

Microwave Assisted Improved Syntheses of Indigoid and Anthraquinoid Dyes

MAMTA DARVEKAR, BHAWNA GHORPADE AND PADMA S. VANKAR*

Facility for Ecological and Analytical Testing (FEAT)

Indian Institute of Technology, Kanpur-208 016, India

E-mail: psv@iitk.ac.in Fax: 0091-512-597844

Rapid and improved approaches to indigoid and anthraquinoid dyes have been developed using microwave irradiation. Reaction between *o*-nitrobenzaldehyde and acetone in aqueous sodium hydroxide yielded indigo which was further functionalized for indigo yellow and tyrian blue. Similarly, anthraquinoid dyes have also been synthesized. Reaction between phthalic anhydride and catechol in presence of catalytic amount of concentrated sulphuric acid gave alizarin in quantitative yield. Alizarin was further functionalized to form alizarin orange.

Our aim is to utilize this energy in synthesizing dyes: like indigo, alizarin which are widely used by dyers. A rapid and improved approach to indigoid and anthraquinoid dyes has been developed using microwave irradiation. The minimum usage of organic or inorganic solvents (*e.g.*, benzene, sulphuric acid), high efficiency, safety, reduced reaction time and simpler experimental procedure make this technique environmentally friendly.

Key Words: Microwave synthesis, Indigoid dyes, Anthraquinoid dyes.

INTRODUCTION

The application of microwaves in organic synthesis has experienced exponential growth within the last eleven years. The usefulness of microwave energy for the preparation of a wide variety of organic compounds using a microwave system shows rate enhancement in reactions both in dry and wet mediums.

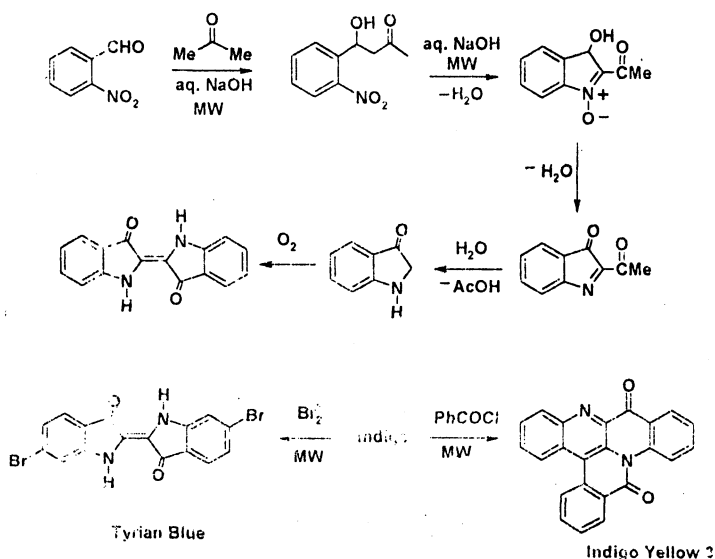
Indigo is a dye that has been used for thousands of years for the blue dyeing of textiles. Indigo and indigoid dyes are vat dyes applicable to both cellulose and protein fibres. Synthetic indigo appeared on the market in 1897. The history of synthetic indigo is closely associated with the history of the BASF Company^{1, 2}. Although today's production plants for dyes are technically very advanced as a result of modernization, but there have always been threats to the environmental pollution and energy depletion despite chemical and technical improvements. Safe environment and usage of minimal energy are the slogans of today. In this regard non-conventional energy sources such as ultrasound³, microwaves⁴⁻⁸, vacuum thermolysis, etc. have been used extensively in recent times. In this regard organic

reactions in wet or dry medium, under microwave irradiation, are at present under extensive examination⁹⁻¹².

Among various methods for the syntheses of indigoid dyes¹³⁻¹⁷, the first one involving two steps was patented by Baeyer¹³ in 1877. However BASF has commercialized another method patented by Heumann¹³ which involved five steps for the synthesis of indigo, but due to high yields in comparison to Baeyer's route this method is still being followed. However, from the ecological point of view the synthesis reported by Heumann involves usage of hazardous chemicals such as hydrogen cyanide, aniline, sodium metal and formaldehyde. The temperature used in the reaction ranges from 80–380°C at various stages. It is obvious that if the Baeyer's synthesis involving only two steps is improved in terms of yield, time and other energy related parameters it could be of commercial value. Our interest in the development of indigo dyes using microwave heating led us to reinvestigate the well known Baeyer's synthesis of indigo.

Since microwave has recently become extremely popular in accelerating organic reactions by providing high heat efficiency (remarkable rate enhancement) and dramatic reduction in reaction times, we considered using microwave irradiation in improving the Baeyer's synthesis for indigo. Indeed it was found that one pot synthesis of indigo employing microwave irradiation was completed in just 20 min in 77% yield. On the other hand, the conventional method reported by Baeyer takes 40 h to yield only 40% of the desired product. Also, the reaction was found to be cleaner when microwave irradiation was used. Likewise, tyrian blue (5,5-dibromoindigo) and indigo yellow 3G were also synthesized by using microwave irradiation with considerable improvement in terms of yields and time (Table-1).

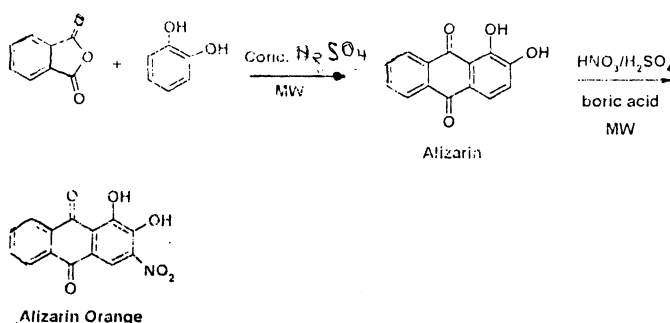
Alizarin¹⁸ is one of the oldest and most important anthraquinoid mordant



Scheme-1. Synthesis of indigoid dyes

dyes. It is derived from the roots of madder and has a brilliant colour. Its synthesis was one of the landmarks of dye chemistry. Synthetic alizarin is considered to be superior to the naturally occurring type because it is pure 1,2-dihydroxy anthraquinone whereas in nature it is present as a glycoside of rubirhythric acid which requires hydrolysis, in the presence of enzyme or dilute acid, to give alizarin. This dye has no affinity for cotton. However, on mordanting with a metal salt such as alum it is readily absorbed by the fibre by complexing the metal ion through the *o*-dihydroxy groups and produces beautiful gamut of colours.

After the first synthesis of alizarin by Graebe and Libermann¹⁹ many syntheses are reported in the literature¹⁹. Commercially, it is synthesized by heating sodium anthraquinone- β -sulfonate (also called silver salt) with aqueous caustic soda and sodium nitrate (or chlorate) in an autoclave at 200°C. The product is a soluble disodium salt, and alizarin is precipitated by acidification. But in this method, fluoropurpurin (1,2,6-trihydroxy anthraquinone) and anthrapurpurin (1,2,7-trihydroxy anthraquinone) are also formed as by-products. More recently alizarin has been prepared by condensation of phthalic anhydride with catechol in the presence of sulphuric acid at 180°C. We became interested in improving this reaction by utilizing microwave irradiation. Indeed it was found that the reaction of phthalic anhydride and catechol in the presence of catalytic amount of sulphuric acid required only 10 min at 60°C for the completion of the reaction. A comparative study with the conventional method shown in Table-1 clearly indicates a dramatic reduction in time and considerable increase in the yield. We have also prepared substituted alizarin such as alizarin orange by nitration of alizarin (**Scheme-2**) in presence of boric acid under microwave irradiation condition which also showed considerable improvement (Table-1). Boric acid, which complexes with the carbonyl groups in anthraquinone, markedly catalyses the electrophilic substitution reaction on the ring which has hydroxyl groups and nitration takes place at the 3rd position. Interestingly, when the reaction mixture was left at room temperature for a couple of days, some 4-substituted nitro product was also formed.



Scheme-2. Synthesis of anthraquinoid dyes

This study documents, for the first time, the usefulness of microwave heating for the preparation of commercially important indigoid and anthraquinoid dyes. The reactions show drastic reduction in reaction times as compared to conventional heating, and cleaner products are formed with high yield. The reactions were performed at 1–2 g scale as well. Thus, we believe that this environmentally safer technology for the syntheses of indigoid and anthraquinoid dyes would find use in dyestuff industry.

EXPERIMENTAL

The reactions were carried out under controlled pressure in a vessel adapted with ATC and APC of milestones MLS-1200 mega reactor in teflon vessels. All the compounds were identified by GC-MS, FT-IR, NMR and gave satisfactory results in comparison with authentic samples. Melting points are in good agreement with literature data. Each reaction was repeated three times to check the yields.

Indigo: Acetone (2 mL) and 1 M NaOH (1 mL) are sequentially added to ortho-nitrobenzaldehyde (1.208 g, 8 mmol) and the mixture subjected to MW irradiation in a teflon vessel at 80 W power and 2.45 GHz for 10 min. One mL of 1 M NaOH was added and again MW irradiation was carried out further for another 10 min. At the end of exposure to microwave, the reaction mixture was cooled to room temperature. The product was then left for air oxidation of the indoxyl moiety for 4 h under basic conditions. The crude product was recrystallized from acetone to yield 77% of indigo. An identical mixture was refluxed for 40 h using conventional heating (oil bath) and subjected to purification to give 40% of the desired product; some polar product was also formed in the controlled experiment which could not be identified.

Indigo Yellow 3G: A mixture of indigo (0.262 g, 1 mmol) and benzoyl chloride (0.181 g, 2 mmol) in nitrobenzene (2 mL) in presence of copper catalyst (0.010 g) was subjected to MW irradiation in a teflon vessel at 80 W power and 2.45 GHz for 10 min. Aqueous work-up followed by extraction with ethyl acetate (50 mL \times 3) gave the product in 65% yield along with 20% starting material and 15% of a very polar compound was obtained. An identical mixture was refluxed for 36 h using conventional heating (oil bath) and subjected to identical work-up and purification to give 45% of the same product and unreacted starting material was also recovered in the controlled experiment.

Tyrian Blue: A mixture of indigo (0.262 g, 1 mmol) and bromine (0.11 mL, 2 mmol) diluted in nitrobenzene was added dropwise and heated in MW in a teflon vessel at 80 W power and 2.45 GHz for 10 min. Aqueous work-up followed by extraction with ethyl acetate (50 mL \times 3) led to the 5,5'-dibromoindigo product obtained in 69% yield and the rest of the starting material was recovered. An identical mixture was refluxed for 20 h using conventional heating (oil bath) and subjected to identical work-up and purification to give 35% of the desired product along with tri- and tetra-brominated products in the controlled experiment.

TABLE-1

Compound	Procedure followed	Reaction time	Reaction temperature (°C)	Recovery product* (%)
Indigo	Microwave	20 min	50	77
Indigo	Conventional	40 h	50	40
Indigo yellow 3G	Microwave	10 min	50	65
Indigo yellow 3G	Conventional	36 h	150	45
Tyrian blue	Microwave	10 min	35	69
Tyrian blue	Conventional	20 h	100	35
Alizarin	Microwave	10 min	60	85
Alizarin	Conventional	8 h	180	65
Alizarin orange	Microwave	15 min	30	98
Alizarin orange	Conventional	6 h	80	68

*The recovery values are based on isolated yields and represent the average of 3 experiments.

Alizarin: Phthalic anhydride (1.48 g, 10 mmol) and catechol (1.10 g, 10 mmol) were mixed with catalytic amount of concentrated H₂SO₄ (2 drops) and the mixture was subjected to MW in a teflon vessel at 120 W power and 2.45 GHz irradiation at 65°C for 10 min. The crude product was an orange reddish dye. Recrystallization with ethanol yielded 85% (2.04 g) of the pure dye. An identical mixture was refluxed for 8 h using conventional heating (oil bath) and subjected to identical work-up and purification to give 65% of the desired product along with unreacted starting material in the controlled experiment.

Alizarin Orange: A mixture of alizarin (0.240 g, 1 mmol) was reacted with 0.5 mL of the mixture of HNO₃/H₂SO₄/H₂O (24 : 59 : 17) along with a small pinch of boric acid in MW in a teflon vessel at 50 W power and 2.45 GHz for 15 min at 30°C. The crude product was recrystallized with ethanol to yield 98% (0.279 g) pure dye. An identical mixture was refluxed for 6 h using conventional heating (oil bath) and subjected to identical work-up and purification to give 68% of the desired product, along with the formation of 4-substituted product.

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Contact:

Professor Xinrong Zhang

Analysis Center, Department of Chemistry

Tsinghua University, Beijing 100084, P.R. China.

Tel: (+86-10) 6278-1688 Fax: (+86-10) 6277-0327

E-mail: xrzhang@chem.tsinghua.edu.cn or zrzhang@ihw.com.cn