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MICROWAVE INDUCED SYNTHESIS OF AZO COMPOUND : A SOLVENT FREE PATH FOR SOME DYES

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ABSTRACT

Synthesis of azo derivatives was carried out under microwave irradiations. The reaction was found to follow diazotization and condensation mechanism with removal of water molecules. Formation of product was confirmed through TLC, M.P. and spectral analysis. The reaction was carried out in a single pot without using solvent in a domestic microwave oven.

Key words: Azo dye, Microwave radiations, One pot synthesis, Dyes, Solvent free path.

INTRODUCTION

Microwave induced organic enhancement *i.e.* MORE technique[1] has several advantages over traditional method of synthesis of organic compound, Some of these advantages are -

(i) Shorter time required for completion of reaction,

(ii) Higher yield,

(iii) Purity of the product,

(iv) Solvent free reaction, and

(v) Energy is not wasted even on bulk heating of the material.

There is an increasing interest in the use of environmentally benign reagent and conditions. Microwave synthesis has various advantages over conventional method.[2-4] In past few years due to numerous advantages, microwave technology has been used widely in household cooking as well as in the field of synthesis of organic compounds like dyes, drugs, proteins, peptides, carbohydrates, heterocyclics etc.

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This non-conventional method has various advantages over conventional method. A lot of work has been done in past decades reactions on are generally of three types -

(i) Reaction between neat reactants, (ii) Reaction of reactants, which are supported on a solid base in dry media like silica, alumina etc. and (iii) Reactions in solvents.

Gedye et al.[5] used microwave ovens for rapid organic synthesis, for the first time and later on, various workers described the utilization and advantages of microwave irradiations for organic synthesis.[5-9] Microwave assisted solvent free synthesis of triphenylmethane derivatives was carried out by Mehta *et al.*[10] A solvent free synthesis of 2-hydrazinobenzothiazole derivatives using microwave has been reported.[11] Microwave assisted solvent free synthesis of substituted chromenes was carried out by Meenakshi *et al.*[12] Solid state induced heterocyclization under microwave irradiations for the synthesis of 2-phenyl-3-hydroxyl-quinoline-4(H)-1 was reported by Heravi *et al.*[13] Microwave assisted solvent free synthesis of anthraquinone derivatives was carried out Jain and Singh.[14] Solvent free improved synthesis of some substituted 1,3-diaryl propanes and 3,5-diaryl-6-carbethoxy cyclohexenone under microwave irradiations was carried out by Jhala *et al.*[15] Solvent free synthesis has also been carried out by other workers.

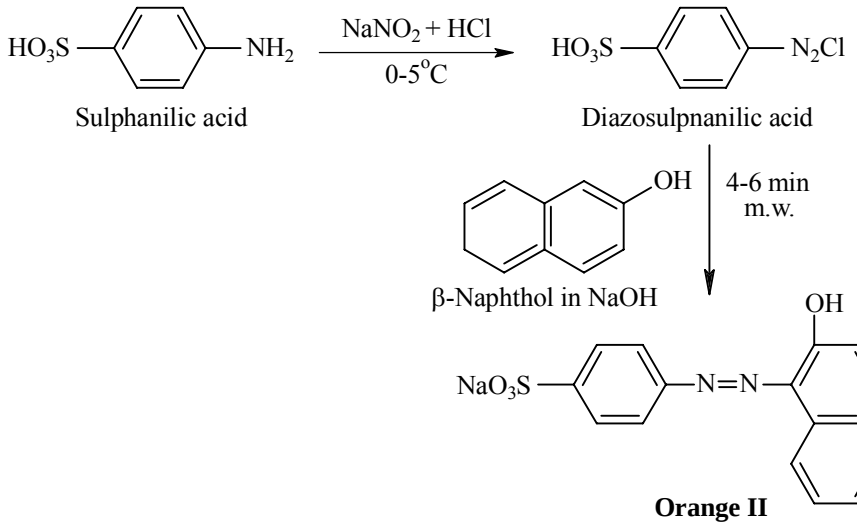
EXPERIMENTAL

Compound **(1)** was prepared by taking diazotized sulphanilic acid and coupling it with β-naphthol in NaOH solution in a vessel. The mixture was irradiated with microwave at low intensity. After formation, it was washed with saturated NaCl solution and then recrystallized with alcohol, where orange crystals were obtained. Its melting point was vrecorded.

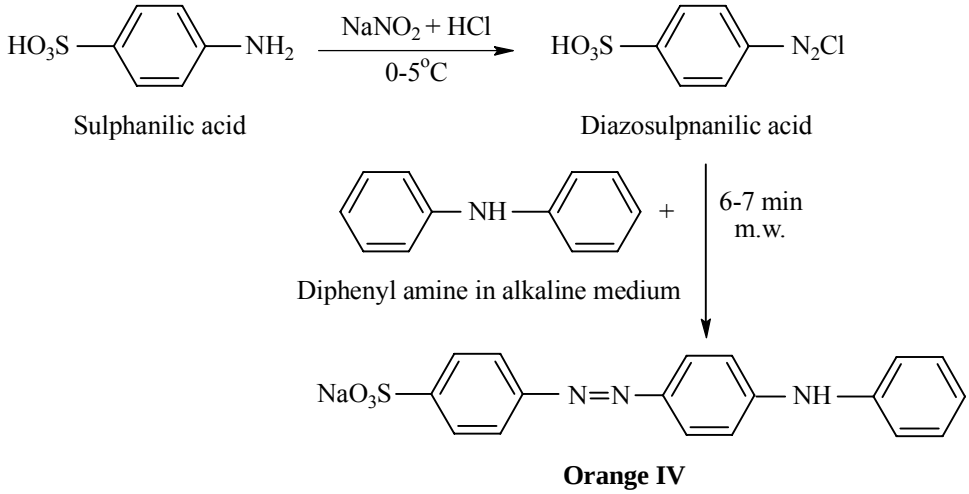
Compound **(2)** was prepared by taking diazotized sulphanilic acid and coupling it with diphenylamine in alkaline solution in a vessel. The mixture was irradiated with microwave at low intensity. After formation, it was washed with water and then recrystallized with alcohol, where yellow-grey crystals were obtained. Its melting point was recorded.

RESULTS AND DISCUSSION

Synthesis of azo derivatives has been carried out in a single pot/few steps without using solvent in a domestic microwave oven. The product formed was monitored through TLC and its structure has been confirmed by spectral studies. Formation of compound *viz*. orange II and orange IV followed the reaction pathway as shown in **Schemes 1** and **2.**



Scheme 1



Scheme 2

Table 1: Physical properties of (1) and (2)

Compound	Molecular formula	Molecular weight	Melting point (°C)	Reaction time (min.)	% Yield
Orange II	$C_{16}H_{11}N_2NaO_4S$	350.32	164	4-6	60.0
Orange IV	$C_{18}H_{14}N_3NaO_3S$	375.39	330	6-7	75.0

Analytical data of compounds

Compound (1)

Elemental analysis – C-54.80%, H-3.14%, O-18.28%, S-9.14%

IR Spectrum : ν_{max} [Nujol (cm^{-1})]

3050 – 3000 - C – H str. (ν)

1300 – 800 - C – C str. (w)

1620 - C = C str. (Aromatic system)

2900 – 2840 - C_{sp3} – H str.

900 – 700 - C – H def. vib.

~1200 - C – O str.

660 - O – H out of plane bending vib. (w)

800 – 770 - C – H out of plane bending (s)

2270 - N_2^+ str. (m)

800 – 600 - C – S str. (w)

1100 – 990 - S = O str. (s)

700 – 600 - S – O str.

Mass Spectrum : m/z

M^+ - (Parent ion peak at m/e = 350; Base peak at m/e = 143 is represented by β-naphthol ion. β-naphthol ion further loses hydrogen to give fragment ion at m/e = 142. Peak of second major fragment ion at m/e = 179 is represented by sulphonic acid sodium salt.

Compound (2)

Elemental analysis – C-57.6%, H-3.73%, O-12.8%, N-11.2%, S-8.53%

IR Spectrum : ν_{max}, [Nujol (cm^{-1})]

2268 - N_2^+ str. (m)

800 – 600 - C – S str. (w)

1122 – 990 - S = O str. (m)

700 – 600 - S – O str. (w)

1320 - C – N str. vib. (s.m.)

3411 – 3533 - N – H str. vib. (Asymmetric and symmetric, m, w)

1675 – 1500 - N – H in plane bending vib. (s)

3020 - C – H str. vib., Aromatic

900 – 650 - N – H out of plan bending (s)

Mass spectrum: m/z

M^+ parent ion peak at m/e = 375; Base peak at m/e = 144 is represented by diphenylamine. Diphenylamine ion further loses hydrogen to give fragment ion at m/e = 143. Peak of second major fragment ion at m/e = 179 is represented by sulphonic acid sodium salt.

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