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^{13}C NMR and Mass Spectral Analysis of 2, 5-Diarylamino-3, 6-Dichloro-1, 4-Benzoquinones Synthesized By Microwave Irradiation

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Abstract: The substituted p-benzoquinones are potentially bioactive and they represent a class of compound with wide spectrum of biological activity. The microwave synthesis has received attention as new strategy for the organic synthesis due to the fact that many reactions seem to proceed with much alacrity under such conditions as opposed to thermal-assisted reactions. Apart from the enhanced reaction rate and higher yield, solvent free MWI method provided several advantages such as safe, clean and green reaction conditions, opportunity to work with open vessel, possibility to upscale the synthesis to multi-gram amount, reproducibility and convenient work-up. The characterization was done by ^{13}C NMR and mass Spectral analysis.

Keywords: microwave, p-benzoquinone, physico-analytical analysis, spectral analysis, ^{13}C NMR.

I. INTRODUCTION

Organic reactions are usually slow as they depend upon thermal energy involving external heating. In the last decade there has been considerable concern for energy crisis. The rapid heating of foodstuffs in microwave oven is routinely used by a significant proportion of mankind. Thus microwave-induced heating has gained large acceptance with synthetic organic chemists as non-conventional mode of heating. In recent years, the concept of microwave-induced organic reaction enhancement (MORE) has been demonstrated to not only to dramatically accelerate many organic reactions, but also to improve yields and selectivity [1]. People have recognized other potential applications of this method of heating and scientists engaged in a number of disciplines have applied the rapid heating associated with it to the number of useful processes. These include the preparation of samples for analysis [2], waste treatment [3], polymer technology [4], ceramics [5], alkanes decomposition [6], drug release/targeting [7] and hydrolysis of proteins and peptides [8]. Organic synthesis is an area which can benefit significantly from this technology and it has the potential to become the chemist's round bottom flasks of the future.

Traditionally commercial microwave ovens are used as convenient source of energy in chemical laboratories for the efficient heating of water, moisture analysis and weight ashing procedure of biological and geological materials. Application of microwave technology through catalytic hydrogenesis of alkenes, hydro cracking of bitumen obtained from coal tar sand, degradation of polyhalogenated hydrocarbon, polymer, ceramic technology and waste management.

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.[9-20]

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 [21]. Benzoquinones derivatives containing "3,6-dichloro-1 ,4-benzoquinone" moiety exhibit potent antibacterial , antifungal , antimalarial , antiviral , pesticide and anticancer activities [22-26]. 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.

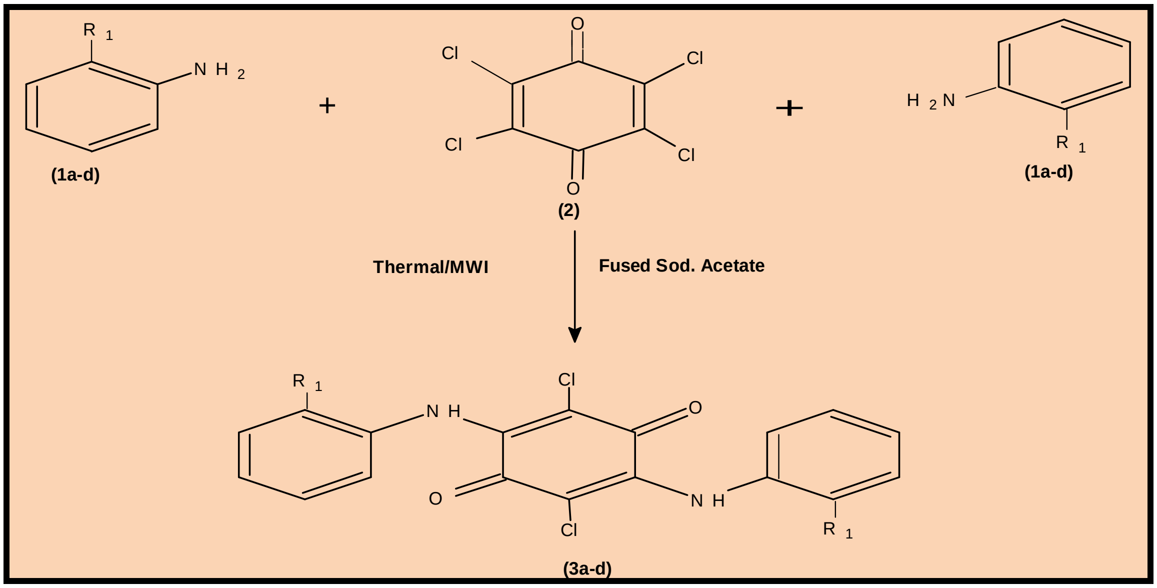
II. MATERIAL AND METHODS

Reagent-grade chemicals were used without further purification. The microwave induced reactions were carried out in an open borosil glass vessel under atmospheric pressure in domestic microwave oven model LG MS-194W operating at 160 W generating 2450 MHz frequency.

The final temperature of the reaction mixture was measured by introducing a glass thermometer into the homogenized reaction mixture. All the melting points were determined in open glass capillary and are uncorrected. UV/VIS. spectra were recorded in Perkin-Elmer Lambda 15 UV/VIS. spectrophotometer.IR spectra were measured on FT IR Perkin-Elmer (Spectrum RX1) spectrometer (ν_{max} in cm^{-1}) using KBr disc. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ / DMSO-d_6 at 300MHz on a Bruker DRX-300 spectrometer. The chemical shifts, are given in ppm, relative to internal reference, tetramethylsilane (TMS) with notations, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet. Fast atom bombardment mass spectra (FAB MS) were recorded at room temperature (m/z (%, fragment)) on a Joel SX-102/DA-600 Mass spectrometer/ Data system using Aragon/Xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV

A. Experimental Synthetic scheme of 2, 5-diarylamino-3, 6-dichloro-1, 4-Benzoquinones

In the present investigation 2, 5-diarylamino-3, 6-dichloro-1, 4-benzoquinone derivatives **(3)** were prepared according to the synthetic scheme proposed by Meister, Lucius and Bruning[11].The title compounds were synthesized by condensing mono substituted aniline **(1)** (2 mol) with tetrachloro-*p*-benzoquinone **(2)** (1 mol) in ethanolic medium in presence of fused sodium acetate under both the conventional (thermal) and microwave irradiation **(Scheme 1)**.



Scheme1. Synthesis of 2, 5-Dianilino-3, 6-Dichloro-1, 4-Benzoquinones
R_1=H, CH_3, OCH_3, F

The following substituted benzoquinone derivatives **(3a-d)** were synthesized:
(3a). 3, 6-Dichloro-2, 5-dianilino-1, 4-benzoquinone (BQ I)
(3b).3,6-Dichloro-2,5-bis(2$'$-methylanilino)-1,4-benzoquinone (BQ II)
(3c).3,6-Dichloro-2,5-bis(2$'$-methoxyanilino)-1,4-benzoquinone (BQ III)
(3d).3,6-Dichloro-2,5-bis(2$'$-fluoroanilino)-1,4-benzoquinone (BQ IV)

The title compounds **(3a-d)** were synthesized by condensing (2 mmol) mono substituted anilines (aniline, o-toluidine, o-anisidine and o-fluoroaniline) **(1a-d)** with (1 mmol) tetrachloro-p- benzoquinones **(2)** in presence of (1 mmol) anhydrous sodium acetate. The reaction mixture(in borosil beaker) kept inside an alumina bath was then placed inside the microwave oven and irradiated for the specified period in cycles of 10 second each followed by 30 second rest. The reproducibility of the whole experiment in the microwave condition was ensured by carrying out every reaction five times on the marked reproducible spots [23] in microwave oven. The internal conditions of temperature and power were controlled by means of selecting solvent free conditions (to avoid temperature fluctuation due to overheating of solvent), alumina bath[24] (for homogeneous heating), controlling power (minimum 160 Watts) and irradiation span (in cycles of 10 seconds each followed by 30 seconds rest). On completion of reaction as monitored by silica gel TLC (Benzene/acetone 60:40), the reaction mixture was cooled to room temperature and solid obtained was washed with hot water and finally with 30% ethanol. Products were recrystallized from benzene/Dimethylformamide.

III. ESULT AND DISCUSSION

A. ^{13}C NMR Spectra and mass Spectral Analysis

^{13}C ^{NMR} spectral studies are used as an additional tool for the complete characterization of newly synthesized organic compounds. As compared to ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy has two distinct advantages.

1) The common range of energy absorption for ^{13}C NMR is wide δ 0-200 relative to TMS, contrasted with δ 0-15 for ^{1}H NMR. Thus fewer peaks overlap in ^{13}C NMR spectra.
2) As only 1.1% of carbon in a compound is ^{13}C thus possibility of ^{13}C-^{13}C coupling is negligible and it is not observed. Therefore, in proton
3) Decoupled ^{13}C NMR spectrum each magnetically non-equivalent carbon gives a single unsplitted peak.

So the fewer peak overlapping and unsplitted signals make ^{13}C NMR spectra easier to interpret. Keeping this in mind ^{13}C NMR spectra of all the substituted p-benzoquinones (3a-d) were recorded on FT NMR spectrometer at 300MHz frequency in DMSO solvents. The chemical shift value and inference derived are given in Table I.

Table-I The chemical shift value according to ^{13}C NMR spectra

Compound	δ (ppm)	Assignment
3a	124.8-145.8 (8) 172.9 (1)	C_1-C_6, C_7 , C_9, C_{10} , C12 and C_{13} -C_{19} (Aromatic C) C_8 and C_{11} (>C=O)
3b	17.9 (1) 125.6-144.2 (8) 172.9 (1)	C_1 and C_{20} (-CH_3) C_3-C_8, C_{10} , C_{11} and C_{13} -C_{19} (Aromatic C) C_9 and C_{12} (>C=O)
3c	55.9 (1) 110.6-152.2 (8) 172.8 (1)	C_1 and C_{20} (-OCH_3) C_3-C_8, C_{10} , C_{11} and C_{13} -C_{19} (Aromatic C) C_9 and C_{12} (>C=O)
3d	126.6-162.1 (8) 171.2 (1)	C_1-C_6, C_7 , C_9, C_{10} , C_{12} and C_{13} -C_{19} (Aromatic C) C_8 and C_{11} (>C=O)

The fast atom bombardment mass spectra (FAB MS) of the substituted 2, 5-dianilino-3, 6 dichloro-1, 4-benzoquinones (3a-d) were recorded at room temperature on a Mass spectrometer using Aragon/Xenon as the FAB gas. Mass fragmentation of the title compounds (3a-d) along with m/z values and relative intensity of the fragments are given in Table II.

Table II-Mass fragmentation of the title compounds (3a-d) along with m/z values and relative intensity of the fragments

Compound	FAB MS (298 ^{0}C) **m/z** (%, fragment)
3a	**359** (30%, M^+), **361** (16%, M^++2), **358** (28%, M^+-H), **329** (25%, M^+-2NH), **324** (10%, M^+-Cl), **326** (6.6%, M^++2 - Cl), **307** (10%, M^+ -2C_2H_2), **266** (9%, M^+-H-C_6H_5N), **208** (72%, unsym. rDA frag.), **165** (15%, sym. rDA frag.), **136** (70%, rDA frag.-CO), **91** (30%, $C_6H_5N^+$), **77** (40%, $C_6H_5^+$).
3b	**387** (100%, M^+), **389** (66%, M^++2), **386** (15%, M^+-1), **351** (35%, M^+-HCl), **333** (17%, M^+-2HCN), **315** (15%, M^+-2HCl), **307** (48%), **289** (25%), **279**(10%, M^+(386)-$C_7H_7^+$), **277**(11%, M^+(333) -2CO), **242** (8%, M^+(279) -Cl), **233**(17%, M^+ -2C_6H_5), **215** (10%, M^+(242) -HCN), **203** (15%), **191** (8%), **177** (25%, rDA fragment), **107** (20%, $C_7H_7^+$).

3c	**419** (80%, M^+), **421** (66%, M^++2), **418** (48%, M^+-1), **388** (25%, M^+-OCH_3), **387** (20%, M^+-CH_3OH), **356** (18%, M^+-2OCH_3), **336** (25%), **315**(5%), **273**(12%), **260** (18%, M^+(312)-2CO), **245** (16%, M^+(260)-NH), **228** (15%, M^+(260) -CH_3OH), **209** (14%, M^+(245)-HCl), **178** (18%, M^+(356) -symm. rDA fragment), **152** (30%, M^+(178)-CO), **120** (35%), **107** (58%, $C_7H_7O^+$), **76** (22%, $C_6H_4^+$).
3d	**395** (40%, M^+), **397** (28%, M^++2), **399** (12.5%, M^++4), **391** (27%, M^+- 2H_2), **375** (25%, M^+ – HF), **361**(20%, M^+(375) - N), **345** (68%, M^+ – C_4H_2), **329** (57%, M^+ (345) – O), **322** (100%, M^+-2HCl), **307** (72%, M^+ (322) – NH), **302** (5%, M^+(375) - C_6H_1), **286** (0%, M^+ (375) - C_6H_3N), **285** (0%, M^+ – C_6H_5NF), **277** (9%, M^+ (329) – C_4H_4), **249** (6%, M^+ (345) – C_6H_5F), **242** (4%, M^+ (277) – Cl), **232** (3%, M^+ (249) – OH), **192** (8%, M^+ (286) - C_6H_3F), **176** (15%, M^+ (285) – C_6H_5NF), **120** (20%, M^+ (176) - 2CO), **89** (32%, $C_6H_3N^+$)

IV. CONCLUSION

Microwave-assisted synthesis is a convenient way toward the goal of green chemistry. Highly substituted, 2, 5-Dianilino-3, 6-Dichloro-1, 4-Benzoquinones (3a-d), have been synthesized .Mass fragmentation of the title compounds along with m/z values and relative intensity of the fragment and ^{13}C NMR characterize the derivatives of 2, 5-Dianilino-3, 6-Dichloro-1, 4-Benzoquinones.

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