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To cite this article: Manabendra Saha , Sanchita Roy , Subrata Kumar Chaudhuri & Sanjay Bhar (2008) Microwave-assisted ammonium formate-mediated Knoevenagel reaction under solvent-free conditions – a green method for C–C bond formation, Green Chemistry Letters and Reviews, 1:2, 113-121, DOI: [10.1080/17518250802141200](https://doi.org/10.1080/17518250802141200)

To link to this article: <https://doi.org/10.1080/17518250802141200>



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Published online: 09 Sep 2008.



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ORIGINAL ARTICLE

Microwave-assisted ammonium formate-mediated Knoevenagel reaction under solvent-free conditions – a green method for C–C bond formation

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(Received 4 August 2007; revised 7 April 2008; final form 18 April 2008)

Syntheses of structurally varied densely functionalized olefins have been accomplished (23 examples) through microwave-assisted ammonium formate-mediated Knoevenagel condensation of differently substituted aromatic aldehydes with ethyl cyanoacetate, cyanoacetamide, malononitrile, and malonic acid under solvent-free condition in good yield (76–95%) and high purity. The said reactions occur within very short period of time (0.75–3 min) in eco-friendly conditions involving an operationally simple procedure, eliminating any kind of inorganic support, toxic reagent and organic solvent.

Keywords: alkenes; ammonium salts; microwave heating; solvent-free reaction; solid-phase synthesis

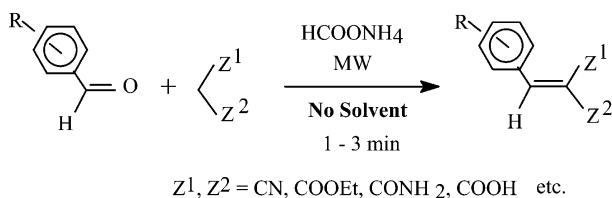
Introduction

Knoevenagel reaction (1) is an important reaction for C–C bond formation and finds immense applications as synthetic intermediates for fine chemicals (2) and bioactive molecules (3). Numerous catalysts have been developed for this important reaction including Lewis bases (4a) like pyrrolidine, piperidine or sodium ethoxide, Lewis acids like Zn(II) (4b) and Bi(III) (4c) chloride, Lewis acid–Lewis base combination, namely, TiCl₄/pyridine (4d) in THF, inorganic support like aluminum oxide (4e) and zeolite (4f), oxidants (potassium tribromide (4g), functionalized silica gel (4h), IR-mediated Tonsil Actisil FF-promoted heterogeneous phase (4i), N,N'-dialkylimidazolium ionic liquids in combination with glycine (4j) and many others. However, many of the aforesaid protocols involve the use of costly as well as toxic reagents and organic solvents, complicated experimental set-up and inorganic supports causing disposal problems. In view of the recent issues of “Chemical Safety” (5) regarding exposure, contamination, storage and disposal of chemical substances relating to a chemical process, development of organic reactions under solvent-free conditions (6) have emerged as an important theme with utmost contemporary interest. Specially, it has often been observed that the solvent-free organic reactions, besides experimental simplicity (7) and eco-friendliness, are enormously accelerated (8) and furnish the products with improved yield (6) and better selectivity (6) compared to the analogous homoge-

neous reactions in various organic solvents. Solvent-free organic reactions under microwave irradiation (9) have also drawn much attention in recent times due to various advantages in terms of rate acceleration and energy economy. In the pursuit to develop eco-friendly Knoevenagel reactions (10) a comparative study (10a)¹ of the said reaction in ethanol, water and dry-grind approach has come out in the literature. However, this study involves toxic piperidine as one of the reagents and the substrates are limited to aryl-substituted cyanoacetamides. Moreover, some of the aforesaid methods are operative on the surface of basic alumina (10c) or silica gel (10e), even with ammonium acetate (10f), although in dry media during the reaction, involves toxic organic solvents during the product isolation thereby reducing the greenness of the said processes. In addition, the disposal of the leftover solid waste becomes problematic. More important to note is the limited applicability of the said protocols as they are confined with a particular type of donors, namely, cyanoacetamide (10a), malonic acid (10c, 10d), malononitrile (10e) or ethyl cyanoacetate (10f) and often different products (10c, 10d) are obtained from different methods using the same donor. So there is a continuous need for the development of a general methodology for this important transformation applicable to different types of substrates accommodating a variety of substitution patterns under economically viable and environmentally benign conditions. Recently ammonium salts, e.g. ammonium formate (11) has found applications in some organic

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reactions (hydrogen donor in transfer hydrogenation (11a) and as a one-carbon donor (11b) in the synthesis of various heterocyclic skeletons) as a safe and less toxic alternative of various reagents. But its use for Knoevenagel reaction is not reported till date to the best of our knowledge.² In the course of our endeavor (12) to develop new eco-friendly methods for important organic transformations we report herein a simple and efficient protocol for microwave-assisted ammonium formate-mediated Knoevenagel condensation under solvent-free conditions without using any kind of inorganic support (Scheme 1).



Scheme 1.

Results and discussion

A mixture of equimolecular amounts of aldehyde, active methylene compound and dry ammonium formate was irradiated in microwave for the stipulated period of time (0.75–3 min) in the absence of any organic solvent and the product was isolated by adding crushed ice to the reaction and subsequent filtration. The general procedure of the experiment is operationally very simple. Detailed results have been shown in Table 1.

As shown in Table 1, several aldehydes having different reactivities due to bearing a wide range of substituents underwent smooth Knoevenagel condensation with a variety of donors, namely, ethyl cyanoacetate, cyanoacetamide, malononitrile and malonic acid to give differently functionalized olefins within very short time (0.75–3 min) in very good yield and purity. The products of this reaction serve as important intermediates for the synthesis of complex molecular skeletons through Michael reaction and cycloaddition owing to their attributes as electrophilic olefins to behave as Michael acceptors and dienophile. It is very important to note that especially the deactivated aldehydes with electron-donating substituents (entries (3, 4, 6, 10, 12, 13, 14, 17, 18, 19, 21, and 22 in Table 1) react extremely well with a variety of donors under the present ammonium formate-mediated reaction within much less period of time (1–2 min) compared to many analogous reactions taking much longer time (4,10) (minutes

to hours) to be complete. This reduces energy consumption as well as mitigating energy dissipation. Acid labile groups like methylenedioxy also survived during the said reaction (entries 10 and 22). Relatively unreactive aryl alkyl ketone has been found to react with a more reactive donor, namely, malononitrile, to give the product in good yield (86% conversion by ¹H-NMR, isolated yield 74%) within a very short period of time (entry 20). Thermally labile aldehydes, like α,β -unsaturated aldehyde (entries 7 and 15 and heteroaryl aldehyde (entries 9 and 16) also responded very efficiently, yields are a little less in the case of heteroaryl aldehyde due to the formation of some by-products owing to little decomposition during the reaction. Aliphatic aldehyde remained inert under the said reaction condition. The aforesaid reactions did not take place in the absence of ammonium formate.

The most important attribute of the present protocol is the complete elimination of organic solvent in the reaction medium as well as during product isolation. We have observed that the microwave-mediated analogous procedure (10f) using ammonium acetate needs a much longer time (8–15 min of continuous exposure) for completion of reaction, causing substantial decomposition due to excessive absorption of microwave energy. This causes the formation of a gummy material after the reaction due to contamination with various unidentified side-products, wherefrom the isolation of pure product is very cumbersome and needs repetitive treatment with various organic solvents. Therefore, efficacy and greenness of that process (10f) are significantly reduced. During the present ammonium formate-mediated procedure, formation of the by-products is minimum. This is due to very little exposure of the reaction mixture to the microwave.

After the completion of the reaction, the products are isolated in practically pure form simply by adding crushed ice to the reaction mixture followed by filtration of the solidified granular material from the aqueous medium. Moreover, in contrast to many reported protocols (4e, 4f, 4h–4j, 10c, 10e), the present method completely does away with the use of any inorganic support. So, the question of the involvement of organic solvents during product isolation from the support does not arise. The use of toxic organic solvent is therefore totally eliminated. In addition, one can thus get rid of the problems of the disposal of the leftover inorganic support.

Ammonium formate is needed in stoichiometric amount and this can be recovered by recrystallization from the aqueous filtrate left after product isolation. Moreover, ammonium formate is known to be much

Table 1. Ammonium formate-mediated microwave-assisted solvent-free Knoevenagel reaction.

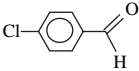

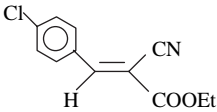
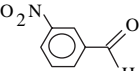

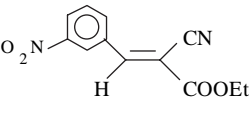
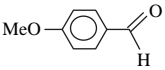

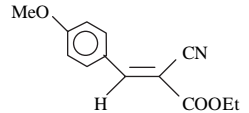
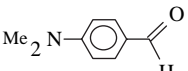

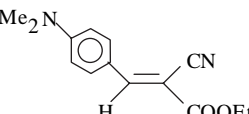
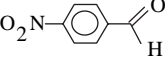

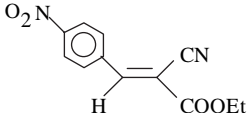
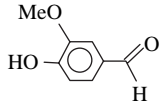

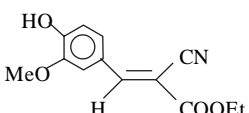
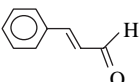

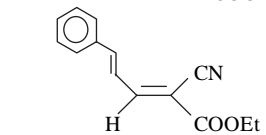
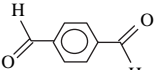

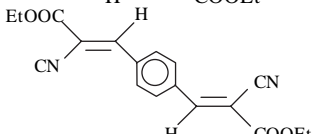
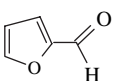

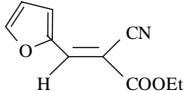
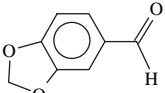

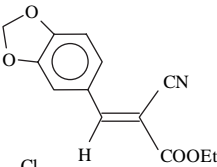
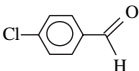

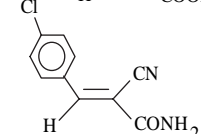
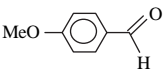

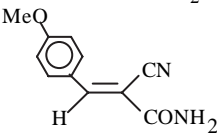
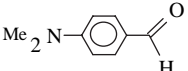

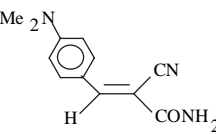
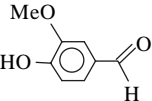

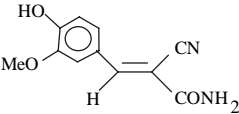
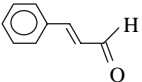

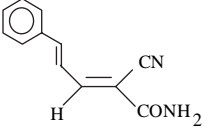
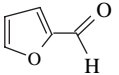

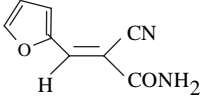
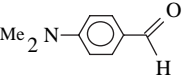

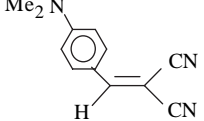
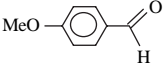

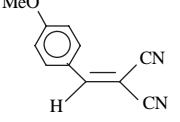
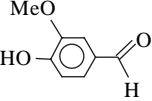

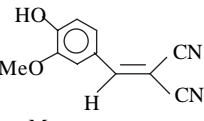
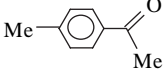

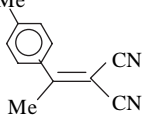
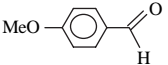

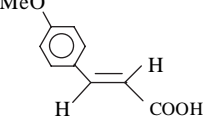
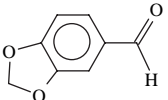

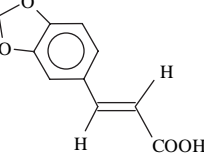
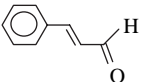

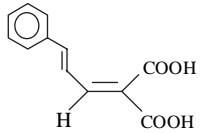
| Entry | Aldehyde | Nucleophile | Product | Time (min) | Yield ^a (%) |
|-------|---|---|--|------------|------------------------|
| 1 |  |  |  | 1.0 | 90 (4d, 4h) |
| 2 |  |  |  | 1.5 | 87 (4d, 4e) |
| 3 |  |  |  | 2.0 | 80 (4b, 4d) |
| 4 |  |  |  | 1.5 | 95 (4d, 4i) |
| 5 |  |  |  | 1.5 | 87 (4d, 4i) |
| 6 |  |  |  | 1.5 | 84 (4b, 4h) |
| 7 |  |  |  | 3.0 | 89 (4c, 4g) |
| 8 |  |  |  | 1.0 | 86 (4d) |
| 9 |  |  |  | 0.75 | 76 (4d, 4i) |
| 10 |  |  |  | 1.5 | 88 (10f) |
| 11 |  |  |  | 2.0 | 84 (4b, 4h) |
| 12 |  |  |  | 2.0 | 85 (4i) |
| 13 |  |  |  | 1.5 | 94 (4d, 4i) |

Table 1 (Continued)

| Entry | Aldehyde | Nucleophile | Product | Time (min) | Yield ^a (%) |
|-------|---|---|--|------------|------------------------|
| 14 |  |  |  | 1.5 | 87 (4b, 4e) |
| 15 |  |  |  | 2.0 | 85 (4b, 4e) |
| 16 |  |  |  | 0.75 | 81 (4d, 4i) |
| 17 |  |  |  | 1.0 | 80 (4b, 4e) |
| 18 |  |  |  | 1.0 | 85 (4d, 4h) |
| 19 |  |  |  | 1.0 | 76 (4b, 4e) |
| 20 |  |  |  | 1.0 | 74 ^b |
| 21 |  |  |  | 2.0 | 69 (78 ^c) |
| 22 |  |  |  | 1.0 | 65 (13) |
| 23 |  |  |  | 1.0 | 87 (10d) |

^aYield of isolated pure products fully characterized spectroscopically.^bMp 92°C; IR (KBr) 2225 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 2.42 (3H, s), 2.62 (3H, s), 7.48 (2H, d, *J* = 9.0 Hz), 7.31 (2H, d, *J* = 9.0 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ 21.06, 24.12, 113.08, 113.24, 127.16, 127.85 (2C), 129.82, 128.88 (2C), 133.05, 143.45. Anal. found C 79.33%, H 5.41%, N 15.23%. Calcd for C₁₂H₁₀N₂, C 79.10%, H 5.53%, N 15.37%.^cPercentage (%) of conversion determined by ¹H-NMR (300 MHz) of the crude reaction mixture after treatment with diazomethane, remainder starting material.

less toxic than many of the conventional reagents (4a–4d, 10a). Therefore, the present microwave-assisted ammonium formate-mediated solvent-free protocol has set out to minimize the use of toxic reagents and organic solvents and significantly reduce energy consumption, energy dissipation and dispersal of harmful chemicals in the environment. Therefore, it can be called a relatively GREEN technology. Attempts to carry out the same ammonium formate-mediated reaction in various organic solvents either failed or led to incomplete conversion even after prolonged reflux for 8–10 hours. These observations show the high efficacy of the solvent-free protocols compared to those in solution. No conversion took place using other ammonium salts, like ammonium chloride, ammonium oxalate or ammonium sulfate. In addition, it takes a much longer time (4–6 hours) with ammonium formate under solvent-free conditions if the reaction is carried out thermally (100°C) instead of microwave and that leads to the formation of a considerable amount of unidentified by-products, depleting the yield and purity of the desired products.

In a paper by Kaupp et al. (10g), structurally simple *p*-substituted aryl aldehydes (three with cyanoacetamide and two with methyl cyanoacetate) were studied for Knoevenagel reaction without any solvent and catalyst, where the reactions were carried out at high temperature (150–170°C) for one hour. We have done several reactions of ethyl cyanoacetate and cyanoacetamide with a greater variety of aryl aldehydes bearing different substituents at different locations in our microwave-mediated method and came out with very good results, as evident from Table 1. We also attempted some thermal reactions of ethyl cyanoacetate and cyanoacetamide following the condition of Kaupp et al. (10g), with some thermolabile aldehydes which we have studied in our ammonium formate-mediated microwave condition (entries 7, 9, 10, 15, 16, and 22 in Table 1). After one hour of heating at 150°C we ended up with tarry materials in all cases containing an inseparable mixture of undefined compounds (as shown in thin layer chromatography (TLC) experiments) with indefinite composition. The products in each case of the aforesaid entries in our solvent-free microwave-assisted ammonium formate-mediated method were obtained in good yield and high purity (entries 7, 9, 10, 15, 16, and 22 in Table 1) within much less time than the earlier thermal method (10g). In view of the above-mentioned aspects our method seems to differ from and have greater advantages and wider applicability compared to the method reported by Kaupp et al. (10g). We could minimize the formation of the side-products with vulnerable aldehydes in our

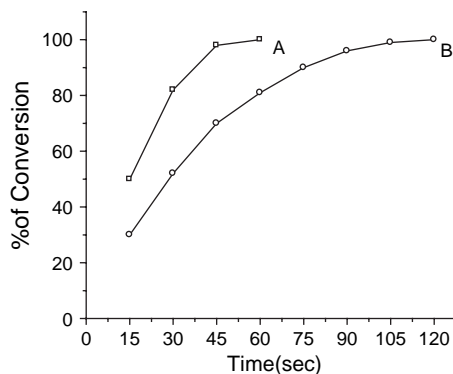


Figure 1. Progress of the microwave-assisted ammonium formate-mediated solvent-free Knoevenagel reactions between (a) ethyl cyanoacetate and *p*-chlorobenzaldehyde and (b) ethyl cyanoacetate and *p*-methoxybenzaldehyde. A: Ammonium formate-mediated reaction of *p*-chlorobenzaldehyde with ethyl cyanoacetate (entry 1 in Table 1). B: Ammonium formate-mediated reaction of *p*-methoxybenzaldehyde with ethyl cyanoacetate (entry 3 in Table 1).

method because the reaction mixture was never exposed to the microwave irradiation continuously. Rather, it was exposed for a short period of time “with an installment of 15 seconds each at a power level of 300 Watts followed by intermittent cooling,” as mentioned in the Experimental section. The progress (measured in terms of percentage (%) of conversion determined by ¹H-NMR analysis of the reaction mixture at different time intervals) of the microwave-assisted ammonium formate-mediated solvent-free Knoevenagel reactions between (i) ethyl cyanoacetate and *p*-chlorobenzaldehyde and (ii) ethyl

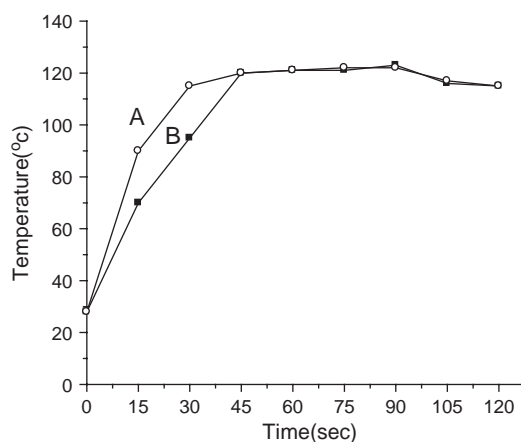


Figure 2. Comparative picture of the temperature profile for two different microwave-assisted ammonium formate-mediated solvent-free Knoevenagel reactions. A: Reaction between *p*-methoxybenzaldehyde with cyanoacetamide (entry 12 in Table 1). B: Reaction between *p*-methoxybenzaldehyde with ethyl cyanoacetate (entry 3 in Table 1).

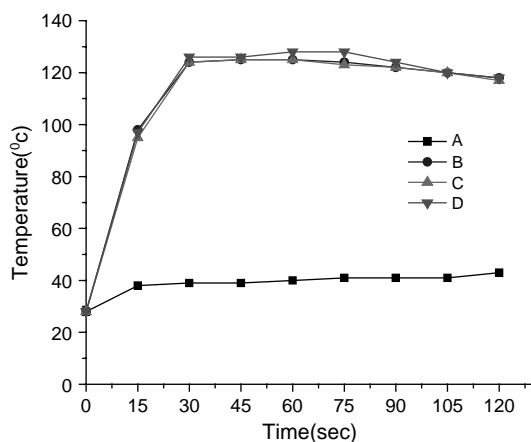


Figure 3. Comparative picture of the temperature rise due to microwave irradiation of the reaction product, reagent, mixture of reagent with product and the actual reaction. A: Temperature profile of the pure product (obtained after the ammonium formate-mediated reaction between *p*-chlorobenzaldehyde and ethyl cyanoacetate (entry 1 in Table 1)) irradiated under microwave. B: Temperature profile of only ammonium formate irradiated under microwave. C: Temperature profile of the binary mixture of ammonium formate and the aforesaid product irradiated under microwave. D: Temperature profile of the ammonium formate-mediated reaction between *p*-chlorobenzaldehyde and ethyl cyanoacetate under microwave irradiation (entry 1 in Table 1).

cyanoacetate and *p*-methoxybenzaldehyde have been shown in Figure 1.

The technique of “intermittent cooling” was applied for two reasons. Firstly, to avoid fluctuation of power level and ensure the exposure to uniform power level operative within the short period of time. Secondly, due to the presence of highly polar ionic reagent (ammonium formate) and gradual accumulation of the polar products with progress of reaction involving polar transition state (*I*), more and more absorption of microwave energy took place causing thermal heating of the reaction mixture (no appreciable heating occurred if the reaction did not proceed at all even after prolonged microwave irradiation, for example, in the absence of ammonium formate). Therefore, it was necessary to cool the reaction mixture intermittently after each 15 seconds of microwave exposure to minimize decomposition of sensitive substrates and products. Representative temperature profiles (two examples) with the progress of the reactions have been shown in Figure 2.

We have observed that ammonium formate, being an ionic species, absorbs microwave energy more rapidly than the Knoevenagel adduct itself (Figure 3). And the temperature profile of the reaction matches with that of ammonium formate itself as well as a

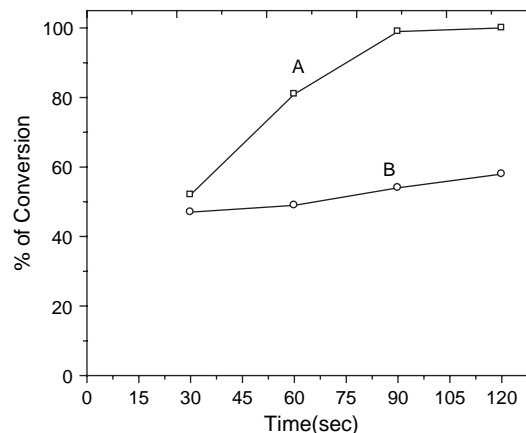


Figure 4. Comparison between ammonium formate and ammonium acetate in microwave-assisted solvent-free Knoevenagel reaction between *p*-methoxybenzaldehyde and ethyl cyanoacetate. A: Ammonium formate-mediated reaction of *p*-methoxybenzaldehyde with ethyl cyanoacetate. B: Ammonium acetate-mediated reaction of *p*-methoxybenzaldehyde with ethyl cyanoacetate.

binary mixture of ammonium formate and Knoevenagel adduct, as evident in Figure 3. The exact reason for this observation is not yet clear but it might be due to more efficient absorption of microwave energy by the ionic reagent, namely, ammonium formate, coupled with the exothermicity of the aforesaid reactions.

The “intermittent cooling” technique was applied to an analogous reaction in the presence of ammonium acetate in place of ammonium formate. The

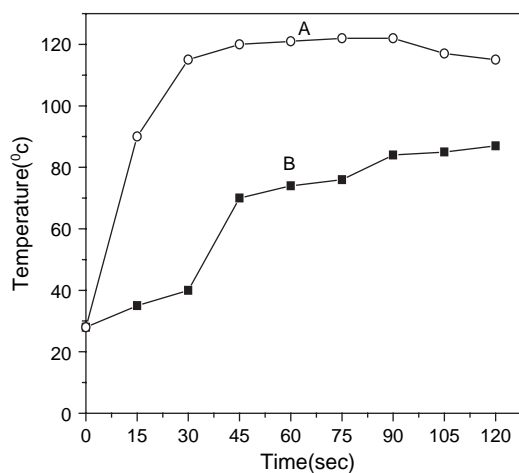


Figure 5. Comparative temperature profile of the ammonium formate-mediated and ammonium acetate-mediated Knoevenagel reaction under microwave irradiation. A: Microwave-mediated reaction between *p*-methoxybenzaldehyde and ethyl cyanoacetate in the presence of ammonium formate. B: Microwave-mediated reaction between *p*-methoxybenzaldehyde and ethyl cyanoacetate in the presence of ammonium acetate.

reaction with ammonium acetate, as discussed earlier, went much slower than that with ammonium formate as evident from Figure 4.

In addition, the temperature profiles for these two reactions are significantly different, as shown in Figure 5.

From the aforesaid observations it seems that the temperature profile for this type of reaction shows consistency with the progress of reaction. This might be due to the relative difference of the exothermicity. It can be roughly correlated with the extent of conversion of the aforesaid reactions. Therefore, the present microwave-assisted ammonium formate-mediated solvent-free protocol for Knoevenagel reaction accommodating a variety of substitution patterns to generate densely functionalized olefins is unique of its kind. It is superior and more utilitarian compared to an analogous method using ammonium acetate in terms of rate (as reflected from the comparative profiles of the progress of reaction in Figure 4), yield, product isolation and purity of the product.

From the comparative picture of the toxicological reports (14) ammonium formate and ammonium acetate seem to possess comparable toxicity. From other available information (14) ammonium formate may cause more irritation on skin contact, ingestion and inhalation compared to ammonium acetate, if taken in excess. However, both the aforesaid reagents do not possess severe toxicity. In the light of the above discussions ammonium acetate might appear to be more commercially acceptable than ammonium formate. However, the present ammonium formate-mediated protocol quite possibly overrides the detriments of using ammonium formate. This procedure is economically attractive and environmentally acceptable in terms of beneficial attributes like improved rate of reaction, higher yield, easier product isolation, simplified purification, reduced consumption of energy and minimized use of toxic organic solvents (in most of the cases, totally eliminated). Ammonium formate-mediated microwave-assisted solvent-free procedure for Knoevenagel reaction described so far thus possesses greater merits, more advantages and wider applicability in comparison to the analogous method using ammonium acetate.

Ammonium formate in this reaction plays its role to provide a combination (1, 4d) of acid and base catalysis. A schematic representation of the plausible reaction pathway has been delineated in Figure 6. Presumably, ammonium formate, under microwave irradiation, reversibly dissociates partly to formic acid and ammonia (as evident from a little smell of ammonia coming out from the reaction mixture during intermittent cooling and appearance of a deep blue material indicative of cuproammonium

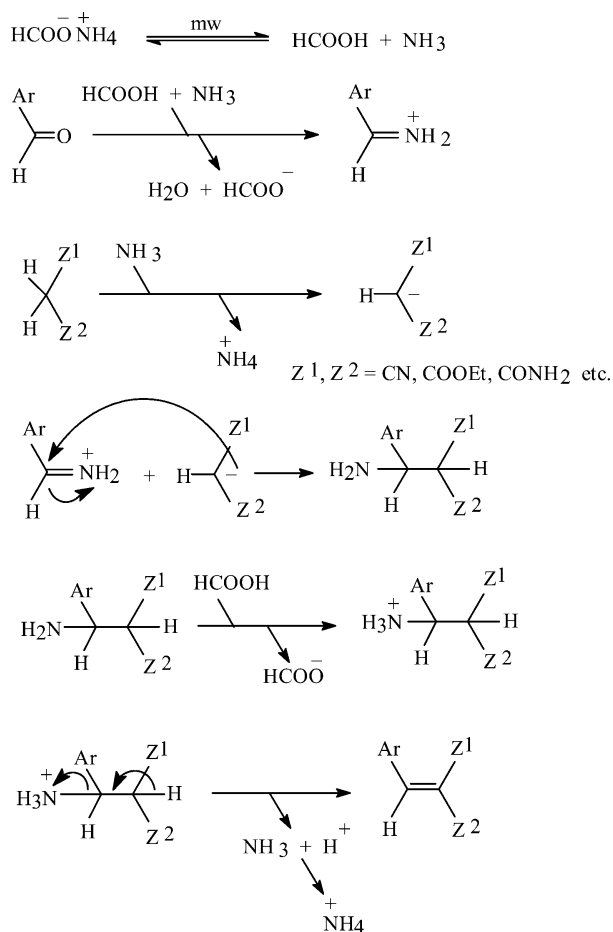


Figure 6. A schematic representation of the plausible reaction pathway.

complex when a white-colored binary mixture of anhydrous cupric sulfate and excess amount of anhydrous ammonium formate is irradiated with microwave for more than 10 seconds). Ammonia might form the iminium species with the aryl aldehyde *in situ*, which being more electrophilic than a formyl group undergoes nucleophilic attack by the active methylene donors under feebly basic condition. Subsequent β -elimination would be assisted by the acidity rendered by the formic acid and the undissociated ammonium cations with regeneration of ammonium formate. There might be some loss of ammonia from the system during microwave irradiation. The use of stoichiometric amount of ammonium formate was therefore probably necessary. Ammonium acetate (pH of 1.0 M aqueous solution is 6.98) is more sluggish than ammonium formate (pH of 1.0 M aqueous solution is 5.90) in the present reaction might be due to its lower acidity and less propensity for dissociation into ammonia and acetic acid under microwave irradiation, although the exact reason is not yet clear to us.

Conclusion

The present ammonium formate-mediated solvent-free protocol for Knoevenagel reaction provides a GREEN access to a range of functionalized olefins with varied substituents through an operationally simple and economically viable route using easily accessible materials.

Experimental section

Representative procedure for microwave-assisted ammonium formate-mediated Knoevenagel reaction

p-Anisaldehyde (1.32 g, 10 mmol), ethyl cyanoacetate (1.13 g, 10 mmol) and ammonium formate (630 mg, 10 mmol) were intimately mixed in a hard glass microwave-resistant vessel fitted with a CaCl₂ drying tube. The mixture was subjected to microwave irradiation (Model 800T, BPL, India) for 2.0 minutes (with an installment of 15 seconds each at a power level of 300 Watts followed by intermittent cooling). After completion of reaction (monitored by TLC on silica gel during cooling after each installment), crushed ice (20 g) was added to the reaction mixture and stirred well. The solid product, precipitated in a granular form, was filtered, washed well with water and dried to furnish ethyl 2-cyano-3-(4'-methoxyphenyl)-propenoate (*4b*, *4d*) (1.84 g, 80%) in practically pure form (by ¹H-NMR).

Acknowledgements

Financial support from CSIR, New Delhi, Govt. of India [Grant No. 01(1673)/00/EMR-II dated 07-12-2000] is gratefully acknowledged. S.R. thanks UGC, New Delhi, Govt. of India and M.S. thanks CSIR, New Delhi, Govt. of India, respectively, for offering Senior Research Fellowships to them. Thanks to Professor S.R. Raychaudhuri of Jadavpur University and Mr N. Dutta of IACS, Kolkata for necessary assistance. Infrastructural support from DST-FIST programme and financial assistance from UGC-CAS-programme in Chemistry, Jadavpur University are also acknowledged.

Notes

1. We attempted a few reactions from this paper but failed to reproduce them.
2. We did not have any reference for the use of ammonium formate in Knoevenagel reactions on SciFinder Scholar Search.

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