secondary 1-heteroaryl alcohols (Table 3). Good to excellent yields were obtained in all cases, although the reaction time was extended to 17 h for the oxidation of 1-(2-furyl)-2-methyl-1propanol and the thienyl analog, which gave, respectively, 74% and 65% yields (Table 3, entries 3 and 4). The sluggishness in these two cases is attributed to steric hindrance from the isopropyl group.

The reaction was, also, extended to a variety of secondary

Run	Substrate	Time (h)	Product	Yield $(\%)^b$
1	OH OH	4 (17)		87 (87)
2	S OH	4 (17)	S S	88 (90)
3	OH OH	4 (17)		66 (74)
4	S OH	4 (17)	S O	48 (65)

Table 3. Oxidation of different 1-heteroaryl alcohols by acetone using water-soluble [Ir(COD)Cl]2-BQC as the catalyst.^a

^aReaction conditions: substrate (2.5 mmol), [Ir(COD)Cl]₂ (0.01 mmol), BQC (0.15 mmol), Na₂CO₃ (2.5 mmol), water (10 mL), acetone (5 mL), 90 °C, N_2 . ^bYields refer to isolated ketones.

Table	4.	Oxidation	of	different	aliphatic	alcohols	by	acetone	using	water-soluble	[Ir(COD)	$Cl]_2 - BQC$
as the	cat	talyst. ^a										

Run	Substrate	Time (h)	Product	Yield (%) ^b
1	OH	4	°	76
2	ОН-ОН	4 (17)	o=	15 (25)
3 ^{<i>c</i>}	ОН-	17	<⊨o	80
4	OH	4 (17)	O L	21 (31)
5	OH	4 (17)	°	21 (30)
6 ^{<i>c</i>}	OH	17	°	91
7	OH	4	O O	23
8 ^c	OH	17	O O	80
9 ^c	OH	20	O O	72

^aUnless stated otherwise, the reaction conditions are: substrate (2.5 mmol), [Ir(COD)Cl]₂ (0.01 mmol), BQC (0.15 mmol), Na₂CO₃ (2.5 mmol), water (10 mL), acetone (5 mL), 90 °C, N₂. ^bYields refer to isolated ketones.

 $^c\text{Substrate}$ (1 mmol), $\left[\text{Ir}(\text{COD})\text{Cl}\right]_2$ (0.025 mmol), and BQC (0.375 mmol).

Run	Substrate	Catalyst	Time (h)	Product	Yield $(\%)^b$
1	OH	[Ir(COD)Cl] ₂ –BQC	1	0	100
2	OH	[Ir(COD)Cl] ₂ -TPPTS	4	 0	100
3	OH	PtCl ₂ (COD)–BQC	4	0	98
4	OH	PdCl ₂ (PhCN) ₂ -BQC	4		100
5	OH	[Rh(COD)Cl]2-BQC	4		100
6	OH	[Ir(COD)Cl] ₂ –BQC	1.5	O C	100
7	OH	[Ir(COD)Cl] ₂ –BQC	17	O L	50
8 ^c	OH	[Ir(COD)Cl] ₂ –BQC	17	O L	100
9	OH	[Ir(COD)Cl] ₂ -BQC	17	O V	13
10 ^c	OH	[Ir(COD)Cl] ₂ –BQC	17	O V	100

Fable 5. Oxidation of different allylic alcohols by acetone using various water-soluble catalysts.^a

^aUnless stated otherwise, the reaction conditions are: substrate (2.5 mmol), [Ir(COD)Cl]₂ (0.01 mmol), BQC

(0.15 mmol), Na2CO3 (0.5 mmol), water (10 mL), acetone (5 mL), 90 °C, N2.

^bYields were estimated by ¹H NMR.

^cSubstrate (1 mmol), [Ir(COD)Cl]₂ (0.025 mmol), and BQC (0.375 mmol).

aliphatic alcohols (Table 4). However, these inactivated alcohols proved to be sluggish substrates under our standard conditions, and only poor yields were obtained. Fortunately, a higher catalyst:substrate ratio (2.5 mol%) and longer reaction times greatly improve the yields (Table 4, entries 3, 6, 8, and 9). Remarkably, cyclooctanol showed a higher reactivity than cyclohexanol and the former was oxidized in 76% yield with only 0.4 mol% of $[Ir(COD)Cl]_2$ after 4 h (Table 4, entry 1).

To investigate the extent of $[Ir(COD)Cl]_2$ -BQC oxidation, different allylic alcohols have been studied (Table 5). The oxidation of 1-octen-3-ol afforded 3-octanone as the sole product after only 1 h of reaction time (Table 5, entry 1). The reaction performed in the absence of acetone led to the same result after 4 h. However, this reaction was not optimized. The isomerization of allylic alcohols to saturated carbonyl compounds is an important reaction in organic chemistry that still suffers from several drawbacks (14). Surprisingly, the water-soluble catalytic systems reported for the isomerization of allylic alcohols are rare, despite their synthetic utility (15). Thus, other water-soluble catalysts were tested for the oxidation of 1-octen-3-ol (Table 5, entries 2-5). Excellent to full conversions to the isomerization product were obtained except in the case of RuCl₃-BQC, which is inactive. Although these reactions were not optimized, the result obtained with [Ir(COD)Cl]₂-BQC is promising since its catalytic frequency for the isomerization of 1octen-3-ol (125 h⁻¹ at 90 °C) is slightly better than the reported activities for other water-soluble catalysts based on $[RuCl_2(\eta^6-arene){P(CH_2OH)_3}]$ (4–67 h⁻¹ at 75 °C) (15*a*), $Rh_2(SO_4)_3$ (30 h⁻¹ at 80 °C) (15b), $RhCl_3$ (60 h⁻¹ at 70 °C) (15b), and (COD)RhCl(PAr₃) (15–48 h⁻¹ at 104 °C) (15c). We are currently continuing to investigate the isomerization of allylic alcohols in the aqueous phase. The oxidation of 1Scheme 1. Proposed mechanism for the Oppenauer-type oxidation and isomerization of allylic alcohols.



phenyl-2-propen-1-ol, under the same conditions, also gave propiophenone as the isomerization product, with full conversion (Table 5, entry 6), whereas cyclic allylic alcohols are, surprisingly, oxidized to their corresponding unsaturated ketones albeit in low yields (Table 5, entries 7 and 9). Fortunately, under the conditions used for the oxidation of aliphatic alcohols (Table 4, entry 3), isophorol and 3-methyl-2-cyclohexenol were fully converted to their corresponding unsaturated ketones (Table 5, entries 8 and 10). Bäckvall and co-workers (9*a*) have also reported that 1-octen-3-ol was isomerized under their reaction conditions to 3-octanone using ruthenium complexes, while 2-cyclohexenol was converted to an unsaturated ketone. Although the structure of the water-soluble active complex is not identified, a rational mechanism for this Oppenauer-type oxidation, including the isomerization process, is presented in Scheme 1.

Since no iridium mirror (black metallic iridium) was observed after the reactions and the aqueous phases remained as clear-brown solutions, we carried out mercury poisoning experiments (see the Experimental section) to rule out the possibility of catalysis by colloidal metal. Mercury poisoning is a well-known and widely used test to distinguish between heterogeneous and homogeneous processes (16). The addition of a large excess of mercury(0) (Hg:Ir molar ratio of 872) with vigorous stirring did not suppress the catalysis.

Table 6. Oxidation of 1-phenylethanol by acetone catalyzed by water-soluble $[Ir(COD)CI]_2$ – BQC using different amounts of Na₂CO₃.^{*a*}

Run	Na ₂ CO ₃ (mmol)	Yield (%) ^l
1	0	0
2	0.25	88
3	0.5	98
4	1	100
5	1.5	100
6	2	100
7	2.5	100

^aReaction conditions: substrate (2.5 mmol), [Ir(COD)Cl]₂ (0.01 mmol), BQC (0.15 mmol), Na₂CO₃ (0–2.5 mmol), water (10 mL), acetone

(5 mL), 90 °C, N₂, 4 h.

^bYields were estimated by ¹H NMR.

These results suggest that nanoparticles are not the key species in the present system and that the process is likely homogeneous.

The first step of the proposed mechanism would involve the formation of iridium alkoxide II (9a, 17). Stoichiometric amounts of Na₂CO₃ were used in our experiments. However, oxidation of 1-phenylethanol with smaller amounts of Na₂CO₃ also gave excellent results (Table 6). When the reaction was performed in the absence of base, its remarkable effect was particularly noticeable because no reaction occurred (Table 6, entry 1). This effect of base in Oppenauer-type oxidations has been observed in previous reports (9a, 9b). Consequently, the primary role of the base is to facilitate formation of iridium alkoxide complex II. This latter species can undergo β -hydride elimination of the coordinated alkoxide to produce the desired ketone and iridium hydride species **IV**, via complex **III** where the ketone is still coordinated to the metal (η^2 -ketone ligand). β -hydride elimination from metal alkoxides has been observed (17, 18) and proposed for hydrogen transfer reactions (9a, 19). In our case, the production of ortho-hydroxypropiophenone from 4-chromanol is in agreement with the formation of complex III. Comparison of the oxidation rates for PhCH(OH)CH₂ and PhCD(OH)CH₂, under the same conditions (Fig. 1), indicates that the ratelimiting step does not involve β -hydride elimination from **II** since the isotope effect is low $(k_{\rm H}/k_{\rm D} = 1.2)$. The reaction of acetone with IV would produce complex V, which leads to iridium isopropoxide VI by insertion of acetone into the Ir— H bond. An exchange of alkoxy moiety would regenerate species II and liberate isopropanol. In the case of allylic alcohols, an additional pathway for the isomerization process is proposed. Three mechanisms have been proposed for transition metal catalyzed isomerization of allylic alcohols. The first one involves a π -allyl metal hydride complex (20), while a second one is based on metal hydride addition-elimination (21). A third mechanism, suggested by Trost and Kulawiec (22), involves the coordination of allylic alcohol as a bidentate ligand and the formation of metal alkoxide species. Our results from oxidation with [Ir(COD)Cl]₂-BQC (Table 5) are consistent with the alkoxide mechanism. Thus, in the case of allylic alcohols, ${\rm I\!I}$ is reorganised as ${\rm I\!I}_{\rm isom}$ to allow the coordination of Ir with R_2 (R_2 is an olefinic moiety). $II_{isom.}$ undergoes β -hydride elimination to produce the





enone hydride species $III_{isom.}$. This latter is expected to evolve in two different ways depending on the steric requirements of the enone. In the case of bulky substrates such as isophorol, $III_{isom.}$ releases the enone through path A and follows the catalytic cycle for the Oppenauer-type oxidation. This is in agreement with previous reports regarding the isomerization of allylic alcohols catalyzed by ruthenium complexes (21, 22). The steric unhindered enones, on the other hand, are not released and allow $III_{isom.}$ to rearrange to π -oxallyl species $IV_{isom.}$ through path B. Protonation with another allylic alcohol molecule liberates the saturated ketone and regenerates the initial species $II_{isom.}$.

Summary

In conclusion, the system composed of $[Ir(COD)CI]_2$ and the cheap water-soluble ligand BQC is a new and highly efficient catalyst for Oppenauer-type oxidation of benzylic, 1heteroaromatic, aliphatic, and allylic secondary alcohols. The system showed much better activity than the waterinsoluble analogs. The catalytic process is likely homogeneous and the mechanism proposed for this Oppenauer-type oxidation including the isomerization process is based on iridium-alkoxide species.

Experimental

Materials and instruments

All the substrates, BQ, and BQC were purchased from Aldrich Chemical Co. and used without further purification. [Rh(COD)Cl]₂, RuCl₃·xH₂O, PdCl₂(PhCN)₂, and [Ir(COD)Cl]₂ were acquired from Strem Chemical Co.

TPPTS was prepared according to the literature method (23) and PhCD(OH)CH₃ was prepared using $LiAlD_4$ (24).

Routine NMR measurements were performed on a Bruker AC-200 spectrometer at 200 MHz and 50 MHz, respectively, for ¹H and ¹³C, using tetramethylsilane (TMS) as an internal standard and CDCl₃ as the solvent.

Typical procedure for this Oppenauer type oxidation with acetone

In the glass liner of a 45 mL autoclave, under an atmosphere of nitrogen, [Ir(COD)Cl]₂ (0.01 mmol), BQC (0.15 mmol), and Na₂CO₃ (2.5 mmol) were dissolved in degassed water (10 mL) at room temperature. Next a solution of the substrate (2.5 mmol) in degassed acetone (5 mL) was introduced. The autoclave, was then flushed several times with 80 psi (1 psi = 6.894757 kPa) of N₂ and then placed in an oil bath at 90 °C for the required reaction time. The autoclave was cooled to room temperature and the mixture was extracted three times with degassed diethyl ether (20 mL). The combined organic layers were dried (MgSO₄), evaporated to dryness, and then analyzed by TLC and ¹H and ¹³C NMR. Literature data and (or) authentic samples were used for comparison. The ¹H NMR spectra for all samples showed the presence of remaining substrate (where the conversions were not complete), the product, and small amounts of 4-hydroxy-4-methyl-2-pentanone formed by aldol condensation of acetone. In the case of isolated yields, the ketones were purified using column chromatography with ethyl acetate - petroleum ether (5:95) as the eluent.

The recycled aqueous phase obtained, after removal of solvents under a nitrogen atmosphere, was reused with only a fresh charge of solution consisting of the alcohol (2.5 mmol) in degassed acetone (5 mL).

Mercury poisoning experiments

Three experiments were performed to determine the effect of mercury (0) on the reaction.

A solution of $[Ir(COD)CI]_2$ (13.4 mg, 0.02 mmol) and BQC (0.3 mmol, 142 mg) in water (20 mL) was stirred in the presence of excess mercury (7 g, 34.9 mmol, ca. 872 equiv.) for 24 h. The solution was decanted from the mercury and divided into two equal parts, which were used for the Oppenauer-type oxidation of 1-phenylethanol for 4 h. After 1 h of reaction time, one autoclave was cooled to room temperature, vented, and opened under a nitrogen atmosphere. Next 3.5 g of Hg(0) was added to the clear-brown catalytically active solution and the autoclave was then purged with nitrogen, resealed, and stirred for 30 min. The mixture was then heated at 90 °C for the remaining reaction time. The two experiments showed the same excellent catalytic activity.

A third experiment was done just to confirm the previous ones. In this experiment, the oxidation was initiated in the presence of excess Hg(0) (872 equiv.). The result was identical to the previous ones.

These experiments indicate that Hg(0) does not react with the precatalyst $[Ir(COD)Cl]_2$ and that the process is likely homogeneous.

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