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Ultrasound Assisted Diazotization and Diazo Coupling Reactions Using Trichlorotriazine[1]

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Abstract—A high rate and efficient procedure for the synthesis of azo dyes has been developed. This concluded the sequential diazotization-diazo condensation of aromatic amines such as 4,4'-sulfonyldianiline with $NaNO_2$, or trichlorotriazine with coupling agents under ultrasound irradiation at room temperature. This method applied to several types of coupling agents led to corresponding azo dyes in high yield within short reaction time. The mild reaction conditions and inexpensive procedure are clear advantages of this method.

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INTRODUCTION

Azo dyes are compounds that contain azo groups linked to the methane or aromatic sp^2-hybridized carbon atom. Azo dyes make a well-known class of organic photoactive materials due to their excellent optical switching properties and high chemical stability [1, 2]. These materials are widely used in heat transfer printing and textile industries [3, 4], optical data storage [5], and photo-refractive polymers [6].

The diazotization and diazo coupling reactions usually include protonation of nitrous acid under strong acidic conditions and azo coupling carried out at low temperature and involve a nucleophilic coupling component [7, 8].

The conventional acid-base catalyzed synthesis of azo compounds is not environmentally friendly. The diazotization and diazo coupling reactions are complicated usually by side reactions. For example, reaction temperatures above 10°C generally can promote phenol formation in aqueous media and subsequent coupling of phenol with undecomposed diazonium salts producing azo phenols.

On the other hand, green chemistry has become a major driving force for organic chemists to develop environmentally benign methods for organic compounds. For example, ultrasound irradiation can enhance the reaction of economical and ecological efficiency [9, 10].

As a part of novel selective and environmentally friendly method for the heterocyclic and pharmaceutical compounds [11–13], herein, we report an efficient and environmentally friendly reaction of diazotization and diazo coupling using TCT under ultrasound irradiation at room temperature.

RESULTS AND DISCUSSION

Diazonium salts are versatile compounds in organic chemistry. However, their low thermal stability limits application of these reagents. According to the novel method 4,4'- sulfonyldianiline was rapidly converted to the corresponding azo dyes under ultrasound irradiation with high yield using TCT at room temperature (Scheme 1).

Equimolar amounts of 4,4'-sulfonyldianiline, sodium nitrite, and TCT in 10 mL of H_2O were stirred at 0–5ºC for 15 min to produce a homogeneous solution of diazonium salt. This was followed by addition of equimolar amount of a coupling agent upon stirring. Progress of the reaction was monitored by TLC. Upon completion of the reaction (30–45 min), the crude product was filtered off and recrystallized from EtOH/H_2O.

Influence of TCT amount and nature of solvents upon reaction time and yield was studied. The corresponding data are listed in Table 1.

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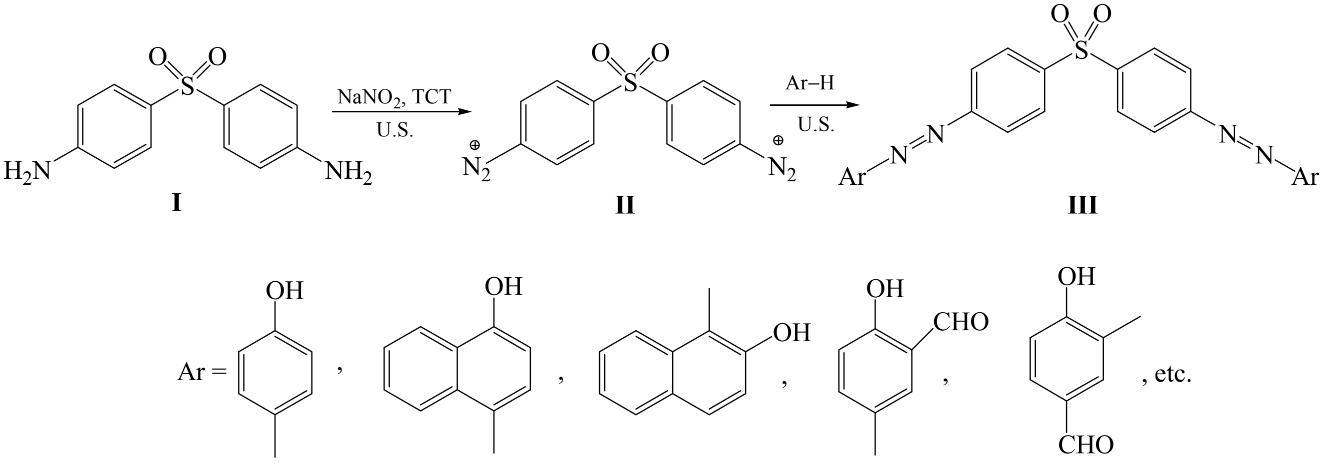
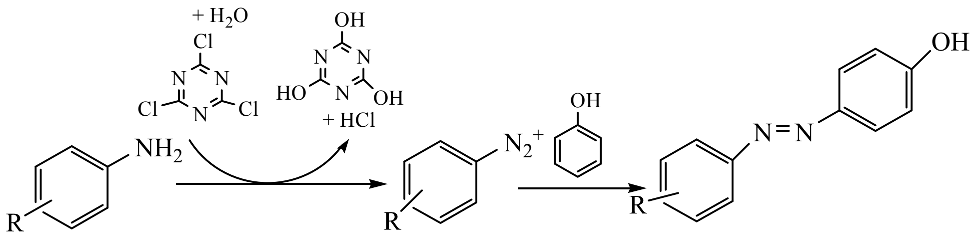
[1] The text was submitted by the authors in English.

Scheme 1. Ultrasound assisted synthesis of azo dyes.



Scheme 2. Estimated mechanism of azo dyes synthesis.



According to the above data (Table 1), 3 mmol of TCT and water media was the most efficient for the synthesis of the azo dye **IIIa**. An estimated mechanism of the aqueous TCT catalyzed process is presented in Scheme 2.

The optimized conditions were applied to synthesis of compounds **IIIa–IIIi**. It is noteworthy that the side processes were not observed (Table 2).

Table 1. Effect of solvents and a catalyst amount on the synthesis of **IIIa**

Catalyst amount (mmol) per 1 mmol substrate	Solvent	Time, min	Yield, %
1	H_2O	60	74
3	H_2O	30	86
5	H_2O	30	82
3	CH_3CN	–	–
3	$CHCl_3$	–	–
3	EtOH	60	89

In the course of ongoing research we studied the catalytic efficiency of K10, KSF, and HY-Zeolite compared to TCT of azo dye **IIIa** in water media at room temperature. The resulting data are presented in Table 3. TCT as a Bronsted acid promoter proved to be a better choice than K10, KSF and HY-Zeolite as Lewis acids in this process.

EXPERIMENTAL

Materials and measurements. All reagents were purchased from Merck and Fluka. Melting points were measured by an Electrothermal 9100 apparatus. Ultrasound apparatus Astra 3D (9.5 L, 45 kHz frequency and the transducers from TECNO-GAZ were used. IR spectra were recorded with a Shimadzu IR-470 spectrometer. ^{1}H NMR spectra were measured by a 500 MHz Bruker DRX-500 in $CDCl_3$ or DMSO-d_6 solvents with TMS internal standard. Element analysis was carried out with a Carlo-Erba EA1110CN-NO-S analyzer and in good agreement with the calculated values.

Typical ultrasound assisted synthesis of 4,4'-[4,4'-sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]diphenol using TCT.

Table 2. Ultrasound assisted synthesis of azo dyes **IIIa–IIIi**

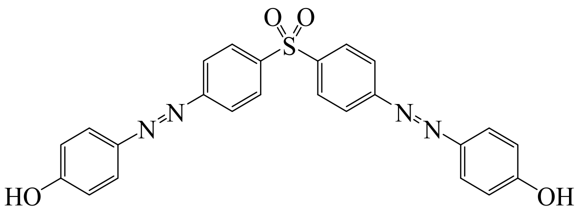
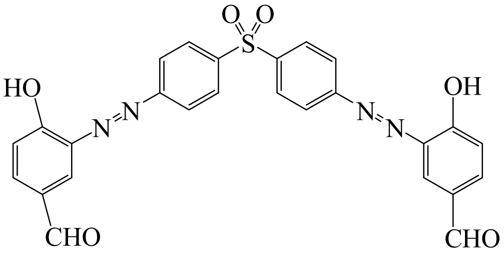
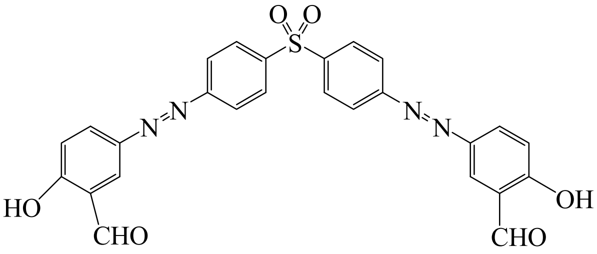
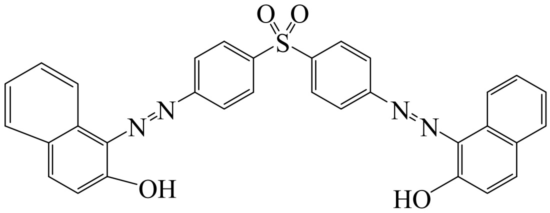
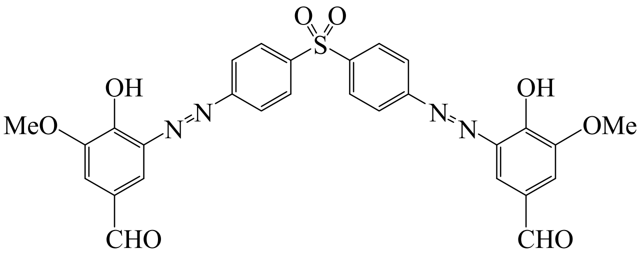
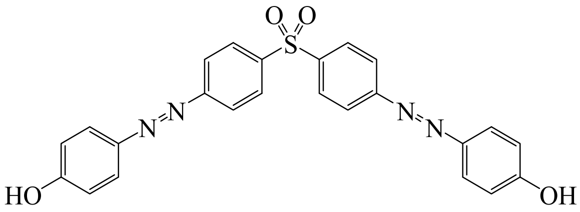
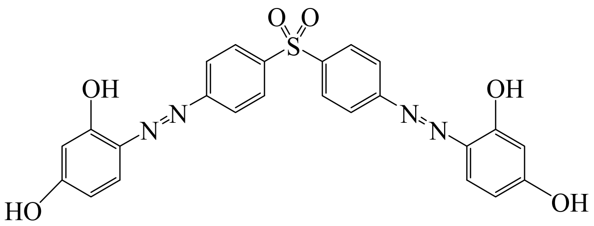
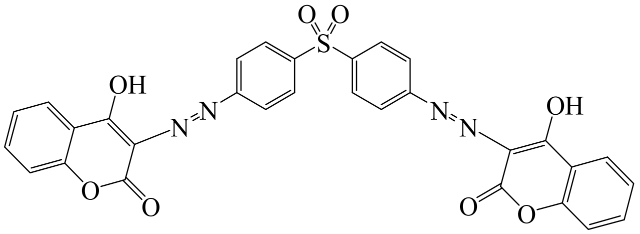
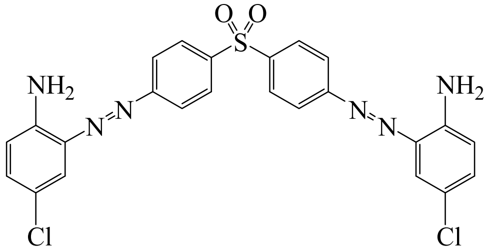
Comp. no.	Structure	Time, min	Yield, %
IIIa		13	86
IIIb		15	83
IIIc		11	97
IIId		11	87
IIIe		15	85
IIIf		12	95

Table 2. (Contd.)

Comp. no.	Structure	Time, min	Yield, %
IIIg		11	97
IIIh		14	89
IIIi		13	86

4,4'-Sulfonyldianiline (4 mmol, 1.12 g), sodium nitrite (8 mmol, 0.55 g), 0.05g TCT and 10 mL of H_2O were charged into an open pyrex glass vessel and ultra sound irradiated in a water bath at room temperature for 3 minutes to produce a homogeneous diazonium salt solution. Phenol (8 mmol, 0.75 g) was added to the diazonium salt and the mixture stirred for 10 minutes. Upon completion of the diazo coupling reaction, the crude product was filtered off and washed with water and recrystallized from EtOH/H_2O. 4,4'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]diphenol was accumulated in 13 min, yield 86%.

Table 3. Comparative study of synthesis of **3a** using K10, KSF and HY-Zeolite

Catalyst	Amount, mmol of substrate	Time, min	Yield, %
K10	0.1g	90	70
KSF	0.1g	75	74
HY-Zeolite	0.1g	120	65
TCT	3 mmol	30	86

4,4'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)diphenol] (IIIa). mp 263°C decomp., IR (KBr), ν, cm^{-1}: 3254, 2993, 1618, 1600, 1558, 1103. ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ_H, ppm: 6.9 d (2H, J = 8.7 Hz), 7.8 d (2H, J = 8.7 Hz), 7.9 d (2H, J = 8.5 Hz), 8.1 d (2H, J = 8.5 Hz), 10.6 s (1H). Calculated, %: C 62.87; H 3.96; N 12.22. $C_{24}H_{18}N_4O_4S$. Found, %: C 62.77; H 3.69; N 12.06.

3,3'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]bis(4-hydroxylbenzaldehyde) (IIIb). mp 272°C decomp., IR (KBr), ν, cm^{-1}: 3363, 2968, 1658, 1600, 1571, 1166. ^{1}H NMR 500 MHz, DMSO-d_6), δ_H, ppm: 6.1 br.s (1H), 6.93 d (1H, J = 7.2 Hz), 6.95 d (2H, J = 7.9 Hz), 7.6 d (2H, J = 7.2 Hz), 7.7 d (2H, J = 7.9 Hz, 9.7 s 1H. Calculated, %: C 60.69; H 3.53; N 10.89. $C_{26}H_{18}N_4O_6S$. Found, %: C 60.56; H 3.86; N 10.93.

5,5'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]bis(2-hydroxybenzaldehyde) (IIIc). mp 268°C decomp., IR (KBr), ν, cm^{-1}: 3390, 3062, 2856, 1658, 1616, 1581, 1151. ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ_H, ppm: 7.2 d (2H, J = 8.9 Hz), 8.02 d

(4H, *J* = 8.5 Hz), 8.09 d.d (2H, *J* = 2.05, *J* = 8.9 Hz), 8.1 d (4H, *J* = 8.7 Hz), 8.2 d (2H, *J* = 2.6 Hz), 10.3 s (2H), 11.7 br.s (2H). Calculated, %: C 60.69; H 3.53; N 10.89. $C_{26}H_{18}N_4O_6S$. Found, %: C 60.59; H 3.57; N 10.71.

1,1'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]dinaphthalen-2-ol (IIId). mp 280°C decomp., IR (KBr), ν, cm^{-1}: 3396, 3068, 2927, 1685, 1579, 1500, 1492, 1143. ^1H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm: 7.4 t (1H, *J* = 7.3 Hz), 7.6 t (1H, *J* = 7.1 Hz), 7.7 d (1H, *J* = 7.4 Hz), 7.92 d (1H, *J* = 9.6 Hz), 7.97 d (2H, *J* = 8.8 Hz), 8.07 d (2H, *J* = 10.8 Hz), 8.4 d(1H, *J* = 8.0 Hz), 15.7 s (1H). Calculated, %: C 68.80; H 3.97; N 10.03. $C_{32}H_{22}N_4O_4S$. Found, %: C 68.57; H 3.66; N 10.35.

3,3'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]bis(4-hydroxy-2*H*-chromen-2-one) (IIIe). mp 275°C decomp., IR (KBr), ν, cm^{-1}: 3458, 3101, 1745, 1625, 1506, 1535, 1145 cm^{-1}. ^1H NMR spectrum (500 MHz, DMSO-d_6), δ_H, ppm: 7.34–7.38 m (2H), 7.7 t (1H, *J* = 7.38), 7.91 d (2H, *J* = 8.2 Hz), 7.97 br.d (1H), 8.1 d (2H, *J* = 8.6 Hz), 15.2 br.s (1H). Calculated, %: C 60.60; H 3.05; N 9.42. $C_{30}H_{18}N_4O_8S$. Found, %: C 60.68; H 3.09; N 9.43.

4,4'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]dinaphthalen-1-ol (IIIf). mp 269°C decomp., IR (KBr), ν, cm^{-1}: 3425, 3049, 2999, 1627, 1591, 1535, 1477, 1257. ^1H NMR spectrum (500 MHz, DMSO-d_6), δ_H, ppm: 6.6 d (2H, *J* = 10.0 Hz), 7.5 t (2H, *J* = 7.1 Hz), 7.6 br (2H), 7.7 t (2H, *J* = 7.5 Hz), 7.9 d (4H, *J* =7.1 Hz), 8.0 d (4H, *J* = 7.1 Hz), 8.2 d (2H, *J* = 10.0 Hz), 8.3 d (2H, *J* = 7.6 Hz), 11.7 s (2H). Calculated, %: C 68.80; H 3.97; N 10.03. $C_{32}H_{22}N_4O_4S$. Found, %: C 68.76; H 3.46; N 10.10.

5,5'-[4,4'-Sulfonylbis(4,1-phenylene)bis(diazene-2,1-diyl)]bis(4-hydroxy-3-methoxybenzaldehyde (IIIg). mp 278°C decomp., IR (KBr), ν, cm^{-1}: 3419, 3087, 2943, 2840, 1685, 1593, 1492, 1139. ^1H NMR spectrum (500 MHz, DMSO-d_6), δ_H, ppm: 3.9 s (3H), 7.5 br (2H), 7.8 br (2H), 8.2 s (2H), 9.8 s (1H), 11.5 br.s (1H). Calculated, %: C 58.53; H 3.86; N 9.75. $C_{28}H_{22}N_4O_8S$. Found, %: C 58.64; H 3.54; N 9.80.

CONCLUSIONS

An efficient, simple, and environmentally friendly synthesis of azo dyes under the action of ultrasound irradiation was developed. The method has some advantages such as mild reaction conditions, short reaction time, high yield, and simple procedure.

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