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Green Approach for Synthesis of Some Substituted Dihalo-1, 4-Benzoquinones by Microwave Irradiation and Its Spectral Studies

Manoj Kumar Batra ¹ and Chhavi Batra ²

¹Department of Chemistry, S.P.C Government College, Ajmer, Rajasthan, India

²Department of Pure & Applied Chemistry, M D S University, Ajmer, Rajasthan, India

ABSTRACT: Microwave-assisted organic synthesis has attracted attention in recent years due to enhanced reaction rates, high yields, improved purity, and ease of work up after the reaction and ecofriendly reaction conditions compared to the conventional methods. In this work microwave-assisted synthesis of 2,5-diarylamino- 3,6-dihalo-1,4-benzoquinones by the condensation of substituted anilines and chloranil has been reported on the inorganic solid support of silica gel. Characterization was done by its physico-analytical and spectral study.

KEYWORDS: Microwave-assisted, 2,5-diarylamino- 3,6-dihalo-1,4-benzoquinones, spectral, physico-analytical

I. INTRODUCTION

Microwave chemistry is becoming increasingly popular both in industry and in academia. Microwaves can accelerate the rate of reaction, provide better yields and higher purity, uniform and selective heating with lower energy usage, achieve greater reproducibility of reactions and help in developing convenient and cleaner synthetic routes. Based on experimental data it has been found that microwave-enhanced chemical reaction rates can be faster than those of conventional heating methods. Reactions conducted using microwaves are cleaner and more eco-friendly than conventional heating methods. Microwaves heat the compounds directly; therefore, usage of solvents in the chemical reaction can be reduced or eliminated. Synthesis without solvent, in which reagents are absorbed on mineral support, has a great potential as it offers an eco-friendly green protocol in synthesis. The use of microwaves has also reduced the amount of purification required for the end products of chemical reactions involving toxic-reagents.[1-12] 1, 4-Benzoquinones are found in animal and plant cells and they play prominent role in cellular respiration processes like bioenergetics transport agents, oxidative phosphorylation and electron transfer[13]. Benzoquinones derivatives containing "3,6-dichloro-1 ,4-benzoquinone" moiety exhibit potent antibacterial [14], antifungal [15], antimalarial [16] , antiviral [17], pesticide[18] and anticancer[19] activities. In this paper, some novel 2,5-diarylamino- 3 ,6-dichloro-1 ,4-benzoquinones, are synthesised under solvent-free conditions on the solid support of silica gel from monosubstituted anilines and 2,3 ,4,5-tetrachloro-1 ,4- benzoquinones (chloranil) using microwave technology.

II. REVIEW OF LITERATURE

Early microwave radiation is used in organic synthesis reaction, the last 60 years of electromagnetic pulse to the acrylic acid, acrylic acid, meth acrylic acid polymerization. Usually microwave-assisted organic reaction mechanism is divided into two kinds, one for the thermal effect, the microwave-assisted organic synthesis reaction mechanism, the microwave-assisted organic synthesis reaction mechanism. Microwave heating speed and uniform, showing no temperature gradient, no hysteresis effect. Microwave can effectively accelerate the chemical reaction, which can be polar organic heating; the other for the non-heating effect: the microwave will accelerate the molecular motion of the reactants; the reactant temperature will rise rapidly. Though many synthetic strategies[20-24]have been reported for the preparation of dihalo 1 ,4 benzoquinone derivatives, most of them include use of expensive, commercially non-available or hazardous reagents, drastic reaction conditions, longer reaction time and cumbersome work-up procedure. The use of silica gel solid support in organic synthetic protocol, especially when coupled with MWI, not only reduce the reaction time and enhance the yield considerably, but also eliminates the requirement of catalyst and solvent from reaction step thus simplify the work-up procedures[25] .

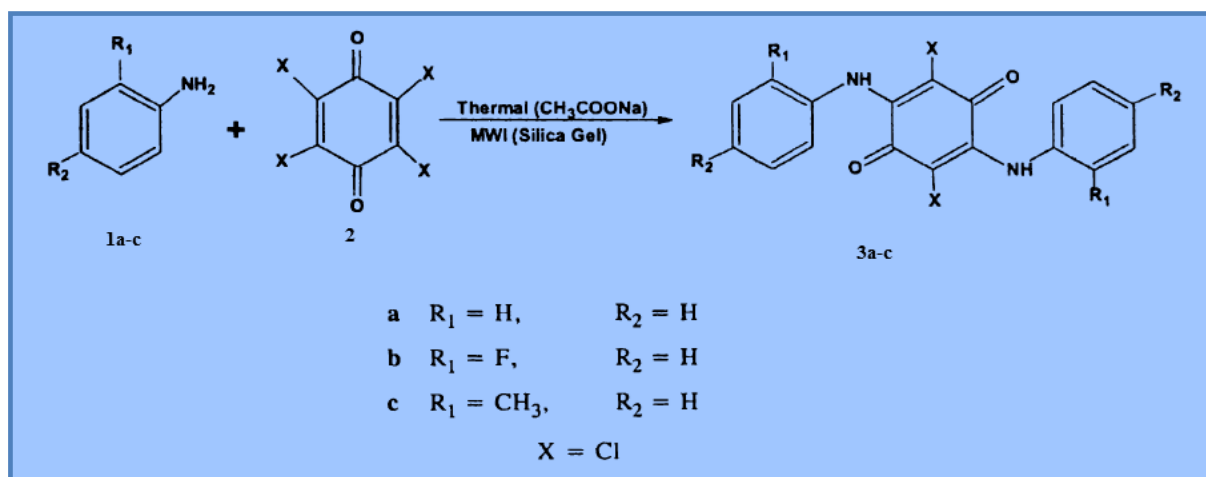
III. EXPERIMENTAL METHODOLOGY

Reagent-grade chemicals were used without further purification. Anhydrous Silica gel 60 (0.063-0.2 mm) was used as solid support after dehydration under microwave irradiation (800 W) for 4 minutes. Microwave reactions were carried out in LG Microwave oven, Model No. LG MS -194W (2450 MHz, 800W), UV/visible spectra were recorded on Perkin-Elmer Lambda 15 UV/vis spectrophotometer. FT IR spectra were recorded on Perkin-Elmer (Spectrum RX1) spectrometer using KBr pellets. ¹HNMR spectra were recorded on Bruker DRX-300 spectrometer (300 MHz) in DMSO-*d*₆ with tetramethylsilane (TMS) as internal standard. Elemental analyses were performed using Elementar Vario EL III Carlo Erba 1108 elemental analyser. Temperature of the reaction mixture was measured through Eutech IR Non-Contact Handheld thermometer (-18 to 260^oC) with LASER sighting, Model No 35625-10. Melting points were determined on a Thomas Hoover melting-point apparatus and are reported uncorrected. UV/vis. maxima, λ_{max}, are given in nm, chemical shifts, δ, for ¹HNMR, are given in ppm, relative to internal reference, TMS and IR frequency, ν, in cm⁻¹.

Microwave method (Solid Phase): A mixture of 2 mmol mono substituted anilines (**1a-c**) and 1mmol chloranil (**2**) were solved in 5 ml of EtOH at room temperature and the solution was adsorbed in anhydrous microwave transparent silica gel solid support (5 g) in a small beaker. The mixture was dried in air and kept in alumina bath in the microwave oven followed by irradiations for the specific time. After the completion of the reaction as monitored by TLC, whole of the reaction mixture was treated with hot-water. The reaction product was extracted with Dimethylformamide (DMF); the extract was filtered, dried and then the solvent was removed. The product (**3a-c**) was first washed with Petroleum ether (40-60 ^oC) and then recrystallized from DMF/Benzene.

IV. RESULTS AND DISCUSSION

2,5-Diarylamino-3,6-dichloro-1,4-benzoquinone derivatives **3** were prepared by the condensation of monosubstituted aryl amine **1a-i** with 2,3,4,5-tetrachloro-1,4- benzoquinone **2** on the inorganic solid support of silica gel under microwave irradiation (Scheme 1).



Scheme-1

The structures of the synthesized 2,5-diarylamino-3,6- dichloro-1,4-benzoquinones **3a-c** were confirmed from physico-analytical (Table 1) and spectral data (Table 2). The % element found for CHN elements are in close agreement with their calculated values (Table 1).

Table-1 Physico-analytical data of 2,5-diarylamino-3,6-dichloro-1,4-benzoquinones 3a-c

Compd. No.	Molecular formula	m.p. (°C)	% CHN, Calcd. (Found)		
			C	H	N
3a	C ₁₈ H ₁₂ Cl ₂ N ₂ O ₂	248	60.16 (60.13)	3.34 (3.31)	7.79 (7.72)
3b	C ₁₈ H ₁₀ F ₂ Cl ₂ N ₂ O ₂	318	54.71 (54.70)	2.55 (2.52)	7.08 (7.05)
3c	C ₂₀ H ₁₆ Cl ₂ N ₂ O ₂	198	61.97 (61.92)	4.16 (4.12)	7.19 (7.16)

The UV spectrum of all the synthesized benzoquinones derivatives exhibits a broad band at 390 nm, which is characteristic of dichloro 1, 4-benzoquinones (Table 2). IR absorption band at 1640-1660 cm⁻¹ gives the values indication of presence of (C = O) group in the compounds and the band at 3230-3242 cm⁻¹ confirms the presence of (N-H) linkage in the synthesized substituted p-benzoquinones (3a-c). In ¹H NMR, δ values at 6.8-7.7 and 8.30 are due to aromatic and NH (D₂O exchangeable) protons, respectively. Singlet appearing at δ 2.28 and 3.87 are due to methyl and methoxy protons, respectively.

Table-2 Spectral of 2, 5-diarylamino-3, 6- dichloro-1, 4-benzoquinones 3a-c

Comp No.	U.V. λ _{max} (cm ⁻¹)	IR(KBr) ν _{max} (cm ⁻¹)	¹ HNMR DMSO (δ)
3a	388	3239(NH) 1651(CO)	7.12-7.40(m,10H,ArH) 8.30(s,2H,NH,D ₂ O ex.)
3b	360	3240(NH) 1656(CO)	7.21-7.64(m, 8H, Ar-H) 8.28(s,2H,NH,D ₂ O ex.)
3c	367.2	3242(NH) 1652(CO)	2.28(s, 6H, 2CH ₃) 7.08-7.26(m, 8H, Ar-H) 8.20(s,2H,NH,D ₂ O ex.)



V. CONCLUSION

Microwave-assisted synthesis is a convenient way toward the goal of green chemistry. Highly substituted, 2, 5-diaryl-amino-3,6-dichloro-1,4-benzoquinones 3a-c, have been synthesized. The Use of silica gel as solid support has excluded the need of excess organic solvents and external bases, keeping the environment ecofriendly. We believe that in the future many more microwave-assisted reactions will be developed which will simplify time consuming conventional procedures thereby increasing the overall efficiency of the processes and reducing pollution of the environment through the use of solvent free reaction protocols.

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