

Iminium salt mediated nitro decarboxylation of α , β -unsaturated acids for the synthesis of β -nitro styrenes under non-conventional conditions

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Abstract: Iminium Salt Mediated Nitro decarboxylation of α , β - Unsaturated Acids has been taken up under conventional and non – conventional conditions. Vilsmeier - Haack (VH) Reagent is used as a source for the generation of iminium salt. Equimolar mixture of either DMF/SOCl₂ or DMF/POCl₃ is used for the preparation of VH reagent. Reactions afforded good yield of products under conventional conditions with longer reaction times. Microwave irradiated reactions not only reduced the reaction times but enhanced the yield of products from good to excellent.

Keywords: Nitration; α , β - unsaturated acids; vilsmeier-haack (VH) reagent; solvent- free; microwave.

1. Introduction

Nitration is one of the oldest and the most extensively studied reactions. It is the most acceptable and favored route for the manufacture of precursors, explosives, for dyes and intermediates, and industrial solvents. The most common nitrating system currently adopted at the industrial scale is represented by the classic “acid mixture” (HNO₃/H₂SO₄/H₂O), which involves two phases viz. the aromatic phase and the mixed acid phase. The reaction occurs exclusively in the acid phase in which aromatics are sparingly soluble. The rate controlling step involves electrophilic attack of nitronium ion on the aromatic ring. The reaction is known to be irreversible and first order in [Aromatic species] and [Nitric acid]. Among the drawbacks, which are often reported with this reaction include poor selectivity, waste disposal, and process safety. Aromatic nitro compounds are key synthons in the preparation of many dyes, plastics, perfumes, explosives, and Pharmaceuticals¹⁻⁴.

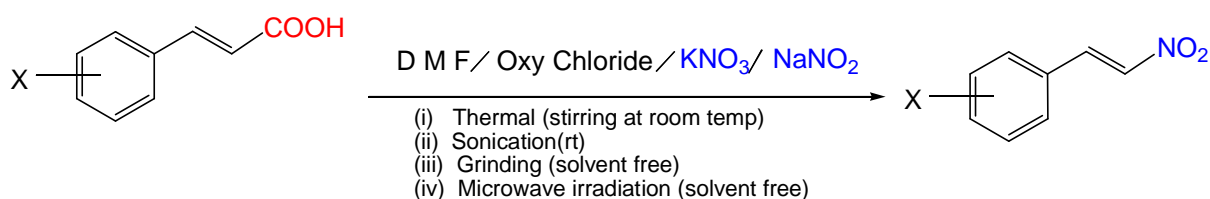
Iminium salt is an intermediate in many organic reactions such as the Beckmann rearrangement, Vilsmeier-Haack reaction, Stephen reaction and the Duff reaction. Iminium cation has the general structure [R₁R₂C=NR₃R₄]⁺ and is as such a protonated or substituted imine.⁵⁻¹¹ VH reagents could be prepared from equimolar quantities of amide [formamide, N, N’- dimethyl formamide (DMF), or N, N’-diethyl formamide (DEF)], and oxy halides such as POCl₃ and SOCl₂. Organic compounds in general and hydrocarbons with excess pi-electrons in particular undergo formylation very easily on synthetic scale.¹²⁻¹⁹ Recent reports on Vilsmeier-Haack (VH) reactions revealed that these reactions afforded bromo derivatives when VH reagent²⁰ is taken with KBr or NBS.

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Hunsdiecker- Borodin reaction (HBR) is one of the most versatile reactions in organic synthesis for the conversion of α , β -unsaturated aromatic carboxylic acids to β -bromo styrenes.²¹ Over a period of years this reaction underwent several modifications as evidenced from earlier publications.²²⁻²⁹ Recent research findings of Jayaprakash Das et al³⁰ and also from our laboratory and revealed that nitro decarboxylation of aromatic α , β -unsaturated carboxylic acids could be achieved conveniently to synthesize β -Nitro styrenes under solution phase and solvent free conditions within good yields with high regio- selectivity. Since more than one decade our group is also actively working on exploiting 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 ultra sound) to assist various organic transformations.³¹⁻³³ These reports revealed dramatic rate enhancements followed by significant hike in the yield of products. Encouraged by the earlier results coupled with a zeal to search for less expensive and operationally simple methods the authors have embarked on the present study under Vilsmeier- Haack conditions.

2. Results and discussion

The α , β -unsaturated carboxylic acids such as Cinnamic acids underwent nitro decarboxylation when treated with VH reagent (DMF/SOCl₂ and DMF/POCl₃) in presence of KNO₃ and NaNO₂ afforded good yields of products under stirred conditions at room temperature. In this study KNO₃ and NaNO₂ were used as catalysts for the generation of nitronium ions.



Scheme 1. Oxy Chloride = POCl₃ or SOCl₂; X = electron donating or withdrawing groups

To check the generality of the reaction an array of unsaturated acids were used as substrates under present reaction conditions as shown in Scheme-11. The products (nitro styrene derivatives for Cinnamic acids and nitro olefins for α , β -unsaturated aliphatic acids) were characterized by physical data (melting/boiling points; table -1), ¹H-NMR, Mass spectra and found to be in consonance with literature reports.^{30,31} But the rate data presented in tables 2 and table S1 and S2 (see supporting information) clearly indicated that reaction times were too long for thermal reactions even though the yields are fairly appreciative. However, the reaction times decreased substantially from several (14 to 15) hours to few minutes under solvent-free (mortar-pestle) grinding conditions followed by a fairly good increase in the product yield. This observation could be attributed to an increase in the fraction of activated species supplemented by the heat energy generated due to the friction in grinding process. By and large similar rate enhancements were observed in the case of ultrasonically assisted reactions. The observed rate accelerations could be explained due to cavitation, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an ultrasonically assisted (irradiated) liquid. Cavitation induces very high local temperatures in the reaction mixture and enhances mass transfer.³⁴⁻³⁶ On the other hand in microwave irradiated reactions, the reaction times further reduced dramatically to only few seconds. The yields also enhanced from good to excellent showing the catalytic effect of non-conventional energy to activate the reactive species in this study. The observations are in accordance with the literature reports that the chemical reactions are accelerated because of selective absorption of microwave (MW) energy by polar molecules, nonpolar molecules being inert to the MW dielectric loss.^{37,38}

Table 1. Melting points of β -Nitro Styrenes in the present study

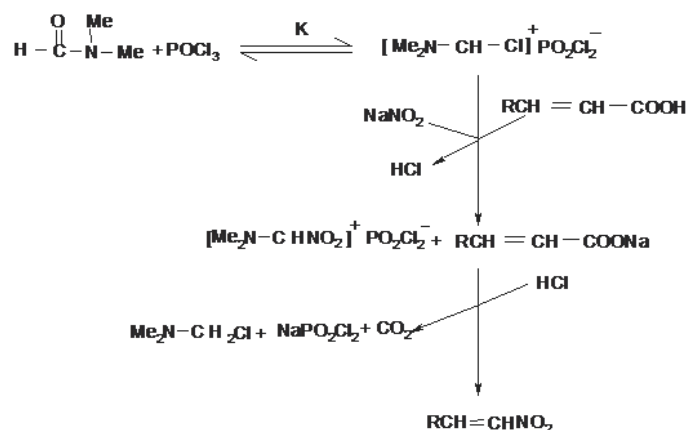
Entry	α , β -unsaturated carboxylic acid	Product	Melting Point ($^{\circ}$ C)	
			Present Work	Reference
1	CA	β -Nitro Styrene	58 - 62	57 - 58 ^{39,40}
2	4-Cl CA	4-Cl β -Nitro Styrene	115-118	113-114 ³⁹⁻⁴¹
3	4-OMe CA	4-OMe β -Nitro Styrene	82 -88	85-87 ³⁹⁻⁴¹
4	4-Me CA	4-Me β -Nitro Styrene	104- 106	103 ^{40, 41}
5	4-NO ₂ CA	4-NO ₂ β -Nitro Styrene	98-103	94-96 ^{39, 41}
6	4-OH CA	4-OH β -Nitro Styrene	166 -172	133-134 ^{39, 41}
7	AA ^a	1-Nitro ethene	100-102 ^a	98.5 ^{a,43}
8	CRA ^a	1-Nitro Propene	131-133 ^a	70 ^{a,42}
9	2-Me CA	2-Me β -Nitro Styrene	115-118	114-116 ⁴⁵
10	2-Cl CA	2-Cl β -Nitro Styrene	48-54	47-49 ⁴⁴

a) Note: For Entries (7 and 8) products are liquids. Therefore corresponding boiling points are given in the table.

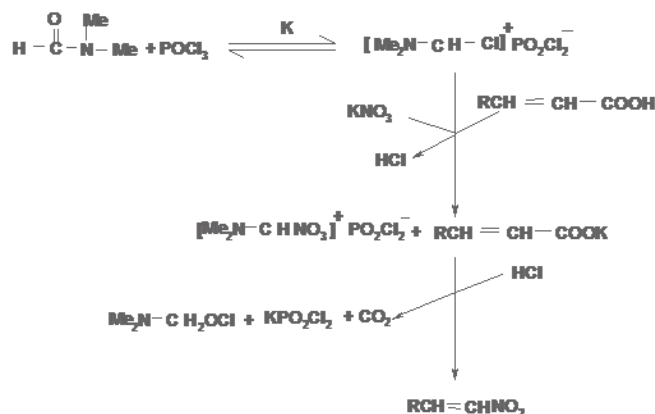
Table 2. Nitro decarboxylation of Cinnamic acid under various conditions

Entry	Reagents	Solvent	KNO ₃		NaNO ₂	
			RT (h)	Yield (%)	RT (h)	Yield (%)
1	SOCl ₂	DCE	14	18	15	15
2	POCl ₃	DCE	14	22	15	18
3	DMF/ SOCl ₂	DCE	14	64	15	60
4	DMF/ POCl ₃	DCE	14	70	15	65
5	SOCl ₂	ACN	14	25	15	20
6	POCl ₃	ACN	14	30	15	24
7	DMF/ SOCl ₂	ACN	14	74	15	72
8	DMF/ POCl ₃	ACN	14	78	15	75

Literature reports and earlier publications from our laboratories clearly depicted that VH reagents (DMF/POCl₃ or DMF/SOCl₂) generate a variety of cationic, nonionic and dipolar intermediates containing chloro methyliminium moiety. Mechanism of nitration with NaNO₂ in the present study could be explained due the *in situ* generation of nitro methyliminium ion due to the reaction of NaNO₂ with chloro methyliminium ion intermediate as shown in Scheme-2. Nitro methyliminium ion thus produced interacts with unsaturated acid and affords β -nitro styrene as the main product.

Scheme 2. Mechanism of nitration with NaNO_2

Mechanism of nitration with KNO_3 could be explained in similar lines given in scheme -2. A detailed sequence of steps is given in Scheme-3.

Scheme 2. Mechanism of nitration with KNO_3

3. Conclusion

In summary, the authors developed a protocol for iminium Salt Vilsmeier-Haack Reagent (VHR) triggered Nitro decarboxylation of α , β - Unsaturated Acids for the synthesis of β - nitro styrenes under conventional and non – conventional conditions. Equimolar mixture of either DMF/ SOCl_2 or DMF/ POCl_3 is used as source for the generation of iminium salt. Reactions afforded good yield of products under conventional conditions with longer reaction times. Non conventional methods (Microwave irradiated, sonicated and mortar-pestle) not only reduced the reaction times but enhanced the yield of products from good to excellent. The present finding is more advantageous because the reactions are conducted with economically cheap and readily available reagents. The reactions occur under mild and under environmentally safe conditions with a simple work up at room temperature.

4. Experimental

NMR spectra were recorded on Bruker UXNMR/XWIN-NMR Avance-300 MHz, and GEMINI spectrometers. Chemical shifts are reported downfield from TMS ($\delta=0$) for ^1H NMR. EI-MS spectra were recorded on a Shimadzu GC-MS instrument (GCMS-QP2010 plus).

General Procedure for preparation of Vilsmeier-Haack Reagent: The Vilsmeier Haack (VH) adduct is prepared afresh before use from Oxychloride (POCl_3 or SOCl_2) and dimethyl formamide (DMF). To a chilled (at -5°C) oxychloride in dichloroethane (DCE) or acetonitrile (Me CN), calculated amount of dimethyl formamide (DMF) was slowly added drop wise, which resulted in a slurry indicating the formation of VH reagent. The reagent thus obtained is stored under cold conditions.

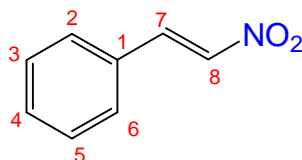
General Procedure for solvent mediated Synthesis of β -Nitro Styrenes under Vilsmeier-Haack conditions: A centi molar (0.01mol) organic substrate, (unsaturated acids), 0.01 mole of KNO_3 or NaNO_2 and about 0.015 mole of VH reagent and solvent (Me CN) were taken in a previously cleaned in a Round bottom flask and stirred for about 12 to 16 hours at room temperature. After completion of the reaction, as confirmed by TLC, the reaction mixture is treated with 5% sodium thiosulphate solution, followed by the addition of ethyl acetate. The organic layer was separated, dried over Na_2SO_4 and evaporated under vacuum, purified with column chromatography using pet ether: ethyl acetate (3:2) as eluent to get pure product.

General Procedure for Ultrasonically assisted (Sonicated) Vilsmeier-Haack Synthesis of β -Nitro Styrenes: To a centi molar (0.01mol) unsaturated acid, 0.01 mole of KNO_3 or NaNO_2 , about 0.015 mole of VH reagent and solvent (Me CN) were added in a clean in a round bottom flask and clamped in a Sonicator at room temperature. After completion of the reaction, as ascertained by TLC, the reaction mixture is treated with 5% sodium thiosulphate solution, followed by the addition of ethyl acetate. The separation and purification procedure is by and large similar to the above procedure.

General Procedure for Microwave Assisted Vilsmeier-Haack Synthesis under solvent free conditions: A centimolar (0.01mol) organic substrate (unsaturated acids), 0.01 mole of KNO_3 or NaNO_2 and about 0.015 mole of VH reagent were taken in a previously cleaned 50 mL beaker. About 500 mg of silica gel were added to the contents and mixed thoroughly and placed in Laboratory Microwave oven (CEM – 908010, bench mate model, 300W laboratory microwave reactor) and irradiated for few seconds. After completion of the reaction, as checked by TLC, the reaction mixture is worked up as detailed in earlier section to get pure product.

General Procedure for solvent free (Grinding) Vilsmeier-Haack Synthesis of β -Nitro Styrenes: A centi molar (0.01mol) organic substrate, (unsaturated acids), 0.01 mole of KNO_3 or NaNO_2 and about 0.015 mole of VH reagent and solvent (Me CN) were taken in a previously cleaned mortar and ground with a pestle. Completion of the reaction is ascertained by TLC. The separation and purification procedure is by and large similar to the above procedure.

Spectra of certain β -Nitro Styrenes:



β - Nitro styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 6.40-6.44 (d, 1H, H-8, $J=18\text{Hz}$); 7.80 (d, 1H, H-7, $J=18\text{ Hz}$); 7.48 (d, 2H, H-2, and H-6, $J=7.95\text{ Hz}$); 7.62-7.65 (m, 3H, H-3, H-4, H-5). EI-MS m/z -149 (100), 77(68), 103(71), 51(48), 90(36).

2-Chloro β - Nitro styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 6.68 (d, 1H, H-8, $J=18.5\text{ Hz}$); 8.32 (d, 1H, H-7, $J=18.5\text{ Hz}$); 7.60 (dd, 1H, H-5, $J=10\text{ Hz}$, $J=8.0\text{ Hz}$); 7.28 (dd, 1H, H-4, $J=9.0\text{ Hz}$, $J=7.5\text{ Hz}$); 7.64 (d, 1H, H-3, $J=8.5\text{ Hz}$); 7.75 (d, 1H, H-6, $J=8.0\text{ Hz}$). EI-MS m/z - 183(100), 185(32), 148(48), 137(85), 76(58), 51(22), 111(28).

2-Methyl β -Nitro styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.95 (s, 3H, Me); 6.78 (d, 1H, H-8, $J=18.5$ Hz); 8.28 (d, 1H, H-7, $J=18.5$ Hz); 7.35 (dd, 1H, H-5, $J=9.5$ Hz, $J=8.5$ Hz); δ 7.18 (dd, 1H, H-4, $J=10$ Hz, $J=8.5$ Hz.); 7.54 (d, 1H, H-3, $J=8.0$ Hz); 7.78 (d, 1H, H-6, $J=9.5$ Hz). EI-MS m/z - 163(100), 117(55), 148(15), 91(74), 72(34), 51(26).

4-Hydroxy β -Nitro styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 10.45 (s, 1H, Ar-OH); 6.58 (d, 1H, H-8, $J=18$ Hz) δ 8.12 (d, 1H, H-7, $J=18$ Hz); 7.28 (d, 2H, H-3 and H-5, $J=9.0$ Hz.); 7.76 (d, 2H, H-2 and H-6, $J=8.5$ Hz). EI-MS m/z -165(100), 119(34), 137(42), 93(46), 148(15), 51(28).

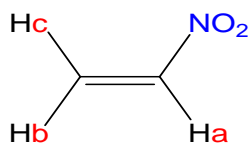
4-Chloro nitro Styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 6.68 (d, 1H, H-8, $J=18.0$ Hz); 8.28 (d, 1H, H-7, $J=18.0$ Hz); 7.24 (d, 2H, H-2 and H-6, $J=8.0$ Hz); 7.68 (d, 2H, H-3 and H-5, $J=8.5$ Hz). EI-MS m/z - 183(100), 185(32), 148(55), 137(92), 76(64), 51(28), 111(19).

4-Nitro β -Nitro styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 6.62 (d, 1H, H-8, $J=18$ Hz); 8.18 (d, 1H, H-7, $J=18.0$ Hz); 7.42 (d, 2H, H-2 and H-6, $J=9.0$ Hz) δ 7.78 (d, 2H, H-3 and H-5, $J=9.5$ Hz). EI-MS m/z -194(100), 148(34), 122(23), 76(65), 51(16).

4-Methyl β -Nitro Styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 3.02 (s, 3H, CH_3); 6.68 (d, 1H, H-8, $J=18$ Hz); 7.85 (H-7, d, 1H, $J=18.0$ Hz), 7.44 (d, 2H, H-2 and H-6, $J=8.0$ Hz), 7.65 (d, 2H, H-3 and H-5, $J=8.0$ Hz). EI-MS m/z -163(100), 117(42), 148(20), 91(84), 72(26), 51(32).

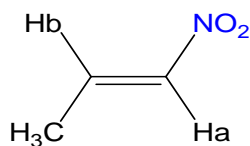
4-Methoxy β -Nitro Styrene: $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 3.82 (s, 3H, CH_3); 6.45 (d, 1H, H-8, $J=18.0$ Hz); 7.88 (d, 1H, H-7, $J=18.0$ Hz); 7.75 (d, 2H, H-2 and H-6, $J=8.0$ Hz), 7.48 (d, 2H, H-3 and H-5, $J=8.5$ Hz). EI-MS m/z -179(72), 133(100), 77(38), 89(46), 63(34).

1-Nitro Ethene:



$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 5.92 (dd, 1H, Hb, $J=11.3$ Hz, $J=1.5$ Hz); 6.65 (dd, 1H, Ha, $J=15.5$ Hz, $J=11.3$ Hz); 7.25 (dd, 1H, Hc, $J=15.5$ Hz, $J=1.5$ Hz). EI-MS m/z -73(100).

1-Nitro Propene:



$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 2.12 (d, 3H, CH_3 , $J=6.9$ Hz); 7.00 (d, 1H, Ha, $J=16.5$ Hz.), δ 7.18 (m, 1H, Hb); EI-MS m/z -87(100), 41(88), 46(57), 72(28), 15(36).

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