Catalysis Letters Vol. 94, Nos. 1–2, April 2004 (© 2004)

Metallophthalocyanines as potent catalysts for cyclopropanation of olefins with ethyldiazoacetate

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Received 23 September 2003; accepted 28 January 2004

Copper, manganese and iron phthalocyanines were found to be highly efficient catalysts for cyclopropanation of olefins using ethyldiazoacetate as carbene precursor. In general copper(II)-phthalocyanine was found to be the most active catalyst followed by the Mn(II)Pc and Fe(II)Pc. Ni(II)Pc and Co(II)Pc were found to be the less active catalysts for this reactions.

KEY WORDS: metallophthalocyanine; carbene; cyclopropanation; diazoesters; olefin.

1. Introduction

The development of new transition metal catalysts and design of effective strategies for their applications have brought a renaissance in the synthetic uses of diazocarbonyl compounds for carbenoid transformations [1–3]. Cyclopropanation of olefins with diazoesters is an important synthetic transformation as cyclopropanes find broad utility as synthetic intermediates in the preparation of pharmaceuticals and agrochemicals [4,5]. Many efficient methods based on the use of copper and rhodium complexes as homogeneous catalysts have been reported in the literature for this transformation [6–8]. The use of heterogeneous and heterogenized homogeneous catalysts for synthetic transformations is an area of current interest owing to the ease of separation and recycling of the catalysts. In this context some methods based on the use of copper complexes supported on the insoluble supports have been reported in the literature for cyclopropanation of olefins with diazoesters [9,10]. However these methods are associated with the limitations such as lower yields of the products, lower catalytic activity towards cyclopropanation as compare to dimerization and longer addition time with ethyldiazoacetate (EDA). Among the various catalysts studied metalloporphyrins were found to be the efficient catalysts for this transformation due to their stability and better yields of the products [11–12]. Metallophthalocyanine complexes (MPc) structurally similar to metal porphyrins, are easily accessible, more stable to degradation than porphyrins, have been extensively used to catalyze a variety of organic reactions [13–20]. Metallophthalocyanines being insoluble in common organic solvents can be easily separated from the reaction mixture for reuse and there are no pore size limitations associated with their use. In continuation to our studies on transition metal catalyzed synthetic transformations [21–28], herein we report for the first time cyclopropanation of olefins with EDA using metallophthalocyanines as heterogeneous catalysts (scheme).

2. Experimental

2.1. Materials

Copper, iron, manganese, nickel and cobaltphthalocyanines were prepared according to the literature procedures. All olefins used were commercially available and distilled before use.

2.1.1. Typical experimental procedure for cyclopropanation of olefins

To a stirred and refluxed solution of 4-methylstyrene (236 mg; 2 mmol) in dry xylene (5 mL) containing 5 Å molecular sieves (100 mg) and Cu(II)-phathalocyanine (Cu(II)Pc 29 mg; 0.05 mmol, 5 mol%), was added the solution of EDA (114 mg; 1 mmol) in dry xylene drop wise for a period of 0.5 h under nitrogen atmosphere. Progress of reaction was monitored by TLC (Hexane/Ethylacetate, 2 : 1) and after completion of the reaction Cu(II)Pc and molecular sieves were removed by filtration. The filtrate obtained was evaporated under vacuum to give an oil, which was purified by passing through the silica gel column using (Hexane/Ethyl acetate, 4 : 1) as eluent. Evaporation of the solvent yielded ethyl-2-(*p*-methylphenyl) cyclopropylcarboxylate (183 mg; 90%). Similarly other cyclopropanes were prepared.

3. Results and discussion

To evaluate the catalytic efficiency of various metallophthalocyanines, the reaction of 4-methylstyrene

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1011-372X/04/0400–0057/0 © 2004 Plenum Publishing Corporation

with EDA was studied by using different metallophthalocyanines as catalysts and xylene as solvent, with olefin/EDA molar ratio 2 : 1 in the presence of molecular sieves. These results are summarized in table 1 and show that Cu(II)Pc is the most active catalyst followed by Mn(II)- and Fe(II)phthalocyanines. Ni(II)- and Co(II)-phthalocyanines were found to be very less active for this reaction. To examine the versatility of Cu(II)Pc catalyst, a variety of olefins were reacted with the carbene generated from EDA using olefin/EDA molar ration 2 : 1 under similar reaction conditions [8]. These results are presented in table 2 and clearly indicate that Cu(II)Pc is very active heterogeneous catalyst for these reactions. The results obtained also show that aromatic substituted alkenes afforded better yields of products as compared to aliphatic alkenes. Further, aromatic substituted alkenes bearing electron-donating groups on benzene ring were found to be more reactive (table 2, entry **2,3).** The cyclopropanation of 4-methylstyrene with EDA was also carried out in different solvent like xylene, benzene, 1,2-dichloroethane, acetonitrile under similar reaction condition. Among the various solvents studied xylene was found to be best solvent for these reactions. Copper and other metallophthalocyanine catalysts used in these reactions could be easily recovered by filtration and reused several times without any significant loss in their activity.

Table 1
Cyclopropanation of 4-methylstyrene by EDA using different metal phthalocyanines as catalysts[a]

Entry	Substrate	Catalyst (mol %)	Yield[b] (%)
1	4-Methylstyrene	Cu(II) Pc	90
2	4-Methylstyrene	Fe(II)Pc	55
3	4-Methylstyrene	Mn(II)Pc	40
4	4-Methylstyrene	Ni(II)Pc	20
5	4-Methylstyrene	Co(II)Pc	10

[a] Metal phthalocyanine (5 mol%), 4-methylstyrene/EDA (2 : 1) in 5 mL of xylene in the presence of 5 Å molecular sieves under N_2 atmosphere at refluxing temperature.

[b] Isolated yields.

Table 2
Copper (II) phthalocyanine catalyzed cyclopropanation of olefins with EDA[a]

Entry	Olefin	Reaction time (h)	Yield[b] (%)
1	Styrene	5	80
2	4-Methylstyrene	3	90
3	3-Methylstyrene	3.5	85
4	α-Methylstyrene	2.5	92
5	Methylmethacrylate	6.5	70
6	*Trans* Methylcinnamate	6.0	55
7	Vinylcyclohexane	8.5	48
8	Norbornylene	10.0	72
9	4-Chlorostrene	8.5	70

[a] Metal phthalocyanine (5 mol%), olefin/EDA (2 : 1) xylene (5 mL) in the presence of 5 Å molecular sieves under N_2 atmosphere at refluxing temperature.

[b] Isolated yields.

4. Conclusion

In summary we have demonstrated for the first time copper, manganese, and iron phthalocyanines to be highly efficient heterogeneous catalysts for cyclopropanation of olefins using EDA as carbene precursor. The simple preparation, easy separation of the catalyst, simple workup and better yields of cyclopropanes make the metallophthalocyanines ideal heterogeneous catalysts for cyclopropanation of olefins.

Acknowledgment

We are thankful to Director, IIP for his kind permission to publish these results. Suman L. Jain and Vishal B. Sharma are thankful to CSIR, New Delhi, for the award of research fellowship.

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