

Short communication

Cerium complexes with phthaloylbis(pyrazolone) ligands as an efficient catalysts for cresols dioxygenation

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Abstract

New cerium complexes with acetato phthaloylbis(1-phenyl-3-methyl-4-pyrazol-5-one) ligands were superior as catalyst for dioxygenation of 3,5-dialkoxyresols into 4-hydroxy-3,5-dialkoxybenzaldehyde. Especially, cerium complexes (1:1) with *ortho*-isomer gave 84% yield of 4-hydroxy-3,5-dimethoxybenzaldehyde as the best catalyst in positional isomers in anhydrous methanol and 55% yield even in methanolic aqueous solution. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Cerium complexes; Phthaloylbis(pyrazolone); Hydroxydialkoxybenzaldehyde; Cresols dioxygenation

1. Introduction

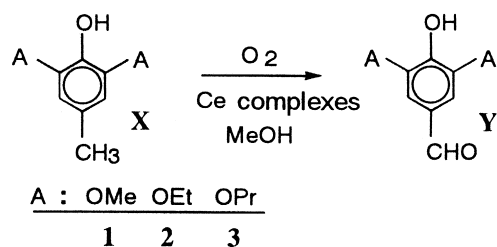
4-Hydroxy-3,5-dialkoxybenzaldehyde **Y** is an important chemical intermediate in the production of chemicals and pharmaceuticals [1]. In general, the synthesis of 4-hydroxy-3,5-dimethoxybenzaldehyde **Y1** from 3,5-dimethoxyresol **X1** by direct oxidation is difficult because of the difficulty in oxidizing only the methyl group on the aromatic ring which also has a free hydroxy group [2–4]. Using cerium triacetate as catalyst for dioxygenation, compound **X1** gave compound **Y1** in high yield without the formation of quinone and dimers [5] when treated in anhydrous methanol [6] (Scheme 1).

But, when the moisture was present in the reaction system, cerium triacetate as catalyst was then inactivated by the excess coordination of water with metal. As results, the yield of compound **Y1** decreased drastically.

The stabilization of catalyst is required to prevent the further aquation by coordinating cerium triacetate with the ligands having a strong affinity with metal ion [7,8]. A novel family of phthaloylbis(1-phenyl-3-methyl-4-pyrazol-5-one) ligands **L** was designed as Fig. 1 shows, in which two acylpyrazole subunits are linked by phthaloyl isomers **a**(*o*-), **b**(*m*-) and **c**(*p*-), and the structure would cause a steric hindrance.

This paper describes an attempt to develop an efficient catalyst for cresol dioxygenation using new cerium complexes in anhydrous methanol or methanolic aqueous solution. Also, the cerium complexes with phthaloylbis(1-phenyl-3-methyl-4-pyrazol-5-one) ligands have been investi-

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Scheme 1.

gated in order to explore the effect of positional isomer.

2. Experimental

2.1. Instrumentation

Routine HPLC data was recorded with a Shimadzu LC-9C type apparatus using an internal standard in a mixture of acetonitrile, water and phosphoric acid. The structure of all the obtained compounds was proven with the aid of ^1H and ^{13}C NMR spectra. High resolution MS spectra were recorded on Shimadzu GCM 9100-MK type.

2.2. Catalyst and materials

3,5-Dialkoxyresol was prepared according to the procedure reported previously [9]. Anhydrous methanol of the purge and trap grade was

purchased from Aldrich. Cerium complexes were prepared according to the procedure reported previously [6,10].

2.3. General procedure

Dioxygenation was carried out in a 50-ml autoclave equipped with a magnetic stirrer in a glass tube at the desired pressure under constant temperature, using anhydrous methanol or methanolic aqueous solution of the materials and catalysts. After a fixed time, the mixture was evaporated using an evaporator to remove the solvents, the residue was diluted with dimethylsulfoxide and acetonitrile in a 20-ml volumetric flask containing *o*-toluic acid as internal standard [10]. The percentage of products was determined by HPLC in a mixed solution of acetonitrile (150 ml)/water (750)/phosphoric acid (0.6) using a reversed column (YMC-AM-312-ODS).

3. Results and discussion

The maximal yield of compound **Y** in Table 1 indicates the effect of cerium complexes under different conditions. The cerium complexes **IIa–c** of 1:1 ligand to cerium stoichiometry

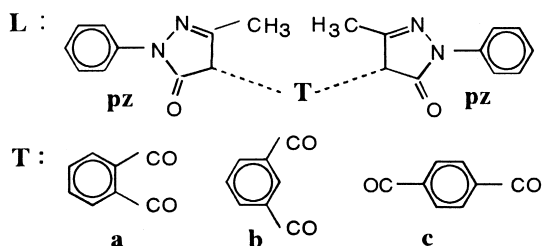
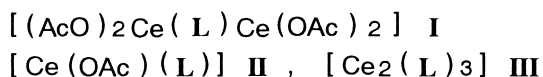


Fig. 1. Cerium complexes as catalyst.

Table 1
Effect of cerium complexes on the yield. DMC: 0.06 mmol, catalyst: 0.005 mmol, MeOH: 10 ml, O_2 : 3 kg cm^{-2}

Entry	Catalyst	XA	Temperature (°C)	Time (h)	Yield (Y%)
1	Ia	1	130	6	29
2	Ib	1	130	6	53
3	Ic	1	130	6	60
4	IIa	1	130	3	84
5	IIb	1	130	3	58
6	IIc	1	130	3	75
7	IIIa	1	140	6	19
8	IIa	2	130	3	81
9	IIa	3	130	3	79
10	OAc^a	1	120	3	82

^aCe(OAc)₃.

(entries 4–6) were more active than cerium complexes **Ia–c** of 2:1 ligand to cerium stoichiometry (entries 1–3) with the corresponding ligands.

When cerium complex **IIa** (entry 4) was used instead of cerium complex **Ia** (entry 1), the yield of compound **Y** increased drastically from 29 to 84% yield. Especially, cerium complex **IIa** (entry 4) with *o*-isomer gave 84% yield of the best catalyst in positional isomer and the yield was better than 82% yield of cerium triacetate monohydrate (entry 10) being the best catalyst hitherto reported [6].

On the other hand, cerium complex **IIIa** had a weak effect on the efficiency of the reaction because compound **X** and dioxygen is difficult to react in the coordination sphere of cerium complex in which all acetate ligands are substituted by ligand **L** having a strong affinity (entry 7).

In the use of *m*-isomer **Lb**, the yield increments did not have a very remarkable effect in complexes **Ib** and **IIb** (entries 2 and 5).

Using *p*-isomer **Lc**, the effect by *para*-attack [11] was remarkable, from 60% yield of **Ic** to 75% yield of **IIc** (entries 3 and 6). The structure of **IIc**, alternative to that of **IIa** and **IIb**, seems to be a complex of 2:2 ligand to cerium stoichiometry employing conventional three-dimensional computer-graphic techniques.

The yield into compound **Y** differing substituent was also held in high levels for the dioxygenation of compound **X2** and **X3** obtained by replacing methoxy group with ethoxy and propoxy (entries 4, 8 and 9).

In anhydrous methanol, compound **X1** by the catalyst of cerium triacetate gave the desired compound **Y** more than 82% yield (entry 10, Fig. 2). But, even with the addition of 2% of water, the yield of compound **Y** decreased drastically by 4% from 82% as Fig. 2 shows. In methanolic aqueous solution, the reaction was totally inhibited [12]. Inactivation of cerium triacetate as catalyst is based on the exceeding coordination of water instead of acetato ligands around the cerium ion.

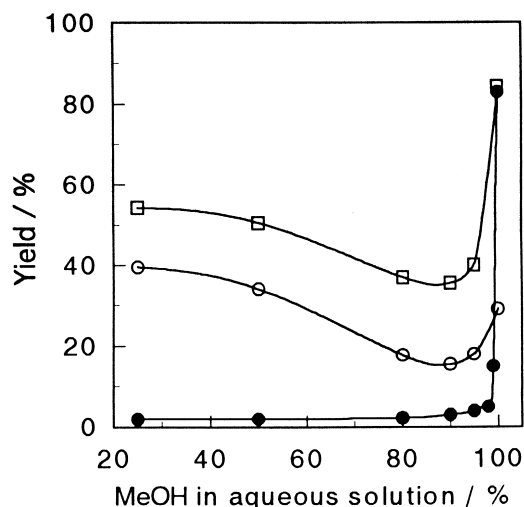
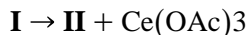


Fig. 2. DMC: 0.06 mmol, catalyst: 0.005 mmol, MeOH: 10 ml, O_2 : 3 kg cm^{-2} , ●:Ce(OAc)₃, ○:Ia, □:IIa.

After the dioxygenation by cerium complex **I** in methanolic aqueous solution, a yellowish green precipitate from the residue was obtained by chromatographical separation was identified as complex **II** using analytical technique.



Ce(OAc)₃ reproduced from complex **I** was very poor as catalyst in methanolic aqueous solution as shown in Fig. 2. The apparent yield of compound **Y** by complex **I** is attributable to the cerium complex **II** obtained as the other byproduct, that is, the complex **II** increased the yield of compound **Y** in methanolic aqueous solution.

4. Conclusion

Cerium complex with acetato *ortho*-phthaloylbis(1-phenyl-3-methyl-4-pyrazol-5-one) gave high yield of 4-hydroxy-3,5-dialkoxybenzaldehyde for dioxygenation in anhydrous methanol and even in methanolic aqueous solution by overcoming the inactivation on chelation of cerium triacetate.

Acknowledgements

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