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Highly Efficient Dehydrogenation of Secondary Alcohols Catalyzed by Iridium–CNP Complexes[1]

Dawei Wang, Keyan Zhao, Shuyan Yang, and Yuqiang Ding

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education,
School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, Jiangsu Province, China
e-mail: wangdw@jiangnan.edu.cn; yding@jiangnan.edu.cn

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Abstract—A new highly practical method is presented for dehydrogenation of secondary alcohols to the corresponding ketones catalyzed by the iridium–CNP complexes. The reactions are compatible with substrates bearing diverse functional groups and proceed efficiently under mild conditions.

Keywords: dehydrogenation, carbonyl compounds, ketones, iridium–CNP complex, alcohols

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INTRODUCTION

Dehydrogenation of secondary alcohols to the corresponding carbonyl compounds provides a practical route to ketones and is of great importance in synthetic chemistry and fine chemical industry [1–7]. Conventional routes for this transformation involve the use of stoichiometric amounts of oxidants such as dichromate and permanganate but these reagents produce large amounts of solid waste and are hazardous to the environment [8–10]. Oxidative dehydrogenation of alcohols using solid catalysts and atmospheric air or molecular oxygen avoids the environmental problem, producing water as the only byproduct [11–15]. In this aspect, Ru [16], Ir [17], and Fe-catalysis [18] has attracted considerable interest, and mild oxidants such as H_2O_2 [19], O_2 [20], and acetone [21] have been used. Transfer dehydrogenation of alcohols that uses unsaturated organic compounds as the hydrogen acceptors increases the selectivity of the carbonyl group and overcomes the safety problem, providing a new route for alcohol transformation [22]. Meanwhile, the practical application of oxidative dehydrogenation of alcohols is still hampered by the unsatisfied selectivity toward carbonyls and the safety concerns connected with the use of flammable solvents under oxidative atmosphere [23].

Our interest in developing new catalysts to adjust transition metal reactivity has led to the recent discovery of CNP iridium complexes with carbon, nitrogen, and phosphine coordinated to iridium [24–28]. We have synthesized the CNP iridium complexes with catalytic activity enhanced by the phosphine ligand and the counter-ion (Scheme 1). These iridium-CNP complexes have shown high catalytic activity in alkylation of amines. Here, we report dehydrogenation of secondary alcohols realized by the use of iridium-CNP complexes as catalysts in a good yield.

RESULTS AND DISCUSSION

In order to evaluate the effectiveness of various iridium catalysts and to optimize the catalytic activity and selectivity, 1-phenylethanol was chosen as the model substrate in the reaction of dehydrogenation (Table 1). Styrene was used as the hydrogen acceptor, being converted to ethylbenzene.

We recently found that complexes **IIa, IIb, IIc**, and **IId** can also affect the catalytic Oppenauer-type oxidation of secondary alcohols, while complexes **Ia** and **Ib** had a poor catalytic activity for converting 1-phenylethanol to acetophenone with 2 mol % catalysts loading, 1 equiv. of K_2CO_3, dioxane as the reaction solvents, and at 110°C during a period of 12 h (Table 1, entries 1–6). Using **IIb** as a catalyst, polar and less-polar solvent were subsequently evaluated. The results showed that these solvents are less effective in comparison with toluene (Table 1, entries 7–10). Thus we selected **IIb** as the preferred catalyst and toluene as the preferred solvent. The screening of various organic and inorganic bases indicated that *t*-BuOK gave a significant higher product yield (Table 1, entry 16). It

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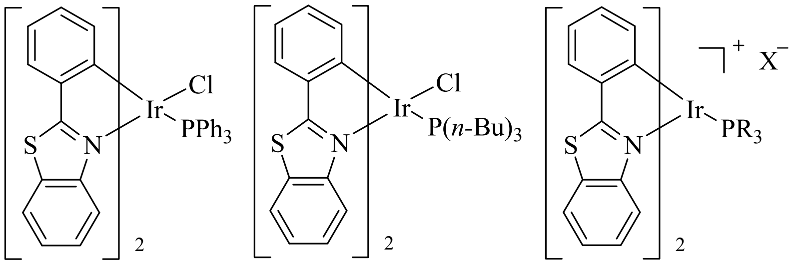
[1] The text was submitted by the authors in English.

Scheme 1. Benzothienyl skeleton Ir(III)–CNP complexes



Ia **Ib** **II**

IIa: R = PPh_3, X = OTf; **IIb**: R = *n*-Bu, X = OTf ; **IIc**: R = *n*-Bu, X = BF_4; **IId**: R = *n*-Bu, X = SbF_6.

should be noted that nearly all the catalysts with coordination anion gave excellent yields (Table 1, entries 17–19).

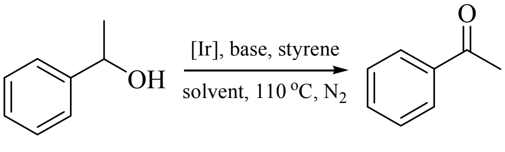
With the optimized conditions established, we next examined the generality of the catalyst system. A series of alcohols were tested under the optimized conditions and the results are summarized in Table 2. As can be seen, all secondary alcohols are converted into the corresponding carbonyl compounds in high yields. The effect of substituents in the aromatic ring was also investigated, and irrespective of the position or the electronic nature of the substituent the products are formed in good yields (Table 2, entries 1–16). Heterocyclic secondary alcohols (Table 2, entries 17–19) as well as benzhydrol (Table 2, entry 20) are also oxidized under the optimal reaction conditions with good yields.

EXPERIMENTAL

General procedure. The obtained products were characterized by ^1H NMR spectra. NMR spectra were obtained on Bruker Advance 400 and 300 in $CDCl_3$ solution. Chemical shifts are reported in ppm downfield from tetramethylsilane. TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

Typical procedure for the synthesis of IVa. Catalyst **IIb** (2 mol %, 0.02 mmol), 1-phenylethanol (1 mmol), styrene (1 mL), potassium *tert*-butoxide, and toluene (1 mL) were added to a Schlenk tube under a nitrogen atmosphere. The mixture was heated under 110°C for 12 h and then cooled to room temperature. The reaction was monitored by TLC and the yield was determined by GC analysis. Below, the ^1H NMR spectra of the products are given.

Table 1. Screening of optimized reaction conditions for dehydrogenation of 1-phenylethanol (**IIIa**)[a,b]

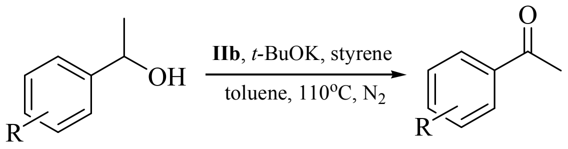


IIIa **IVa**

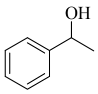
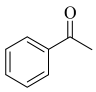
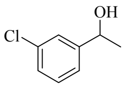
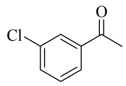
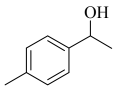
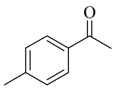
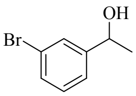
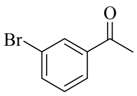
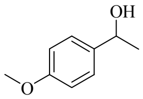
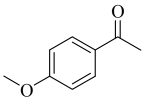
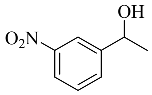
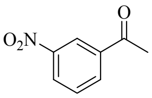
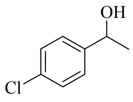
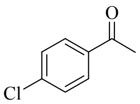
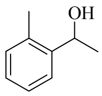
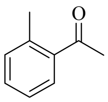
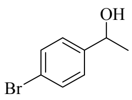
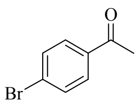
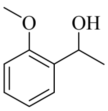
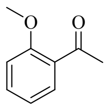
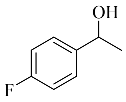
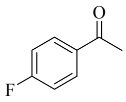
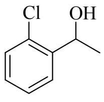
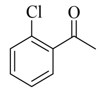
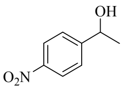
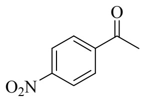
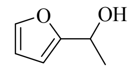
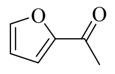
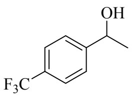
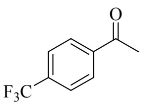
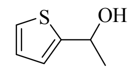
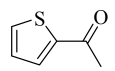
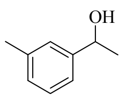
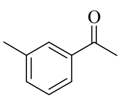
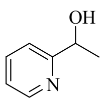
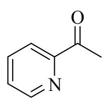
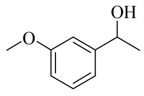
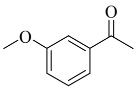
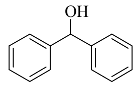
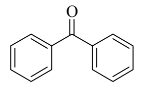
Entry	Catalyst	Base	Solvent	Yield, %
1	**Ia**	K_2CO_3	Dioxane	24
2	**Ib**	K_2CO_3	Dioxane	30
3	**IIa**	K_2CO_3	Dioxane	45
4	**IIb**	K_2CO_3	Dioxane	47
5	**IIc**	K_2CO_3	Dioxane	46
6	**IId**	K_2CO_3	Dioxane	45
7	**IIb**	K_2CO_3	DMSO	58
8	**IIb**	K_2CO_3	DMF	54
9	**IIb**	K_2CO_3	Toluene	67
10	**IIb**	K_2CO_3	MeCN	52
11	**IIb**	–	Toluene	38
12	**IIb**	KOH	Toluene	64
13	**IIb**	Et_3N	Toluene	35
14	**IIb**	Na_2CO_3	Toluene	63
15	**IIb**	Cs_2CO_3	Toluene	79
16	**IIb**	*t*-BuOK	Toluene	89
17	**IIa**	*t*-BuOK	Toluene	87
18	**IIc**	*t*-BuOK	Toluene	85
19	**IId**	*t*-BuOK	Toluene	87

[a] Reagents and conditions: under a nitrogen atmosphere, 1-phenylethanol (1 mmol), styrene (1 mL), Cat [Ir] loading (2 mol %), base (1 mmol), Solvent (1 mL), 110°C, 12 h. [b] The yield was determined by GC.

Table 2. Catalytic dehydrogenation of various secondary alcohols[a,b]



III **IV**

Entry	Alcohol	Product	Yield, %	Entry	Alcohol	Product	Yield, %
1			**IVa** (89)	11			**IVk** (91)
2			**IVb** (95)	12			**IVl** (92)
3			**IVc** (86)	13			**IVm** (94)
4			**IVd** (88)	14			**IVn** (87)
5			**IVe** (86)	15			**IVo** (88)
6			**IVf** (87)	16			**IVp** (85)
7			**IVg** (87)	17			**IVq** (92)
8			**IVh** (88)	18			**IVr** (94)
9			**IVi** (92)	19			**IVs** (95)
10			**IVj** (93)	20			**IVt** (85)

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[a] Reagents and conditions: under a nitrogen atmosphere, secondary alcohol (1 mmol), styrene (1 mL), Cat **IIb** loading (2 mol %), *t*-BuOK (1 mmol), toluene (1 mL), 110°C, 12 h. [b] The yield was determined by GC.

Acetophenone (IVa) [29]. 400 MHz, δ, ppm: 7.97–7.95 m (2H), 7.58–7.54 m (1H), 7.48–7.44 m (2H), 2.61 s (3H).

1-(*p*-Tolyl)ethanone (IVb) [29]. 400 MHz, δ, ppm: 7.85 d (*J* = 8 Hz, 2H), 7.25 d (*J* = 8 Hz, 2H), 2.57 s (3H), 2.41 s (3H).

1-(4-Methoxyphenyl)ethanone (IVc) [29]. 400 MHz, δ, ppm: 7.93 d (*J* = 8.8 Hz, 2H), 6.92 d (*J* = 8.8 Hz, 2H), 3.86 s (3H), 2.54 s (3H).

1-(4-Chlorophenyl)ethanone (IVd) [29]. 400 MHz, δ, ppm: 7.88 d (*J* = 8.8 Hz, 2H), 7.42 d (*J* = 8.8 Hz, 2H), 2.58 s (3H).

1-(4-Bromophenyl)ethanone (IVe) [30]. (270 MHz) δ 7.65 d (*J* = 9 Hz, 2H), 7.42 d (*J* = 8 Hz, 2H), 2.43 s (3H).

1-(4-Fluorophenyl)ethanone (IVf) [30]. 400 MHz, δ, ppm: 8.00–7.96 m (2H), 7.15–7.11 m (2H), 2.58 s (3H).

1-(4-Nitrophenyl)ethanone (IVg) [30]. 400 MHz, δ, ppm: 8.33–8.30 m (2H), 8.13–8.10 m (2H), 2.68 s (3H).

1-[4-(trifluoromethyl)phenyl]ethanone (IVh) [31]. 400 MHz, δ, ppm: 8.09 d (2H*J* = 8.0 Hz), 7.74 d (2H, *J* = 8.0 Hz), 2.65 s (2H).

1-(*m*-Tolyl)ethanone (IVi) [31]. 270 MHz, δ, ppm: 7.74–7.28 m (4H), 2.55 s (3H), 2.38 s (3H).

1-(3-Methoxyphenyl)ethanone (IVj) [29]. (300 MHz), δ, ppm: 7.1–7.6 m (4H), 3.9 s (3H), 2.6 s (3H).

1-(3-Chlorophenyl)ethanone (IVk) [30]. 400 MHz, δ, ppm: 7.93–7.92 m (1H), 7.84–7.82 m (1H), 7.55–7.52 m (1H), 7.43–7.39 m (1H), 2.59 s (3H).

1-(3-Bromophenyl)ethanone (IVl) [31]. 400 MHz, δ, ppm: 8.20 m (1H), 7.99 d (1H, *J* = 8.21 Hz), 7.87 d (1H, *J* = 8.20 Hz), 7.50 m (1H), 2.68 s (3H).

1-(3-Nitrophenyl)ethanone (IVm) [31]. 400 MHz, δ, ppm: 8.77 d (*J* = 2.0 Hz, 1H), 8.44–8.41 m (1H), 8.30–8.28 m (1H), 7.71–7.67 m (1H), 2.69 s (3H).

1-(*o*-Tolyl)ethanone (IVn) [30]. 270 MHz, δ, ppm: 7.67–7.18 m (4H), 2.53 s (3H), 2.51 s (3H).

1-(2-Methoxyphenyl)ethanone (IVo) [31]. 400 MHz, δ, ppm: 7.78 d (1H, *J* = 6.90 Hz), 7.70 m (1H), 7.26 d (1H, *J* = 7.77 Hz), 7.17 m (1H), 3.99 s (3H), 2.71 s (3H).

1-(2-Chlorophenyl)ethanone (IVp) [32]. 400 MHz, δ, ppm: 7.56–7.53 m (1H), 7.41–7.30 m (3 H), 2.64 s (3H).

1-(Furan-2-yl)ethanone (IVq) [32]. 500 MHz, δ, ppm: 7.58–7.59 d (*J* = 0.8, 1H), 7.18–7.19 d (*J* = 3.4, 1H), 6.53–6.54 d.d (*J* = 3.5, 1.6, 1H), 2.49 s (3H).

1-(Thiophen-2-yl)ethanone (IVr) [32]. 300 MHz, δ, ppm: 7.69–7.70 d (*J* = 3.6, 1H), 7.63–7.64 d (*J* = 4.2, 1H), 7.11–7.14 t (*J* = 4.2, 1H), 2.57 s (3H).

1-(Pyridin-2-yl)ethanone (IVs) [32]. 400 MHz, δ, ppm: 8.68–8.67 m (1H), 8.04–8.02 m (1H), 7.84–7.80 m (1H), 7.48–7.45 m (1H), 2.72 s (3H).

Benzophenone (IVt) [31]. 400 MHz, δ, ppm: 7.81–7.79 m (4H), 7.61–7.57 m (2H), 7.50–7.46 m (4H).

CONCLUSIONS

In conclusion, a new highly practical method is presented for dehydrogenation of secondary alcohols to the corresponding ketones by means of the iridium–CNP complexes as catalysts. All secondary alcohols were converted into the corresponding carbonyl compounds in high isolated yields under a nitrogen atmosphere. The reactions are compatible with substrates bearing diverse functional groups and the substitution patterns of alcohols have little influence on the formation of the desired products.

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