

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 HNO₃ 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 (O.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 % Na₂CO₃ 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.

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TABLE-1
EFFECT OF ADDITIVE PEG ON METAL NITRATE MEDIATED
NITRO DECARBOXYLATION OF CINNAMIC ACID
UNDER SOLVENT FREE CONDITIONS

Entry	Fe(NO ₃) ₃		$Mn(NO_3)_2$	
Entry	Time (min)	Yield (%)	Time (min)	Yield (%)
PEG-200	45	90	45	88
PEG-300	60	86	60	83
PEG-400	30	88	30	87
PEG-600	30	86	30	85
PEG-3000	60	76	60	80
PEG-6000	35	88	30	87

The products were characterized by ¹H NMR, mass spectra and physical data with authentic samples and found to agree well with earlier reports [25,27].

β-Nitro styrene: Mass: (m/z) 149; ¹H NMR: δ 6.4 (d 1H, β-CH), δ 7.3-7.65 (m 5H, Ar-H) δ 7.8 (d 1H, α-CH).

1-Nitro propene: Mass: (*m/z*) 87; ¹H NMR: δ 2.12 (d 3H, CH₃), δ 7.0 (d 1H, α-CH), δ 7.15 (m 1H, β-CH).

Effect of PEG and metal nitrate on the reactivity: The results (Table-1) show that the reactions afford very good to excellent yields within 1 h when the reactants are ground in a mortar with a pestle, in presence of laboratory desk top *d*-block metal nitrates such as ferric nitrate and manganese nitrate. Further, the reactions underwent smoothly with all the poly(ethylene glycols) (molecular weights ranging from PEG-200 to PEG-6000). However, among the different PEGs used in the present study, PEG-400 has been found to be much more

effective than other PEGs. It is evident that due to the grinding of reactants in a mortar with a pestle, mechanical energy is converted to heat energy, which could be utilized for activation of molecules. Since the grinding is done under solvent free conditions, bulk and speedy activation of molecules can be expected. Majority of such activated molecules might undergo chemical change and afford products in good to excellent yields. Basically poly(ethylene glycol) is an alcohol which is capable of binding with transition metal nitrates such as Fe(III) nitrate and Mn(II) nitrate to form to give [M(NO₃)_{x-1}(PEG)], a ternary complex containing PEG in the metal coordination spheres. The complex thus formed is as an effective catalyst to trigger the nitration reaction through the generation of active nitronium ion as shown in **Scheme-I**.

Effect of structure on reactivity: The results (Table-2) revealed that the reaction is sensitive to the structural variation of cinnamic acid, when the nitro decarboxylation reaction is conducted with cinnamic acids in presence of PEG-400 and metal nitrates reaction rates accelerated with the introduction of electron donating groups and retarded with electron withdrawing groups.

Conclusion

In summary, we have accomplished poly(ethylene glycol) supported Fe(III) nitrate and Mn(III) nitrate as efficient reagents for the synthesis of β -nitro styrenes from α , β -unsaturated carboxylic acids under solvent-free and mineral acid-free conditions using cost-effective grind-stone technology. The



where **R** = Alkyl (or) Aryl group; MNO₃ = Metal nitrate

Scheme-I: Plausuble mechanism of nitrodecarboxylation of unsaturated acid

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

	Fe(NO ₃) ₃		Mn(NO ₃) ₂	
Entry	Time	Yield	Time	Yield
	(min)	(%)	(min)	(%)
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.

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