

Metal nitrate driven nitro Hunsdiecker reaction with α,β -unsaturated carboxylic acids under solvent-free conditions

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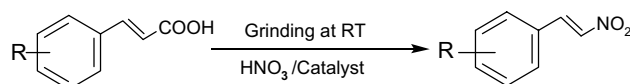
Abstract—Hunsdiecker reactions with α,β -unsaturated carboxylic acids were conducted under solvent-free conditions in the presence of a few drops of HNO_3 together with a variety of metal nitrates [$\text{Mg}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$], $\text{Al}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, AgNO_3 , $\text{ZrO}(\text{NO}_3)_2$, $\text{UO}_2(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_2$] or ammonium nitrate. α,β -Unsaturated aromatic carboxylic acids underwent nitro decarboxylation to afford β -nitro styrenes in moderate to good yields, while α,β -unsaturated aliphatic carboxylic acids underwent decarboxylation to yield the corresponding nitro derivatives.

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Recently, interest in the development of economically simple and environmentally safe methods in synthetic organic chemistry has increased.¹ Recent reviews and publications^{2–5} in this field highlight the importance of organic synthesis under solvent-free conditions which is not only simple, but also satisfies both economical and environmental demands by replacing toxic solvents. Organic reactions performed under solvent-free conditions have gained much attention because of their enhanced selectivity, mild reaction conditions and associated ease of manipulation. The use of solid acid catalysis is potentially more attractive because of the ease of removal and recycling of the catalyst and the possibility that the solid might influence the selectivity. The classical Hunsdiecker–Borodin reaction is an important reaction in organic synthesis that affords β -halostyrenes in a single step from α,β -unsaturated and saturated aliphatic and aromatic carboxylic acids in the presence of $\text{Ag}(\text{I})$ and molecular bromine.⁶ Several groups^{7–13} have modified this reaction replacing toxic reagents such as bromine and $\text{Ag}(\text{I})$. Our group is also investigating the use of a variety of eco-friendly materials such as metal ions and surfactants as catalysts and non-conventional energy sources (such as microwave and ultrasound) to assist various organic transformations such as Vilsmeier–Haack and nitration reactions.¹⁴ Recent work¹⁵ by Das et al. revealed that nitro decarboxylation of

aromatic α,β -unsaturated carboxylic acids can be achieved using nitric acid (3 equiv) and catalytic AIBN (2 mol %) in MeCN. Even though considerable efforts were made to use simple materials as catalysts, not much attention has been directed towards the solvent-free Hunsdiecker–Borodin reaction. In the present investigation, decarboxylative nitration of α,β -unsaturated aliphatic and aromatic carboxylic acids has been explored under solvent-free conditions.

α,β -Unsaturated aromatic carboxylic acids such as cinnamic acids afforded β -nitrostyrenes, while aliphatic unsaturated acids gave nitroalkenes in moderate to good yields and regioselectivity when treated with a metal nitrate in the presence of a few drops of HNO_3 in a mortar followed by grinding for about 1–2 h. To check the generality of the reaction, an array of substituted cinnamic acids were used as substrates under the present reaction conditions (Scheme 1). The yields of the major products are compiled in Tables 1–3. The products were characterized by IR, ^1H NMR and mass spectroscopy and by comparison of physical data with those of authentic samples.¹⁶



Scheme 1. Catalyst = $\text{Mg}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, AgNO_3 , $\text{ZrO}(\text{NO}_3)_2$, $\text{UO}_2(\text{NO}_3)_2$, $\text{Th}(\text{NO}_3)_2$ or ammonium nitrate.

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Table 1. Nitro Hunsdiecker reaction in the presence of d-block metal nitrates under solvent-free conditions^a

Entry	Cinnamic acid (CA)	Ni(NO ₃) ₂		Zn(NO ₃) ₂		ZrO(NO ₃) ₂		Cd(NO ₃) ₂		Hg(NO ₃) ₂	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	CA	1.75	45	1.75	49	1.75	46	1.75	46	1.75	43
2	4-ClCA	2.00	40	2.00	42	2.00	45	2.00	42	2.00	41
3	4-MeOCA	1.50	46	1.50	54	1.50	56	1.50	48	1.50	53
4	4-MeCA	1.50	48	1.50	48	1.50	56	1.50	48	1.50	50
5	4-O ₂ NCA	2.00	42	2.00	40	2.00	42	2.00	42	2.00	48
6	4-HOCA	1.50	60	1.50	56	1.50	56	1.50	62	1.50	58
7	Acrylic acid	1.50	44	1.50	42	1.50	44	1.50	45	1.50	42
8	Crotonic acid	2.00	45	2.00	46	2.00	45	2.00	48	2.00	48
9	3-Phenyl crotonic acid	1.50	42	1.50	43	1.50	46	1.50	44	1.50	46
10	2-ClCA	2.00	46	2.00	42	2.00	45	2.00	42	2.00	45
11	2-MeCA	1.50	52	1.50	50	1.50	52	1.50	52	1.50	50

^a All reactions were performed at room temperature.**Table 2.** Nitro Hunsdiecker reaction in the presence of s-block, p-block and inner transition metal nitrates under solvent-free conditions^a

Entry	Cinnamic acid (CA)	Mg(NO ₃) ₂		Sr(NO ₃) ₂		Al(NO ₃) ₃		UO ₂ (NO ₃) ₂		Th(NO ₃) ₂	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield (%)
1	CA	1.75	60	1.75	63	1.75	58	1.75	62	1.75	62
2	4-ClCA	2.00	54	2.00	58	2.00	60	2.00	62	2.00	64
3	4-MeOCA	1.50	62	1.50	63	1.50	60	1.50	63	1.50	62
4	4-MeCA	1.50	58	1.50	61	1.50	60	1.50	58	1.50	58
5	4-O ₂ NCA	2.00	54	2.00	56	2.00	53	2.00	50	2.00	54
6	4-HOCA	1.50	62	1.50	60	1.50	62	1.50	63	1.50	60
7	Acrylic acid	1.50	52	1.50	48	1.50	56	1.50	55	1.50	56
8	Crotonic acid	2.00	53	2.00	51	2.00	55	2.00	52	2.00	52
9	3-Phenyl crotonic acid	1.50	54	1.50	56	1.50	54	1.50	54	1.50	54
10	2-ClCA	2.00	45	2.00	48	2.00	46	2.00	40	2.00	46
11	2-MeCA	1.50	52	1.50	49	1.50	52	1.50	48	1.50	50

^a All reactions were performed at room temperature.**Table 3.** Nitro Hunsdiecker reaction in the presence of AgNO₃ or NH₄NO₃ under solvent-free conditions^a

Entry	Cinnamic acid (CA)	AgNO ₃		NH ₄ NO ₃	
		Time (h)	Yield (%)	Time (h)	Yield (%)
1	CA	1.75	30	1.75	50
2	4-ClCA	1.50	32	1.50	52
3	4-MeOCA	1.50	35	1.50	46
4	4-MeCA	1.50	33	1.50	45
5	4-O ₂ NCA	2.00	32	2.00	43
6	4-HOCA	1.50	32	1.50	45
7	Acrylic acid	1.50	35	1.50	45
8	Crotonic acid	2.00	36	2.00	46
9	3-Phenyl crotonic acid	1.50	36	1.50	34
10	2-ClCA	2.00	32	2.00	42
11	2-MeCA	1.50	38	1.50	45

^a All reactions were performed at room temperature.

A perusal of the results presented in Tables 1–3 indicated that Mg(NO₃)₂, Sr(NO₃)₂, Al(NO₃)₃, UO₂(NO₃)₂ and Th(NO₃)₂ afforded the best yields and hence are the catalysts of choice in the nitro Hunsdiecker reaction under solvent-free conditions.

In summary, we have investigated the nitro Hunsdiecker reaction with α,β -unsaturated aliphatic and aromatic carboxylic acids under solvent-free conditions. The reaction occurs under mild environmentally safe conditions

and involves a simple work-up at room temperature. Thus, the present method is convenient for the synthesis of β -nitrostyrenes and nitroalkenes, some of which are known to exhibit biological activity.

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16. *General procedure for the synthesis of β -nitrostyrenes*: Cinnamic acid (0.01 mol), metal nitrate (0.015 mol) and a few drops of nitric acid were taken in a mortar and ground for about 1–2 h. After completion, as ascertained by TLC, the reaction mixture was treated with 2% sodium carbonate solution, followed by the addition of dichloromethane or dichloroethane. The organic layer was separated, dried over Na₂SO₄ and evaporated under vacuum, then purified by column chromatography using ethyl acetate:hexane (3:7) as eluent to afford the pure product.