RESEARCH ARTICLE

Comparison among the Synthesis of Some Azomethine Derivatives by Classical and Non-classical Methods

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ABSTRACT

In this time, most researchers toward about preparation of compounds according to green chemistry. This research describes the preparation of 2-fluoro-5-(substituted benzylideneamino) benzonitrile under reflux and microwave methods. Six azomethine compounds (B1-6) were synthesized by two methods under reflux and assisted microwave with the comparison between the two methods. Reflux method was prepared of azomethine (B1-6) by reaction of 5-amino-2-fluorobenzonitrile with some aldehyde derivatives with (50–100) mL of absolute ethanol and some quantity of GAA and time is limited between (2–5) hours with a yield between (60–70) percent with recrystallization for appropriate solvents. But the microwave-assisted method was synthesized of compounds B (1-6) under domestic microwave with a small number of solvents (2-3) mL without catalyst and time is (2–3) minutes with yield (85–93) percent. TLC verified all prepared compounds, FTIR, Elemental analysis, and ^{1}H-NMR spectroscopy.

Keywords: Classical and non-classical synthesis, Domestic microwave, Fluorocyano azomethine compounds, Green chemistry.

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INTRODUCTION

Microwave-assisted synthesized one of the most important inorganic and inorganic chemistry fields to prepare compounds such as Schiff bases, heterocyclic unit, macrocycle derivatives, complexes compound.[1] Microwave irradiation can convert electromagnetic energy into heat.[2] Synthesis of compounds through the use of (MW) oven has been widely used in organic and inorganic chemistry, used as an energy source. A comparison can be made between the traditional method and the non-traditional method by knowing the following information, transmission and absorption of conventional heating is entirely different from microwave energy, classical heating is an easy warming method, and energy is transported from the superficial to the most prominent part by conduction and convection.[3] But non-classical method (domestic MW irradiation) makes efficient internal heating by directly coupling irradiation energy with the reaction mixture.[4]

In the past period was the use of classical methods in organic synthesis such as reflux, sand oil, fusion, grinding, but now many researchers have used other methods such as photosynthesis, microwave irradiation, ultraviolet and infrared irradiation for the production of chemical compounds characterized by being more purity, high yield, low cost, short time, environment friendly, less dangerous to human life.[5]

Sustainable or green chemistry is one of the most important fields in chemistry, especially organic synthesis, because this method has some advantages; sustainable chemistry focuses on the environmental impact of chemistry, preventing pollution, reducing toxicity in organic compounds.[6]

The use of microwave irradiation to accelerate organic chemical reactions was first synthesized by Gedye *et al*. and Giguere *et al*.[7,8] Then, some other researchers prepared other compounds within the same method.[9]

EXPERIMENTAL

All chemical derivatives used were supplied from MERCK, CDH, BDH, and Sima-Aldrich. Melting point measuring device was sourced from Stuart company type SMP4. The Fourier transform infrared of the synthesized compounds were recorded in the region 4000–600 cm^{-1} using Shimadzu, type FT-IR 8400, the proton nuclear magnetic resonance device is BRUKER 400MHz spectrometer in DMSO-d6, elemental analysis (CHNS-O) from EURO-VECTOR, Italy, Domestic microwave device has been equipped from LG company.

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Table 1

Compound	*(C=N) cm^{-1}*	*C≡N cm^{-1}*	*(-CH) cm^{-1} aliphatic*	*(-CH) cm^{-1} aromatic*	*(C-F) cm^{-1}*	*others*
B1	1631	2243	2850	3080	713	NO_2 1346 and 1519
B2	1622	2254	2883	3075	713	-
B3	1620	2231	2876	3107	715	OH 3361 cm^{-1}
B4	1620	2231	2839	3097	714	-
B5	1631	2232	2848	3078	719	OH 3447 cm^{-1}
B6	1606	2233	2831	3089	716	-

Traditional Method

Synthesis of 2-fluoro-5-(substituted-amino) benzonitrile

We take equal numbers of moles from 5-amino-2-fluorobenzonitrile (0.1 mol, 0.136 gm) in 50 mL absolute ethanol with (1 mol) from some aldehyde derivatives with three drops of glacial acetic acid, and the reaction mixture is transferred to the hot plate with stirring (reflux) for appropriate time according to the substituted group in aldehyde, the solid product was collected by filtration then washed with ethanol and recrystallized from an appropriate solvent

Microwave Method

In a small vessel, put (0.1 mol) of 5-amino-2-fluorobenzonitrile and (0.1 mol) from substituted aldehyde in a small quantity of absolute ethanol, the mixture had been moved to the domestic microwave oven. The reaction mixture was irradiated by microwave at (340–670) watts, the solid precipitate was washed with ethanol. Physical properties for compounds (B1–B6) are listed in the Scheme (1) illustrates the equations of this reaction.

DISCUSSION

Imine or Schiff bases are previously known compounds, but this research synthesized some imine derivatives via two methods under microwave and conventional, with a comparison between these methods.

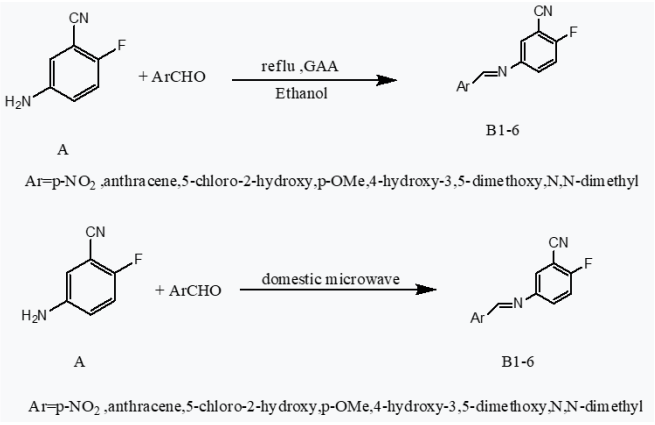
Compounds (B1-B6) were prepared under conventional process with catalyst (GAA) and the reaction time between (2–5) hours, the volume of solvent between (50–100mL). But the same compounds (B1–B6) were synthesized under microwave irradiation without any catalyst, short time for the reaction, and solvent volume (2–3mL).

The microwave method in organic synthesis has several advantages, such as all synthesized compounds used free or minimal amounts of solvent; this method can be considered environmentally y friendly (Green chemistry). This method can also reduce pollution by using a small amount of solvent. Another important adjective for this reaction has concise time comparison with classical method (reflux), moreover simple reaction and low cost because in this research was used domestic microwave oven; finally, the yield in a non-classical method is a high yield compound than the classical method

5-amino-2-fluorobenzonitrile was treated with some aromatic aldehyde compounds to give 2-fluoro-5-(substituted-amino) benzonitrile (B1–B6) all compounds were identified by Fourier transform infrared, H-NMR, elemental analysis.

Table 2

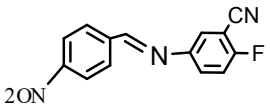
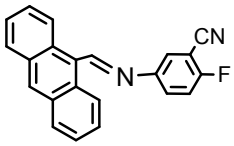
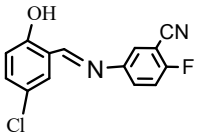
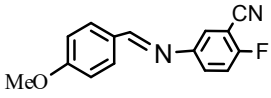
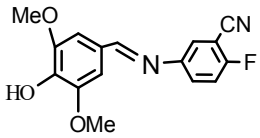
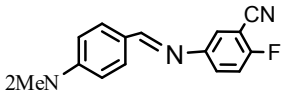
Compound	*%C*		*%H*	*%N*
B1	calculate	62.4	3.01	15.61
	found	61.98	3.05	15.45
B2	calculate	81.47	4.04	8.64
	found	81.39	4.10	8.53
B3	calculate	61.22	2.94	10.20
	found	61.19	2.87	10.11
B4	calculate	70.86	4.36	11.02
	found	70.71	4.27	11.00
B5	calculate	64.00	4.36	9.33
	found	64.12	4.27	9.25
B6	calculate	71.89	5.28	15.72
	found	70.99	5.17	15.70



Scheme 1

The FT-IR of compounds (B1–B6) showed a new band at (1631–1606) cm^{-1} for (imine group) (C=N), good evidence for this reaction is disappeared of the amino group in 5-amino-2-fluorobenzonitrile at (3103 and 3290) cm^{-1}, nitrile group was appeared at (2243–2230) $cm^{-1,}$ (C-F) at (713–719) cm^{-1} moreover (C-H) aliphatic and aromatic at (2831, 2883), (3078,3107)cm^{-1} respectively all values for infrared spectrophotometry for compounds (B1–B6) are listed in Table 1.

Table 3

No.	*Structure*	*Method*	*Time*	*m.p*	*Yield%*
B1		M.W	3 min	156-158℃	91
		reflux	2 hrs.	156-158°C	78
B2		M.W	4.5 min	178-180°C	98
		reflux	3.5 hrs.	178-180°C	82
B3		M.W	4 min	122-124°C	93
		reflux	3 hrs.	122-125°C	89
B4		M.W	2 min	118-119°C	91
		reflux	1.5 hrs.	116-119°C	76
B5		M.W	5 min	113-114°C	95
		reflux	4 hrs.	112-114°C	87
B6		M.W	2 min	146-147°C	92
		reflux	1.15 hrs.	144-147°C	79

H-NMR for compounds (B1–B6) showed a peak at (8.66–9.01) ppm attributed for imine group (CH=N), and multiple peaks at (7.15–7.89) ppm due to of protons in aromatic rings, all compounds (B1–B6) were dissolved in DMSO-d6.

All elemental analysis for compounds (B1-B6) proven suggested formulas by comparison between calculate and theoretical values. Table 2 are listed for the elemental analysis for the compounds (B1–B6)

Table 3 below, illustrates reaction time for classical and microwave methods, structures, melting points, and yield for all compounds (B1–B6).

CONCLUSION

Microwave irradiation in my research is better than reflux or classical heating for the reaction of primary amine (5-amino-2-fluorobenzonitrile) with some aldehyde derivatives because this method is environmentally friendly, high yield, low cost, and short time comparison with the reflux process. Moreover, irradiation of microwave in this research was under the domestic microwave. Both methods gave the same melting points for the synthesized compounds.

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