

SHORT COMMUNICATION

SYNTHESIS OF 2,2-DIMETHYL-4-PHENYL-[1,3]-DIOXOLANE USING ZEOLITE ENCAPSULATED Co(II), Cu(II) AND Zn(II) COMPLEXES

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ABSTRACT. Zeolite encapsulated Co(II), Cu(II) and Zn(II) complexes with 2-methyl benzimidazole (Mebzlh) have been used to catalyze the reaction of styrene oxide with acetone under reflux condition. The yield of the isolated product using various catalysts range from good to excellent and the efficiency of the recycled catalyst was excellent.

KEY WORDS: Epoxide, 1,3-Dioxolane, Zeolite encapsulated catalyst, Styrene oxide

INTRODUCTION

1,3-Dioxolanes are widely used as protecting groups for the carbonyls and 1,2-diols in synthetic chemistry of carbohydrates and steroids [1]. They are generally prepared from oxiranes with carbonyl compounds in the presence of Bronsted [2] or Lewis acids such as BF₃ [3], CuSO₄ [4], Bi(III) [5], Sn(IV) [6], Ti(IV) [7], Ir(II) [8], Ru(III) [9], Re(VI) [10], zeolite [11], KSF clay [12] and HBF₄ [13] as catalysts has been reported. But these methods have suffered from drawbacks like low yields and require relatively long reaction times. The use of anhydrous zinc [14] and magnesium halides [15] as catalysts in the preparation of dioxalanes yields rearranged product instead of expected ones. The same reaction was carried out with FeCl₃ [16] and Me₃SiCl [17], gave the corresponding halohydrins, and the use of SnCl₄ and TiCl₄ produced little or no product [3]. Recently, Seung-Han Lee *et al.* [18], reported the use of copper(II) triflate catalyst in acetone for the formation of 1,3-dioxalane with good yields, but the time required is 4 h.

Encapsulated metal complexes in zeolite are potential catalysts for various selective organic transformations such as hydrogenation [19-21], oxygenation [22] and cycloaddition [23] reactions. In view of their potential catalytic activity, transition metal complexes containing nitrogen heterocycles have attracted considerable attention in recent years. Zatorski *et al.* [11] reported the formation of 1,3-dioxolanes from styrene oxide and acetone in the presence of HY, HUSY (ultra stabilized) and HZSM-5 zeolite catalysts, here the yields are too low. To our knowledge, there are no reports available for the synthesis of 1,3-dioxolane using benzimidazole complexes encapsulated inside zeolite as catalyst.

In our laboratory, we reported the catalytic activity of zeolite encapsulated Co(II), Cu(II) and Zn(II) complexes of 2-methyl benzimidazole in phenol hydroxylation reaction [24]. The present paper describes the synthesis of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane from styrene oxide and acetone in good yields using zeolite encapsulated Co(II), Cu(II) and Zn(II) complexes of 2-methyl benzimidazole as catalysts. The catalyst can be reused several times with good selectivity for 1,3-dioxolanes.

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EXPERIMENTAL

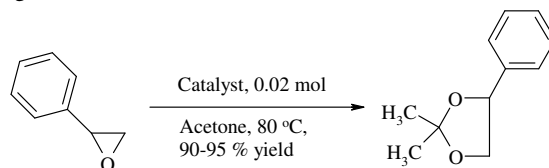
Materials and methods. Protonated form of zeolite-Y [H-Y] and ZSM-5 [H-ZSM-5] were purchased from Sud-chemie (India). Acetone was purchased from s.d.fine-chemicals (India) and styrene oxide from Aldrich (Germany) and were used as such and catalysts were synthesized according to the known procedures [24]. The product was identified by comparison with authentic sample. The purity of the product was checked by TLC and GLC by using Shimadzu 14B gas chromatograph (Japan) fitted with FID detector and BP-5 capillary column.

Synthesis of catalyst. Zeolite-Y and ZSM-5 encapsulated Co(II), Cu(II) and Zn(II) complexes of 2-methyl benzimidazole, synthesized by flexible ligand method and characterized by different physico-chemical method, which is already reported by us [24]. [Metal % found in the complex by ICP method: [Co(Mebzlh)]-Y (10.45 %), [Co(Mebzlh)]-ZSM-5 (1.5 %), [Cu(Mebzlh)]-Y (1.8 %), [Cu(Mebzlh)]-ZSM-5 (0.8 %), [Zn(Mebzlh)]-Y (3.6 %) and [Zn(Mebzlh)]-ZSM-5 (0.8 %)] Y is the zeolite complex formed.

Synthesis of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane. In a 50 mL double necked round bottom flask, styrene oxide (1 mmol), acetone (3 mL) and catalyst (2 mmol) were taken and then refluxed at 80 °C for 30 min on an oil bath with continuous stirring. The progress of the reaction was monitored by TLC and GLC. After the completion of the reaction, catalyst was separated and thoroughly washed with ethyl acetate, then dried in the oven at 100 °C. Then the reaction was repeated to test the catalytic activity of the used catalyst.

RESULTS AND DISCUSSION

In the present investigation, the reaction between 1 mmol of styrene oxide and acetone was carried out at 80 °C in presence of 2 mmol of catalyst gives 2,2-dimethyl-4-phenyl-[1,3]-dioxolane in excellent yield and with 100% selectivity within 30 min (Scheme 1). The condition was optimized by considering varying temperature, substrate and catalyst ratio and time. The results are given in Table 1.



Scheme 1. Synthesis of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane.

It was observed that ZSM form of complexes are more efficient than ZY form of complexes and among the Co(II), Cu(II) and Zn(II) encapsulated complexes, Zn(II) encapsulated complex was found to be most efficient for the formation of 1,3-dioxolane. A maximum conversion of 90% was observed with catalyst [Zn(Mebzlh)]-ZSM-5 and the order of formation of product for different catalyst is as follows:

[Zn(Mebzlh)]-ZSM-5 > [Cu(Mebzlh)]-ZSM-5 > [Zn(Mebzlh)]-Y = [Co(Mebzlh)]-ZSM-5 > [Cu(Mebzlh)]-Y = [Co(Mebzlh)]-Y as shown in Table 2.

The catalyst was recycled twice and no leaching of metal complex was observed. The results are given in Table 3.

Table 1. Effect of different parameters on the yield of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane using [Zn(Mebzlh)]-ZSM-5 catalyst.

Entry	Reaction condition (°C)	Substrate to catalyst ratio	Time (min)	Yield (%)
1	RT	1:2	30	25
2	50	1:2	30	55
3	80	1:2	30	90
4	80	1:1	30	75
5	80	1:3	30	95
6	80	1:2	10	50
7	80	1:2	60	92

Table 2. Comparison of catalytic activity of various complexes for the formation of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane.

Entry	Catalyst	Yield (%)
1	H-Z-Y	5
2	H-ZSM-5	15
3	[Co(Mebzlh)]-Y	30
4	[Co(Mebzlh)]-ZSM-5	40
5	[Cu(Mebzlh)]-Y	30
6	[Cu(Mebzlh)]-ZSM-5	60
7	[Zn(Mebzlh)]-Y	40
8	[Zn(Mebzlh)]-ZSM-5	90

Reaction condition: substrate:catalyst = 1:2, time = 30 min, temperature = 80 °C.

Table 3. Catalytic activity of the fresh and recycled [Zn(Mebzlh)]-ZSM-5 catalyst for the formation of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane.

Entry	Recycle	Yield (%)
1	Fresh	90
2	1 st run	89
3	2 nd run	87

Reaction condition: substrate: catalyst = 1:2, time = 30 min, temperature = 80 °C.

CONCLUSIONS

This catalytic method can be applied for the synthesis of 2,2-dimethyl-4-phenyl-[1,3]-dioxolane in excellent yield, by reacting styrene oxide and acetone within short duration of time. The methodology employed is simple and reusability of catalyst makes this protocol useful for carrying out this transformation.

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REFERENCES

- Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, John Wiley and Sons: New York; **1999**.

2. Bucsi, I.; Meleg, A.; Molnar; Bartok, M. *J. Mol. Catal. A: Chem.* **2001**, 168, 47.
3. Torok, D.S.; Figueroa, J.J.; Scott W.J. *J. Org. Chem.* **1993**, 58, 7274.
4. Hanzlik, R.P.; Leinwetter, M. *J. Org. Chem.* **1978**, 43, 438.
5. Mohammad poor-Baltork, I.; Khosropour, A.R.; Aliyan, H. *Synth. Commun.* **2001**, 31, 3411.
6. Tangestaninejad, S.; Habibi, M.H.; Mirkhani, V.; Moghadam, M. *J. Chem. Res.* **2001**, 9, 365.
7. Iranpoor, N.; Zeynizadeh, B. *J. Chem. Res. (S)* **1998**, 8, 466.
8. Adams, R.D.; Barnard, T.S.; Brosius, K. *J. Organomet. Chem.* **1999**, 582, 358.
9. Iranpoor, N.; Kazemi, F. *Synth. Commun.* **1998**, 28, 3189.
10. Zhu, Z.; Espenson, J.H. *Organometallics* **1997**, 16, 3658.
11. Zatorski, L.W.; Wierzchowski, P.T. *Catal. Lett.* **1991**, 10, 211.
12. Steinbrink, H.; Chemische Werke Huls AG, GP (DOS) 1086241, **1959**; *Chem. Abstr.* **1962**, 56, 5969.
13. Gevorkyan, A.A.; Kazaryan, P.I.; Avakyan, O.V.; Vardanyan, R.A. *Khim. Geterotsykl. Soedin.* **1991**, 1, 33; *Chem. Abstr.* **1991**, 115, 8633x.
14. Rickborn, B.R.; Gerkin, M. *J. Am. Chem. Soc.* **1971**, 93, 1693.
15. Hudrlik, P.F.; Misra, R.N.; Withers, G.P.; Hudrlik, A.M.; Rona, R.J.; Arcoleo, J.P. *Tetrahedron Lett.* **1976**, 8, 1453.
16. Kagan, J.; Firth, B.E.; Shih, N.Y.; Boyajian, C. *J. Org. Chem.* **1977**, 42, 343.
17. Harvey, D.J.; Glazener, L.; Stratton, C.; Johnson, D.B.; Hill, R.M.; Horning, E.C.; Horning, M.G. *Res. ommun. Chem. Pathol. Pharmacol.* **1972**, 4, 247.
18. Lee, S.H.; Lee, J.C.; Li, M.X.; Kim, N.S. *Bull. Korean Chem. Soc.* **2005**, 26, 221.
19. Kowalak, S.; Weiss, R.C.; Balkus Jr., K.J. *J. Chem. Soc. Chem. Commun.* **1991**, 1, 57.
20. Bakus Jr., K.J.; Welch, A.A.; Gande, B.E. *Zeolites* **1990**, 10, 721.
21. Chatterjee, D.; Bajaj, H.C.; Das, A.; Bhatt, K.N. *J. Mol. Catal.* **1994**, 92, 235.
22. Gerrits, P.P.K.; Devos, D.; Starzyk, F.T.; Jacobs, P.A. *Nature* **1994**, 369, 543.
23. Keshavaraja, A.; Hegde, V.R.; Pandey, B.; Ramaswamy, A.V.; Kumar, P.; Ravindranathan, T. *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 2143.
24. Nethravathi, B.P.; Mahendra, K.N. *J. Porous Mater.* **2010**, 17, 107.