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Direct oxidation of alcohols to carboxylic acids over ruthenium hydride catalyst with diphenyl sulfoxide oxidant

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ABSTRACT

In the present work, a new method for the synthesis of carboxylic acids over ruthenium hydride catalyst is reported. Direct oxidation of alcohols to their corresponding carboxylic acids with diphenyl sulfoxide oxidant over RuHCl(CO)(PPh₃)₃ catalyst was investigated. Mild reaction conditions, short reaction times and excellent yields make this method as an appealing way for preparation of carboxylic acids.

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Synthesis of carboxylic acids is one of the most fundamental transformations in chemistry. Because of their unique and important roles, a number of synthetic methods have been developed for this manner and new synthetic strategies are still in demand [1-11]. Due to the high activity of ruthenium based catalysts, the ruthenium-catalyzed reactions have attracted considerable attention in the past decade. Among them, ruthenium hydride catalysts have played a great role in these transformations. The remarkable feature of these catalysts is their ability in catalyzing reductive carbon-carbon bond formation [12-19]. In recent years, RuHCl(CO)(PPh₃)₃ has been employed as catalyst for diaryl ketone synthesis by coupling of arylboronic acids with aryl aldehydes [20], post-polymerization functionalization of conjugated polyisoperene [21], synthesis of (*E*)-styryl ketones from styrene [22] and conversion of dialdehydes and keto aldehydes to lactones [23]. The high catalytic activity of RuHCl(CO)(PPh₃)₃ in the oxidation of alcohols to aldehydes [15,16,24–30], prompted us to investigate its ability in the oxidation of aldehydes to their corresponding carboxylic acids.

Recently, we reported the catalytic activity of homogeneous $[RuHCl(CO)(PPh_3)_3]$ in the oxidation of alcohols with styrene oxide and heterogeneous $[RuHCl(CO)(PPh_3)_3]$ in the synthesis of unsaturated carbonyl compounds [31,32].

Herein, we report the application of ruthenium hydride catalyst, [RuHCl(CO)(PPh₃)₃], in the direct oxidation of alcohols to their corresponding carboxylic acids with diphenyl sulfoxide (Scheme 1).

The $[RuHCl(CO)(PPh_3)_3]$ complex was prepared *via* method reported in the literature [33]. To optimize the reaction conditions, the oxidation of benzyl alcohol **1a** in the presence of $RuHCl(CO)(PPh_3)_3$ was chosen as model reaction (Table 1). First, the catalyst amount was optimized in the model reaction. The highest yield was obtained with 4 mol% of catalyst after 2.5 h in THF at 70 °C. Increasing the catalyst amount to 5 mol% did not affect the yield, but by decreasing the catalyst amount to 3 mol%, the yield was reduced (entries 1-5). The solvent effect was also examined. The results showed that among toluene, DMF, DCE and THF; THF and DCE gave better yields (entries 4 and 6-8). From environmental points of view and green chemistry, all reactions were carried out in THF. The optimum reaction time was 2.5 h. Increasing the reaction time had no obvious effect on the yield but at shorter reaction times, the yield decreased significantly (entries 9 and 10). The reaction temperature was also optimized in the model reaction. The highest yield was observed at 70 °C while at lower temperature (50 °C), the vield was 32%, while no better yield was obtained at 90 °C (entries 11 and 12). Finally, when dimethyl sulfoxide was used as oxidant, the yield was 43%. Notably, in the absence of diphenyl sulfoxide, only aldehyde is produced, and no corresponding acid product was observed [15,16,24-30].

Under the optimized reaction conditions, several primary alcohols (including benzylic and linear ones) were selected as reactants and their oxidation was investigated with diphenyl sulfoxide in the presence of RuHCl(CO)(PPh₃)₃ at 70 °C in THF (Table 2) [37]. Substituted benzyl alcohols were efficiently converted to their corresponding substituted benzoic acids with diphenyl sulfoxide in the presence of catalytic amounts of RuHCl(CO)(PPh₃)₃ (entries 1–7). It seems that the substituents in the benzylic alcohols have no significant electronic effect on the product yield. A series of substituted *N*-(2-hydroxyethyl)benzamides were also oxidized to their corresponding carboxylic acids in high to excellent yields with diphenyl sulfoxide in the presence of [RuHCl(CO)(PPh₃)₃] (entries 9–11). To check the ability of this catalytic system in the full oxidation of linear alcohols, the oxidation of cinnamyl

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Scheme 1. Ruthenium hydride-catalyzed direct oxidation of alcohols to carboxylic acids with diphenyl sulfoxide as oxidant.

alcohol was carried out and the cinnamic acid was produced in high yield (entry 12). In all reactions, diphenyl sulfoxide oxidant was converted to diphenyl sulfide. On the other hand, small amounts of corresponding aldehydes were also detected as by-product. Therefore, the conversions and yields were determined by GC and the carboxylic acids were purified and identified by spectroscopic techniques.

The results of this catalytic system were compared with some of those reported in the literature (Table 3). As can be seen, the [RuHCl(CO)(PPh₃)₃]/DPSO catalytic system, can be considered as an efficient and simple catalytic system for direct oxidation of alcohols to carboxylic acids.

In summary, we demonstrated a novel ruthenium catalyzed strategy for oxidation of primary alcohols with diphenyl sulfoxide under mild conditions which produced a diverse range of carboxylic acids in good to excellent yields. Our studies revealed that DPSO can be employed as oxygen atom source and alcohol may serve both as hydrogen donor and precursor for nucleophilic reaction.

Spectral data

Benzoic acid (**3a**):

Colorless crystal; Mp 121–123 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.51 (t, 2H, *J* = 16 Hz), 7.63 (t, 1H, *J* = 8 Hz), 7.95 (d, 2H, *J* = 4 Hz); 12.99 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 128.55, 129.23, 130.69, 132.58, 167.30.

4-Methylbenzoic acid (**3b**):

White solid, Mp 178–179 °C; ¹H NMR (400 MHz, CDCl₃): δ =2.37 (s, 1H), 7.31 (d, 2H, *J*=8 Hz), 7.84 (d, 2H, *J*=8 Hz), 12.82 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =21.10, 127.96, 129.10, 129.30, 143.01, 167.29.

4-Hydroxybenzoic acid (**3c**):

White solid, Mp 210–214 °C; ¹H NMR (400 MHz, CDCl₃): δ = 6.93 (d, 2H, *J* = 8.4), 7.77 (d, 2H, *J* = 8.4), 9.79 (s, 1H), 10.63 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 115.8, 128.4, 132.1, 163.3, 191.0.

4-Fluorobenzoic acid (3d):

White solid, Mp 182–184 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (t, 2H, *J* = 8 Hz), 7.99–8.03 (m, 2H), 13.07 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 115.50, 115.72, 132.03, 132.13, 166.11, 166.36. *2-Chlorobenzoic acid* (**3e**):

White solid, Mp 137–138 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.42–7.55 (m, 3H), 7.79 (d, 2H, *J*=8 Hz) 13.44 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 127.21, 130.58, 130.76, 131.50, 132.56, 166.28. 4-*Nitrobenzoic acid* (**3f**):

White solid, Mp 237–239 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.27 (d, 2H, *J* = 8 Hz), 8.38 (d, 2H, *J* = 8 Hz), 12.92 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 183.4, 151.6, 133.9, 130.4, 124.7.

2,2'-Biphenyldicarboxylic acid (3g):

White solid; Mp 224–226 °C; ¹H NMR (400 MHz, CDCl₃): δ = 6.94–8.16 (m, 8H), 12.47 (bs, 2H); ¹³C NMR (100 MHz, CDCl₃): δ =126.9, 129.4, 130.3, 131.0, 142.9, 167.9; IR (KBr): 3064, 2994, 2885, 2818, 2645, 2567, 1686, 1597, 1577, 1453, 1407, 1297, 1273, 1136, 1049, 1105, 1049, 1003, 921, 796, 754, 703 cm⁻¹; EIMS *m*/*z*, 244.04 (M⁺), 242.00, 196.66, 181.03, 152.02, 138.96, 114.97, 98.48, 88.95, 75.96, 70.00, 57.35; calcd for C₁₄O₄H₁₀: 242.23; found: 242.00.

2-Benzamidoacetic acid (3h):

White solid; Mp 185–188 °C; ¹H NMR (400 MHz, DMSO-d₆): δ = 3.95 (d, 2H, *J* = 4 Hz), 7.49 (t, 2H, *J* = 8 Hz), 7.55 (t, 2H, *J* = 4 Hz), 7.89 (d, 1H, *J* = 8 Hz), 8.87 (t, 1H, *J* = 6 Hz), 12.64 (bs, 1H); ¹³C NMR (100 MHz): δ = 41.2, 127.2,128.2,128.3,131.4,133.7,166.4, 171.3; IR (KBr): 3343, 3075, 2938, 1742, 1602, 1556, 1490, 1416, 1395, 1336, 1317, 1305, 1257, 1181, 1078, 999, 943, 849, 806, 723 cm⁻¹; EIMS *m/z*, 179.09 (M⁺), 135.04, 104.87, 83.07, 76.99, 69.06, 57.04, 51.01, 45.03, 43.08, 41.08; calcd for C₉O₉NO₃: 179.17, found: 179.09.

Table 1

Optimization of conditions in the reaction o	f 1a with sulfoxides	catalyzed by RuHCl(CO)(PPh ₃) ₃ . ^a .
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Ph ^S Ph +	R OH Catalyst Solvent	$\rightarrow Ph^{S}Ph + R^{O}$	ОН		
Entry	Oxidant	Solvent	Catalyst amount (mol%)	T (°C)	Yield (%) b
1	DPSO	THF	1	70	17
2	DPSO	THF	2	70	46
3	DPSO	THF	3	70	78
4	DPSO	THF	4	70	90
5	DPSO	THF	5	70	90
6	DPSO	Toluene	4	70	63
7	DPSO	DMF	4	70	45
8	DPSO	DCE	4	70	93
9 ^c	DPSO	THF	4	70	90
10 ^d	DPSO	THF	4	70	54
11	DPSO	THF	4	50	32
12	DPSO	THF	4	90	90
13	DMSO	THF	4	70	43

^a All reactions were carried out with 1 mmol of benzyl alcohol, and 1 mmol of sulfoxide, catalyst, and solvent (2 mL) in a screw capped test tube.

^b The yields refer to pure isolated material.

^c The reaction time is 4 h.

^d The reaction time is 1.5 h.

Table	2

Ruthenium hydride-catalyzed	direct oxidation of alcohols t	o carboxylic acids wi	ith diphenyl sulfoxide. ^a

Entry	Alcohol 1	Carboxylic acid 3	Yield (%) ^b	Conversion (%)c	Selectivity (%)
1	ОН	0	90	93	96
	√″_1a	3a			
2	ОН	OH	89	92	97
	1b	H ₃ C 3b			
3	НО	ОН	85	88	96
	1c	HO 3c			
4	F	ОН	92	95	97
r	1d	F 3d	00	03	00
5	CI	ОН	90	92	90
6	le	CI 3e	93	96	97
-		ОН			
7 ^c	OH	O_2N \sim 3f O_2 OH	81	86	94
8	HO 1g	3g	88	90	08
0	N OH	N OH	00	50	56
9	՝ հ Օ	3h	87	89	98
	H ₃ C H	H-C N H OH			
10	li O	3i 0	89	92	97
	O ₂ N H	O ₂ N H OH			
11	lj Cl O	3j CI O	88	92	96
12	Ік	3к О	76	80	95
		ОН			
		~ 31			

^a All reactions (except for 1g) were performed using alcohol (1 mmol), diphenyl sulfoxide (1 mmol), and catalyst (4 mol%) in THF (2 mL) at 70 °C for 2.5 h.

^b The yields refer to GC yield.

^c The reaction was performed using alcohol (1g, 1 mmol), diphenyl sulfoxide (2 mmol), and catalyst (8 mol%) in THF (2 mL) at 70 °C for 2.5 h.

2-(4-Methylbenzamido)acetic acid (3i):

2-(4-Nitrobenzamido)acetic acid (3j):

Light brown solid; Mp 152–154 °C; ¹H NMR (400 MHz, CDCl₃): δ =3.97 (d, 2H, J=8 Hz), 8.11 (d, 2H, J=8 Hz), 8.33 (d, 2H, J= 8 Hz), 9.28 (t, 1H, J=5 Hz), 13.14 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =41.3, 123.6, 128.8, 139.3, 149.1, 164.8, 170.9; IR (KBr): 3316, 3110, 1706, 1641, 1601, 1541, 1425, 1351, 1297, 1231, 1108, 1013, 930, 874, 831, 801, 786, 716 cm⁻¹; EIMS *m/z*,179.10, 150.08, 120.09, 104.09, 92.10, 76.13, 50.16, 45.15; calcd for $C_9H_8N_2O_5;$ 224.1712, found: 224.03.

2-(2-Chlorobenzamido)acetic acid (3k):

White solid; Mp 158–162 °C; ¹H NMR (400 MHz, CDCl₃): δ =3.92 (d, 2H, J=8 Hz), 7.40–7.49 (m, 3H), 7.51 (t, 1H, J=4 Hz), 8.79 (t, 1H, J=4 Hz), 12.71 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =40.9, 127.0, 129.0, 129.9, 130.8, 132.6, 136.2, 166.6, 170.9; IR (KBr): 3289, 3082, 1721, 1626, 1597, 1596, 1553, 1469, 1437, 1402, 1350, 1321, 1259, 1230, 1173, 1052, 999, 947, 842, 760 cm⁻¹; EIMS *m*/*z*, 213.01 (M⁺), 168.52, 139.18, 111.16, 75.04, 55.94, 57.11, 50.19, 43.16; calcd for C₉H₈NO₃Cl: 213.01, found: 213.62.



White solid; Mp 129–132 °C; ¹H NMR (400 MHz, CDCl₃): δ = 6.56 (d, 1H, *J* = 8 Hz), 7.43–7.73 (m, 5H), 7.90 (d, 1H, *J* = 8), 11.61 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 173.9, 147.16, 135.1, 130.9, 128.9, 128.3, 118.4.

Table 3

Comparison of the results obtained with [RuHCl(CO)(PPh₃)₃]/styrene oxide catalytic system with some of those reported in the literature.

Catalyst	Catalyst amount	Yield (%)	Time (h)	Ref.
[RuHCl(CO)(PPh ₃) ₃]/DPSO	4 mol%	76-93	2.5	Present work
CuCl/ ^t BuOOH	5 mol%	76-99	1-6	[10]
PS-TEMPO/NaClO	10 mol%	77-98	20-48	[6]
Pt-C/Air	1.95 wt.%	99	1-16	[9]
TPAP/NMO	10 mol%	26-100	-	[11]
KMnO ₄	4 mmol	5-91	4-18	[34]
OsO ₄	4 wt.%	50-85	-	[35]
CAN	2.2 eq	42-95	4	[36]

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- [37] General information. Melting point was measured using Stuart Scientific SMP2 apparatus in sealed capillary and not corrected. Solvents and liquid alcohols were distilled prior to use. The products were purified by silica gel chromatography (Merck KGaA, Silica Gel 60).¹H and ¹³C NMR (400 and 100 MHz) spectra were recorded on a Bruker-Avance 400 MHz spectrometer. FT-IR spectra were recorded on a Platform II spectrometer from Micromass; El mode at 70 eV. Elemental analysis was done on a LECO, CHNS-932 analyzer.

Typical procedure for the ruthenium hydride-catalyzed direct oxidation of alcohols to carboxylic acids with diphenyl sulfoxide: Benzyl alcohol **1a** (108.1 mg, 1 mmol), diphenyl sulfoxide **2** (202.3 mg, 1 mmol), [RuHCI(CO)(PPh₃)₃] (39.1 mg, 0.04 mmol) and THF (2 mL) were placed in a screw capped test tube. The test tube was purged with argon and sealed. The mixture was stirred at 70 °C for 2.5 h. After the reaction was completed, the solvent was removed under reduce pressure. The residue was purfied by silica gel chromatography (petroleum ether/ethyl acetate=6/1) and recrystallized from H₂O-methanol to give the compound **3a** as a white crystal.