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An efficient method for the olefination of aldehydes with ethyl diazoacetate using iron (II) phthalocyanine as catalyst

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A variety of aliphatic and aromatic aldehydes were smoothly converted to the corresponding olefins in excellent yields with ethyldiazoacetate using iron (II) phthalocyanine as catalyst in the presence of triphenylphosphine as reducing agent.

KEY WORDS: Olefination; iron (II) phthalocyanine; aldehydes; ethyl diazoacetate.

1. Introduction

The formation of carbon–carbon double bond is an important synthetic transformation as olefins find broad utility especially in the areas of natural products and polymer synthesis [1]. Transition metal catalyzed olefination of aldehydes with diazoacetates in the presence of trialkylphosphine/trialkylstilbene as reducing agent has come out to be an efficient method for the construction of carbon–carbon double bond in the recent years. A variety of transition metal based systems such as methyltrioxorhenium [2], $MoO_2(S_2(Net)_2)$ [3], Cu(I) salts [4] and $RuCl_2(PPh_3)_3$ [5] have been reported to be effective catalysts for this transformation. Among the transition metals iron has been singled out as a nontoxic metal and in this context, recently Woo *et al*. [6] reported the olefination of aldehydes with ethyldiazoacetate using iron (II) porphyrin complex as catalyst in the presence of triphenylphosphine as reducing agent.

Metallophthalocyanines (MPc) structurally similar to metal porphyrins, are easily accessible, more stable to degradation and cost effective than porphyrins, have been extensively used to catalyze a variety of organic reactions [7–12]. Metallophthalocyanines being insoluble in common organic solvents can be easily separated from the reaction mixture for reuse. In continuation to our studies on transition metal catalyzed synthetic transformations [13–17], herein we report for the first time a highly efficient catalytic method for the olefination of aldehydes with ethyldiazoacetate using iron (II) phthalocyanine Fe(II) Pc 1 as catalyst in the presence of triphenylphosphine as reducing agent (scheme 1).

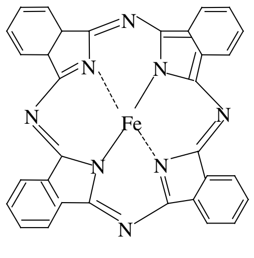
2. Experimental

2.1. Materials

Iron phthalocyanine [18] was prepared according to the literature procedures. All aldehydes used were commercially available.

2.1.1. Typical experimental procedure for olefination of aldehydes

To a stirred suspension of benzaldehyde (1.08 g, 10 mmol), $N_2CHCOOEt$ (2.28 g, 20 mmol) and triphenylphosphine (3.14, 12 mmol) in dry toluene (20 ml) was added Fe (II) phthalocyanine (0.28 g, 0.5 mmol, 5 mol%) under nitrogen atmosphere at room temperature (20 °C). Stirring was continued for 3.5 h. The solvent was evaporated under vacuum and the residue obtained was purified by passing through the silica gel column using hexane/ethylacetate (9:1) as eluent. Evaporation of the solvent yielded *trans*-ethylcinnamate (1.61 g, 92%), which was identified by comparing the physical and spectral data with that of authentic sample. Similarly other olefins were prepared.



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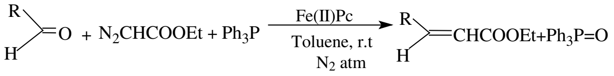

$$\mathrm{RHC{=}O} + N_2CHCOOEt + Ph_3P \xrightarrow[\text{Toluene, r.t}\ N_2\ \text{atm}]{\text{Fe(II)Pc}} \mathrm{RHC{=}CHCOOEt} + Ph_3P{=}O$$

Scheme 1.

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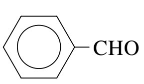
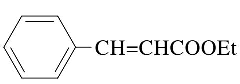
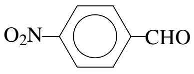
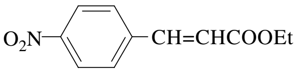
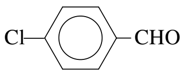
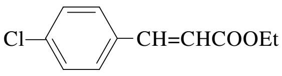
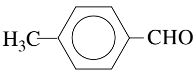
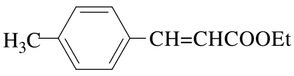
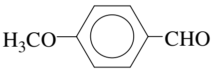
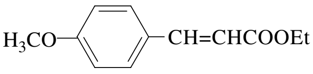
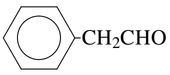
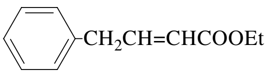
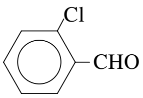
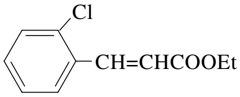
Table1
Iron (II)phthalocyanine catalyzed olefination of aldehydes.[a]

Entry	Aldehyde	Product	Reaction Time (*h*)	Yield[b]
1			3.5	92
2			2.0	96
3			2.5	94
4			4.5	90
5			6.0	85
6			8.5	65
7			3.0	92

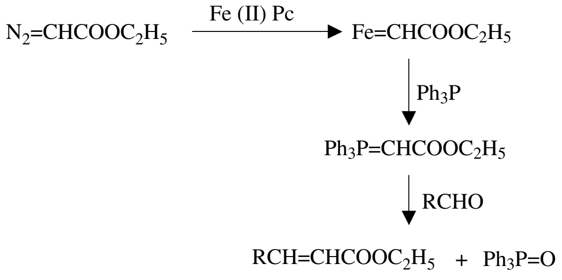
[a] Reaction conditions: Aldehyde (10 mmol), Ph_3P (12 mmol), $N_2CHCOOEt$ (20 mmol), Fe (II)Pc (0.5 mmol) in dry toluene (20 ml) at room temperature under N_2 atm.

[b] Isolated yields

3. Results and discussion

A variety of aliphatic and aromatic aldehydes were reacted with ethyldiazoacetate using catalytic amount of iron (II) phthalocyanine in the presence of triphenylphosphine to yield corresponding olefins in excellent yields with high *trans* selectivity [9]. These results are presented in table 1. Among the various aldehydes studied those containing electron withdrawing groups were found to be more reactive (table 1 entries 2, 3 and 7) as compared to those substituted with electron donating groups (table 1 entries 4 and 5). The presence of triphenylphosphine was found to be essential for this reaction and reaction did not proceed in the absence of triphenylphosphine. The formation of triphenylphosphine oxide was also observed during the reaction, which may be due to the transfer of oxygen from aldehyde to triphenylphosphine. To evaluate the catalytic effect of the Fe (II) Pc, the olefination of 4-nitrobenzaldehyde was carried out in the absence of catalyst under similar reaction conditions and no olefination product was observed in the absence of the catalyst.

The mechanism of this reaction is not clear at this stage and the reaction probably involves the transfer of carbene moiety generated from ethyldiazoacetate to phosphorous in the presence of Fe (II) Pc. The *in situ* ylide thus generated may react with aldehyde to yield corresponding olefin as shown in scheme 2. The further studies in this direction are under investigation.



Scheme 2.

4. Conclusion

In summary we have demonstrated for the first time Fe (II)Pc to be highly efficient heterogeneous catalyst for the olefination of aldehydes with ethyldiazoacetate in the presence of triphenylphosphine under very mild conditions. The simple preparation and easy separation of the catalyst for reuse and excellent yields of the products make this a facile method for the olefination of aldehydes.

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References

[1] B.E. Maryanoff and A.B. Reitz, Chem. Rev. 89 (1989) 863.
[2] W.A. Herrmann and M. Wang, Angew. Chem. Int. Ed. Engl. 30 (1991) 1641.
[3] X. Lu, H. Fang and Z. Ni, J. Organomet. Chem. 373 (1989) 77.
[4] Y. Liao and Y.-Z. Huang, Tetrahedron Lett. 30 (1990) 1641.
[5] O. Fujimura and T. Honma, Tetrahedron Lett. 39 (1998) 625.
[6] G.A. Mirafzal, G. Cheng and L.K. Woo, J. Am. Chem. Soc. 124 (2002) 176.
[7] C. Perollier and A.B. Sorokin, Chem. Commun. (2002) 1548.
[8] B. Meunier and A. Sorokin, Acc. Chem. Res. 30 (1997) 470.
[9] A. Sorokin, S. De Suzzoni-Dezard, D. Poullain, J.P. Noel and B. Meunier, J. Am. Chem. Soc. 118 (1996) 7410.
[10] A. Hadasch, A. Sorokin, A. Rabion, L. Fraisse and B. Meunier, Bull. Soc. Chim. Fr. 134 (1997) 1025.
[11] A. Sorokin and B. Meunier, J. Chem. Soc. Chem., Commun. (1994) 1799.
[12] A. Sorokin, J.L. Seris and B. Meunier, Science 268 (1995) 1163.
[13] V.B. Sharma, S.L. Jain and B. Sain, Tetrahedron Lett. 44 (2003) 383.
[14] S.L. Jain and B. Sain, J. Mol. Catal. 176 (2001) 101.
[15] V.B. Sharma, S.L. Jain and B. Sain, Tetrahedron Lett. 44 (2003) 3235.
[16] S.L. Jain, V.B. Sharma and B. Sain, Tetrahedron Lett. 44 (2003) 4385.
[17] S.L. Jain, V.B. Sharma and B. Sain, Tetrahedron Lett. 45 (2004) 1233.
[18] J.E. Backvall, R.B. Hopkins, H. Grennberg, M.M. Mader and A.K. Awasthi, J. Am. Chem. Soc. 112 (1990) 5160.