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Synergic Effects of Ionic Liquid and Microwave Irradiation in Promoting Trifluoromethylpyrazole Synthesis

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Abstract The synthesis of 5-trifluoromethyl-1-phenyl-1*H*-pyrazoles from the reactions of 4-alkoxy-1,1,1-trifluoro-3-alken-2-ones [$CF_3C(O)CH{=}C(R^1)OR$, where R = Me, Et; R^1 = H, Me, Bu, *i*-Bu, Ph, 4-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, 4-IC_6H_4, fur-2-yl] with phenyl hydrazine in the presence of ionic liquid [BMIM][BF_4] is reported. Synergic effects of ionic liquid and microwave irradiation in promoting pyrazole synthesis have been shown for the first time.

Keywords Microwave Irradiation · Ionic Liquid · Pyrazole · Catalysis · Halogenated compounds

1 Introduction

In recent decades, there has been an extensive search for new synthetic methodologies which minimize environmental impacts. The use of nonvolatile solvents and more economic energy sources to promote organic reactions has been one of the most prominent tactics in this effort. The development and use of ionic liquids have emerged as a fascinating technology because, in addition to their negligible vapor pressure and recyclability, they present unique physicochemical properties such as tunable polarity, high thermal stability and miscibility with a number of organic solvents [1, 2]. With regard to alternative energy sources, the use of microwave ovens for synthesis has been accepted as a way of reducing reaction times, often by orders of magnitude, and of increasing product yields when compared to conventional methods [3, 4]. A key advantage of modern scientific microwave equipment is the ability to control very specific reaction conditions, monitoring temperature, pressure, and reaction times. Several methods have been developed for performing reactions using microwaves, including under solvent-free conditions, with the adsorbtion of reactants onto inorganic supports such as silica (or clays) and in ionic liquids [5].

Enabling technologies and methodologies have been established and combined to afford various environmentally benign processes for laboratory scale synthesis and for the production of fine chemicals. In this context, a recent trend in this area is microwave-assisted synthesis using ILs as solvent, co-solvent, catalyst, and/or template [6]. Due to their ionic nature, ILs allow highly effective interactions with microwave (MW) energy for the rapid generation of products with generally high yields [7].

Our research group has developed a general procedure for preparing β-alkoxyvinyl trihalomethyl ketones and we have exhaustively studied the versatility of the β-alkoxyvinyl trihalomethyl ketones in heterocyclic synthesis [8]. Recently, we have published a number of works related to the minimization of environmental impacts through the use of ionic liquids [9–11] or solvent-free reactions [12, 13]

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and by using ultrasound [14, 15] or MW [12, 13] to promote the reactions. Our current review about heterocyclic synthesis in ionic liquid [16] has demonstrated that there is a lack of reports dealing with pyrazole synthesis in this media. Substituted pyrazoles are important synthetic targets in the pharmaceutical industry because the pyrazole motif makes up the core structure of numerous biologically active compounds, including blockbuster drugs such as Celecoxib [17] and Sildenafil [18]. Although several methods have been developed, regioselective synthesis of the pyrazole ring remains a significant challenge for organic chemists [19–22]. In this context, our aim in this work is to demonstrate the synergic effects of ionic liquid and microwave irradiation in promoting the synthesis of trifluoromethyl pyrazoles.

2 Experimental

2.1 General

The experiments were performed in a Discover CEM MW using the mode of operation: with and without simultaneous cooling. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) and Bruker DPX-200 (^{1}H at 200.13 MHz and ^{13}C at 50.32 MHz) in $CDCl_3$/TMS solutions at 298 K. Mass spectra were registered in a HP 5973 MSD connected to a HP 6890 GC and interfaced by a Pentium PC. The GC was equipped with a split-splitless injector, cross-linked to a HP-5 capillary column (30 m, 0.32 mm i.d.), and helium was used as the carrier gas. The melting points were measured using a Microquímica MQAPF 301. The ionic liquid 1-butyl-3-methyl imidazolium tetrafluoroborate [BMIM][BF_4] was prepared according to procedures from the literature [23]. The enones **1a–k** were obtained from the acylation reaction of enol ether or acetal with trifluoroacetic anhydride in accordance with the methodology developed in our laboratory [24]. Phenylhydrazine was obtained commercially.

2.2 Preparation and Characterization of Pyrazoles (**3a–k**)

Conventional method Enones **1a–k** (1 mmol), phenylhydrazine **2** (1.2 mmol) and ionic liquid ([BMIM][BF_4]) (1 mmol) were placed into a round-bottom flask equipped with a stir bar. After the mixture was stirred for the times and temperatures indicated in Scheme 1, the products were isolated with chloroform (5 mL) and washed with water (3 × 5 mL). The chloroform was evaporated under vacuum (reduced pressure) and the products were obtained in a pure form without further purification.

Microwave irradiation A 10 mL microwave vessel equipped with a standard cap (vessel commercially furnished by Discover CEM) was filled with 1 mmol of enone **1a–k**, 1.2 mmol of phenylhydrazine **2** and 1 mmol of ionic liquid ([BMIM]BF_4]). After the vessel was sealed, the sample was irradiated for the times and temperatures as indicated in Scheme 1, which was plotted in Synergies Version 3.5.9 software applying the power of 200 W as the maximum level of irradiation and a maximum level of internal vessel pressure of 250 psi. The irradiation power was in the range of 6–30 W for reactions at 100 °C, with simultaneous cooling, and at 14–46 W for reactions at 150–200 °C, without simultaneous cooling. The reaction mixture was subsequently cooled to 50 °C by compressed air. The products were isolated with chloroform (5 mL) and washed with water (3 × 5 mL). The chloroform was evaporated under vacuum (reduced pressure) and the products were obtained in a pure form without further purification. For the data of compound **3a–e**, ^{1}H NMR spectra were found to be identical with the one described in Ref. [12, 25, 26].

2.2.1 5-Trifluoromethyl-1,3-diphenyl-1H-pyrazole (3e)

The crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC 803591). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 01223-336033.

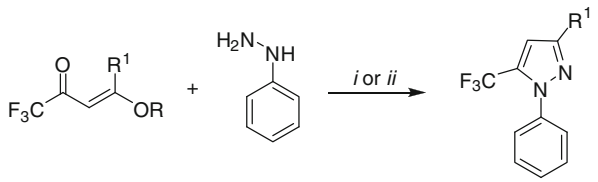
2.2.2 5-Trifluoromethyl-3-(4-methylphenyl)-1-phenyl-1H-pyrazole (3f)

$C_{17}H_{13}F_3N_2$ M.p.:127–130 °C; Yield: 89%, ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.38$ (s, 3H, Me), 7.07 (s, 1H, H4), 7.22 (*d*, 2H, Ar), 7.46–7.56 (m, 5H, Ph), 7.74 (*d*, 2H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 21.3$ (CH_3), 105.9 (q, ^{3}J 2, C4), 119.7 (q, ^{1}J 268, CF_3), 125.6 (q, J 1.4, C_{ortho}),125.6, 128.8, 129.0, 129.2, 129.5, 138.5, 139.1 (C–Ar), 133.7 (q, ^{2}J 39, C5), 151.6 (C3); MS (70 eV): $m/z = 302$ (100), 281 (42), 77 (20).

2.2.3 5-Trifluoromethyl-3-(4-fluorophenyl)-1-phenyl-1H-pyrazole (3g)

$C_{16}H_{10}F_4N_2$ M.p.: 58–60 °C; Yield: 89%; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.07$ (s, 1H, H4), 7.39 (*d*, 2H, Ar), 7.50–7.55 (m, 5H, Ar), 7.83 (*d*, 2H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 105.8$ (q, ^{3}J 3, C4), 115.8 (*d*, ^{2}J 22, CAr), 119.67 (q, ^{1}J 269, CF_3), 125.6 (q, J 1.4, C_{ortho}), 125.6 (C–Ar), 129.1, 129.3, (C–Ar), 127.6 (*d*, ^{3}J 8, C–Ar), 127.9 (*d*, ^{4}J 3, C–Ar), 133.98 (q, ^{2}J 39, C5), 150.7

Scheme 1 Synthesis of compounds **3a-k**



1a-k **2** **3a-k**

i: [BMIM][BF_4], 25-150°, 1-3 h *ii*: [BMIM][BF_4], MW (100-200 °C), 6 min

				Conventional	MW
Enone	R	R^1	Prod.(s)	Yield[a] (%)	Yield[a] (%)
1a	Et	H	**3a**[b]	80	80
1b	Me	Me	**3b**	93	92
1c	Me	*i*-Bu	**3c**	91	90
1d	Me	Bu	**3d**	92	91
1e	Me	Ph	**3e**	85	82
1f	Me	4-Me-C_6H_4	**3f**	89	83
1g	Me	4-F-C_6H_4	**3g**	89	82
1h	Me	4-Cl-C_6H_4	**3h**[c]	90	82
1i	Me	4-Br-C_6H_4	**3i**[d]	96	94
1j	Me	4-I-C_6H_4	**3j**	-	96
1k	Me	Fur-2-yl	**3k**	72	56

[a]Yield of isolated products. [b] A mixture of regioisomers was isolated in conventional heating and under MW in a molar ratio of 1:1. [c] A mixture of regioisomers was isolated in conventional heating and under MW in a molar ratio of 10:1. [d] A mixture of regioisomers was isolated in conventional heating and under MW in a molar ratio of 5:1. [e] Reaction performed in 10 min.

(C3), 163.05 (*d*, ^1J 248, C–Ar); MS (70 eV): *m/z* = 306 (100), 285 (42), 273 (9), 77 (12).

2.2.4 3-(4-Chlorophenyl)-5-trifluoromethyl-1-phenyl-1H-pyrazole (3h)

$C_{16}H_{10}ClF_3N_2$ Oil; Yield: 90%; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.08$ (s, 1H, H4); 7.38 (*d*, 2H, H–Ar), 7.47–7.55 (m, 5H, Ar), 7.79 (*d*, 2H, H–Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 105.9$ (q, ^3J 2, C4), 119.6 (q, ^1J 268, CF_3), 125.6 (q, $J = 1.4$, C_{ortho}), 125.6 (C–Ar), 127.0, 128.9, 129.1, 129.4, 130.2, 134.47, 139.0 (C–Ar), 134.0 (q, ^2J 38 C5), 150.5 (C3); MS (70 eV): *m/z* = 322 (100), 301 (61), 267 (20), 77 (19).

2.2.5 5-(4-Chlorophenyl)-3-trifluoromethyl-1-phenyl-1H-pyrazole (3h)

$_{16}H_{10}ClF_3N_2$ Oil; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 6.74$ (s, 1H, H4); 7.16 (*d*, 2H, H–Ar), 7.29 (*d*, 2H, H–Ar), 7.47–7.55 (m, 5H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 105.6$ (q, ^3J 2, C4), 121.6 (q, ^1J 268, CF_3), 127.5, 128.6, 128.8, 129.2, 129.6, 133.1, 138.9 (C–Ar), 143.4 (C5); MS (70 eV): *m/z* = 322 (100), 301 (36), 267 (13), 77 (10).

2.2.6 3-(4-Bromophenyl)-5-trifluoromethyl-1-phenyl-1H-pyrazole (3i)

$C_{16}H_{10}BrF_3N_2$ Oil; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.08$ (s, 1H, H4), 7.13–7.52 (m, 7H, Ar), 7.72 (*d*, 2H, Ar); ^{13}C

NMR (400 MHz, $CDCl_3$): $d = 105.9$ (q, ^3J 3, C4),119.6 (q, ^1J 267, CF_3), 125.4 (q, J 1.4, C_{ortho}), 125.5 (C–Ar),127.3, 129.1, 129.4, 130.2, 131.7, 131.92, (C–Ar), 134.1 (q, ^2J 39, C5),150.4 (C3). MS (70 eV): $m/z = 366$ (100), 347 (21), 267 (17), 133 (12), 77 (30).Due the low concentration of *1,3*-isomer, the signals of C5 were not observed.

2.2.7 5-(4-Bromophenyl)-3-trifluoromethyl-1-phenyl-1H-pyrazole (3i)

$C_{16}H_{10}BrF_3N_2$ Oil; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 6.75$ (s, 1H, H4), 7.07 (*d*, 2H, Ar), 7.45 (*d*, 2H, Ar), 7.51–7.57 (m, 5H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 105.6$ (q, ^3J 2, C4),121.1 (q, ^1J 269, CF_3), 122.6, 125.4, 128.0, 128.7, 129.2, 129.8, 130.6, 138.9 (C–Ar), 143.3 (q, ^2J 39, C3),143.4 (C5); MS (70 eV): $m/z = 366$ (100), 347 (31), 267 (23), 133 (47), 77 (44).

2.2.8 3-(4-Iodophenyl)-5-trifluoromethyl-1-phenyl-1H-pyrazole (3h)

$C_{16}H_{10}IF_3N_2$ M.p.: 76–79 °C;^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 7.09$ (s, 1H, H4), 7.51–7.62 (m, 7H, Ar), 7.76 (*d*, 2H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 105.9$ (q, ^3J 3, C4), 119.6 (q, ^1J 269, CF_3), 94.3, 125.6, 127.5, 129.1, 129.4, 131.3, 137.9, 139.5 (CAr), 134.1 (q, ^2J 38, C5), 150. 6 (C3); MS (70 eV): $m/z = 414$ (100), 393 (9), 218 (16), 55 (53).

2.2.9 5-Trifluoromethyl-3-(fur-2-yl)-1-phenyl-1H-pyrazole (3k)

$C_{14}H_9F_3N_2O$ Oil;^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 6.47$ (dd, 1H, H13), 6.79 (*d*, 1H, H12), 7.04 (s, 1H, H4), 7.48–7.53 (m, 6H, Ar); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 105.7$ (q, ^3J 3, C4), 119.5 (q, ^1J 269, CF_3), 107.1, 111.4, 144.1, 146.9 (Fur-2-yl), 125.7, 129.0, 129.3, 138.7, (CAr), 133.5 (q, ^2J 39, C5), 142.5 (C3); MS (70 eV): $m/z = 278$ (100), 249 (22), 139 (22), 77 (50).

3 Results and Discussion

We started the studies with the reaction of β-alkoxyvinyl trihalomethyl ketones **1a–k** with phenylhydrazine **2** in the presence of ionic liquid under conventional heating. Based on previous observations of good results for cyclocondensation reactions [9–11], the ionic liquid selected for these reactions was [BMIM][BF_4]. The reaction times were of 1 h for alkyl enones and 3 h for nonsubstituted and aryl/heteroaryl enones and temperatures were of 25 °C for alkyl enones and 150 °C for nonsubstituted and aryl/heteroaryl enones (Scheme 1). Pyrazoles **3a–k** were obtained in moderate to excellent yields (60–96%). Synthesis of compound **3c**, in 75% yield, was described in the literature [25] in two steps: (i) ethanol reflux for 3 h, (ii) addition of a mixture of dichloromethane and sulfuric acid 96% and heating at 40 °C for 2 h. This comparison demonstrates that the reaction of enones **1a–k** with phenylhydrazine **2** in [BMIM][BF_4] is a more versatile and efficient method to obtain a series of 1-phenyl-5-trifluoromethyl-1*H*-pyrazoles from alkyl and aryl/hetroaryl enones when compared with molecular solvents. The reaction in [BMIM][BF_4] resulted in products in only one step, in a reduced reaction time and in excellent yields.

Subsequently, to investigate the synergic effects of ionic liquid and microwave irradiation in promoting trifluoromethyl pyrazole synthesis, we carried out all the reactions under MW irradiation, using [BMIM][BF_4]. We applied the times and temperatures established in our previous studies of pyrazoles synthesis using microwave irradiation [12]. From the results (Scheme 1), we found that the microwave irradiation condition were superior, because they furnished the pyrazoles **3a–k** in better yields (56–96%) and a shorter time (6 min) than did the conventional method. The regioselectivity of the products was the same for both methods, for all substituted enones studied. However, the conventional method was more sensitive to the enone structure, since enones containing 4-alkyl substituents were more reactive and presented shorter reaction times and lower temperatures, while 4-aryl-substituted enones required a longer reaction time and higher temperature. In addition, to formation of pyrazole **3k** under MW conditions was necessary 10 min, and the yield was not satisfactory (56%). Synthesis of compounds **3a–d** in toluene using a domestic microwave oven, or in K-10 under solvent-free conditions is described in literature [12]. Compound **3a** was isolated as a mixture of dehydrated pyrazole and 1,5-regioisomer (ratio of 2:1) and compounds **3b–d** were obtained in 85–91% yields. Results for the reactions combining the use of microwave irradiation and ionic liquid were similar to those for the reactions performed in microwave under solvent-free conditions for products **3a**, **3b**, **3d** [12], however regioselectivity was higher in the presence of ionic liquids.

Recently, Martinez-Palou published a review [7] showing synergic effects of ionic liquids and MW for important reactions. Some of these are cyclocondensation reactions leading to 2-aminothiophenes, tiotetrahydropyrimidinones, 4-*H*-pyrans, triazines and imidazoles, and the ionic liquids were used as specific functions, such as acid catalyst, liquid support or co-solvent. There is not report of any heterocyclic synthesis in a simple ionic liquid, such as [BMIM][BF_4], in MW. We believed that the synergic effects of ionic liquid and MW in promoting this reaction is due ionic nature of ILs. This fact allows highly effective interactions with MW energy generating products in short time

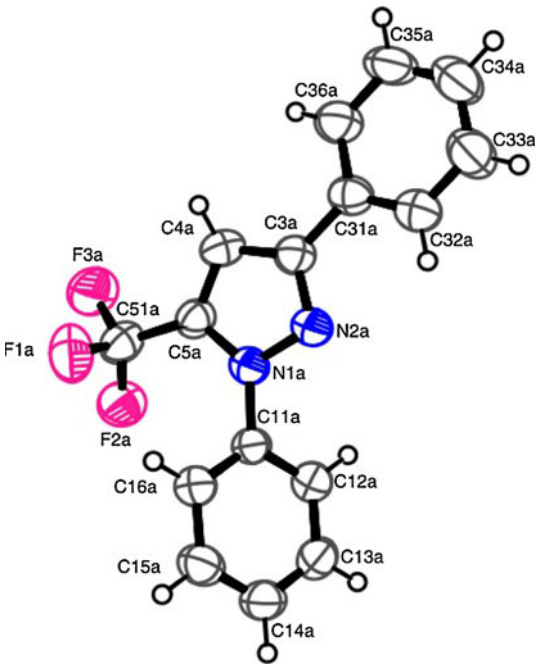


Fig. 1 ORTEP3 [29] obtained from crystal structure of pyrazole **3e**

and with high yields [7]. Therefore, based on a systematic study, we have described, for the first time, the combined use of [BMIM][BF_4] and MW in pyrazole synthesis and have shown their synergic effect to promote the reaction. In addition, using this new method, we have described six new 5-trifluoromethyl-1-phenyl-3-aryl-1*H*-pyrazoles.

All the isolated products were characterized by ^{1}H and ^{13}C NMR, and MS spectral data and were also compared with literature data [12, 25, 26]. An interesting finding was the magnetic resonance behavior observed in compounds **3a–i** (*1,5*-isomer) in the ^{13}C NMR spectral. The signal of ortho carbon of the phenyl group (125.0–126.0) appeared as a quartet because of a through-space ^{13}C–^{19}F coupling with $J = 1.5$ Hz [27, 28]. The solid compound **3e** was submitted to X-ray diffraction and the crystallographic data revealed that it was a *1,5*-isomer, as shown in the ORTEP of Fig. 1.

4 Conclusion

In conclusion, this paper has described an efficient method for pyrazole synthesis that combines the use of ionic liquid and MW. The corresponding system was shown to be a synergic promoting effects, resulting in shorter reaction times and better yields when compared with the classical method. The extremely simple operational procedure and the high aggregate value of the product may facilitate medicinal chemical studies in various fields.

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