CHEMIJA. 2013. Vol. 24. No. 1. P. 59–66

The green synthesis of new azo dyes derived from salicylic acid derivatives catalyzed via baker's yeast and solid acid catalysis

Abbas Teimouri[1]*,

Alireza Najafi Chermahini[2],

Mohammad Hassan Ghorbani[3]

[1] *Chemistry Department, Payame Noor University, 19395-4697, Tehran, I. R. of Iran*

[2] *Department of Chemistry, Isfahan University of Technology, Isfahan, 841543111, Iran*

[3] *Department of Biology, Falavarjan Branch, Islamic Azad University, Falavarjan, Isfahan, Iran*

The synthesis of a series of new azo dyes containing 4-sulfonyl azide benzenediazonium salt, salicylic acid, 2-hydroxy benzoic acid, and 2,4-dihydroxy benzoic acid derivatives over eco-friendly baker's yeast, modified montmorilonite K10, zeolites and sulphated zirconia are described. These inexpensive, noncorrosive and reusable catalysts were found to exhibit bifunctional catalytic properties for these reactions. No considerable decrease in the efficiency of the catalysts was observed after four cycles of operation. The new method totally avoids the use of acid, alkali or toxic solvents in diazotization and azocoupling reactions.

Key words: environmental compatibility, diazotization, azocoupling, dyes, baker's yeast, clays, zeolite, sulfated zirconia

INTRODUCTION

Azo dyes constitute the largest group of commonly available dyes and pigments [1]. Due to their colour, azo dyes are used as pigments, [2] indicators of solvent polarity of molecular environments [3] and chemical environments [4]. They are also widely used as histological stains [5] and in the colorimetric analysis of pharmaceuticals [6–8]. The pharmaceutical importance of compounds with an arylazo group has been extensively reported in the literature [9–10]. The oxidation-reduction behaviours of these compounds play an important role in their biological activity [11].

The formation of diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions and azo coupling carried out at low temperature in the presence of nucleophilic coupling components. These conventional acid-base catalyzed processes are effective for the near quantitative formation of the desired products. But the main limitation of such synthetic processes is their environmental incompatibility. The acidic and basic effluents from the laboratory and industry produce permanent damage to the environment and disturb the ecological balance [12]. Clays have been long used as acidic catalysts and existence of both Lewis and Bronsted acid sites. In addition, clays are low-cost, widely available materials, and synthetic organic chemists have largely used them in a variety of acid-catalysed reactions [13]. Montmorillonite clay is able to function as an effcient solid acid catalyst in organic transformations with excellent product, regio- and stereo-selectivity [14]. Nowadays more and more heterogeneous Bronsted acids, e. g. zeolites are utilized. Zeolites are

* Corresponding author. E-mail: a_teimouri@pnu.ac.ir

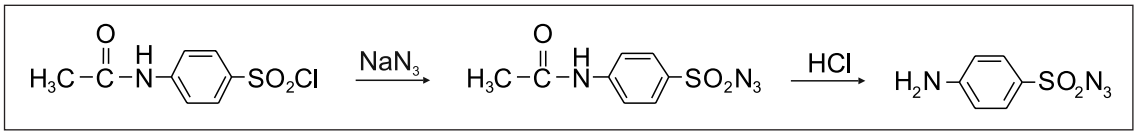


Fig. 1. Synthesis of 4-aminobenzene-1-sulfonyl azide

preferred from an economical perspective as well as from an ecological viewpoint, the excellent catalytic abilities are due to the presence of Bronsted and Lewis acid centers in the zeolite structure [15]. Zirconia has an attractive considerable interest based on its potential use as a catalyst support, Zirconia is active and its activity is due to acidic, basic, oxidizing and reducing surface properties [16].

Salicylic acid (SA) is the first chemically synthetic compound used for therapeutic means as analgesic, antipyretic and antirheumatic drugs [17]. Salicylic acid (SA) belongs to a group of plant phenolics widely distributed in plants and is now considered as a hormone-like substance, which plays an important role in the regulation of plant growth and development (transpiration, stomatal closure, seed germination, fruit yield, glycolysis, flowering and heat production) [18–19]. In recent years, SA has received particular attention because its accumulation is essential for expression of multiple modes of plant disease resistance. Salicylic acid has been used primarily as an intermediate in the production of agrochemicals, dyes and colorant products. Synthesis of azo dyes and their derivatives have attracted a lot of attention [20–21]. Recently synthesis and evaluation of 5-aminosalicylic acid azo systems as prodrug for tissue in inflammatory bowel disease have been interesting [22–23].

The use of biocatalysis in organic synthesis has been increasing day by day because of its various advantages. Among the biocatalysts used in organic synthesis, baker's yeast (*Saccharomyces cerevisiae*) [24] is gaining prime importance in synthetic organic chemistry [25, 26] as yeast catalyzes variety of organic transformations. Baker's yeast has the ability to catalyze the cyclocondensations leading to bioactive heterocycles, such as benzimidazoles [27], dihydropyridines [28], dihydropyrimidines [29], polyhydroquinolines [30], benzothiazoles [31], benzotriazoles [32], quinoxaline [33], isoxazolines [34], polyhydroquinolines [35], benzotraizole oxides [30], 1,4-dihydropyridines [32], and 3,4-dihydropyrimidine-2-(1H)-ones [28].

Recently we have synthesized a new group of azo dyes containing an azide group [36]. As part of our ongoing research program for exploring the bifunctional catalytic properties [37], herein we describe a new process for diazotization and diazocoupling reactions using modified montmorilonite K10, zeolites, baker's yeast and sulfated zirconia as a catalyst toward the synthesis of new azo dyes derived from salicylic acids. These interesting dyes contain both sulfonyl azide and salicylic acid derivatives. In addition, the sulfonyl azide moiety is a reactive part and can be applied as a source of nitrene in organic reactions.

RESULTS AND DISCUSSION

This paper describes a facile and modified synthesis of azo dyes without using conventional acid or base, namely, in the presence of modified montmorilonite K10, zeolites, baker's yeast and sulfated zirconia. The 4-aminobenzene-1-sulfonyl azide was synthesized from the reaction of 4-acetamidobenzene-1-sulfonyl chloride with sodium azide followed by acid hydrolysis (Fig. 1).

4-Aminobenzene-1-sulfonyl azide, a dilute $NaNO_2$ solution and an active catalyst were mixed to a paste and then cooled down to 0–5 °C (Fig. 2). The diazonium-catalyst complex formed was subsequently coupled with various coupling components, such as salicylic acid **1**, methyl salicylate **2**, ethyl salicylate **3**, n-propyl salicylate **4**, n-butyl salicylate **5**, n-pentyl salicylate **6**, methyl-2,4-dihydroxy benzoate **7**, ethyl-2,4-dihydroxy benzoate **8**, salicylaldehyde **9**, salicylamide **10**, 2,4-dihydroxy banzamide **11**, salicylaldoxime **12**, respectively. Dyes were obtained generally in good yields – 58–85% (Table). The azo dyes derived from salicylic acids were separated from the catalyst by extraction with dichloromethane. The excess solvent was removed under vacuum. The generality of the process is proved by performing the reaction with all the catalysts, with 4-aminobenzene-1-sulfonyl azide and with coupling agents. After the formation of the diazonium-catalyst complex, the edge hydroxyls of the catalyst platelets are believed to get converted into –ONa species by consuming the Na ions from $NaNO_2$ solution used for diazotization. This –ONa species helps to maintain the pH of the medium neutral or slightly alkaline for a quantitative coupling of the diazonium ion with the coupling agent. Control reactions were carried out with the same reagents in the presence of mineral acids like HCl by following the conventional procedure for comparing the yields. All yields are found to be slightly lower than the values obtained using mineral acid. The clay catalysts were washed free of anions, dried at 110 °C for 2 h, and calcined at 430 °C for 2 h. This enriched the catalyst with acid sites and removed any organic or carbonate impurities (which are not catalytically active). On wetting, the layers move apart by the entry of water molecules, thereby, the catalyst swells and the existing interlayer cations become easily exchangeable. Acid activation definitely improves the catalytic activity of the catalyst by making its surface more accessible for the reactant molecules due to the increased pore size and pore volume and by increasing the number of Bronsted and Lewis sites. On acid activation both strength and the number of sites increased.

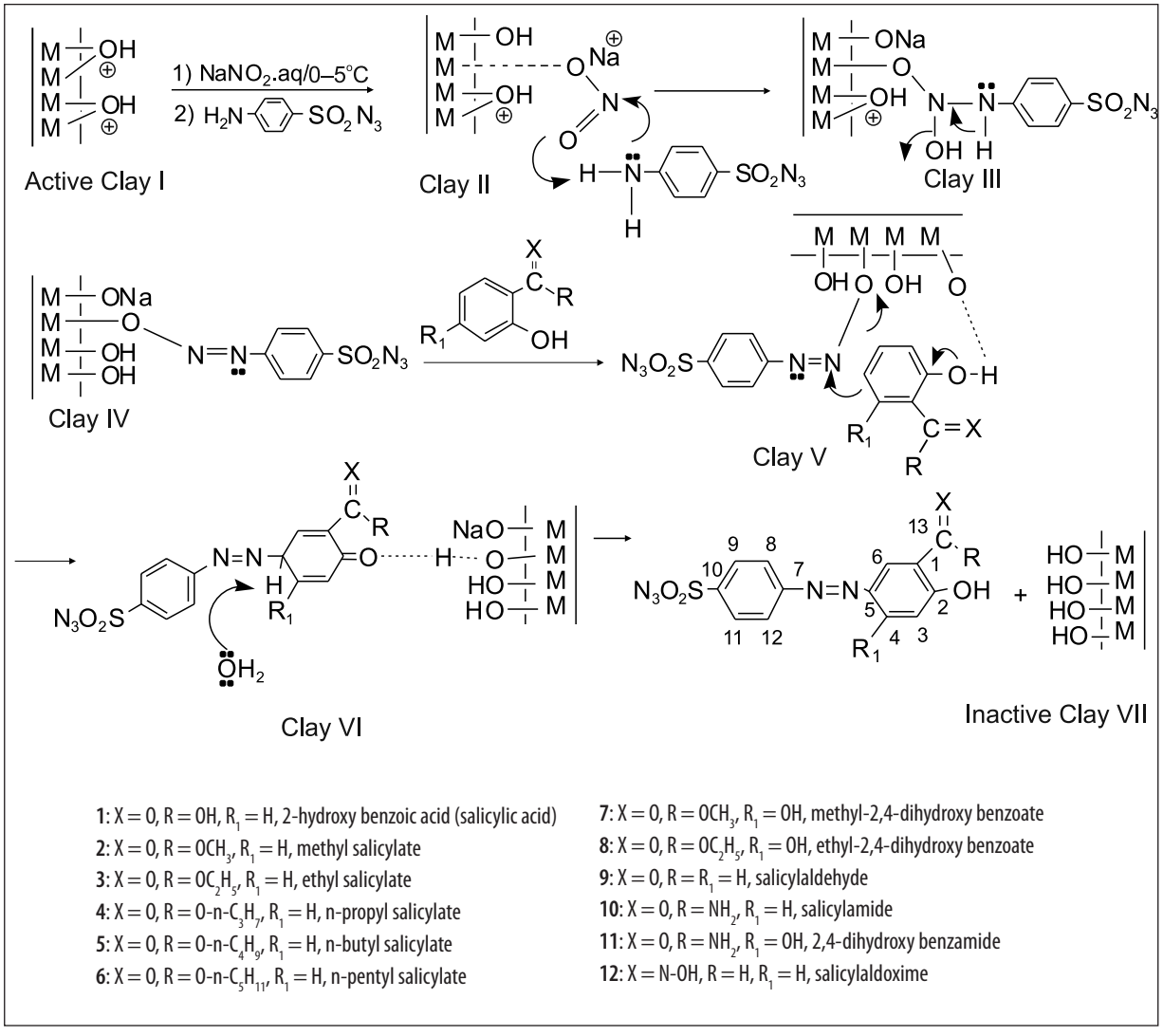


Fig. 2. Mechanism of diazotization and azocoupling

The mechanism for diazotization and azocoupling reactions is depicted on Fig. 2. Initially, the catalyst is activated by losing water molecules to retain acidic and basic sites I. Next $NaNO_2$ adsorbs over the surface of the catalyst on acidic sites II. In the next stage, salicylic acid groups initiate a neucleophilic addition reaction with the adsorbed nitrite ion to produce intermediate III. Elimination of water (by catalyst) from III gives IV. Rearrangement of IV on the surface of the catalyst produces the adsorbed diazonium salt V. Finally, the added coupling agent adsorbs by the surface of the catalyst forming new intermediate VI. Deprotonation from the adsorbed salicylic acid groups VI is followed by the desorption of azo dye from the inactive catalyst VII.

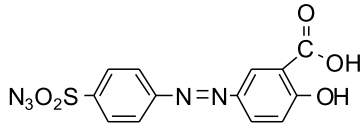
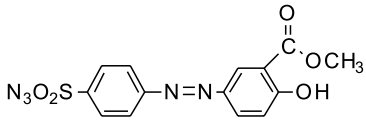
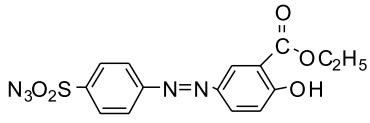
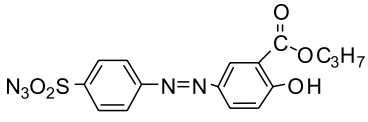
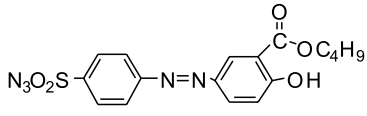
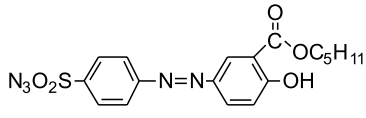
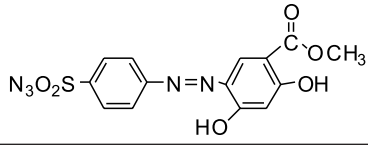
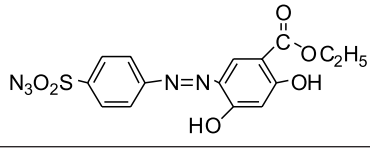
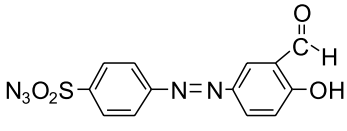
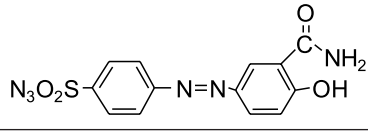
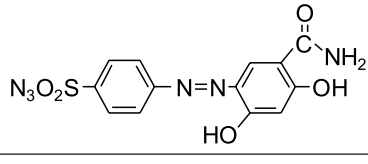
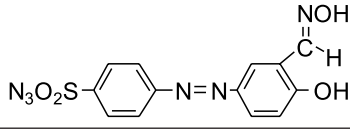
Then, we report an efficient and economic synthesis of a series of new azo dyes under relatively milder reaction conditions by employing yeast. It was interesting to observe that azo dyes were synthesized in good yields catalyzed by dry baker's yeast in dichloromethane. In order to get the best experimental condition, we have considered the reaction of diazotization and azocoupling in the presence of baker's yeast as a standard model reaction. The use of water or water / ethanol as a solvent gave poor yields.

To examine the catalytic efficiency of baker's yeast, the model reaction was run in the absence of yeast in dichloromethane. There was no conversion even after 40 h.

Baker's yeast has a variety of enzymes. These enzymes might be accelerating the diazotization and may be catalyzing the diazocoupling by dehydrogenation involving hydride ion transfer and the subsequent abstraction of a proton.

Recycling of the modified montmorillonite K10, zeolites and sulphated zirconia catalysts in four successive runs led to slight decrease in conversions. The catalysts (after the removal of the azo dyes) were washed several times with acetone and dried at 110 °C in an air oven for 1 h. The oven-dried samples were calcined at 450 °C for 3 h in a furnace and used for performing the reactions. The SZ is reusable and we were able to reach turnover numbers of >4 without significant loss in activity. This activity and stability compare quite well with, for example, clay-based catalysts.

Table. **Diazotization and azocoupling reaction of *p*-aminobenzene-1-sulfonyl azide with coupling components over baker's yeast, modified K10, zeolite and sulphated zirconia**

Entry	Product	% Yield[a]			
		Modified K10	Baker's yeast	Zeolite	SZ
1		65	70	60	85
2		60	65	60	70
3		55	70	60	75
4		55	70	50	80
5		65	70	60	75
6		65	60	60	75
7		65	60	65	80
8		65	60	60	80
9		65	65	50	70
10		60	60	50	75
11		65	70	65	85
12		60	75	60	80

[a] isolated yields.

EXPERIMENTAL

Montmorillonite K10 is procured from Aldrich. Dry baker's yeast was purchased from Angel Yeast Company Limited (Hubei, China) and stored in a refrigerator. For synthesis of ZSM-5, hydrated aluminum sulfate (Merck) and sodium silicate solution (Merck) were the sources of aluminum and silicon, respectively. The tetrapropylammonium bromide (Merck) was used as the structure-directing template [38].

Amorphous hydrated zirconia was synthesized by hydrolysis of $ZrCl_4$ (Merck, for synthesis) with a concentrated (25%) solution of ammonia according to the procedure described earlier [39].

Salicylic acid, 2,4-dihydroxy benzoic acid, and salicylamide and 4-acetamidobenzenesulfonyl chloride were procured from Merck. Salicylaldehyde and salicylaldoxime were purchased from Aldrich and were used without further purification. Methyl salicylate, ethyl salicylate, n-propyl salicylate, n-butyl salicylate, n-pentyl salicylate, methyl-2,4-dihydroxy benzoate and ethyl-2,4-dihydroxy benzoates were prepared by a modified procedure according to Vogel [40].

Melting points reported were determined by an open capillary method. UV spectra were recorded on a JASCO V-570 UV/Vis/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer. NMR spectra were recorded on a Bruker 500 Ultrasheild NMR and DMSO-d_6 used as a solvent.

Catalyst preparation

Synthesis of catalyst Zn^{2+}-montmorillonite K-10

Solution of 0.5 M zinc chloride was prepared by dissolving the equivalent amount of salt in deionized and distilled water. A diluted montmorillonite suspension was prepared by adding the montmorillonite powder (5 g) into the deionized and distilled water (200 ml). The pillaring reaction was carried out under continuous vigorous stirring by dropwise adding the pillaring solution into the montmorillonite suspension over a period of 10 min. The resulting slurry was refluxed for 8 h and then stirred at room temperature for 24 h. The catalysts were filtered and washed with demineralised water until free from anions. The sample was dried at 100 °C temperature, then after grinding calcined for 3 h at 400 °C under airflow.

Synthesis of ZSM-5 and HZSM-5

ZSM-5 zeolite was synthesized according to the procedure described earlier. The solid phase obtained was filtered, washed with distilled water several times, dried at 120 °C for 12 hours and then calcined at 550 °C for 6 hours. And followed by ion exchange with NH_4NO_3 solution (three times), the acid hydrogen form of the compound is prepared by transferring the oven-dried compound to a tube furnace. Ammonium zeolite is heated for 3 hours to ensure the thermal decomposition of NH_4^+ ions. Over the course of this process, zeolite should turn from a white to brown / black color [38].

Synthesis of sulfated zirconia

Zirconia was dried at 393 K for 12 h. Sulfated zirconia (SZ) was prepared by suspending ZrO_2 in a solution of 0.5 M H_2SO_4. After 90 min stirring the mixture was filtered and washed with 0.05 M H_2SO_4. The precipitate was dried at 383 K and calcined for 1 h at 823 K with subsequent cooling in either a desiccator or under ambient conditions [39].

General procedure for diazotization and diazocoupling reaction 1–12

In a typical experiment, to a cooled mixture of modified montmorilonite K10, zeolites and sulphated zirconia catalysts (3 g) in (25 ml) H_2O, 1.38 g (20 mmol) of $NaNO_2$ in (15 ml) H_2O were added dropwise for a period of 1 h and stirred in an ice bath. To this solution 4-aminobenzene-1-sulfonyl azide (1.98 g 10 mmol) was added slowly. To this mixture the nucleophilic coupling components were added at ice cold temperature and stirred for 3–4 h and then filtered.

The similar reaction was performed by varying the amount of baker's yeast from 1 to 3 g per 10 mmol of the reactants. It was observed that when 2 g of baker's yeast were used, the coupling was found to be complete.

The azo dyes formed were extracted from the catalyst using dichloromethane. The solvent was removed by evaporation under vacuum. The solid product was filtered under suction, dried, and recrystallized from dichloromethane and petroleum ether. In some cases, the product was oil, in which case separation was achieved by extraction into dichloromethane.

5-{2-[4-(Azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzoic acid (1)

Decomposition point: 170–172 °C; λ_{max} (DCM) 226, 356 nm; FTIR: 3 425, 2 924, 2 144, 1 662, 1 617, 1 577, 1 373, 1 175 cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ: 12.32 (br, OH), 8.37 (d, J = 2.10 Hz, H_6), 8.18 (d, J = 8.82 Hz, 2H), 8.07 (d, J = 8.69 Hz, 2H), 7.8 (q, H_4), 7.15 (d, J = 8.87 Hz, H_3). ^{13}C NMR (500 MHz, DMSO-d6) δ: 113.9, 118.5, 123.5(2), 126.9, 128.8(2), 138.3, 144.4, 155.2, 164.6, 166.8, 171. Anal. calcd. for $C_{13}H_9N_5O_5S$ (347.03): C, 44.96; H, 2.61; N, 20.16. Found: C, 44.70; H, 2.71; N, 20.01.

Methyl 5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzoate (2)

Decomposition point: 116–118 °C; λ_{max} (DCM) 224, 356.5 nm; FTIR: 3 296; 2 956; 2 137; 1 686; 1 619; 1 576; 1 374; 1 167; 1 143 cm^{-1}; ^1H NMR (500 MHz, DMSO-d6) δ: 11.13 s (OH), 8.33 (d, J = 2.23 Hz, H_6), 8.19 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.61 Hz, 2H), 7.9 (q, H_4); 7.19 (d, J = 8.86 Hz, H_3), 3.92 (s, CH_3). ^{13}C NMR (500 MHz, DMSO-d6) δ: 52.6, 114.7, 118, 123.6(2), 126, 129, 128.9(2), 138.4, 144.4, 155.2, 163.1, 167.7. Anal. calcd. for $C_{14}H_{11}N_5O_5S$ (361.05): C, 46.54; H, 3.07; N, 19.38 %. Found: C, 46.60; H, 3.03; N, 19.38.

Ethyl 5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzoate (3)
Decomposition point: 92–94 °C; λ_{max} (DCM) 224, 355 nm; FTIR: 3 299, 2 135, 1 687, 1 621, 1 576, 1 362, 1 119 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d6) δ: 11.20 s (OH), 8.38 (d, *J* = 2.21 Hz, H_6), 8.21 (d, *J* = 8.45 Hz, 2H), 8.03 (d, *J* = 8.36 Hz, 2H), 7.94 (q, H_4); 7.21 (d, *J* = 8.95 Hz, H_3), 4.4 (q, 2H), 1.37 (s, CH_3). ^{13}C NMR (500 MHz, DMSO-d6) δ: 13.9, 61.6, 114.7, 118.8, 123.6(2), 127, 128.6, 129.4(2), 144.4, 146.8, 155.3, 163.2, 167. Anal. calcd. for $C_{15}H_{13}N_5O_5S$ (375.06): C, 48.01; H, 3.49; N, 18.66. Found: C, 47.84; H, 3.20; N, 18.36.

n-Propyl 5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzoate (4)
Oil; λ_{max} (DCM) 224, 355 nm; FTIR: 3 285, 3 073, 2 970, 2 128, 1 672, 1 614, 1 586, 1 375, 1 171 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d6) δ: 11.16 (s, OH), 8.35 (d, *J* = 2.45 Hz, H_6), 8.17 (d, *J* = 8.60 Hz, 2H), 8.02 (d, *J* = 8.51 Hz, 2H), 7.93 (q, H_4), 7.29 (d, *J* = 8.93 Hz, H_3), 4.2 (t, 2H), 1.6 (m, 2H), 1.06 (t, CH_3). ^{13}C NMR (500 MHz, DMSO-d6) δ: 12.5, 21.5, 65.2, 114.8, 118.8, 123.5(2), 127.1, 128.3, 129.3(2), 138.5, 146.4, 155.3, 164.2, 167.6. Anal. calcd. for $C_{16}H_{15}N_5O_5S$ (389.08): C, 49.11; H, 3.50; N, 17.96. Found: C, 49.39; H, 3.88; N, 17.99.

n-Butyl 5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzoate (5)
Oil; λ_{max} (DCM) 226, 355.5 nm; FTIR: 3 183, 3 073, 2 962, 2 127, 1 673, 1 614, 1 586, 1 375, 1 170 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d6) δ: 11.12 (s, OH), 8.33 (d, *J* = 2.41 Hz, H_6), 8.19 (d, *J* = 8.66 Hz, 2H), 8.01 (d, *J* = 8.57 Hz, 2H), 7.88 (q, 1H), 7.23 (d, *J* = 8.91 Hz, H_3), 4.33 (t, 2H), 1.76 (m, 2H), 1.44 (m, 2H), 0.89 (t, CH_3). ^{13}C NMR (500 MHz, DMSO-d6) δ: 13.7, 21.6, 28.3, 65, 114.1, 117.2, 123.5(2), 127.2, 128.8, 129.7(2), 135.5, 146.6, 155.1, 164, 168.4. Anal. calcd. for $C_{17}H_{17}N_5O_5S$ (403.1): C, 50.62; H, 4.25; N, 17.36. Found: C, 50.42; H, 4.40; N, 17.46.

n-Pentyl 5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzoate (6)
Oil; λ_{max} (DCM) 224, 355.5 nm; FTIR: 3 181, 3 073, 2 959, 2 127, 1 674, 1 614, 1 586, 1 377, 1 172 cm^{-1}; ^{1}H NMR (DMSO-d6) δ: 11.2 (1H, s, –OH); 8.35 (1H, d, *J* = 2.49 Hz, H_6); 8 (2H, d, *J* = 8.57 Hz, phenyl); 8.15 (2H, d, *J* = 8.56 Hz, phenyl); 7.76 (1H, q, H_4); 7.19 (1H, d, *J* = 8.9 Hz, H_3); 4.2 (2H, t, ethyl), 1.8 (2H, m, ethyl) 1.68 (2H, m, ethyl) 1.35 (2H, m, ethyl) 0.88 (3H, t, methyl); ^{13}C NMR (DMSO-d6) δ: 13.7, 21.2, 27.6, 29.3, 65.2, 114.5, 116.8, 124.1(2), 127.8, 128.6, 129.3(2), 138.6, 146.2, 155.8, 164.3, 168. Anal. calcd. for $C_{18}H_{19}N_5O_5S$ (4.17.1): 51.79; H, 4.59; N, 16.78. Found: C, 51.58; H, 4.37; N, 16.52.

Methyl-5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2,4-hydroxybenzoate (7)
Decomposition point: 118–121 °C; λ_{max} (DCM) 226, 356 nm; FTIR: 3 343, 3 205, 2 958, 2 132, 1 646, 1 504, 1 358, 1 147 cm^{-1}; ^{1}H NMR (DMSO-d6) δ: 10.71 (1H, s, –OH); 10.42 (1H, s, –OH); 8.21 (1H, d, *J* = 0.71 Hz, H_6); 7.37 (2H, d, *J* = 8.67 Hz, phenyl); 7.98 (2H, d, *J* = 8.66, phenyl); 6.29 (1H, d, *J* = 0.71 Hz, H_3); 3.81 (3H, s, methyl); ^{13}C NMR (DMSO-d6) δ: 51.9, 102.4, 103.9, 108.3(2), 120.5, 131.5(2), 147.1, 155.2, 162.7, 164.2, 169.61, 169.62. Anal. calcd. for $C_{14}H_{11}N_5O_6S$ (377.1): C, 44.56; H, 2.94; N, 18.56. Found: C, 44.50; H, 2.62; N, 18.40.

Ethyl-5-{2-[4-(azidosulfonyl)phenyl]-1-diazenyl}-2,4-hydroxybenzoate (8)
Decomposition point: 70–72 °C; λ_{max} (DCM) 224, 356 nm; FTIR: 3 341, 2 983, 2 129, 1 624, 1 663, 1 587, 1 515, 1 375, 1 169 cm^{-1}; ^{1}H NMR (DMSO-d6) δ: 10.80 (1H, s, –OH); 10.4 (1H, s, –OH); 8.14 (1H, d, *J* = 0.72 Hz, H_6); 7.36 (2H, d, *J* = 8.41 Hz, phenyl); 7.98 (2H, d, *J* = 8.41 Hz, phenyl); 6.28 (1H, d, *J* = 0.72 Hz, H_3); 4.27 (2H, q, ethyl), 1.28 (3H, t, methyl); ^{13}C NMR (DMSO-d6) δ: 15.9, 60.6, 102.4, 104, 108.2(2), 120.5, 123.6, 131.4(2), 146.8, 162.8, 164.19, 169.2, 169.3. Anal. calcd. for $C_{15}H_{13}N_5O_6S$ (391.1): C, 46.04; H, 3.35; N, 17.89. Found: C, 45.88; H, 3.21; N, 17.28.

5-{2-[4-(Azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzaldehyde (9)
Decomposition point: 146–148 °C; λ_{max} (DCM) 226, 355.5 nm; FTIR: 3 446, 2 840, 2 750, 2 144, 1 663, 1 616, 1 565, 1 373, 1 169 cm^{-1}; H NMR (DMSO-d6) δ: 11.7 (1H, br, –OH); 10.35 (1H, s, –HCO); 8.22 (1H, d, *J* = 2.53 Hz, H_6); 8.07 (2H, d, *J* = 8.13 Hz, phenyl); 8.19 (2H, d, *J* = 8.13 Hz, phenyl); 8.11 (1H, q, H_4); 7.20 (1H, d, *J* = 8.8 Hz, H_3); ^{13}C NMR (DMSO-d6) δ: 118.5, 123.5(2), 124.8, 129.8(2), 129.4, 129.9, 144.7, 146.8, 155.3, 164.3, 190.2. Anal. calcd. for $C_{13}H_9N_5O_4S$ (331.2): C, 47.13; H, 2.74; N, 21.14. Found: C, 46.90; H, 2.80; N, 22.0.

5-{2-[4-(Azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzamide (10)
Decomposition point: 138–140 °C; λ_{max} (DCM) 224, 356 nm; FTIR: 3 397, 3 363, 3 186, 2 140, 1 635, 1 577, 1 362, 1 119 cm^{-1}; ^{1}H NMR (DMSO-d6) δ: 13 (1H, s, –OH); 8.66 (1H, d, *J* = 2.29 Hz, H_6); 8.37 (1H, br, -NH); 8.08 (2H, d, *J* = 8.59 Hz, phenyl); 8.23 (2H, d, *J* = 8.59 Hz, phenyl); 7.87 (1H, br, -NH); 7.83 (1H, q, H_4); 7.10 (1H, d, *J* = 7.75 Hz, H_3); ^{13}C NMR (DMSO-d6) δ: 114.3, 117.3, 118.2, 123.4(2), 128(2), 129, 134.1, 144.3, 156.1, 161, 172. Anal. calcd. for $C_{13}H_{10}N_6O_4S$ (346.1): C, 45.09; H, 2.91; N, 24.27. Found: C, 45.27; H, 2.66; N, 24.40.

5-{2-[4-(Azidosulfonyl)phenyl]-1-diazenyl}-2,4-hydroxybenzamide (11)
Decomposition point: 120–122 °C; λ_{max} (DCM) 224, 358 nm; FTIR: 3 427, 3 363, 3 320, 3 215, 2 958, 2 361, 2 133, 1 638, 1 617, 1 506, 1 358, 1 173 cm^{-1}; ^{1}H NMR (DMSO-d6) δ: 10.71 (1H, s, –OH); 10.42 (1H, s, –OH); 8.22 (1H, br, -NH); 7.93 (2H, d, *J* = 8.4 Hz, phenyl); 8.06 (2H, d, *J* = 8.39 Hz, phenyl); 8.15 (1H, d, *J* = 0.73 Hz, H6) 7.74 (1H, br, -NH); 6.21 (1H, d, *J* = 0.73 Hz, H_3); ^{13}C NMR (DMSO-d6) δ: 102.5, 103.9, 108.3, 124.6(2), 128.6(2), 131, 143.7, 156, 162, 164, 169. Anal. calcd. for $C_{13}H_{10-}$

N_6O_5S (362.2): C, 43.10; H, 2.78; N, 23.36. Found: C, 42.87; H, 2.70; N, 23.20.

5-{2-[4-(Azidosulfonyl)phenyl]-1-diazenyl}-2-hydroxybenzaldehyde oxime (12)

Decomposition point: 142–144 °C; λ_{max} (DCM) 226, 354 nm; FTIR: 3419, 2963, 2131, 1618, 1575, 1396, 1167 cm^{-1}; ^1H NMR (DMSO-d6) δ: 9.8 (1H, br, –OH); 9.23 (1H, s, aldehyde); 8.34 (1H, d, J = 2.5 Hz, H6); 7.94 (2H, d, J = 8.19 Hz, phenyl); 8.10 (2H, d, J = 8.2 Hz, phenyl); 7.80 (1H, q, H4); 7.58 (1H, s, –NOH); 6.93 (1H, d, J = 7.49 Hz, H_3); ^{13}C NMR (DMSO-d6) δ: 115.8, 119.2, 122.9, 125.7(2), 126.7, 130.8(2), 151.8, 152.2, 153.5, 156.7, 160.6. Anal. calcd. for $C_{13}H_{10}N_6O_4S$ (346.1): C, 45.09; H, 2.91; N, 24.27. Found: C, 44.79; H, 2.63; N, 24.10.

CONCLUSIONS

To summarize, we have developed a highly efficient 'green' method for synthesis of several novel azo dyes catalyzed by eco-friendly clay catalysts (modified montmorrilonite K-10), zeolites, sulfated zirconia and baker's yeast with better recycling options and totally avoiding the use of acid, alkali and toxic solvents in diazotization and azocoupling reactions. The structures of adducts were confirmed by their NMR, FTIR, UV, MS spectra and elemental analysis. Thanks are due to Mrs. Sahar Salehi for recording the XRD pattern of the compound.

ACKNOWLEDGEMENTS

Support from the Research Council of Payame Noor University in Isfahan and help of Isfahan University of Technology and Islamic Azad University are gratefully acknowledged.

Received 22 October 2012
Accepted 28 November 2012

References

1. H. Zollinger, *Color Chemistry*, 3rd edn., Verlag Helvetica Chimica Acta, Switzerland (2003).
2. W. Herbst, K. Hunger, *Industrial Organic Pigments: Production, Properties, Applications*, Verlagsgesellschaft mbH, Germany (1997).
3. V. Buss, L. Eggers, J. C. Lindon, G. E. Tranter, J. L. Holmes, *Encyclopedia of Spectroscopy and Spectrometry*, Academic Press, USA (2000).
4. A. A. Olaniyi, F. O. Ogungbamila, *Experimental Pharmaceutical Chemistry*, Shaneson C. I. Ltd., Ibadan (1991).
5. N. M. Rageh, *Spectrochim. Acta Part A*, **60**, 103 (2004).
6. A. C. Bratton, J. E. K. Marshall, *J. Biol. Chem.*, **128**, 537 (1939).
7. P. Nagaraja, H. S. Yathirajan, C. R. Raju, R. A. Vasantha, M. S. Nagendra, M. S. Hemantha Kumar, *IL Farmaco*, **58**, 1295 (2003).
8. H. D. Revanasiddappa, B. Manju, *IL Farmaco*, **56**, 615 (2001).
9. H. G. Garg, R. A. Sharma, *J. Med. Chem.*, **12**, 1122 (1996).
10. E. J. Modest, H. N. Schlein, G. E. Foley, *J. Pharmacol.*, **9**, 68 (1957).
11. L. K. Ravindranath, S. R. Ramadas, S. B. Rao, *Electrochim. Acta*, **28**, 601 (1983).
12. J. H. Clark, *Chemistry of Waste Minimization*, Chapman and Hall, London (1995).
13. J. K. Thomas, *Chem. Rev.*, **105**, 1683 (2005).
14. B. Singh, J. Patial, P. Sharma, S. G. Agarwal, G. N. Qazi, S. Maity, *J. Mol. Catal. A: Chem.*, **266**, 215 (2006).
15. M. Bregolato, V. Bolis, C. Busco, et al., *J. Catal.*, **245**, 283 (2007).
16. D. Pietrogiacomi, M. C. Campa, S. Tuti, V. Indovina, *Appl. Catal., B*, **41**, 301 (2003).
17. J. R. Vane, R. M. Botting, *Am. J. Med.*, **104**, (3A) 2S (1998).
18. I. Raskin, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, **43**, 439 (1992).
19. D. F. Klessig, J. Malamy, *Plant Mol. Biol.*, **26**, 1439 (1994).
20. A. Brzezinski, G. B. Rankin, D. L. Seidner, B. A. Lshner, *Cleve. Clin. J. Med.*, **62**, 317 (1995).
21. G. B. Bonner, W. B. Ruderman, in: K. D. Rainsford (ed.), *Inflammopharmacology*, Kluwer Academic, Norwell, MA (1993).
22. S. S. Dhaneshwar, N. Gairola, M. Kandpal, G. Vadnerkara, L. Bhatt, *Bioorg. Med. Chem.*, **15**, 4903 (2007).
23. S. S. Dhaneshwar, M. Kandpal, G. Vadnerkara, B. Rathi, S. S. Kadam, *Bioorg. Med. Chem. Lett.*, **17**, 1897 (2007).
24. P. Darrigo, H. E. Hogberg, G. Pedrocchi-Fantoni, S. Servi, *Biocatal. Biotransform.*, **9**, 299 (1994).
25. R. Csuk, B. I. Glanzer, *Chem. Rev.*, **91**, 49 (1991).
26. S. Servi, *Synthesis*, 1 (1990).
27. G. Renard, D. A. Lerner, *New J. Chem.*, **31**, 1417 (2007).
28. J. H. Lee, *Tetrahedron Lett.*, **46**, 7329 (2005).
29. A. Kumar, R. A. Maurya, *Tetrahedron Lett.*, **48**, 4569 (2007).
30. A. Kumar, R. A. Maurya, *Tetrahedron Lett.*, **48**, 3887 (2007).
31. P. Csaba, C. Majdic, M. Tosa, R. Misca, F. D. Irimie, *Biotechnol. Lett.,* **6**, 325 (2001).
32. W. Baik, T. H. Park, B. H. Kim, Y. M. Jun, *J. Org. Chem.*, **60**, 5683 (1995).
33. M. V. Baez, A. E. Robinsohn, M. J. Legaspi, M. E. Hedrera, B. M. Fernandez, *J. Planar Chromatogr.*, **16**, 28 (2003).
34. K. Ramarao, *Pure Appl. Chem.*, **64**, 1141 (1992).
35. H. A. Dabbagh, Y. Mansoori, *Dyes Pigm.*, **54**, 37 (2002).
36. H. A. Dabbagh, A. Teimouri, A. Najafi Chermahini, *Appl. Catal., B*, **76**, 24 (2007).
37. V. R. Choudhary, D. Panjala, S. Banerjee, *Appl. Catal., A*, **231**, 243 (2002).
38. U. B. Demirci, F. Garin, *J. Mol. Catal. A: Chem.*, **193**, 139 (2003).
39. A. I. Vogel, A. R. Tatchell, B. S. Furnis, A. J. Hannaford, P. W. G. Smith, *Vogel's Textbook of Practical Organic Chemistry*, 5th edn., Prentice Hall (1996).

Abbas Teimouri, Alireza Najafi Chermahini,
Mohammad Hassan Ghorbani

NAUJŲ AZODAŽIKLIŲ ŽALIOJI SINTEZĖ IŠ SALICILO RŪGŠTIES DARINIŲ, KATALIZUOJAMA KEPIMO MIELĖMIS IR KIETAISIAIS RŪGŠTINIAIS KATALIZATORIAIS

Santrauka
Aprašyta kelių naujų azodažiklių sintezė naudojant katalizatoriais kepimo mieles, modifikuotą montmorilonitą K10, ceolitus ir cirkonio dioksidą.