



Poly(ethylene glycol) Supported Metal Nitrates as Well-Organized Reagents for Hunsdiecker Conversion of α,β -Unsaturated Acids to β -Nitrostyrenes under Solvent and Acid-Free Conditions

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Poly(ethylene glycol) (PEG) supported metal nitrates such as ferric nitrate and manganese nitrate were accomplished as well-organized reagents for Hunsdiecker conversion of α,β -unsaturated acids to β -nitrostyrenes under acid-free and solvent free conditions using grind-stone technique. However, in the case of unsaturated aliphatic acids, nitro alkene derivatives were obtained as products. PEG-400 was found the best among the other PEGs (PEG-200,300, 400, 600, 3000 and 6000) used in this protocol.

Keywords: PEG supported metal nitrates, β -Nitrostyrenes, α,β -Unsaturated acids, Hunsdiecker conversion.

INTRODUCTION

Solvent and acid free organic synthesis captured the attention of chemistry community all over the world because of their importance to prevent environmental pollution, improve green reaction conditions followed by enhanced selectivity [1-11]. Stimulated by these striking features coupled with other green-chemistry principles we too have focused our attention to design, improve and execute green synthetic protocols [12-20]. In previous publication [19] we reported the synthesis of β -nitrostyrenes and nitroalkenes respectively from α,β -unsaturated aromatic and aliphatic acids using metal nitrates and few drops of HNO_3 by grinding all the ingredients in a mortar with a pestle. In another publication [20], we have explored poly(ethylene glycols) (PEGs) as efficient catalysts in these reactions under acid-free conditions. Recent literature reports revealed that PEGs are cost-effective and user-friendly additives/solvents to enhance and facilitate several organic transformations [21-27]. Enthused by these results we have tried to further improve the greenery of the reactions. In this part of the work, we have employed PEGs (PEG-200,300, 400, 600, 3000 and 6000) as additives along with d -block metal nitrates like Fe(III) and Mn(II) nitrates under acid-free and solvent free conditions.

EXPERIMENTAL

Grind-stone method of β -nitro styrene synthesis: Known amounts of unsaturated acid (0.1 mol), PEG (0.02 mol) and Fe(III) or Mn(II) nitrate (0.12 mol) were taken in a mortar and ground with a pestle till the reaction mixture became homogeneous. After completion of the reaction, as confirmed by TLC, about 2 % Na_2CO_3 solution was added to the reaction mixture till it is neutralized. Reaction product was extracted by dichloromethane (DCM) or dichloroethane (DCE), dried with sodium sulfate and purified by column chromatography. Binary solvent mixture of ethyl acetate and hexane (3:7) was used as eluent to obtain pure product.

RESULTS AND DISCUSSION

All the reactants (α,β -unsaturated acid, PEG and metal nitrate) are taken in a clean mortar and ground with a pestle till the reaction is completed, as ascertained by TLC. The reactions with aromatic carboxylic acid such as cinnamic acid afforded β -nitro styrenes, while the aliphatic carboxylic acid such as crotonic acid afforded nitroalkenes in good yield of products with high regioselectivity. Initially the reactions are conducted with cinnamic acid, metal nitrate and different PEGs are to select the best PEG. The observed results are presented in Table-1.

TABLE-2
NITRO DECARBOXYLATION OF CINNAMIC ACIDS IN
PRESENCE OF PEG-400 AND METAL NITRATES
UNDER SOLVENT FREE CONDITIONS

Entry	Fe(NO ₃) ₃		Mn(NO ₃) ₂	
	Time (min)	Yield (%)	Time (min)	Yield (%)
Cinnamic acid	30	88	30	87
4-Chloro cinnamic acid	60	86	60	83
4-Methoxy cinnamic acid	30	88	30	87
4-Methyl cinnamic acid	30	86	30	85
4-Nitro cinnamic acid	60	76	60	80
4-Hydroxy cinnamic acid	30	92	30	88
Acrylic acid	30	80	30	78
Crotonic acid	60	78	60	78
3-Phenyl crotonic acid	30	76	30	80
2-Chloro cinnamic acid	60	82	60	70
2-Methyl cinnamic acid	30	86	30	78

reactants were ground in a mortar with a pestle till the reaction is completed. The reaction time is generally about 30-60 min. The present finding has advantages such as the use of economically cheap and readily available desktop Fe(III) and Mn(III) nitrates, PEGs and unsaturated acids.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P. Anastas and J. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press: New York (1998).
2. L.E. Kaïm, L. Gautier, L. Grimaud, L.M. Harwood and V. Michaut, *Green Chem.*, **5**, 477 (2003); <https://doi.org/10.1039/B306242B>.
3. G.R. Desiraju and B.S. Goud, ed.: V.V. Boldyrev, *Reactivity of Solids: Present, Past and Future*, Blackwell Sciences: London, p. 223 (1995).
4. K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000); <https://doi.org/10.1021/cr940089p>.
5. G.W.V. Cave, C.L. Raston and J.L. Scott, *Chem. Commun.*, 2159 (2001); <https://doi.org/10.1039/b106677n>.
6. I. Mohammadpoor-Baltork, M. Sadeghi and A.-H. Adibi, *Molecules*, **6**, 900 (2001); <https://doi.org/10.3390/61100900>.
7. J.D. Lou and Z.N. Xu, *Tetrahedron Lett.*, **43**, 6095 (2002); [https://doi.org/10.1016/S0040-4039\(02\)01333-3](https://doi.org/10.1016/S0040-4039(02)01333-3).
8. J.D. Lou and Z.N. Xu, *Tetrahedron Lett.*, **43**, 8843 (2002); [https://doi.org/10.1016/S0040-4039\(02\)02234-7](https://doi.org/10.1016/S0040-4039(02)02234-7).
9. J.D. Lou and Z.N. Xu, *Tetrahedron Lett.*, **43**, 6149 (2002); [https://doi.org/10.1016/S0040-4039\(02\)01345-X](https://doi.org/10.1016/S0040-4039(02)01345-X).
10. J.L. Scott, D.R. MacFarlane, C.L. Raston and M. Teoh, *Green Chem.*, **2**, 123 (2000); <https://doi.org/10.1039/b000825g>.
11. C.L. Raston and J.L. Scott, *Green Chem.*, **2**, 49 (2000); <https://doi.org/10.1039/a907688c>.
12. M.M. Ali, K.C. Rajanna and P.K. Sai Prakash, *Synlett*, **2001**, 251 (2001); <https://doi.org/10.1055/s-2001-10765>.
13. M.M. Ali, S. Sana, Tasneem, K.C. Rajanna and P.K. Saiprakash, *Synth. Commun.*, **32**, 1351 (2002); <https://doi.org/10.1081/SCC-120003631>.
14. K.C. Rajanna, M. Moazzam Ali, S. Sana, Tasneem and P.K. Saiprakash, *J. Dispers. Sci. Technol.*, **25**, 17 (2004); <https://doi.org/10.1081/DIS-120027663>.
15. K.C. Rajanna, M.M. Ali, S. Sana and P.K. Saiprakash, *Chem. Lett.*, **1**, 48 (2000).
16. C. Hunsdiecker and H. Hunsdiecker, *Ber. Dtsch. Chem. Ges.*, **75**, 291 (1942); <https://doi.org/10.1002/cber.19420750309>.
17. R.G. Johnson and R.K. Ingham, *Chem. Rev.*, **56**, 219 (1956); <https://doi.org/10.1021/cr50008a002>.
18. A.G. Smith, *Organic Synthesis*, Wiley Interscience: New York (1993).
19. S. Ramgopal, K. Ramesh, A. Chakradhar, N.M. Reddy and K.C. Rajanna, *Tetrahedron Lett.*, **48**, 4043 (2007); <https://doi.org/10.1016/j.tetlet.2007.04.026>.
20. K.C. Rajanna, K. Ramesh, S. Ramgopal, S. Shylaja, P.G. Reddy and P.K. Saiprakash, *Green. Sustain. Chem.*, **1**, 132 (2011); <https://doi.org/10.4236/gsc.2011.14022>.
21. T.J. Dickerson, N.N. Reed and K.D. Janda, *Chem. Rev.*, **102**, 3325 (2002); <https://doi.org/10.1021/cr010335e>.
22. B. Das, V.S. Reddy and M. Krishnaiah, *Tetrahedron Lett.*, **47**, 8471 (2006); <https://doi.org/10.1016/j.tetlet.2006.09.153>.
23. S. Chandrasekhar, N.R. Reddy, S.S. Sultana, Ch. Narsihmulu and K.V. Reddy, *Tetrahedron*, **62**, 338 (2006); <https://doi.org/10.1016/j.tet.2005.09.122>.
24. J.-H. Li, X.-C. Hu, Y. Liang and Y.-X. Xie, *Tetrahedron*, **62**, 31 (2006); <https://doi.org/10.1016/j.tet.2005.09.138>.
25. S. Chandrasekhar, C. Narsihmulu, B. Saritha and S.S. Sultana, *Tetrahedron Lett.*, **45**, 5865 (2004); <https://doi.org/10.1016/j.tetlet.2004.05.153.f>.
26. B. Das, M. Krishnaiah, P. Thirupathi and K. Laxminarayana, *Tetrahedron Lett.*, **48**, 4263 (2007); <https://doi.org/10.1016/j.tetlet.2007.04.062>.
27. A.I. Vogel, *Text Book of Practical Organic Chemistry*, Longman: London and New York, edn 4 (1986).