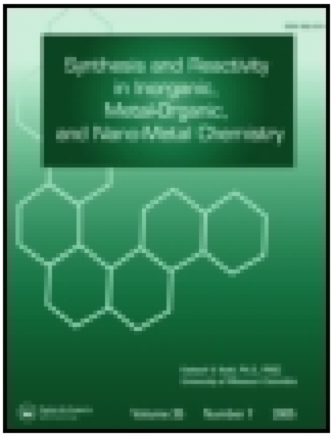

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Effective Oxidation of Alcohols with H_5IO_6 Catalyzed by Nickel(II) Schiff Base Complexes

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Published online: 31 Aug 2010.

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:516–520, 2010

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2010.503180

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Nickel(II)-Schiff base-triphenylphosphine complexes catalyze oxidation of alcohols to carbonyls in presence of minimum amount of periodic acid. The catalytic oxidation was developed in mild conditions and showed good yields. The effects of temperature, time, and concentrations of catalyst and co-oxidant were studied. Higher catalytic activity has been observed for NiL1 compared to the other complexes.

Keywords Ni(II) complex, oxidation, periodic acid, Schiff base

INTRODUCTION

The oxidation of alcohols to the corresponding aldehydes and ketones is a key reaction in synthetic organic chemistry, and numerous oxidizing reagents are available to affect this important reaction.[1–4] Many of these oxidation systems require stoichiometric amounts of metal compounds with concomitant environmental problems. For example, the chromium oxidants are used in vast amounts both in the laboratory and industry.[5] Recent efforts have focused on systems that employ metal compounds only in catalytic amounts together with a stoichiometric oxidant.[6–9] Several reaction conditions have been developed for the oxidation of alcohols to carbonyls, such as $RuCl_3/H_5IO_6$,[10] RuO_4,[11] $RuCl_3/K_2S_2O_8$,[12] Ru–Co bimetallic catalyzed oxidation,[13,14] $Cu(MnO_4)_2$ catalyzed oxidation,[15] TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy)-catalyzed oxidation with sodium hypochlorite,[16–21] Na_2WO_4/H_2O_2,[22] and Cu(II)–salen complex/H_2O_2.[23] The use of transition-metal complexes as catalysts for oxidation reactions has received good attention during the last decades, particularly by the interest in understanding reactions where the metal ion plays a central role in the catalytic reaction. However, despite the extensive studies carried out with cobalt, iron and manganese complexes, only a few investigations have focused on nickel catalysts.[24–26]

Received 20 March 2010; accepted 19 May 2010.
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Very recently, we developed an efficient method for the selective oxidation of alcohols to the corresponding aldehydes and ketones using nickel(II) complex containing triphenylphosphine and a Schiff base as a catalyst in ionic liquid media.[27] As a part of our ongoing research towards nickel catalyzed oxidation chemistry, herein, we report the catalytic oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds using periodic acid at ambient temperature. This procedure is very simple, mild and clean and works efficiently without any additives.

EXPERIMENTAL

The complexes were synthesized according to a reported literature procedure,[27] as shown in Scheme 1.

Catalytic Experiment

A typical experimental procedure was as follows: A solution of nickel complex (11 mg, 0.02 mmol) in 20 cm^3 CH_3CN was added to the solution of substrate (1 mmol) and H_5IO_6 (230 mg, 1 mmol). The reaction mixture was stirred at 70°C for 30 min and the mixture was extracted with ether. The ether solution was analyzed by GC. Products were isolated by distillation.

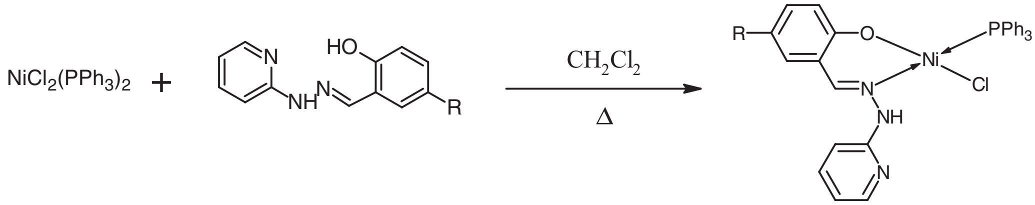
Product Analysis

The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane Restek capillary column (30 m length and 0.25 mm diameter) and a flame ionization detector (FID). Nitrogen gas was used as the carrier gas. The retention times for different compounds were determined by injecting commercially available compounds under identical gas chromatography conditions. The oxidation products are commercially available, and were identified by GC co-injection with authentic samples.

RESULTS AND DISCUSSION

Catalytic Oxidation

Benzylalcohol was selected as a model substrate for optimization of the process. In order to study the effect of time



NiL1: R=H, **NiL2**: R= Cl, **NiL3**: R=Br, **NiL4:** R=NO_2, **NiL5**: R= OCH_3.

SCH. 1. Synthesis of nickel (II) complexes.

on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Figure 1). It was observed that the total reaction time was only 30 minutes. This implies that Ni(II)-complex/CH_3CN-H_5IO_6 catalytic system showed good efficiency. Therefore this catalytic system was studied in detail (Table 2). The oxidation occurred only in poor yield by simply bubbling molecular oxygen through reaction mixture under similar reaction conditions (Table 1, entry 2). To evaluate the catalytic effect of catalyst, the oxidation of benzylalcohol was carried out under similar reaction conditions in the absence of catalyst and no conversion was observed (Table 1, entry 3). Alternatively, the reaction was carried out at room temperature under the same conditions in which the reaction was complete after 210 min (Table 1, entry 4). Further, when the oxidation of benzylalcohol was carried out using less amount of catalyst, the yield was low (Table 1, entry 5). Also the reaction was carried out using low amount of oxidant under same conditions and was observed that the yield was low (Table 1, entry 6).

The oxidation of other benzylic and allylic alcohols was then examined using the optimized reaction conditions. The results for the oxidation of a variety of alcohols are summarized in Table 2. Benzyl alcohols with functional groups were also oxidized smoothly to the corresponding aldehydes in high yields. As expected, secondary alcohols were oxidized more quickly than primary alcohols. Most oxidations of secondary alcohols were completed within 45 min and gave the corresponding ketones cleanly. Oxidation of allylic alcohols to α, β-unsaturated carbonyl compounds has long been of interest. It was found that cinnamaldehyde was obtained from cinnamyl alcohol in ~90% conversion after 30 min of stirring whereas $NaIO_4$/2,2,6,6-tetramethylpiperidine-1-oxyl/NaBr system gives only 18% of aldehyde from the same substrate.[28] Interestingly, catalytic property of nickel(II) complexes is not affected even for chelating substrate (*o*-hydroxy benzylalcohol) as it is in many homogeneous catalytic systems. This present catalytic system requires a very short reaction period of about 30–45 minutes compared to reported catalytic systems.[29]

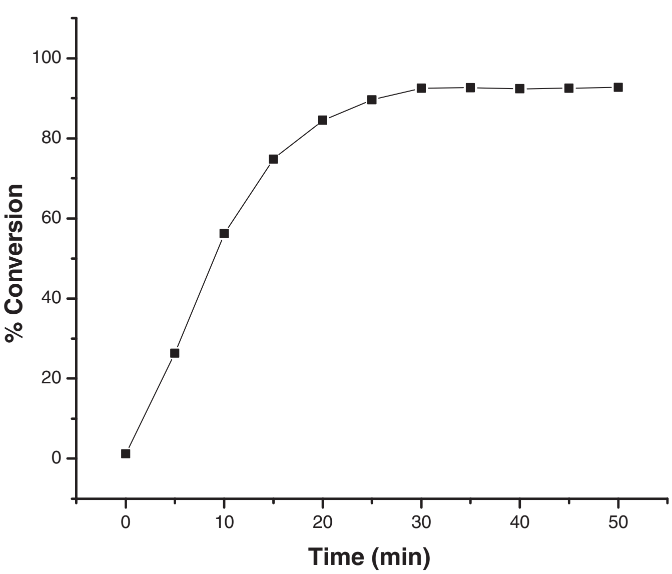


FIG. 1. Effect of time with % conversion.

TABLE 1
Oxidation of benzylalcohol to benzaldehyde[a]

Entry	Reaction time (min)	% Conversion
1	30	92.5
2[b]	300	<20
3[c]	300	NR[d]
4[e]	210	90.6
5[f]	30	56.9
6[g]	30	64.9

[a]Unless otherwise indicated, all reactions were carried out with 1.08g (1 mmol) of benzylalcohol with 11 mg (0.02 mmol) of Ni(II) catalyst 230 mg (1 mmol) of H_5IO_6, stirring at 70°C.

[b]The reaction was carried out under an atmosphere of O_2 instead of H_5IO_6.

[c]The reaction was carried out without Ni(II) catalyst.

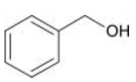
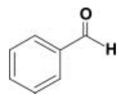
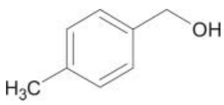
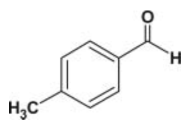
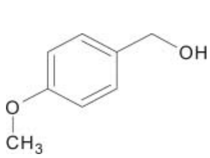
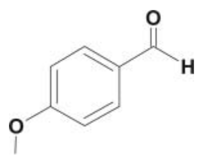
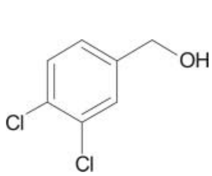
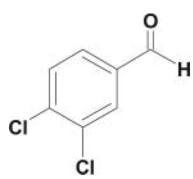
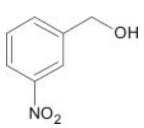
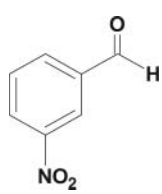
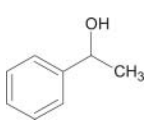
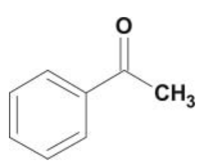
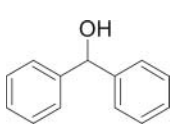
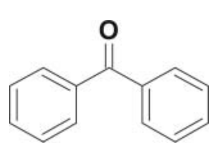
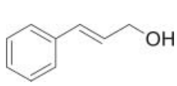
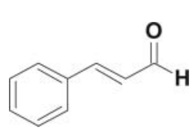
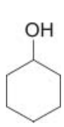
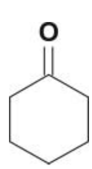
[d]NR = reaction did not occur.

[e]The reaction was carried out at room temperature.

[f]The concentration of Ni(II) catalyst was decreased to 0.01 mmol.

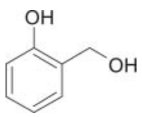
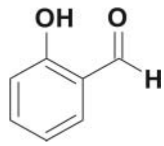
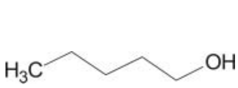
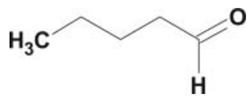
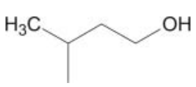
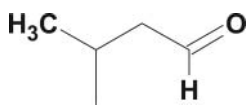
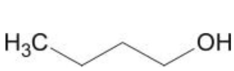
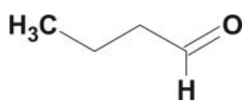
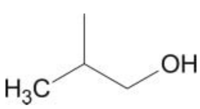
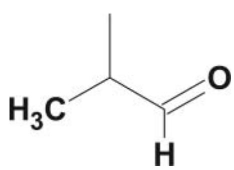
[g]The concentration of the oxidant was decreased to 0.5 mmol.

TABLE 2
Oxidation of alcohols catalyzed by Ni(II) complexes[a] in CH_3CN-H_5IO_6 system

			% Yield of carbonyl compound[b]				
Alcohols	Product	Time (min)	**NiL1**	**NiL2**	**NiL3**	**NiL4**	**NiL5**
		30	92.6	89.5	84.6	85.4	81.0
		30	91.7	86.2	86.9	85.6	80.1
		30	96.4	95.6	84.6	84.6	80.6
		30	90.1	86.2	82.4	88.6	78.4
		40	91.9	85.4	80.1	80.2	80.0
		40	95.6	87.8	89.6	85.2	82.1
		40	92.1	87.2	90.0	80.1	76.3
		35	85.1	90.0	88.3	88.5	79.8
		30	87.1	89.5	82.6	86.1	81.3

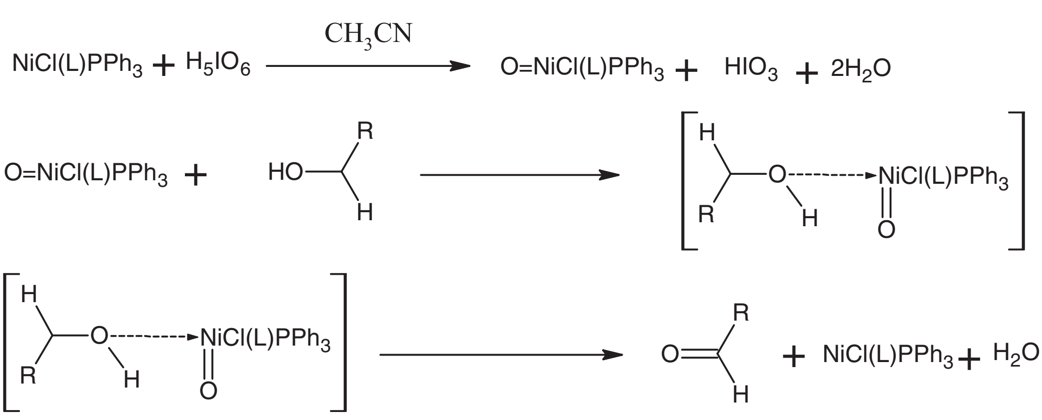
(continued on next page)

TABLE 2
Oxidation of alcohols catalyzed by Ni(II) complexes[a] in CH_3CN-H_5IO_6 system *(continued)*

			% Yield of carbonyl compound[b]				
Alcohols	Product	Time (min)	**NiL1**	**NiL2**	**NiL3**	**NiL4**	**NiL5**
		30	95.7	91.3	77.6	71.9	80.1
		30	76.2	75.5	76.0	73.6	71.2
		40	80.2	76.6	74.6	78.1	76.5
		30	75.7	74.9	72.6	73.1	72.5
		30	72.1	72.6	71.2	76.1	70.0

[a]1 mmol alcohol, 1 mmol H_5IO_6, 0.02 mmol Ni (II) complex, 20 mL CH_3CN, stirring at 70°C.
[b]GC yield, average of three trials.

Spectral evidence for the complex formation between catalyst and substrate was obtained from UV-Vis spectra of catalyst, benzylalcohol and both in CH_3CN. A bathochromic shift of about 15 nm from 350 nm to 365 nm in the spectra of Ni(II) was observed and a hyperchromicity was observed at 365 nm (Figure 2). This may be attributed to the formation of a Ni-substrate complex.[30] On the basis of above discussion, a plausible reaction mechanism is given (Scheme 2).



SCH. 2. Proposed reaction mechanism for the catalytic oxidation of alcohols.

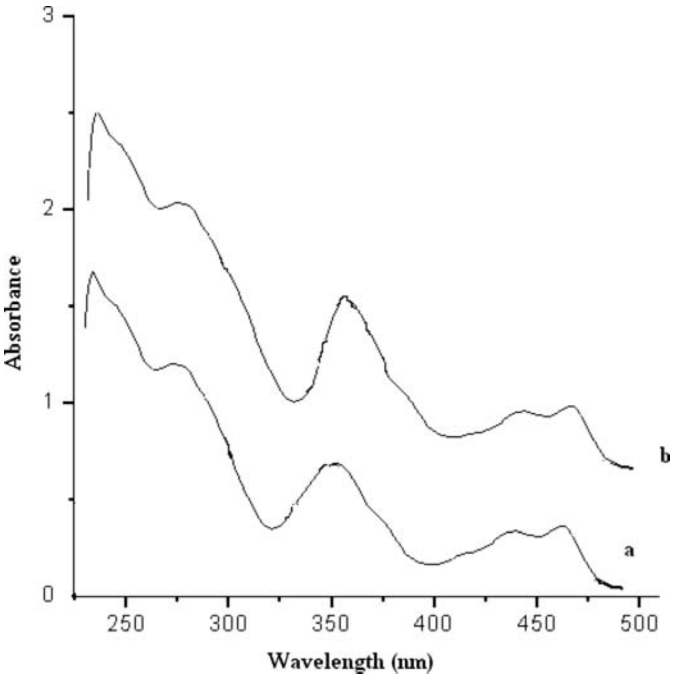


FIG. 2. UV-Vis spectral scans of (a) NiL1 + H_5IO_6 in CH_3CN; (b) NiL1 + H_5IO_6 + Benzylalcohol in CH_3CN.

CONCLUSIONS

In conclusion, the results obtained in this research show that the above square planar nickel (II) complexes are excellent catalysts for the simple, selective and very fast oxidation of alcohols to the corresponding carbonyl compounds with periodic acid in CH_3CN. The system works very efficiently in mild conditions.

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