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Montmorillonite K-10: An efficient and reusable catalyst for the one-pot multi component microwave synthesis of diethyl 1-(4-aryl)-4-phenyl-1*H*-pyrrole-2,3-dicarboxylates

S. Ahammad Kabeer, N. Maheswara Reddy, G. Mohan, B. Mahesh and C. Suresh Reddy*

Department of Chemistry, Sri Venkateswara University, Tirupati, India

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ABSTRACT

An efficient and green one-pot multi component microwave synthesis of diethyl 1-(4-aryl)-4-phenyl-1H-pyrrole-2,3-dicarboxylates has been accomplished under solvent-free conditions from the reaction of benzaldehyde, diethyl acetylenedicarboxylate and nitroalkane with various amines. The merit of the methodology is that the interlamellar structure of the montmorillonite K-10 favoured the reaction in synthesizing the tetra substituted pyrroles with the environmentally benign reaction conditions by offering good product yields.

Keywords: Montmorillonite K-10, Green synthesis, Microwave irradiation, Multi component reaction, Tetrasubstituted pyrroles.

INTRODUCTION

Pyrroles constitute an important class of heterocyclic compounds with wide array of applications both in biological systems and natural products like enzymes, coenzymes and alkaloids [1]. Thus, many synthetic routes were developed for them like multicomponent, tandem reactions and cyclo additions [2]. In recent some heterogeneous catalysts and metal-catalyzed coupling reactions were also developed for the accomplishment of Poly substituted pyrroles from multi-component reactions [3, 4].

In view of the involvement of disadvantages like unsatisfactory yields, harsh reaction conditions and long reaction times in the multi component reactions, the urge of development of new and efficient methodology and catalyst has been received the attention of organic chemistry researchers. As part of our research, we have developed some green methodologies involving the features like solvent free reactions, new and effective catalysts and use of microwave irradiation and sonication energies [5-8].

In such hierarchy, we have investigated the efficient catalyst for the synthesis of diethyl 1-(4-aryl)-4-phenyl-1H-pyrrole-2,3-dicarboxylates and reporting herewith montmorillonite K-10 as an effective clay catalyst. Mmontmorillonite K-10 clays are composed of two silica tetrahedral sheets (negatively charged) with a central alumina octahedral sheet (cationic species) in a sandwich like structure and facilitates the sustenance of multi-component reactions for forming the target products [9].

So herein, we report a facile solvent-free one-pot neat synthesis of diethyl 1-(4-aryl)-4-phenyl-1H-pyrrole-2,3-dicarboxylates *via* four-component reaction of benzaldehyde, diethyl acetylenedicarboxylate and nitroalkane with various amines in the presence of catalytic amount of Montmorillonite K-10 (30mg) under microwave irradiation at 100 °C.

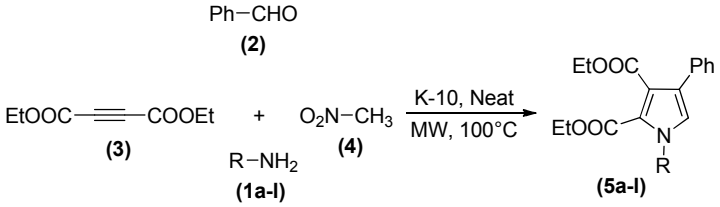
MATERIALS AND METHODS

2.1. General

All reagents were obtained from Sigma-Aldrich and Alfa Aesar and were used directly without further purification. The progress of the reactions was monitored by thin layer chromatography (TLC) on 250 μm silica plates using 7:3 n-hexane and ethyl acetate mixture as an eluent. IR spectra were recorded on Bruker Alpha-EcoATR-FTIR interferometer with single reflection sampling module equipped with ZnSe crystal. The ^{1}H and ^{13}C NMR spectra of compounds were recorded on Bruker instrument at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR in DMSO-d_6 with TMS reference and their chemical shifts were reported in δ scale. Mass spectra were recorded on a Jeol SX 102 DA/600 mass spectrometer and elemental analysis was performed on a Thermo Finnigan Instrument.

2.2. Chemistry

2.2.1. *Synthesis of Diethyl 4-phenyl-1-(o-tolyl)-1H-pyrrole-2,3-dicarboxylate* ***5a:*** A mixture of *o*-toluidine (**1a**, 1 mmol), benzaldehyde (**2**, 1 mmol), diethyl acetylenedicarboxylate (**3**, 1 mmol), nitromethane (**4**, 1mL), and K-10 (30 mg) was taken in an open vessel in CATA-4R Scientific Microwave oven and irradiated at 100 °C (140 W) at ambient pressure in solvent-free condition for 2 min. The reactions were followed by thin layer chromatography (TLC) using hexane/ethyl acetate as an eluent. After completion of the reaction, the mixture was washed with ethyl acetate and filtered to recover the catalyst. The filtrate was evaporated and the crude product was recrystallized from ethanol to afford pure diethyl 4-phenyl-1-(*o*-tolyl)-1*H*-pyrrole-2,3-dicarboxylate (**5a**) in 92% yield.



Entry	R	Entry	R	Entry	R	Entry	R
5a	2(Me)Ph	**5d**	2(OMe)Ph	**5g**	2,5-(Me)Ph	**5j**	2,5-(OMe)Ph
5b	3(Me)Ph	**5e**	3(OMe)Ph	**5h**	3,5-(Me)Ph	**5k**	3,5-(OMe)Ph
5c	4(Me)Ph	**5f**	4(OMe)Ph	**5i**	3,4-(Me)Ph	**5l**	3,4-(OMe)Ph

Scheme 1: K-10 catalyzed synthesis of tetra substituted pyrroles (5a-l)

The same reaction procedure was followed for the synthesis of **5b-l (Scheme 1**). All the compounds are collected as yellow liquids and were characterized by spectral and elemental analyses.

2.2.2. *Diethyl 4-phenyl-1-(o-tolyl)-1H-pyrrole-2,3-dicarboxylate* ***5a:*** Yield: 92%; IR (ZnSe): 1734 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, DMSO): δ 7.48-7.46 (m, 2H), 7.35-7.32 (m, 3H), 7.29-7.20 (m, 4H), 6.89 (s, 1H), 4.35-4.33 (m, 2H), 4.12-4.09 (m, 2H), 2.12 (s, 3H), 1.28 (t, 3H), 1.07 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.33, 158.59, 139.07, 134.97, 133.24, 130.55, 128.76, 128.39, 127.67, 127.23, 126.71, 126.45, 125.16, 124.32, 123.12, 121.56, 61.30, 60.37, 17.46, 14.87, 13.66 ppm; LCMS m/z: 377(M+). Anal. Calcd for $C_{23}H_{23}NO_4$ (%): C, 73.19; H, 6.14; N, 3.71; Found: C, 73.05; H, 6.06; N, 3.67.

2.2.3. *Diethyl 4-phenyl-1-(m-tolyl)-1H-pyrrole-2,3-dicarboxylate* ***5b:*** Yield: 93.5%; IR (ZnSe): 1732 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, DMSO): 7.45 (d, 2H), 7.31 (t, 2H), 7.28 (t, 2H), 7.16 (d, 1H), 7.11 (t, 2H), 6.91 (s, 1H), 4.31-4.27 (m, 2H), 4.17-4.11 (m, 2H), 2.29 (s, 3H), 1.23 (t, 3H), 1.14 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 166.12, 159.94, 139.38, 138.71, 132.87, 128.94, 128.12, 127.76, 127.12, 126.33, 125.91, 125.06, 123.89, 123.15, 121.68, 61.34, 61.44, 21.56, 13.75, 13.96 ppm; LCMS m/z: 377(M+). Anal. Calcd for $C_{23}H_{23}NO_4$ (%): C, 73.19; H, 6.14; N, 3.71; Found: C, 73.09; H, 6.08; N, 3.68.

2.2.4. *Diethyl 4-phenyl-1-(p-tolyl)-1H-pyrrole-2,3-dicarboxylate* ***5c:*** Yield: 92.5%; IR (ZnSe): 1731 (C=O) cm^{-1}; ^{1}H NMR (500 MHz, DMSO): 7.45 (t, 2H), 7.26-7.15 (m, 3H), 7.11 (t, 4H), 6.54 (s, 1H), 4.29-4.25 (m, 2H), 4.09-4.05 (m, 2H), 2.35 (s, 3H), 1.19 (t, 3H), 1.16 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.86, 158.67, 137.56, 135.43, 131.75, 128.42, 128.15, 127.34, 126.54, 125.44, 125.21, 124.13, 123.26, 121.15, 59.94, 61.44, 20.56, 13.86, 13.54 ppm; LCMS m/z: 377(M+). Anal. Calcd for $C_{23}H_{23}NO_4$ (%): C, 73.19; H, 6.14; N, 3.71; Found: C, 73.02; H, 6.02; N, 3.66.

2.2.5. *Diethyl 1-(2-methoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5d:*** Yield: 89%; IR (ZnSe): 1725 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.32 (d, 2H), 7.19-7.14 (m, 3H), 7.08-7.03 (m, 2H), 6.87-6.83 (m, 2H), 6.73 (s, 1H), 4.252-4.17 (m, 2H), 4.02-3.97 (m, 2H), 3.44 (s, 3H), 1.09 (t, 3H), 1.04 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.22, 156.46, 153.22, 133.98, 128.44, 128.06, 127.87, 127.26, 126.75, 125.34, 124.21, 123.89, 121.31, 120.49, 111.77, 60.98, 60.17, 54.62, 13.98, 13.76 ppm; LCMS m/z: 393(M+). Anal. Calcd for $C_{23}H_{23}NO_5$ (%): C, 70.21; H, 5.89; N, 3.56; Found: C, 70.05; H, 5.76; N, 3.49.

2.2.6. *Diethyl 1-(3-methoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5e:*** Yield: 90%; IR (ZnSe): 1726 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.45-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.22 (m, 2H), 6.76 (s, 1H), 6.72-6.68 (m, 2H), 6.43 (t, 1H), 4.29-4.24 (m, 2H), 4.19-4.15 (m, 2H), 3.67 (s, 3H), 1.29 (t, 3H), 1.14 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.89, 156.65, 158. 54, 141.43, 133.56, 129.64, 128.31, 127.69, 127.01, 125.36, 123.66, 123.14, 121.55, 118.12, 114.24, 112.08, 61.27, 60.85, 55.41, 14.14, 13.76 ppm; LCMS m/z: 393 (M+). Anal. Calcd for $C_{23}H_{23}NO_5$ (%): C, 70.21; H, 5.89; N, 3.56; Found: C, 70.02; H, 5.75; N, 3.49.

2.2.7. *Diethyl 1-(4-methoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5f:*** Yield: 90.5%; IR (ZnSe): 1728 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.35-7.32 (m, 2H), 7.32 (t, 2H), 7.26-7.20 (m, 3H), 6.93-6.88 (m, 3H), 4.31-4.26 (m, 2H), 4.18-4.12 (m, 2H), 3.67 (s, 3H), 1.24 (t, 3H), 1.14 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.28, 159.45, 158.36, 133.56, 132.16, 128.32, 127.65, 127.39, 126.55, 125.84, 124.27, 123.13, 121.48, 61.14, 60.39, 55.30, 14.06, 13.56 ppm; LCMS m/z: 393 (M+). Anal. Calcd for $C_{23}H_{23}NO_5$ (%): C, 70.21; H, 5.89; N, 3.56; Found: C, 70.09; H, 5.77; N, 3.51.

2.2.8. *Diethyl 1-(2,5-dimethylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5g:*** Yield: 89%; IR (ZnSe): 1736 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.45 (d, 2H), 7.25 (t, 2H), 7.18 (t, 1H), 7.04 (s, 2H), 6.76 (s, 1H), 6.12 (s, 1H), 4.28-4.22 (m, 2H), 4.04-3.99 (m, 2H), 2.24 (s, 3H), 1.97 (s, 3H), 1.18 (t, 3H), 1.02 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 166.04, 159.31, 138.68, 135.78, 133.26, 132.14, 130.34, 130.04, 129.46, 128.32, 127.47, 126.98, 126.25, 125.24, 124.33, 123.64, 121.49, 61.94, 60.55, 20.67, 16.44 ppm; LCMS m/z: 391(M+). Anal. Calcd for $C_{24}H_{25}NO_4$ (%): C, 73.64; H, 6.44; N, 3.58; Found: C, 73.49; H, 6.32; N, 3.52.

2.2.9. *Diethyl 1-(3,5-dimethylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5h:*** Yield: 91%; IR (ZnSe): 1734 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.42 (d, 2H), 7.25 (t, 2H), 7.16 (t, 1H), 6.96 (s, 1H), 6.82 (d, 3H), 4.26-4.20 (m, 2H), 4.13-4.07 (m, 2H), 2.21 (s, 6H), 1.16 (t, 3H), 1.15 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.74, 160.07, 139.82, 138.37, 133.23, 129.85, 128.45, 127.63, 126.83, 125.31, 124.63, 123.51, 121.56, 60.78, 60.34, 21.15, 13.76, 12.96 ppm; LCMS m/z: 391(M+). Anal. Calcd for $C_{24}H_{25}NO_4$ (%): C, 73.64; H, 6.44; N, 3.58; Found: C, 73.52; H, 6.33; N, 3.54.

2.2.10. *Diethyl 1-(3,4-dimethylphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5i:*** Yield: 91.5%; IR (ZnSe): 1735 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.39 (d, 2H), 7.26 (t, 2H), 7.19-7.14 (m, 1H), 7.10-7.04 (m, 2H), 6.99 (d, 1H), 6.76 (s, 1H), 4.19-4.15 (m, 2H), 4.12-4.08 (m, 2H), 2.19 (s, 6H), 1.18 (t, 3H), 1.09 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 166.22, 159.78, 137.19, 137.02, 136.71, 133.24, 129.77, 128.25, 127.62, 126.55, 125.43, 124.32, 123.17, 121.44, 61.01, 60.57, 19.54, 19.20, 14.04, 13.54 ppm; LCMS m/z: 391(M+). Anal. Calcd for $C_{24}H_{25}NO_4$ (%): C, 73.64; H, 6.44; N, 3.58; Found: C, 73.56; H, 6.34; N, 3.53.

2.2.11. *Diethyl 1-(2,5-dimethoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5j:*** Yield: 89%; IR (ZnSe): 1726 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): 7.39 (d, 2H), 7.22 (t, 2H), 7.16-7.12 (m, 1H), 7.07-7.02 (m, 2H), 6.95 (d, 1H), 6.72 (s, 1H), 4.26-4.23 (m, 2H), 4.13-4.07 (m, 2H), 2.16 (s, 6H), 1.21 (t, 3H), 1.13 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 167.01, 158.55, 136.32, 136.73, 135.44, 132.65, 128.12, 127.74, 127.13, 126.13, 125.37, 124.12, 123.79, 121.45, 61.08, 60.73, 19.74, 19.29, 13.97, 13.66 ppm; LCMS m/z: 423(M+). Anal. Calcd for $C_{24}H_{25}NO_6$ (%): C, 68.07; H, 5.95; N, 3.31; Found: C, 67.79; H, 5.83; N, 3.19.

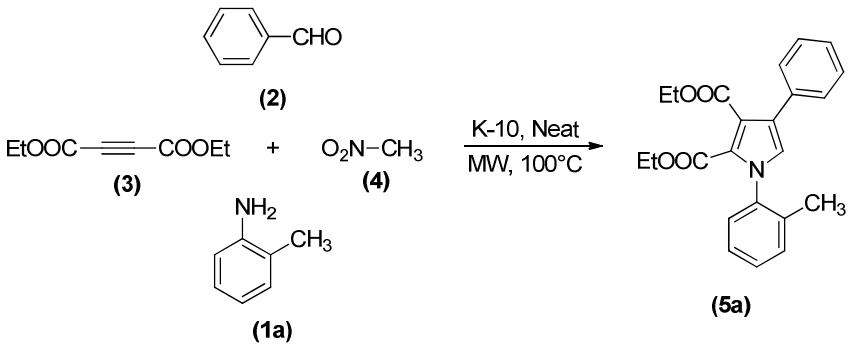
2.2.12. *Diethyl 1-(3,5-dimethoxyphenyl)-4-phenyl-1H-pyrrole-2,3-dicarboxylate* ***5k*****:** Yield: 89.5%; IR (ZnSe): 1727 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): δ 7.42 (d, 2H), 7.31 (t, 2H), 7.26-7.21 (m, 1H), 6.95 (s, 1H), 6.43 (s, 3H), 4.29-4.24 (m, 2H), 4.19-4.13 (m, 2H), 3.63 (s, 6H), 1.25 (t, 3H), 1.16 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz): δ 165.77, 161.71, 158.91, 142.02, 134.16, 127.39, 126.55, 125.92, 125.21, 124.76, 123.45, 121.33, 104.53, 100.22, 60.87, 59.76, 55.38, 14.08, 13.86 ppm; LCMS m/z: 423(M+). Anal. Calcd for $C_{24}H_{25}NO_6$ (%): C, 68.07; H, 5.95; N, 3.31; Found: C, 67.81; H, 5.84; N, 3.22.

2.2.13. *Diethyl 1-(3,4-dimethoxyphenyl)-4-phenyl -1H-pyrrole-2,3-dicarboxylate* ***5l:*** Yield: 923.5%; IR (ZnSe): 1728 (C=O) cm^{-1}; ^1H NMR (500 MHz, DMSO): δ 7.42 (d, 2H), 7.28 (t, 2H), 7.21 (t, 1H), 6.94 (s, 1H), 6.88-6.81 (m, 3H), 4.27-4.21 (m, 2H), 4.17-4.12 (m, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 1.22 (t, 3H), 1.12 (t, 3H) ppm; ^{13}C NMR (DMSO, 125 MHz) δ (ppm) 166.22, 158.78, 148.82, 147.53, 132.78, 131.36, 128.14, 127.44, 126.31, 125.55,

124.42, 123.45, 121.55, 117.37, 110.64, 110.15, 61.07, 60.42, 55.65, 13.76, 13.43 ppm; LCMS m/z: 423(M+). Anal. Calcd for $C_{24}H_{25}NO_6$ (%): C, 68.07; H, 5.95; N, 3.31; Found: C, 67.85; H, 5.83; N, 3.23.

RESULTS AND DISCUSSION

In establishing the reaction procedure we have taken the synthesis of diethyl 4-phenyl-1-(*o*-tolyl)-1*H*-pyrrole-2,3-dicarboxylate from benzaldehyde, *o*-toluidine, dimethyl nitromethane and diethyl acetylenedicarboxylate (**Scheme 2**) as a model and optimized the catalyst concentration and temperature conditions.



Scheme 2: K-10 Catalyzed synthesis of 5a

Initially, both conventional and microwave methods under solvent-free conditions have been investigated at 100°C. Investigation of catalytic action of various compounds like $FeCl_3$, $InCl_3$, $GaCl_3$, and CAN neither completed the reaction nor scale up the higher yield (**Table 1**, **Entry 1-4**). Then we have investigated the action of solid acid catalysts like STA, $FeCl_3.SiO_2$, PS-PTSA, InF_3, and $BF_3.SiO_2$, but the results are unproductive (**Table 1, Entry 5-9**). Then the multicomponent reaction of these reactants motivated us to focus on catalysts with multiple applications. In such analysis we have identified the Montmorillonite K-10 catalyst to obtain the desired product with the anticipated yields by a systematic investigation (**Table 1, Entry 10-16**).

Table: 1 Influence of the catalyst on the synthesis of 5a

Entry	Catalyst (mol%)	Conventional		Microwave	
		Time (h)	Yield[a] (%)	Time (min)	Yield[a] (%)
1	$FeCl_3$ (5)	24	30	14	45
2	$InCl_3$ (5)	18	35	14	55
3	$GaCl_3$(5)	25	30	17	52
4	CAN (5)	18	45	12	53
5	STA(5)	14	75	9	85
6	$FeCl_3.SiO_2$(5)	20	60	15	74
7	PS-PTSA (5)	12	60	8	78
8	InF_3 (5)	18	65	15	75
9	$BF_3.SiO_2$	10	60	6	77
10	K-10 (10mg)	12	65	4	70
11	K-10 (20mg)	10	70	3	80
12[b]	K-10 (30mg)	8	85	2	92, 90, 88, 85
13	K-10 (40mg)	8	82	2	92
14	K-10 (50mg)	10	77	4	89
15	K-10 (60mg)	12	71	5	87

[a]Isolated yield; [b]Catalyst was reused four times.

It is well noticed that natural montmorillonite clays have surface acidity within the limits of nitric acid and sulfuric acid favours the carbocationic reactions. It is a quite interesting factor that the prominent cations present in K-10 easily exchange the available acidic protons of the organic compounds at the interlamellar surfaces [10]. The analysis of Montmorillonite K-10 catalyst the yields are up to 70-92% with varying the catalyst concentration (10mg-60mg). In ultimate we have recorded the optimum concentration of the catalyst with high product yields and reusability as 30mg (**Table 1, Entry 12**). The excessive catalyst concentrations have retarded the product yields significantly (**Table 1, Entry 13-15**).

The extended studies for the identification of optimum temperature, the reactions were performed at various temperatures ranging from 60°C to 100°C and we observed the significant yield of compound **5a** at 100°C itself under conventional conditions for affording compound **5a** with 92% yield with in 2h (**Table 2, Entry 3**). Further enhancement of the reaction temperature had not shown any impact on the reaction time and yield.

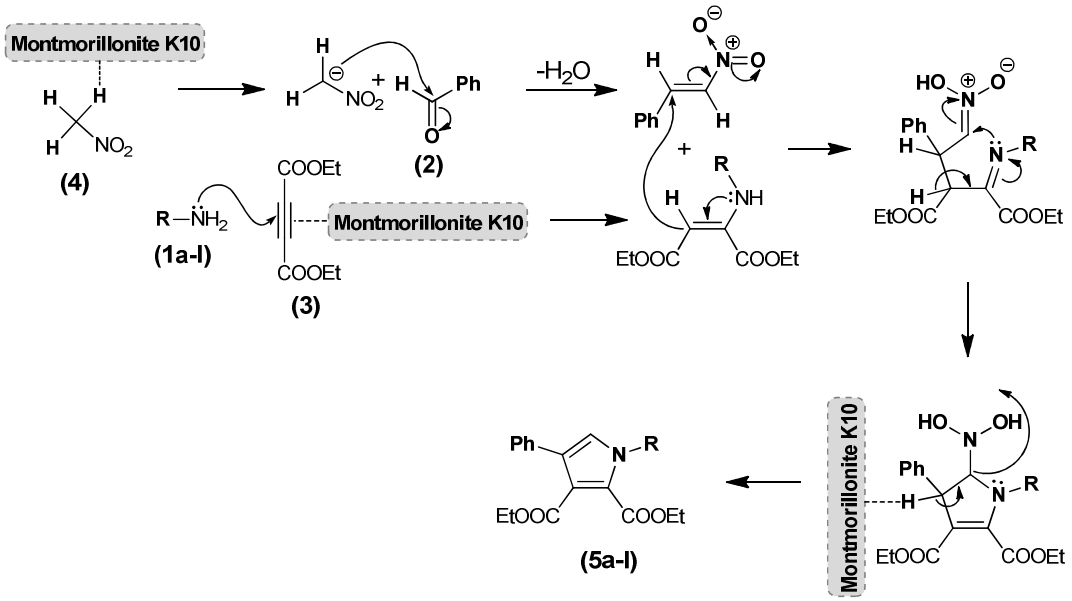
Table: 2 Effect of temperature for the synthesis of 5a

Entry	Temp (°C)	Time (min)	Yield[a] (%)
1	60	240	25
2	80	180	60
3	100	120	92
4	120	120	92
5	140	120	92

[a]*Isolated yield*

The reusability of the Montmorillonite K-10 catalyst has been tested and identified as productive for up to four cycles with 30mg concentration with 92, 90, 88, 85 % of successive yields of **5a** (**Table1, Entry 12**). So these optimized conditions were followed for affording the synthesis of remaining compounds **5b-l**.

The mechanistic pathway of reaction plausibly initiated by the action of Montmorillonite K-10 by abstracting the active proton of the nitromethane, which in the sequence undergo condensation reaction with benzaldehyde and forms nitro substituted alkenes. In the next step the arylamines will reacts with diethyl acetylenedicarboxylates and aryl substituted ethylene-1,2-dicarboxylate. In the next step these two molecules will undergo addition followed by cyclization reactions and forms the required diethyl 1-(4-aryl)-4-phenyl-1*H*-pyrrole-2,3-dicarboxylates as the desired products (**Scheme 3**).



Scheme 3: Plausible Mechanism for the synthesis of title compounds 5a-l

CONCLUSION

In conclusion, we have identified montmorillonite K-10 as an efficient catalyst for the one-pot multi component microwave synthesis of diethyl 1-(4-aryl)-4-phenyl-1*H*-pyrrole-2,3-dicarboxylates with simple operating procedures with good yields.

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