

Ruthenium-catalysed transfer hydrogenation of aromatic aldehydes with dioxane under KOH: assistance of Cannizzaro reaction

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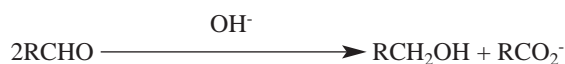
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Aromatic aldehydes are reduced to the corresponding alcohols in dioxane at 80°C in the presence of a catalytic amount of a ruthenium catalyst together with KOH in moderate to good yields.

Keywords: alcohols, aldehydes, Cannizzaro reaction, ruthenium catalyst, transfer hydrogenation

Many reduction methods have been developed and documented for efficient organic transformation.¹ Besides conventional reduction routes, recently, catalytic transfer hydrogenation has been attempted because of the facility and efficiency of reaction.² During the course of our ongoing studies on ruthenium catalysis,^{3–5} we recently found an unusual type of ruthenium-catalysed transfer hydrogenation of ketones by alcohols accompanied by C–C coupling under KOH.^{6,7} In connection with this report, Imai *et al.* partly reported that dioxane can be used as a hydrogen donor in ruthenium-catalysed transfer hydrogenation of aldehyde, giving a low yield of alcohol.⁸ Further, even though aldehydes which have no α -hydrogen are reduced to alcohols under a base (Cannizzaro reaction⁹), the protocol is of little synthetic use since half of the aldehyde is converted into a carboxylate (Scheme 1). Herein we wish to report an efficient ruthenium-catalysed transfer hydrogenation, which is partially assisted by Cannizzaro reaction, of aromatic aldehydes with dioxane under KOH.



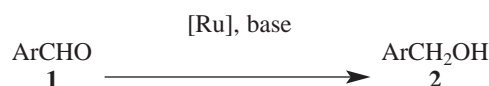
Scheme 1

The results of several attempted reductions of benzaldehyde (**1a**, **1**: Ar = Ph) under various conditions are listed in Table 1 (Scheme 2). Treatment of **1a** in the presence of a catalytic amount of [RuCl₂(=CHPh)(PCy₃)₂] (1 mol%) along with KOH in dioxane at 80°C for 20 h afforded benzyl alcohol (**2a**, **2**: Ar = Ph) in 65% GLC yield (entry 1). This reaction condition was eventually revealed to be the best for obtaining **2a**. Of various ruthenium catalysts employed, [RuCl₂(=CHPh)(PCy₃)₂] is the choice of preference for the effective formation of **2a** (entries 1 and 4–10). The yield of **2a** gradually increased from 24% (3 h), 32% (5 h), 48% (10 h), 57% (15 h) to 65% (20 h) under [RuCl₂(=CHPh)(PCy₃)₂]. If the reaction was performed in the presence of K₂CO₃ in place of KOH, the starting **1a** was recovered almost completely (entry 2). Tuning the amount of KOH was necessary for the effective transformation of **1a** into **2a**. The use of 0.5 equivalent (under 1 mol% [RuCl₂(=CHPh)(PCy₃)₂]) and 2 equivalents (under 2 mol% [RuCl₂(PPh₃)₃]) of KOH to **1a** afforded **2a** in 32% and 43% yields, respectively. Diglyme can be alternatively used as solvent, but the yield of **2a** was lower than that in dioxane (entry 3). Lower reaction temperature resulted in a lower yield of **2a** (entry 6). As is the case for Cannizzaro reaction, the reaction proceeded in the absence of ruthenium catalyst (entry 11).

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Comparing the results of entries 1 and 11 in Table 1, it appears that the present reduction also proceeds via transfer hydrogenation of **1a** by solvent dioxane in the presence of a ruthenium. It is known that dioxane has been used as hydrogen donor in transition metal-catalysed transfer hydrogenation.^{8,10}



Scheme 2

Table 1 Reactions under several conditions^a

Entry	Ruthenium catalyst	Base/solvent	GLC yield/%
1	RuCl ₂ (=CHPh)(PCy ₃) ₂	KOH/dioxane	65
2	RuCl ₂ (=CHPh)(PCy ₃) ₂	K ₂ CO ₃ /dioxane	0
3	RuCl ₂ (=CHPh)(PCy ₃) ₂	KOH/diglyme	43
4	RuCl ₂ (PPh ₃) ₃	KOH/dioxane	41
5	RuH ₂ (PPh ₃) ₄	KOH/dioxane	44
6 ^b	RuH ₂ (PPh ₃) ₄	KOH/dioxane	31
7	Ru ₃ (CO) ₁₂	KOH/dioxane	53
8	RuCl ₃ ·nH ₂ O/1.5dppm ^c	KOH/dioxane	47
9	Cp* ^d RuCl ₂ (CO) ^d	KOH/dioxane	45
10	Cp* ^d RuCl(CO)(PPh ₃) ^d	KOH/dioxane	45
11	-	KOH/dioxane	33

^aReaction conditions: **1** (1 mmol), ruthenium catalyst (0.01 mmol), base (1 mmol), solvent (3 ml), 80°C, for 20 h. ^bAt 50°C. ^cdppm = bis(diphenylphosphino)methane. ^dCp* = η⁵-C₅Me₅.

Given the controlled conditions, with various aromatic aldehydes **1** the corresponding alcohols **2** were formed in the range of 40–82% yields. As shown in Table 2, the product yield was not considerably affected by the position of the substituent on the aromatic ring of **1** (entries 2–4). Electron-donating and –withdrawing substituents on the aromatic ring of **1** also had no significant relevance to the yield of **2** (entries 5–9). In the reaction with 2-bromobenzaldehyde (**1g**), in addition to the alcohol **2g**, debromination product benzyl alcohol was also produced in 2% yield (entry 7). It is known that haloarenes are readily dehalogenated in the presence of a transition metal catalyst under a hydrogen donor.^{10,11} In the case of 4-nitrobenzaldehyde (**1i**), the reaction proceeded with tolerance of the nitro functional group under the present reduction system (entry 9). Poly- (**1j** and **1k**) and heteroaromatic (**1l–1n**) aldehydes were also reduced to afford the corresponding alcohols (**2j–2n**) (entries 10–14). The reduction proceeded likewise with ferrocenealdehyde (**1o**) to give ferrocenemethanol (**2o**) in 57% yield (entry 15). The reaction with terephthalaldehyde (**1p**) under the same conditions afforded 4-(hydroxymethyl)benzaldehyde (**2p**) in 40% isolated yield with concomitant formation of further

Table 2 Ruthenium-catalysed reduction of aldehydes to alcohols^a

Entry	Aldehydes 1 (Ar =)	Alcohols 2	Isolated yield/%
1	Ph (1a)	2a	59
2	2-MeC ₆ H ₄ (1b)	2b	75
3	3-MeC ₆ H ₄ (1c)	2c	82
4	4-MeC ₆ H ₄ (1d)	2d	77
5	4-MeOC ₆ H ₄ (1e)	2e	55
6	3,4-(MeO) ₂ C ₆ H ₃ (1f)	2f	51
7	2-BrC ₆ H ₄ (1g)	2g	70 ^b
8	2,4-Cl ₂ C ₆ H ₃ (1h)	2h	54
9	4-NO ₂ C ₆ H ₄ (1i)	2i	60
10	2-naphthyl (1j)	2j	75
11	9-anthracenyl (1k)	2k	63
12	2-furanyl (1l)	2l	54
13	2-thiophenyl (1m)	2m	64
14	3-pyridyl (1n)	2n	51
15	ferrocenyl (1o)	2o	57
16	4-(CHO)C ₆ H ₄ (1p)	2p	40 ^c

^aReaction conditions: **1** (1 mmol), RuCl₂(=CHPh)(PCy₃)₂ (0.01 mmol), KOH (1 mmol), dioxane (3 ml), 80°C, for 20 h. ^bBenzyl alcohol was also formed in 2% yield. ^c1,4-Benzenedimethanol was also formed in 36% yield.

reduced 1,4-benzenedimethanol (36% yield) (entry 16). On the other hand, the reaction with aliphatic aldehyde 1-octanal afforded a complicated mixture on GLC analysis.

In summary, we have shown that aromatic aldehydes can be reduced to alcohols in the presence of a catalytic amount of a ruthenium catalyst in dioxane as hydrogen donor and solvent under KOH. The present reaction is an efficient catalytic transfer hydrogenation of aromatic aldehydes assisted by Cannizzaro reaction.

Experimental

GLC analyses were carried out with Shimadzu GC-17A equipped with CBP10-S25-050 column (Shimadzu, a silica fused capillary column, 0.33 mm x 25 m, 0.25 μm film thickness) using N₂ as carrier gas. Commercially available organic and inorganic compounds were used without further purification. [Cp*RuCl₂(CO)] and [Cp*RuCl(CO)(PPh₃)] were prepared by the reported method.¹²

General experimental procedure: Aldehyde (1 mmol), [RuCl₂(=CHPh)(PCy₃)₂] (0.01 mmol), KOH (1 mmol) and dioxane (3 ml) were placed in a 5 mL screw-capped vial and allowed to react at 80°C for 20 h. The reaction mixture was filtered through a short silica gel column (CHCl₃-ethyl acetate) to eliminate inorganic salts and concentrated under reduced pressure. The residual oily material was separated by column or thin-layer chromatography to give the corresponding alcohols. All products are known and identified by comparison with authentic samples.

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