

Vilsmeier Haack Adducts as Effective Reagents for Regioselective Nitration of Aromatic Compounds under Conventional and Non-Conventional Conditions

Kamatala Chinna Rajanna*, Mukka Satish Kumar, Purugula Venkanna,
Soma Ramgopal, Marri Venkateswarlu

Department of Chemistry, Osmania University, Hyderabad, India

E-mail: kcrajannaou@yahoo.com

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Abstract

Nitration of aromatic Compounds is triggered by Vilsmeier-Haack reagent (DMF/ POCl_3) or (DMF/ SOCl_2) in the presence of KNO_3 or NaNO_2 under conventional and non-conventional conditions. The reactions afforded corresponding Nitro derivatives in very good yield with high regioselectivity. The results obtained in non-conventional methods (Micro wave irradiation, Grinding, Sonication) are comparable with those obtained under conventional conditions, but the reaction times of former conditions are substantially shorter than that of the latter.

Keywords: Nitration, KNO_3 or NaNO_2 , Vilsmeier-Haack Reagent, Microwave Irradiation (MWI), Grinding, Sonication

1. Introduction

Over the years, Nitration of aromatic compounds has been an area of interest to chemists because Nitro arenes are useful intermediates in the synthesis of organometallic species and pharmaceutically important compounds [1-3]. Direct methods of Nitration of aromatic compounds involve the use of hazardous acid mixture (HNO_3 and H_2SO_4) that is highly toxic, corrosive, and pollutes to the environment, and metal ion catalysts are generally expensive. In view of this, there has been an upsurge in the design and execution of mild methods of Nitration of aromatic compounds [4-17]. Over the past decade, our group has also been actively involved in designing a variety of eco friendly materials using micelle-forming surfactants as catalysts and unconventional energy sources (such as microwave irradiation and ultrasound) to assist Vilsmeier-Haack (VH) reactions [18-20] and Hunsdiecker reactions [21-22]. Dramatic rate accelerations followed by an increase in the product yield were observed in these reactions in all cases. 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 recent reviews and publications in this field prove the im-

portance of solvent-free organic synthesis [23-28] and highlights that this process is not only simple but also satisfies both economical and environmental demands by replacing the toxic solvents.

2. Results and Discussion

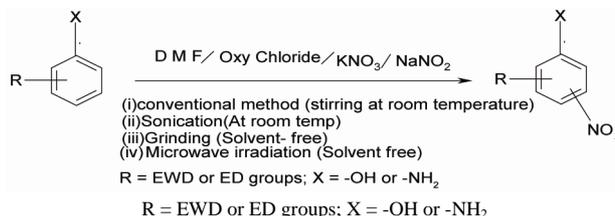
The VH reaction [29-32] is widely used for formylation. It can be applied to introduce an acetyl group on activated aromatic or hetero aromatic compounds, many other conversions can be achieved with this technology. It is one of the most versatile reactions in organic synthesis for the conversion of arenes to corresponding bromo derivatives. In general, (DMF/ POCl_3) or (DMF/ SOCl_2) are used to generate an iminium salt intermediate salt can be used in the synthesis of a large number of heterocyclic compounds. The VH reaction is a mild method known for the introduction of a formyl (-CHO) group to various activated aromatic and hetero aromatic compounds. Recently our group reported that Vilsmeier-Haack (VH) reagents could be effectively used in presence of KBr or NBS for bromination of arenes [20]. Encouraged by this result, we tried to use VH reagent (DMF/ SOCl_2 and DMF/ POCl_3) in presence of KNO_3 and NaNO_2 for nitration reactions. Aromatic compounds such as phenols

and amines underwent nitration 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 reagents for the generation of nitronium ions. Under these conditions only nitro derivatives were obtained. However, in the absence of KNO₃ and NaNO₂ formylated products could be obtained. We have analysed the products carefully to check this point. To check the generality of the reaction an array of aromatic compounds were used as substrates as shown in **Scheme 1**.

An important note that, Nitration of aniline using (HNO₃ and H₂SO₄) forms m-nitro aniline as major product, it is because aniline is a strong activating group forms anilinium salt (C₆H₅-NH₃⁺) with strong acid. But, using VHR and KNO₃ or NaNO₂ can afford o, p-nitro anilines as major products.

The reaction rapidly afforded high yields of the corresponding Nitro derivatives. All the products were characterized by physical data (m.p/b.p), ¹H NMR, and mass

spectra, with authentic samples and found to be satisfactory. To compare these results, aromatic compounds were treated with VH adduct (POCl₃ + DMF) in Acetonitrile under reflux conditions. When aromatic amines and Phenols were reacted with (POCl₃ + DMF) in the presence of KNO₃ or NaNO₂, the reaction indicated corresponding Nitro derivatives. The reaction proceeded rapidly with (POCl₃ + DMF)/(KNO₃ or NaNO₂) over (SOCl₂ + DMF)/(KNO₃ or NaNO₂) to afford high yields of the corresponding Nitro derivatives. Data summarized in **Figures 1-4** and **Tables 1** and **2**. **Figures 1-4** clearly demon-



Scheme 1. Nitration of aromatic compounds with VH reagents and KNO₃/NaNO₂ under conventional and non-conventional conditions.

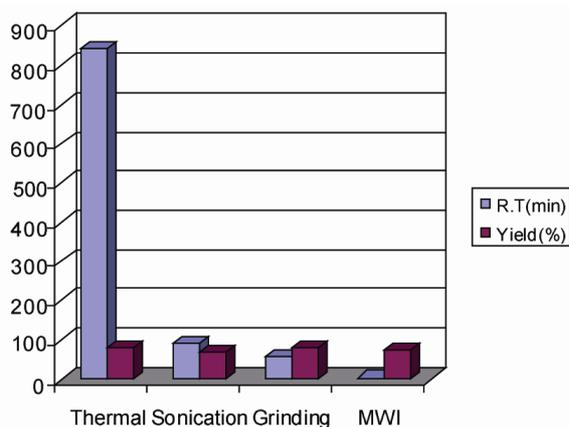


Figure 1. Nitration of Aromatic Compounds with VH reagent (DMF + SOCl₂) and KNO₃.

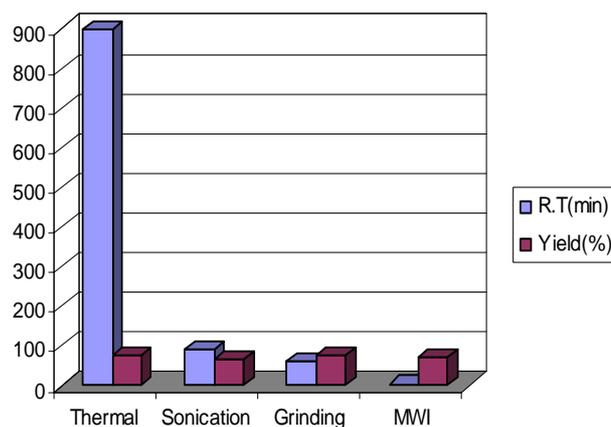


Figure 2. Nitration of Aromatic Compounds with VH reagent (DMF + SOCl₂) and NaNO₂.

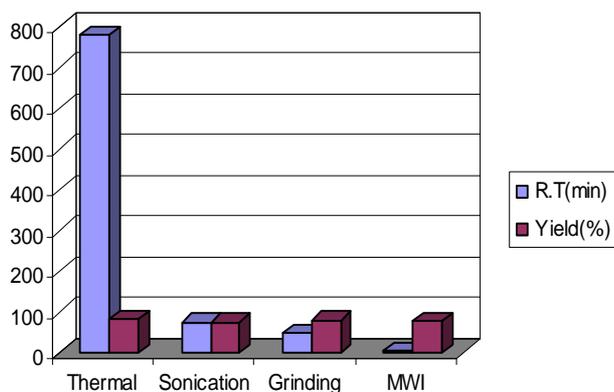


Figure 3. Nitration of Aromatic Compounds with VH reagent (DMF + POCl₃) and KNO₃.

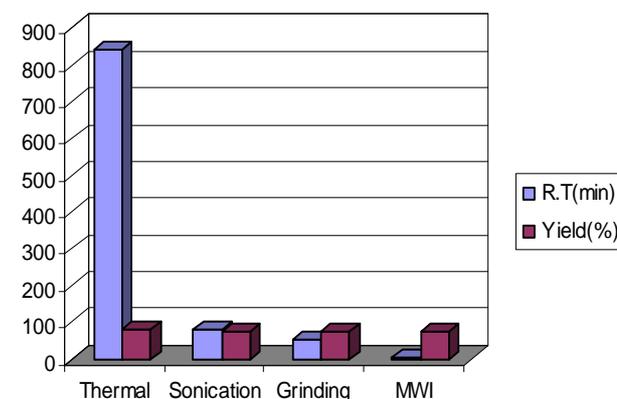


Figure 4. Nitration of Aromatic Compounds with VH reagent (DMF + POCl₃) and NaNO₂.

Table 1. Nitration of certain aromatic compounds under Vilsmeier Haack Conditions.

Entry	Substrate	Thermal (Room temp)				Sonication (Room temp)				Grinding (Solvent free)				Microwave (300 watt) (Solvent free)			
		KNO ₃		NaNO ₂		KNO ₃		NaNO ₂		KNO ₃		NaNO ₂		KNO ₃		NaNO ₂	
		R.T (h)	Yield (%)	R.T (h)	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T (Sec)	Yield (%)
1	Phenol	14	78	15	74	90	70	90	66	60	80	60	74	240	74	250	70
2	o-Cresol	14	82	15	76	90	76	90	72	60	82	60	75	210	76	230	72
3	p-Cresol	14	80	15	74	90	75	90	72	60	80	60	75	220	75	230	70
4	m-Cresol	14	76	15	72	90	70	90	65	60	75	60	70	240	72	240	68
5	o-Cl phenol	14	80	14	75	90	74	90	68	60	80	60	74	240	72	260	70
6	p-Cl phenol	14	75	15	72	90	72	90	65	60	76	60	74	240	70	260	68
7	p-Br phenol	15	74	15	70	90	68	90	64	60	74	60	70	250	70	260	66
8	o-OH benzaldehyde	15	72	16	65	90	68	90	60	60	74	60	68	250	70	250	65
9	p-OH benzaldehyde	15	70	16	62	90	65	90	58	60	70	60	64	260	68	260	62
10	o-OH phenol (R)	14	82	15	78	90	78	90	72	60	84	60	76	210	78	210	75
11	p-OH phenol (Q)	14	80	15	75	90	75	90	70	60	80	60	75	210	76	210	72
12	α , β -Naphthol	16	62	16	58	90	58	90	54	60	62	60	58	300	60	300	56
13	β -Naphthol	16	66	16	60	90	62	90	58	60	66	60	60	300	62	300	58
14	3-OH acetophenone	14	75	15	70	90	72	90	70	60	76	60	72	240	72	250	68
15	Aniline	14	75	15	70	90	68	90	60	60	78	60	72	210	74	260	68
16	4-NH ₂ phenol	14	76	15	72	90	72	90	68	60	75	60	70	210	75	220	65
17	3-NH ₂ phenol	14	74	15	66	90	68	90	62	60	75	60	65	220	70	235	60
18	m-Chloro aniline	16	68	16	60	90	64	90	56	60	66	60	60	260	64	270	60
19	p-Toluidine	14	72	15	68	90	68	90	60	60	74	60	66	220	70	230	62
20	o-Toluidine	14	74	15	70	90	70	90	60	60	75	60	68	220	70	230	64

VHR = (DMF + SOCl₂); SOLVENT = Acetonitrile.

Table 2. Nitration of certain aromatic compounds under Vilsmeier Haack Conditions.

Entry	Substrate	Thermal (Room temp)				Sonication (Room temp)				Grinding (Solvent free)				Microwave (300 watt) (Solvent free)			
		KNO ₃		NaNO ₂		KNO ₃		NaNO ₂		KNO ₃		NaNO ₂		KNO ₃		NaNO ₂	
		R.T (h)	Yield (%)	R.T (h)	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T min	Yield (%)	R.T (Sec)	Yield (%)
1	Phenol	13	82	14	78	75	75	80	72	50	82	50	76	220	78	230	72
2	o-Cresol	13	84	14	80	75	80	80	76	50	85	50	80	210	80	220	76
3	p-Cresol	13	80	14	75	75	76	80	72	50	82	50	76	210	78	210	70
4	m-Cresol	13	78	14	72	75	76	80	70	50	80	50	72	230	76	230	70
5	o-Cl phenol	15	82	15	76	75	74	80	72	50	84	50	76	220	76	240	72
6	p-Cl phenol	13	78	14	75	75	75	80	72	50	80	50	76	220	74	240	70
7	p-Br phenol	14	76	14	72	75	72	80	68	50	78	50	72	250	72	260	66
8	o-OH benzaldehyde	14	75	15	70	75	72	80	66	50	78	50	70	240	72	240	66
9	p-OH benzaldehyde	14	70	15	68	75	68	80	64	50	72	50	65	240	70	240	65
10	o-OH phenol (R)	13	84	14	80	75	80	80	75	50	84	50	80	200	80	200	76
11	p-OH phenol (Q)	13	82	14	78	75	78	80	72	50	80	50	76	200	76	200	72
12	α , -Naphthol	15	64	15	60	75	60	80	54	50	65	50	58	280	62	280	58
13	β -Naphthol	15	60	15	58	75	56	80	52	50	66	50	60	280	64	280	60
14	3-OH acetophenone	13	78	14	70	75	75	80	72	50	76	50	74	240	75	250	70
15	Aniline	13	78	14	72	75	70	80	60	50	76	50	72	230	74	250	65
16	4-NH ₂ phenol	13	78	14	74	75	72	80	68	50	78	50	75	200	75	220	68
17	3-NH ₂ phenol	13	76	14	70	75	68	80	62	50	76	50	72	200	74	220	65
18	m-Chloro aniline	15	68	16	62	75	64	80	58	50	66	50	60	250	66	250	62
19	p-Toluidine	14	75	15	70	75	65	80	60	50	76	50	68	200	72	220	60
20	o-Toluidine	14	76	15	72	75	66	80	60	50	78	50	70	200	74	220	64

VHR = (DMF + POCl₃); SOLVENT = Acetonitrile.

strate that the obtained yields are good to excellent; the $(\text{POCl}_3 + \text{DMF})/(\text{KNO}_3 \text{ or } \text{NaNO}_2)$ system afforded relatively better yields than the $(\text{SOCl}_2 + \text{DMF})/(\text{KNO}_3 \text{ or } \text{NaNO}_2)$ system. This may be because the active electrophile (NO_2^+) is released faster in the case of the $(\text{POCl}_3 + \text{DMF})/(\text{KNO}_3 \text{ or } \text{NaNO}_2)$ system and is available for favorable Nitration over the $(\text{SOCl}_2 + \text{DMF})/(\text{KNO}_3 \text{ or } \text{NaNO}_2)$ system. It is interesting to note that the reaction times under thermal conditions are too long 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 [23-26]. 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 [33-35]. 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 energy by polar molecules, nonpolar molecules being inert to the MW dielectric loss [27,28].

3. Conclusions

In summary, the authors developed a protocol for iminium Salt Vilsmeier-Haack Reagent (VHR) triggered aromatic 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 Details

4.1. General Procedure for Preparation of Vilsmeier-Haack Reagent

The Vilsmeier Haack (VH) adduct is prepared afresh be-

fore use from Oxychloride (POCl_3 or SOCl_2) and dimethyl formamide (DMF). To a chilled (at -5°C) Oxychloride in acetonitrile (MeCN), calculated amount of dimethyl formamide (DMF) was slowly added drop wise, which resulted in slurry indicating the formation of VH reagent. The reagent thus obtained is stored under cold conditions.

4.2. General Procedure for Synthesis of Nitro Arenes under Solvent Phase Conditions Using VH Reagent (Thermal)

A centi molar (0.01 mol) organic substrate, (phenols, anilines), 0.01 moles of KNO_3 or NaNO_2 and about 0.015 moles of VH reagent and solvent (MeCN) were taken in a previously cleaned in a Round bottom flask and stirred for about 12 to 15 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 and ethyl acetate to get pure product.

4.3. General Procedure for Synthesis of Nitro Arenes under Solvent Phase Conditions Using VH Reagent (Sonication)

A centi molar (0.01 mol) organic substrate, (phenols, anilines), 0.01 moles of KNO_3 or NaNO_2 and about 0.015 moles of VH reagent and solvent (MeCN) were taken in a previously cleaned in conical flask at room temperature. After completion of the reaction, as confirmed by TLC, the reaction mixture is further processed for isolation of product as detailed in earlier section.

4.4. General Procedure for Synthesis of Nitro Arenes under Solvent Free Conditions Using VH Reagent (Grinding)

A centi molar (0.01 mol) organic substrate, (phenols, anilines), 0.01 moles of KNO_3 or NaNO_2 and about 0.015 moles of VH reagent in a previously cleaned in mortar grounded with a pestle. After completion of the reaction, as confirmed by TLC, the reaction mixture is further processed according to the above procedure to get pure product.

4.5. General Procedure for Microwave Assisted Vilsmeier-Haack Synthesis of Nitro Arenes under Solvent Free Conditions

A centimolar (0.01 mol) organic substrate (phenols, ani-

lines), 0.01 moles of KNO_3 or NaNO_2 and about 0.015 moles 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 microwave oven (CEM-908010, bench mate model, 300W laboratory microwave reactor). After completion of the reaction, as checked by TLC, the reaction mixture is treated with 5% sodium thiosulphate solution, followed by the same procedure as detailed above to get pure product.

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