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NOTE

Microwave Assisted Synthesis of Arylpyrazoles Using Montmorillonite K-10

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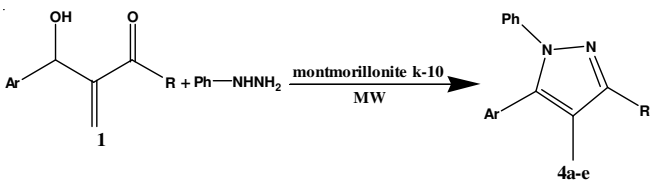
Montmorillonite K-10 clay catalyzed Friedlander condensation of Baylis-Hillman adducts with phenyl hydrazine hydrochloride afforded 1,5-diarylpyrazoles.

Key Words: Arylpyrazole, Montmorillonite K-10, Microwave, Baylis-Hillman.

Heterocyclic compounds are valuable compounds and many applications have been reported. Nitrogen containing five and six membered heterocyclic compounds have been used as a scaffold to synthesize numerous therapeutic molecules[1]. We have synthesized a number of heterocyclic compounds[2-6]. Arylpyrazole is an important class of organic compounds, which received a considerable attention due to their wide range of biological activities and widely used as pharmaceuticals, agrochemicals, antiinflammatory, antiviral, antibacterial[7-13]. In our ongoing research prompted by our interest in multiple component reactions and as part of programs in the area of heterocyclic compounds containing nitrogen[14] and due to the resultant pharmacological interest in compounds which belong to the diarylpyrazoles, although this reaction done previously in other conditions[15,16], herein we report in a different condition using microwave irradiation, one pot reaction, a short time with high yields and easy separation of product for the construction of some 1,5-diarylpyrazole derivatives, *via* condensation of Baylis-Hillman adduct and phenyl hydrazine under microwave irradiation (**Scheme-I**).



Scheme-I

All the chemicals were obtained from Merck or Fluka. All reactions were carried out in a CEM MARS 5TM microwave oven. Silica gel SILG/UV_{254} plates were used for TLC. IR spectra were measured on a Shimadzu IR-470 Spectrophotometer. ^1H and ^{13}C NMR spectra were determined on Bruker 300 DRX AVANCE instrument at 300 and 75 MHz, respectively.

Synthesis of compounds 4a-e: In a reaction a mixture of montmorillonite K10 (0.3 g) was placed in a mortar followed by a Baylis-Hillman adduct (**4a-e**) (1 mmol) and phenyl hydrazine hydrochloride (1 mmol) in 1,2-dichloroetane (5 mL). These materials were then mixed using a pestle for *ca*. 4 min. The homogenized mixture was transferred to a beaker and irradiated with microwaves for 5 min. The progress of reaction was monitored by TLC. The mixture was diluted with CH_2Cl_2 and washed with water and the organic layer was dried ($MgSO_4$). Evaporation of the solvent under vacuum provided a residue which was purified by column chromatography (hexan/ethyl acetate of 8/2) to afford the desired pyrazoles (**4a-e**).

Compound 4a: Orange oil; IR: (KBr, ν_{max}, cm^{-1}): 3056, 2974, 1603, 1593, 1495; ^1H NMR (300 MHz, $CDCl_3$): 1.36 (t, J = 7.6 Hz, 3H), 1.94 (s, 3H), 2.75 (q, J = 7.6 Hz, 2H), 7.21-7.26 (m, 5H), 7.34 (dd, J = 7.6, 1.4 Hz, 1H), 7.55 (dt, J = 8.1, 1.4 Hz, 1H), 7.62 (dt, J = 7.5, 1.30 Hz, 1H), 7.98 (dd, J = 8.1, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 154.4, 149.6, 140.2, 136.1, 133.5, 133.4, 130.0, 129.3, 127.2, 126.7, 125.0, 124.5, 115.3, 20.6, 13.8, 8.5 ppm.

Compound 4b: Orange oil; IR (KBr, ν_{max}, cm^{-1}): 3052, 2970, 2965, 2920, 1607, 1552, 1487, 1351, 1455, 900, 750; ^1H NMR (300 MHz, $CDCl_3$): 1.38 (t, J = 7.5 Hz, 3H), 1.95 (s, 3H), 2.7 (q, J = 7.5 Hz, 2H), 7.20-7.26 (m, 5H), 7.33 (dd, J = 7.5, 1.5 Hz, 1H), 7.58 (dt, J = 8.5, 1.5 Hz, 1H), 7.65 (dt, J = 7.5, 1.30 Hz, 1H), 8.0 (dd, J = 8.5, 1.3 Hz, 1H); ^{13}C NMR (75

MHz, $CDCl_3$): 156.4, 148.2, 141.2, 135.7, 132.2, 135.5, 132.0, 129.7, 128.0, 127.4, 125.5, 124.5, 116.8, 21.8, 14.2, 8.8 ppm.

Compound 4c: Orange oil; IR (KBr, n_{max}, cm^{-1}): 3055, 2972, 2920, 2821, 1590, 1456, 1519, 1340, 750; ^1H NMR (300 MHz, $CDCl_3$): 1.34 (t, *J* = 7.2 Hz, 3H), 2.12 (s, 3H), 2.79 (q, *J* = 7.2 Hz, 2H), 7.20 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.30-7.38 (m, 3H), 7.40 (d, *J* = 8.5 Hz, 2H), 8.30 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.0, 148.0, 143.5, 140.8, 135.5, 132.1, 129.2, 128.8, 127.0, 125.9, 120.2, 23.8, 14.5, 8.9 ppm.

Compound 4d: Orange oil; IR (KBr, ν_{max}, cm^{-1}): 3054, 2962, 2855, 1590, 1568, 1490, 1055, 920, 850, 747, 690; ^1H NMR (300 MHz, $CDCl_3$): 1.41 (t, *J* = 7.5 Hz, 3H), 2.4 (s, 3H), 2.9 (q, *J* = 7.5 Hz, 2H), 7.3 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.25-7.35 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.0, 144.1, 142.2, 137.7, 138.8, 135.5, 132.1, 129.5, 128.8, 128.1, 127.1, 126.0, 115.6, 21.1, 13.5, 9.1 ppm.

Compound 4e: Orange oil; IR (KBr, ν_{max}, cm^{-1}): 3055, 2964, 2916, 2873, 1605, 1509, 1455, 1732, 763; ^1H NMR (300 MHz, $CDCl_3$): 1.38 (t, *J* = 7.5 Hz, 3H), 2.13 (s, 3H), 2.81 (q, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 2H), 7.20-7.26 (m, 3H), 7.31 (m, 2H), 7.35 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.5, 152.3, 145.4, 138.3, 135.6, 131.4, 128.3, 126.5, 125.5, 124.8, 118.5, 21.0, 13.1, 9.0.

Baylis-Hillman adducts were prepared by the reaction of ethyl vinyl ketone, arylaldehydes[17]. For synthesis of 1,5-diarylpyrazole derivatives under microwave, the reaction of Baylis-Hillman adduct (**1**), phenylhydrazine hydrochloride in 1,2-dicloroethane was used (**Scheme-I**). Therefore preparation of all the 1,5-diarylpyrazoles described in this paper, the reaction was complete within 5-8 min on solid support under microwave irradiation in excellent yields (84-90 %) to afford **4a-e** (Table-1).

TABLE-1
THREE-COMPONENT SYNTHESIS
OF SOME 1,5-DIARYLPYRAZOLES

Entry	R	Ar	Product	Yields (%)	Time (min)
1	-Me	Phenyl	**4a**	87	5
2	-Et	*o*-Nitrophenyl	**4b**	84	8
3	-Et	*p*-Nitrophenyl	**4c**	86	7
4	-Et	*m*-Chlorophenyl	**4d**	89	7
5	-Et	*p*-Chlorophenyl	**4e**	90	6

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