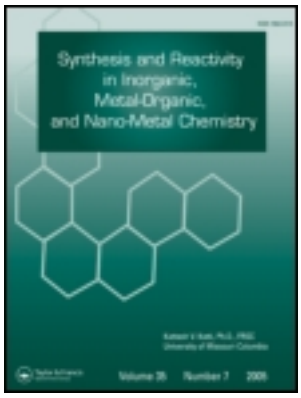

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Oxalylchloride/DMF as an Efficient Reagent for Nitration of Aromatic Compounds and Nitro Decarboxylation of Cinnamic Acids in Presence of KNO_3 or $NaNO_2$ Under Conventional and Nonconventional Conditions

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Oxalylchloride/DMF as an Efficient Reagent for Nitration of Aromatic Compounds and Nitro Decarboxylation of Cinnamic Acids in Presence of KNO_3 or $NaNO_2$ Under Conventional and Nonconventional Conditions

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Nitration of aromatic compounds and cinnamic acids with oxalylchloride/DMF afforded the corresponding nitro derivatives in the presence of KNO_3 or $NaNO_2$ under conventional and nonconventional (ultrasonic and microwave) conditions. The present methodology offers several benefits such as excellent yields, simple work-up procedure, and short reaction times. The yields obtained under present methodology are comparable with those obtained from ($POCl_3$/DMF/KNO_3 or $NaNO_2$) and ($SOCl_2$/DMF/KNO_3 or $NaNO_2$) systems followed by shorter reaction times. The reaction times of sonication and microwave conditions are very shorter than those of the conventional conditions.

Keywords aromatic compounds, cinnamic acids, microwave, nitration, oxalylchloride, sonication

INTRODUCTION

Nitration is one of the most basic and important industrial processes for the synthesis of nitro products, which are widely used as solvents, pharmaceuticals, and intermediates in the manufacture of synthetic dyestuffs and other chemicals.[1–7] Usually, nitration reactions performed under classical conditions using acid mixture are the cause of environmental concerns arising from the disposal of the large excess of mixed acids (concentrated nitric acid and sulfuric acid) employed in these processes. As a result several methods of nitration were designed, which can minimize acid waste. A perusal of literature also reveals that metal nitrates with one nitrate group (MNO_3) are effective only in presence of acids. More so nitration of phenols also occurred in presence of HNO_3 using of a variety of compounds (e.g., CTAB, TBAB, bentonite clay, $Ac_2O/H_5PMo_{10}V_2O_{40}$, $ZnCl_2$ under ultrasonic conditions, oxychloride complex of Zr or Hf, and KSF, $ClNO_2$, ZSTA, metal nitrate/TFA, N_2O_5, and $AcONO_2$) as catalysts.[8–17] For the past few years we have been searching for a more practical process for the nitration phenols using stoichiometric or a small excess amount of nitric acid under mild conditions because the development of environmentally friendly practical procedures for the nitration of aromatic compounds is highly desirable. The mechanism of nitration depends on the nature of bonding between nitrate and substrate. Many methods have been reported by using metal nitrates or nitrites as source of nitronium ion under mild acidic or neutral conditions.[18] In another report it was mentioned that a mixture of $AgNO_3/BF_3$ in acetonitrile could also be employed as an effective nitrating agent. Nitrations with this reagent system are homogeneous, and the silver salt can be recovered as $AgBF_4$.[19] Sulfuric acid on silica-gel has also been used as an inexpensive catalyst for aromatic nitration.[20] But the nitration procedure involved in this protocol contains 70% nitric acid and isopropyl nitrate in addition to solid acidic catalyst. Although it has been shown that these reagents are efficient and selective nitrating systems for phenolic compounds, they are environmentally unfavorable and have other disadvantages including acidic conditions, using unavailable and expensive catalysts or reagents and tedious handling. Recent publications of Jayaprakash Das et al.[21] and several others[22] demonstrated that nitro decarboxylation of α- and β-unsaturated carboxylic acids could be achieved conveniently in solution phase and solvent free conditions with high regioselectivity.

In recent past sonication[23] and microwave irradiation[24] are well known in organic synthesis because their application can enhance the reaction rate, yield, and selectivity of the reactions. Apart from these they can also facilitate reactions under ambient conditions by eliminating requirement of drastic conditions such as temperature, pressure, or concentrations. These reports revealed dramatic rate enhancements followed by significant hike in the yield of products. Encouraged by the striking

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features and applications of ultrasound and microwaves in organic synthesis, coupled with zeal the authors propose to take up nitration of certain aromatic, heteroaromatic compounds and α- and β-unsaturated acids under conventional and nonconventional (US and MW) conditions using a multicomponent reagent oxalyl chloride [$(COCl)_2$]/dimethyl formamide (DMF)/KNO_3 or $NaNO_2$. Recent reports revealed that oxalyl chloride in presence of a small amount of N, N-dimethyl formamide (DMF) forms an iminium salt *in situ*, in the lines of Vilsmeier-Haack reagent (VHR). It is less expensive and operationally simple reagent. Iminium salt thus formed *in situ* generates active nitronium ion.

EXPERIMENTAL

General

All chemicals and solvents purchased from Aldrich (India), Merck (India), Loba (India), and Sd fine (India) were of reagent/AR grade. ^{1}H NMR spectra were recorded at a Varian VNMRS 300, 400, and 500 MHz spectrometer (Palo Alto, CA, USA) with $CDCl_3$. Chemical shifts are reported as values in ppm relative to $CHCl_3$ (7.26) in $CDCl_3$, and TMS was used as internal standard. Mass spectra were recorded on a ZAB-HS mass spectrometer (VG Analytical Ltd., Manchester, UK) using ESI ionization. The instruments used for microwave and ultrasonic reactions were Biotage Initiator + SP Wave model 0.200 W at 2.45 GHz (Sweden), capped at 60 W during steady state (microwave) TCL (BIO-Technics India).

General Procedure for Preparation of $(COCl)_2$+DMF Iminium Salt/Reagent

The previous reagent or adduct is prepared afresh before use from oxalylchloride [$(COCl)_2$] and dimethyl formamide (DMF). To a chilled (at -5°C) solution of oxalylchloride in acetonitrile (MeCN), calculated amount of dimethyl formamide (DMF) was added drop wise, which resulted in slurry indicating the formation of iminium salt. The reagent thus obtained is stored under cold conditions.

General Procedure for Synthesis of Nitro Arenes and β-Nitro Styrenes Under Conventional Conditions Using $(COCl)_2$+DMF Iminium Salt

A centimolar (0.01 mol) organic substrates 0.01 mol of KNO_3 or $NaNO_2$ and about 0.015 mol of $(COCl)_2$+DMF iminium salt

TABLE 1
Comparison study of nitration of certain aromatic compounds under conventional condition using different reagents (yields)

S. No.	Substrate	Product	$SOCl_2$/DMF		$POCl_3$/DMF		$(COCl)_2$/DMF	
			KNO_3	$NaNO_2$	KNO_3	$NaNO_2$	KNO_3	$NaNO_2$
1	Phenol	2-NO_2Phenol	78	74	82	78	85	75
2	*o*-Cresol	2-Me-4-NO_2 Phenol	82	76	84	80	86	83
3	*p*-Cresol	2-NO_2 4-Me Phenol	80	74	80	75	84	82
4	*m*-Cresol	3-Me-4-NO_2 Phenol	76	72	78	72	82	74
5	*o*-Cl Phenol	4-NO_2 2-Cl Phenol	80	75	82	76	84	78
6	*p*-Cl Phenol	2-NO_2 4-Cl Phenol	75	72	78	75	81	79
7	*p*-Br Phenol	2-NO_2 4-Br Phenol	74	70	76	72	80	79
8	*p*-OH Phenol	2-NO_2 Benzene-1,4-diol	80	75	82	78	85	83
9	α-Naphthol	2-NO_2-1-Naphthol	62	58	64	60	74	67
10	β-Naphthol	1-NO_2-2-Naphthol	66	60	60	58	70	68
11	Aniline	4-NO_2-Aniline	75	70	78	72	83	76
12	Benzaldehyde	3-NO_2-Benzaldehyde	76	72	78	72	82	80
13	3-OH-acetophenone	3-OH-4-NO_2-acetophenone	75	70	78	70	81	76
14	4-NH_2-Phenol	4-NH_2-2-NO_2-Phenol	76	72	78	74	82	80
15	4-Cl-Benzaldehyde	4-Cl-3-NO_2-benzaldehyde	62	58	64	60	74	72
16	2-OH Benzaldehyde	2-OH-5-NO_2-benzaldehyde	72	65	75	70	79	77
17	4-OH Benzaldehyde	4-OH-3-NO_2-benzaldehyde	70	62	70	68	78	76
18	Benzoic acid	3-NO_2-benzoic acid	80	75	82	78	85	82
19	Furan	2-NO_2furan	62	58	64	60	78	76
20	Thiophene	2-NO_2thiophene	75	72	78	75	82	79
21	5-methoxy pyridine-2-carboxylic acid	5-methoxy-6-nitropyridine-2-carboxylic acid	74	70	76	72	83	77
22	methyl 2-(5-methoxypyridin-2-yl)acetate	methyl 2-(5-methoxy-6-nitropyridin-2-yl)acetate	80	75	82	78	85	83

Reaction times: 14–16 h ($SOCl_2$/DMF); 13–15 h ($POCl_3$/DMF); 6–8 h [$(COCl)_2$/DMF)].

TABLE 2
Comparison study of nitration of certain cinnamic acids (CA) under conventional condition using different reagents (yields)

S. No.	Cinnamic acids (CA)	Product	$SOCl_2$/DMF		$POCl_3$/DMF		$(COCl)_2$/DMF	
			KNO_3	$NaNO_2$	KNO_3	$NaNO_2$	KNO_3	$NaNO_2$
1	CA	β-NO_2 styrene	74	72	78	75	80	75
2	4-Cl CA	4-Cl β-NO_2 styrene	64	60	72	70	75	72
3	4-OMe CA	4-OCH_3 β-NO_2 Styrene	75	72	80	76	80	75
4	4-Me CA	4-Me β-NO_2 Styrene	72	70	74	72	76	74
5	4-NO_2 CA	4-NO_2 β-NO_2 styrene	60	56	64	60	68	65
6	4-OH CA	4-OH β- NO_2 styrene	76	74	80	75	80	76
7	AA	1–NO_2 Ethene	65	60	68	62	70	65
8	CRA	1–NO_2 Propene	66	62	65	62	72	66
9	2-Me CA	2-Me β-NO_2 styrene	70	64	70	65	75	70
10	2-Cl CA	4-Cl β-NO_2 styrene	62	56	65	60	72	65

Reaction times: 14–16 h ($SOCl_2$/DMF); 12–15 h ($POCl_3$/DMF); 6–8 h [$(COCl)_2$/DMF)].

and solvent (MeCN) were taken in a previously cleaned in a round-bottom flask and stirred for about 6–8 h at room temperature. After completion of the reaction, as confirmed by TLC, the reaction mixture is treated with 5% sodium thiosulfate 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. In case of aromatic compounds nitro aromatic derivatives were obtained while the reactions afforded β-nitro styrenes with cinnamic acids.

General Procedure for Synthesis of Nitro Arenes and β-Nitro Styrenes Using $(COCl)_2$+DMF Iminium Salt (Under Sonication)

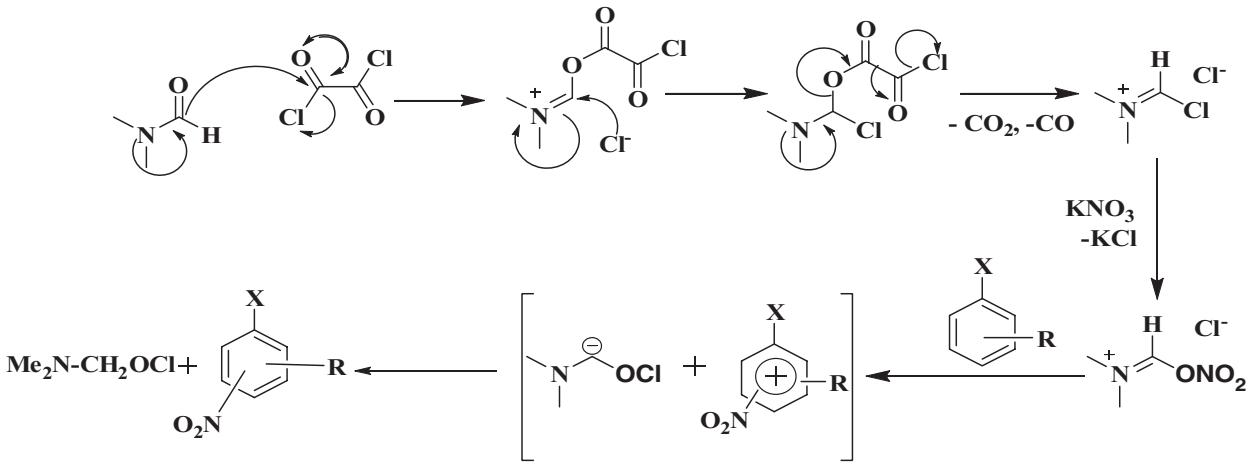
Organic substrate, KNO_3 (or $NaNO_2$), [$(COCl)_2$+DMF] iminium salt, and solvent (MeCN) were taken in a clean conical flask at room temperature and immersed in a sonicator and progress of the reaction monitored by TLC. After completion, the reaction mixture is further processed for the isolation of product as detailed in earlier section.

General Procedure for Microwave Assisted Synthesis of Nitro Arenes and β-Nitro Styrenes Using $(COCl)_2$+DMF Iminium Salt Under Solvent-Free Conditions

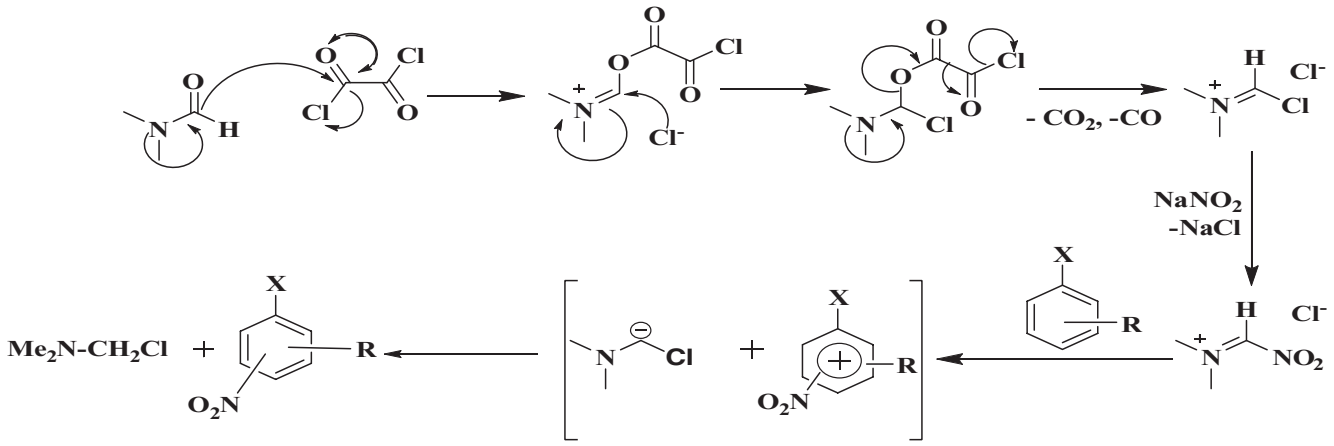
Organic substrate, KNO_3 (or $NaNO_2$), $(COCl)_2$+DMF iminium salt, and the resulting reaction mixture was heated in a controlled microwave synthesizer (Biotage Initiator + SP Wave model 0.200 W at 2.45 GHz, capped at 60 W during steady state) for 5 min (attains temperature 100°C and 2 bar pressure) and progress of the reaction was monitored by TLC. After completion, the reaction mixture is further processed for the isolation of product as detailed in earlier section.

RESULTS AND DISCUSSION

In our recent publication, we developed a general methodology[25] comprising Vilsmeier-Haack reagent[26] [($POCl_3$ or



SCH. 1. Mechanism of nitration of aromatic compound with KNO_3 in presence of oxalylchloride/DMF.

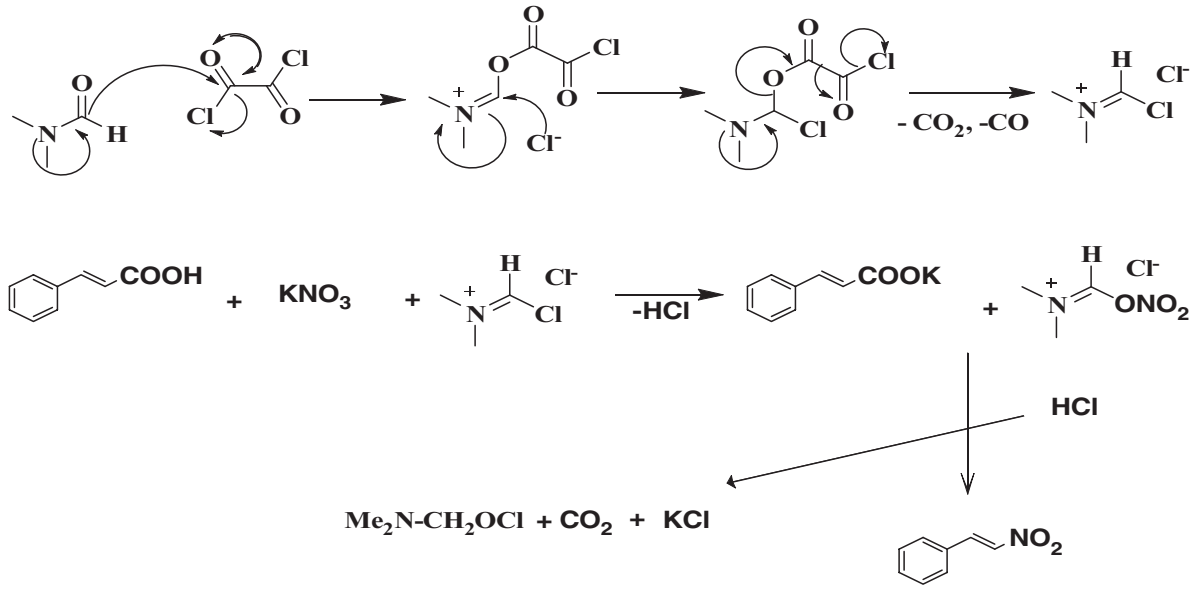


SCH. 2. Mechanism of nitration of aromatic compound with $NaNO_2$ in presence of oxalylchloride/DMF.

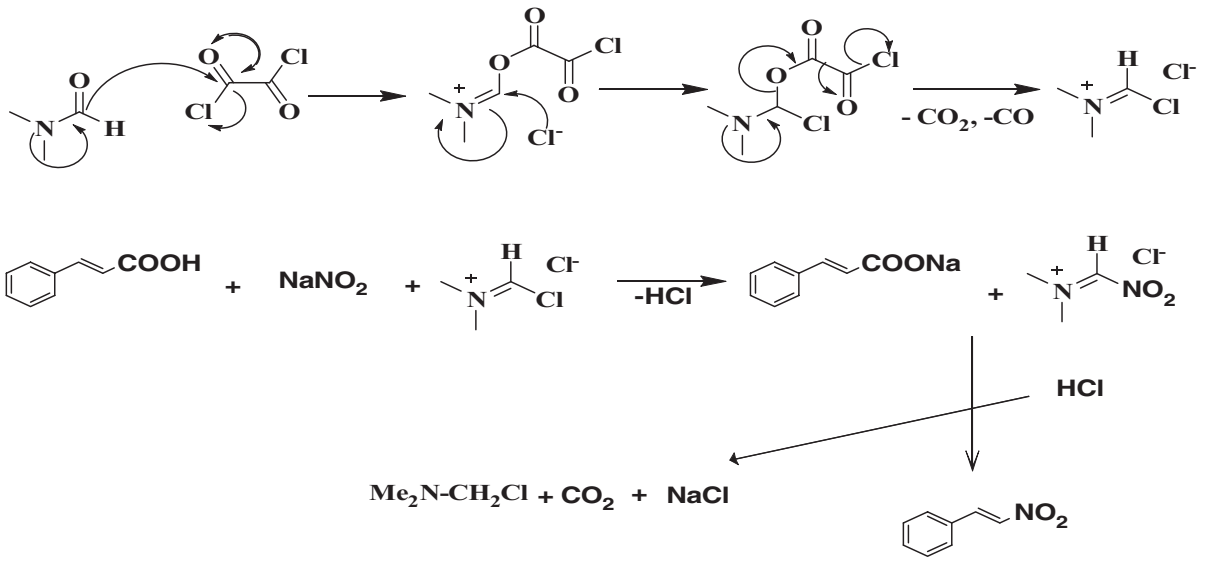
$SOCl_2$)/dimethyl formamide (DMF)] and (KNO_3 or $NaNO_2$) for the synthesis of nitroaromatic compounds and β-Nitro styrenes. Reactions were sluggish with these reagents under conventional conditions. Therefore, a modification is required to enhance the rate of the reaction. Rate of the reaction depends on the ease of *in situ* generation of nitro group due to electrophilic reaction between iminium salt (obtained from the DMF and $POCl_3$ or $SOCl_2$ reagent) and nitrate or nitrite. Recent reports showed that (oxalylchloride/DMF)[27] is better formylating agent than ($POCl_3$/DMF) or ($SOCl_2$/DMF) because the replacement of $POCl_3$ or $SOCl_2$ with oxalylchloride [$(COCl)_2$][28] in reagent enhances the rate of formation of such iminium salt. In this part of the work nitration of aromatic compounds and cinnamic acids were studied using multicomponent reagent (oxalylchloride/DMF/KNO_3 or $NaNO_2$) in acetonitrile medium. The reactions afforded corresponding nitro compounds with excellent yields and shorter reaction times. Results obtained in the present study are compared with DMF/$POCl_3$ and DMF/$SOCl_2$ systems (Tables 1 and 2).

Mechanism of nitration with KNO_3/$NaNO_2$ in the present study could be explained due the *in situ* generation of nitro methyliminium ion due to the reaction of KNO_3/$NaNO_2$ with chloro methyliminium ion intermediate as shown in Schemes 1–4. Nitro methyliminium ion thus produced interacts with substrates and affords nitro aromatics and β-nitro styrenes as the main products.

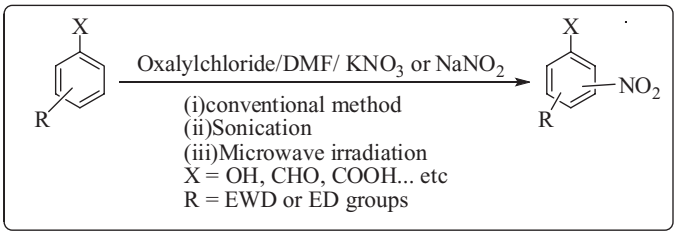
In order to check the generality of the reaction an array of aromatic compounds and Cinnamic acids were used as substrates



SCH. 3. Mechanism of nitro decarboxylation of cinnamic acid with KNO_3 in presence of oxalylchloride/DMF.



SCH. 4. Mechanism of nitro decarboxylation of cinnamic acid with $NaNO_2$ in presence of oxalylchloride/DMF.

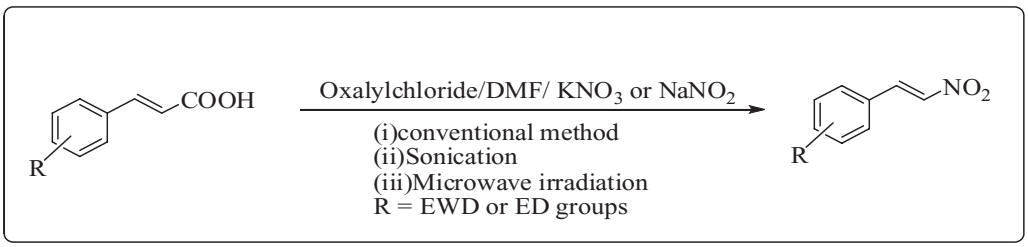


SCH. 5. Nitration of aromatic compounds in presence of oxalylchloride/DMF using KNO_3 or $NaNO_2$.

as shown in Schemes 5 and 6. The reaction rapidly afforded high yields of the corresponding nitro compounds. All the products were characterized and compared with authentic samples. When aromatic compounds were reacted with [$(COCl)_2$+DMF] iminium salt in the presence of KNO_3 or $NaNO_2$, the reaction indicated corresponding nitro derivatives**,** while the reactions afforded β-nitro styrenes with cinnamic acids and data summarized in Tables 3 and 4. It is interesting to note that the reaction times under conventional stirred conditions are long even though the yields are fairly appreciative. However, the reaction times decreased substantially and rate enhancements were observed in the case of nonconventional conditions.

Nonconventional (USA and MWA) Methods

The results obtained from conventional method (Table 1), we focused our attention on nonconventional methods such as ultrasonic and microwave assisted reactions to increase the productivity. Even though the concept of chemical ultrasonics is introduced in 1927, its applications in chemical sciences have been reported only in the past three decades. Gradually it received the attention of chemists all over the world and emerged as a specific branch, namely sonochemistry. Sonochemical technology is capable of enhancing radical formation, improving mass transport, and affecting surface activity[23] have demonstrated that ultrasonic irradiations not only accelerate chemical reactions, but also promote new systems and also reduce the number of steps which are generally required for normal reactions.[29] Observed rate accelerations (Table 2) in ultrasonically assisted reactions are based on the effects resulting from the collapse of acoustic cavitation bubbles that generate regions of extremely high local temperature and pressure.[29] This can cause homogeneous ruptures of covalent bonds and result in



SCH. 6. Oxalylchloride/DMF mediated nitro decarboxylation of cinnamic acids in presence of KNO_3 or $NaNO_2$.

TABLE 3
Nitration of certain aromatic compounds under different conditions using $COCl)_2$/DMF (yields)

S. No.	Substrate	Product	Conventional		Sonication		Microwave	
			KNO_3	$NaNO_2$	KNO_3	$NaNO_2$	KNO_3	$NaNO_2$
1	Phenol	2-NO_2Phenol	85	75	86	80	89	85
2	*o*-Cresol	2-Me-4-NO_2 Phenol	86	83	88	84	93	85
3	*p*-Cresol	2-NO_2 4-Me Phenol	84	82	87	83	90	86
4	*m*-Cresol	3-Me-4-NO_2 Phenol	82	74	87	87	92	84
5	*o*-Cl Phenol	4-NO_2 2-Cl Phenol	84	78	88	87	94	82
6	*p*-Cl Phenol	2-NO_2 4-Cl Phenol	81	79	85	81	91	83
7	*p*-Br Phenol	2-NO_2 4-Br Phenol	80	79	85	80	90	83
8	*p*-OH Phenol	2-NO_2 Benzene-1,4-diol	85	83	87	84	95	85
9	α-Naphthol	2-NO_2-1-Naphthol	74	67	84	77	94	87
10	β-Naphthol	1-NO_2-2-Naphthol	70	68	87	85	90	88
11	Aniline	4-NO_2-Aniline	83	76	86	77	93	86
12	Benzaldehyde	3-NO_2-Benzaldehyde	82	80	86	82	92	86
13	3-OH-acetophenone	3-OH-4-NO_2-acetophenone	81	76	82	80	91	86
14	4-NH_2-Phenol	4-NH_2-2-NO_2-Phenol	82	80	84	82	92	90
15	4-Cl-Benzaldehyde	4-Cl-3-NO_2-benzaldehyde	74	72	76	74	83	82
16	2-OH Benzaldehyde	2-OH-5-NO_2-benzaldehyde	79	77	83	80	89	85
17	4-OH Benzaldehyde	4-OH-3-NO_2-benzaldehyde	78	76	81	87	88	86
18	Benzoic acid	3-NO2-benzoic acid	85	82	87	84	95	88
19	Furan	2-NO_2furan	78	76	82	78	88	79
20	Thiophene	2-NO_2thiophene	82	79	84	82	88	85
21	5-methoxy pyridine-2-carboxylic acid	5-methoxy-6-nitropyridine-2-carboxylic acid	83	77	85	79	89	87
22	methyl 2-(5-methoxypyridin-2-yl)acetate	methyl 2-(5-methoxy-6-nitropyridin-2-yl)acetate	85	83	86	84	89	85

Reaction times: 6–8 h (conventional method); 30–40 min (sonication); 2–3 min (MWI).

the formation of radicals that can enter into a great variety of reactions.[29] It is also reported that sonochemical effects are frequency dependent because variation of frequency can influence the collapse time and hence the size of the bubbles.[30]

Microwave-assisted organic synthesis has proven to be a valuable tool for the efficient synthesis of organic compounds with biological activities.[31,32]. Many reviews have been published recently, which detailed its utility.[33] In MWA systems,

TABLE 4
Nitration of certain cinnamic acids (CA) under different conditions using $COCl)_2$/DMF (yields)

S. No.	Cinnamic acids (CA)	Product	Conventional		Sonication		Microwave	
			KNO_3	$NaNO_2$	KNO_3	KNO_3	$NaNO_2$	KNO_3
1	CA	β-NO_2 styrene	80	75	82	78	80	76
2	4-Cl CA	4-Cl β-NO_2 styrene	75	72	78	72	80	75
3	4-OMe CA	4-OCH_3 β-NO_2 Styrene	80	75	85	76	82	75
4	4-Me CA	4-Me β-NO_2 Styrene	76	74	80	78	78	75
5	4-NO_2 CA	4- NO_2 β-NO_2 styrene	68	65	72	68	70	68
6	4-OH CA	4-OH β-NO_2 styrene	80	76	82	78	80	75
7	AA	1–NO_2 Ethene	70	65	75	70	75	72
8	CRA	1–NO_2 Propene	72	66	76	70	74	70
9	2-Me CA	2-Me β-NO_2 styrene	75	70	76	70	72	68
10	2-Cl CA	4-Cl β-NO_2 styrene	72	65	75	70	75	72

Reaction times: 6–8 h (conventional method); 40–60 min (sonication); 2–3 min (MWI).

reaction times are reduced from several hours to only 2–3 min accompanied by yield enhancements (Table 2). The ability to rapidly heat reactions significantly above the boiling point of the solvent has resulted in dramatic decreases in reaction times and increases in reaction yields for a variety of chemical transformations.[34,35]

CONCLUSION

In this proposed protocol, we developed iminium salt (oxalylchloride/DMF) mediated nitration reaction of aromatic compounds and nitro decarboxylation of cinnamic acids under sonication and microwave irradiation. Microwave and ultrasonically assisted reactions not only reduced the reaction times remarkably but also enhanced the yield of products from good to excellent as compared to those of normal protocol. The presently developed work is more advantageous because the reactions are conducted with economically cheap and readily available reagents.

REFERENCES

1. Anastas, P.T.; Warner, J.C. *Green Chemistry: Theory and Practice*; Oxford University Press, Oxford, England, **1999**.
2. Olah, G.A.; Malhotra, R.; Narang, S.C. *Nitration: Methods and Mechanism*, Feuer, H. editor. VCH, New York, **1989**.
3. Ingold, C.K. *Structure and Mechanism in Organic Chemistry,* 2nd edn.; Cornell University Press, Ithaca, New York, **1969**.
4. Olah, G.A.; Kuhn, S.J. In *Friedel-Crafts and Related Reactions*, Olah, G.A. editor. Wiley-Interscience, New York, **1964**; Vol. 2.
5. Olah, G.A.; Narang, S.C.; Olah, J.A.; Lammertsma, K. *Proc. Natl. Acad. Sci.* **1982**, 4487.
6. Thompson, M.J.; Zeeger, P.J. *Tetrahedron* **1991**, *47*, 8787.
7. Bisarya, S.C.; Joshi, S.K.; Holker, A.G. *Synth. Commun.* **1993**, *8*, 1125.
8. Yang, G.S.; Shi, J.; Li, J. *Korean J. Chem. Eng.* **2003**, *20*, 886.
9. Joshi, A.V.; Baidoosi; Mukhopadhyay, S.; Sasson, Y. *Org. Proc. Res. Dev.* **2003**, *7*, 95.
10. Bahulayan, D.; Narayan, G.; Sreekumar, V.; Lalithambika, M. *Synth. Commun.* **2002**, *32*, 3565.
11. Heravi, M.M.; Bakhtiari, K.; Benmorad, T.; Bamoharram, F.F.; Oskooie, H.A.; Tehrani, M.H. *Monatsh. Chem.* **2007**, *138*, 449.
12. Kamal, A.; Kumar, B.A.; Arifuddin, M.; Patrick, M. *Ultrasonics Sonochem.* **2004**, *11*, 455.
13. Shi, M.; Cui, S.C.; Yin, W.P. *Eur. J. Org. Chem.* **2005**, 2379.
14. Heal, M.R.; Harrison, M.A.J.; Cape, J.N. *Atmosph. Environ.* **2007**, *41*, 3515.
15. Mallick, S.; Parida, K.M. *Catal. Commun.* **2007**, *8*, 1487.
16. Munawar, M.A.; Khalid, M. *J. Chem Soc.* **2004**, *26*, 4.
17. Rodrigues, J.A.R.; de Oliveira Fiho, A.P.; Moran, P.J.S.; Custodio, R. *Tetrahedron* **1999**, *55*, 6733.
18. (a) 18 Rajanna, K.C.; Abdulla; Amina, S.; Arun Kumar, Y.; Arifuddin, M. *Synth. Comm.* **2011**, *41*, 2946–2951. (b) Rajanna, K.C.; Moazzam Ali; Sana, S.; Saiprakash, P.K. *Chemistry Letters*, **2000**, *29*, 48–49. (c) Ramgopal, S.; Ramesh, K.; Chakradhar, A.; Maasi Reddy, N.; Rajanna, K.C. *Tetrahedron Lett.* **2007**, *48*, 4043–4045.
19. Olah, G.A.; Fung, A.P.; Narang, S.C.; Olah, J.A. *J. Org. Chem.* **1981**, *46*, 3533.
20. Joan, M.; Riego, Z.; Sedin, J.; Zaldivar, M.; Nunziata, C.; Marzianot, C.T. *Tetrahedron Lett.* **1996**, *37*, 513.
21. Das, J.P.; Sinha, P.; Roy, S. A nitro-Hunsdiecker reaction: from unsaturated carboxylic acids to nitrostryrenes and nitroarenes. *Org. Lett.* **2002**, *4*, 3055–3048.
22. (a) Ramgopal, S.; Ramesh, K.; Chakradhar, A.; Reddy, N.M.; Rajanna, K.C. Metal nitrate driven nitro Hunsdiecker reaction with α, β-unsaturated carboxylic acids under solvent-free conditions. *Tetrahedron Lett.* **2007**, *48*, 4043–4045. (b) Satish Kumar, M.; Venkanna, P.; Ramgopal, S.; Ramesh, K.; Venkateswarlu, M.; Rajanna, K.C. *Org. Commun.* **2012**, *5*(*2*): 42–49. (c) Anna, M.; Alessandra, G.; Isidoro, G.; Fabio, T.; Benedetto, D.B.; Antonio, F. *Syn. Com.* **2004**, *34*, 3317–3324.
23. (a) Mason, T.J. *Chemistry with ultrasound*, Elsevier Science Publishers Ltd., England, **1990**; (b) Mason, T.J.; Peters, D. *Practical Sono-Chemistry: Power Ultrasound Uses and Applications,* 2nd edn.; Horwood, Cambridge, England, **2003**. (c) Suslick, K.S. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH, London, **1988**. (d) Margulis, M.A. *Advances in Sonochemistry*, Mason, T.J., editor. Greenwich, London, **1990**; 1, 49.
24. (a) Chaouchi, M.; Loupy, A.; Marque, S.; Petit, A. *Eur. J. Org. Chem.* **2002**, 1278. (b) Gedye, R.N.; Smith, F.E.; Westaway, K.C. *Can. J. Chem.* **1988**, *66*, 17. (c) Loupy, A.; Perreux, L.; Liagre, M.; Burle, K.; Moneuse, M. *Pure Appl. Chem.* **2001**, *73*, 161.
25. Rajanna, K.C.; Satish Kumar, M.; Venkanna, P.; Ramgopal, S.; Venkateswarlu, M. *Int. J. Org Chem.* **2011**, *4*, 250–256.
26. Vilsmeier, A.; Haack, A. *Ber.* **1927**, *60*, 119.
27. (a) Barnett, G.H.; Anderson, H.J.; Loader, C.E. *Can. J. Chem.* **1980**, *58*, 409. (b) Salmon, R. *Encyclopedia of Reagents for Organic Synthesis*. Wiley, New York, **2001**.
28. Al'bina, I.; Mikhaleva, A.V.; Ivanov, E.V.; Skital'tseva, I.A.; Ushakov, A.M.; Vasil'tsov, B.A.T. *Synthesis* **2009**, *4*, 587–590.
29. (a) Mason, T.J. Applied sonochemistry. In: *Kirk-Othmer Encyclopedia of Chemical Technology*, Kroschwitz, J.I.; Howe-Grant, M.; editors. Wiley, New York, **1991**. (b) Mason, T.J. *Practical Sonochemistry: User's Guide to Applications in Chemistry and Chemical Engineering, Ellis Horwood Series in Organic Chemistry*; Horwood, New York, **1991**.
30. Mason, T.J.; Cobley, A.J.; Graves, J.E.; Morgan, D. *Ultrason. Sonochem.* **2011**, *18*, 226.
31. Lew, A.; Krutzik, P.O.; Hart, M.E.; Chamberlin, A.R. *J. Comb. Chem.* **2002**, *4*, 95.
32. Kaddar, H.; Hamelin, J.; Benhaoua, H. *J. Chem. Res.* **1999**, 718.
33. (a) Perreux, L.; Loupy, A. *Tetrahedron.* **2001**, *57*, 9199. (b) Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron.* **2001**, *57*, 9225.
34. Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathe, D. *Synthesis* **1998**, 1213.
35. Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J.L.; Petit, A. *Tetrahedron* **1999**, *55*, 10851.