

Oxidation of Alcohols Catalyzed by Ruthenium Complexes with Iodosylbenzene as Oxidant

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Abstract: Five ruthenium complexes such as Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Bipy-Ru-Quin (where Phen=1, 10-phenanthroline, Quin=8-hydroxyquinoline, Bipy=2, 2'-bipyridine) were synthesized and used as catalysts for the oxidation of benzylic and primary aliphatic alcohols with iodosylbenzene as oxidant. The oxidations were carried out at room temperature, affording the corresponding aldehydes and ketones with high selectivity.

Keywords: Alcohols, catalytic oxidation, ruthenium complexes, iodosylbenzene.

Oxidation of primary and secondary alcohols into the corresponding carbonyl compounds plays an important role in organic synthesis¹⁻². Traditional methods for performing such transformations generally involve the use of stoichiometric quantities of inorganic oxidants, notably chromium (VI) reagents³. However, the method is not a good choice from the point of view of environmental safety. Catalytic oxidation methods that employ other metal-containing catalysts will avoid the use of such toxic reagents. Among these catalysts, ruthenium oxides and its complexes have been found to be active towards the oxidation of alcohols. However, the ligands and the methodology employed to prepare this kind of complexes are difficult⁴⁻⁶. We report here the synthesis, spectroscopic characterization and the catalytic behavior of several complexes with Ru(III) and 1, 10-phenanthroline, 8-hydroxyquinoline, and 2, 2'-bipyridine as ligands. A series of alcohols includes benzylic and primary aliphatic alcohols were oxidized to the corresponding aldehydes and ketones in the catalysis of the ruthenium complexes. The oxidations were carried out in acetonitrile using PhIO as oxidant with the ruthenium complexes as catalysts under mild reaction conditions, giving the products in high yields with the selectivity of 100%. It was found that all of the complexes obtained exhibit excellent catalytic activity for the oxidation of alcohols.

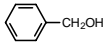
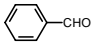
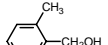
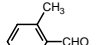
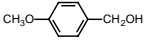
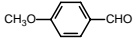
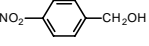
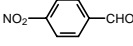
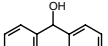
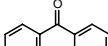
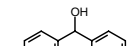
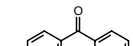
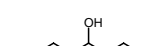
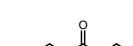
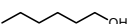

The catalysts, named as Phen-Ru-Phen, Phen-Ru-Bipy, Phen-Ru-Quin, Quin-Ru-Quin and Quin-Ru-Bipy (abbreviated as PRP, PRB, PRQ, QRQ and QRB, respectively, where Phen=1,10-phenanthroline, Quin=8-hydroxyquinoline, Bipy=2,2'-bipyridine) were

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synthesized according to the literatures⁷⁻⁸. The structures of these complexes were well characterized by FT-IR, XPS and ICP determination.

Several factors that influence the catalytic oxidation were investigated using the complexes as catalysts and benzaldehyde as substrate. The optimized catalytic reaction condition for the oxidation of alcohols is as follows: alcohol 0.1 mmol, catalyst 4 mg, oxidant (PhIO): 2.5 eq., solvent: acetonitrile 2 mL, temperature: room temperature (25 °C).

Table 1 Catalytic oxidation of alcohols using PhIO catalyzed by ruthenium complexes^{a, b}

Run	Substrate	Product	PRP ^c	PRB ^c	PRQ ^c	QRQ ^c	QRB ^c
1			100 (8)	100 (4)	100 (2)	100 (1)	100 (5)
2			100 (4)	77 (8)	100 (3)	100 (2)	100 (8)
3			100 (4)	100 (2)	100 (0.5)	100 (0.5)	100 (2)
4			100 (4)	100 (2)	100 (1)	100 (0.5)	100 (2)
5			63 (8)	63 (8)	60 (8)	62 (8)	57 (8)
6			74 (8)	80 (8)	89 (8)	89 (8)	61 (8)
7			73 (8)	73 (8)	77 (8)	61 (8)	58 (8)
8			100 (4)	100 (6)	100 (6)	100 (2)	100 (4)
9	$n\text{-C}_{11}\text{H}_{24}\text{OH}$	$n\text{-C}_{11}\text{H}_{24}\text{CHO}$	28 (8)	100 (8)	85 (8)	100 (6)	100 (8)

Reaction condition: alcohol 0.1 mmol, PhIO 2.5 equiv., cat. 4 mg, CH₃CN 2 mL, 25 °C.

^a Each of the oxidation bears the selectivity of 100%.

^b The conversion and the selectivity of each reaction were obtained by GC determination.

^c Data outside and inside the parenthesis are conversion (%) and reaction time (h), respectively.

We also investigated their catalytic properties for the oxidation of other alcohols. It was very satisfied to find that all these complexes can be used as efficient catalysts in this oxidation system. The results were shown in **Table 1**.

All of the catalysts show promising catalytic activity for the oxidation of benzyl alcohol and its derivatives, but exhibit low catalytic activity for the oxidation of benzhydrol and its derivatives. The reason might consist in the structure hindrance of benzhydrol. Concerning of the two typical aliphatic alcohols, all the catalysts bear better catalytic activities to *n*-hexanol than to dodecanol. Aliphatic alcohols are generally difficult to be oxidized in other catalytic oxidation systems.

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References

1. R. A. Sheldon, J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1981**, p. 350.
2. S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis*, **1994**, 639.
3. G. Cainelli, G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, **1984**.
4. A. L. B. Marques, W. Li, E. P. Marques, J. J. Zhang, *Electrochimica Acta*, **2004** *49*, 879.
5. A. Wolfson, S. Wuyts, D. E. De Vos, *et al.*, *Tetrahedron Lett.*, 2002, *43*, 8107.
6. K. Ebitani, H. B. Ji, T. Mizugaki, K. Kaneda, *J. Mol. Catal. A: Chem.*, **2004**, *212*, 161.
7. G. F. Smith, F. W. Lagle, *J. Org. Chem.*, **1947**, *12*, 781.
8. R. D. Gillard, E. Hill, *J. Chem. Soc., Dalton Trans.*, **1974**, 1217.

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