



## A green alternative to synthesize azo compounds

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### ABSTRACT

Different nitrates were used as sources of nitrosonium ion to obtain diazonium salts. Diverse azo compounds were synthesized in acetonitrile giving very good yields and free of by-products in comparison with traditional synthesis. Among the tested species, the best combination for *para red* synthesis was nitric acid and gaseous hydrogen chloride.

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### 1. Introduction

Diazonium salts are very important intermediates in the synthesis of aromatic compounds [1], and they are precursors of azo compounds which are very useful in the fields of dyes, pigment and advanced materials. Azo dye compounds are widely used as colorants in the textile industries but they have several other applications too [2] as, for example, colorants for digital printing and photography [3]; dyes for drug, food and cosmetic applications. Some dyes have been used in the biomedical field [4] and for molecular recognition [5]. They are also used as chiral receptors [6], liquid crystals [7], new glassy materials [8] and chiral switches in photochemistry [9].

It is well known that diazonium salts are obtained in aqueous acidic phase by the action of nitrous acid on anilines. Later, they can react with different compounds to give products where the nitrogen atoms of the diazonium ion are preserved or not. Specifically, azo dyes are compounds that contain azo groups linked to methine or aromatic  $sp^2$ -hybridized C-atoms. The formation of the diazotizing reagent starts with protonation of nitrous acid under strongly acidic conditions, and azo coupling occurs at low temperature in presence of nucleophilic components. The nucleophiles are usually phenols and aromatic amines and their reactivity toward the weak diazonium salt electrophiles increases when they

have electron donor substituents. It is well known that diazonium ion reactions give poor yields and a lot of by-products, so they are not in accordance with the principles of Green Chemistry [10]. These principles were introduced with the aim to overcome health and environmental problems at the source by developing cleaner chemical processes for the chemical industry through the design of innovative and environmentally benign chemical reactions [11,12,13,14,15,16].

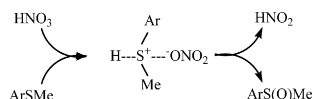
Additionally, the clean production of azo dyes is a classical chemistry problem. For this reason, the study of new synthetic alternatives is a matter of current interest. For instance, the use of a  $CO_2/H_2O$  system has been proposed as possible green *via* [17]; clay catalysts, bentonite, kaolin and K10, have also been used in diazotization and diazo coupling reactions [18]. Various reaction media such as ionic liquids [19,20] or organic solvent as acetonitrile [21,22] or 1,2-dichlorobenzene [23] or dichloromethane [24] or solvent-free conditions have also been studied [25]. The synthesis of new azo compound derivatives from amines that are insoluble in aqueous media is very important and it can pave the way for new technology.

On the basis of the general and continuous interest in the synthesis of azo dyes [26,27], and particularly in the development of synthetic methods for their clean production [28,29], we are currently involved in the study of reaction methodologies to achieve a greener synthetic alternative.

In previous papers, we have reported a catalytic system for sulfoxidation reaction that involves nitrates and halides ions [30,31,32]. The suggested mechanism for the catalytic sulfoxidation

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reaction involved the formation of several nitrogen oxides and nitrous acid [33]. Scheme 1. In these studies, we observed that 4-(methylthio)aniline give as by-product 4-(methylthio)bromobenzene, suggesting the formation of a diazonium salt in the reaction media by diazotization of the aromatic amino group [34]. The behaviour of 4-(methylthio)aniline prompted us to explore potential applications of our catalytic system in the diazonium salt synthesis.



Scheme 1. HNO<sub>2</sub> generation in sulfoxidation reaction.

In this paper, we present an alternative synthesis of known azo compounds, Fig. 1, as *Para Red* or Sudan I and we compare it with traditional synthesis. We have analyzed the results in terms of reported green metric parameters and we demonstrate that the methodology proposed for the azo compounds synthesis fulfill several of the green chemistry principles since the molar ratio between reactants is smaller and produce less amount of waste comparing with traditional methods.

## 2. Material and methods

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were carried out in a 400 MHz Bruker Avance II spectrometer, all NMR experiments were performed in CDCl<sub>3</sub> or D<sub>2</sub>O in accordance with compound solubility. Mass spectra were recorded on a Bruker, MicroTOF Q II equipment, operated with an ESI source operated in (positive/negative) mode, using nitrogen as nebulizing and drying gas and sodium formate 10 mM as internal calibrant. I.R. spectra were carried out Nicolet 55C spectrophotometer. The melting points were measured in open glass-capillaries using Electrothermal type 9100 point apparatus and are uncorrected.

The solvents used were Merck analytical grade or Mallinckrodt HPLC grade. The Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, FeBr<sub>3</sub>, FeCl<sub>3</sub>, HBr (48%), HCl (37%), HNO<sub>3</sub> (65%) were commercially available samples and used as received. Substrates 4-(nitro)aniline, aniline, 4-(methyl)aniline, 1-naphthylamine, 1,2-phenyldiamine, 4-(amine)-3-(hydroxy)naphthalensulphonic acid, β-naphthol and α-naphthol were also obtained from commercial suppliers. The products were identified by <sup>1</sup>H NMR and/or MS-GC and found to be identical to authentic samples.

### 2.1. General procedure

Several reaction conditions were screened to optimize the synthesis of *para red*, compound **1**, Fig. 1. Once reached, these conditions were used to obtain all the other colorants. No efforts were done to optimize the methodology for each particular compound.

#### 2.1.1. Classical synthesis of azo compounds

Classical synthesis was performed in aqueous media by the known procedure [35]. The amine (3.0 mmol) was dissolved in 60.0 mL of water with concentrate HCl (3.0 mL), this solution was cooled in ice. The solution temperature was maintained at (0–5)°C and an aqueous cold solution of sodium nitrite (14.5 mmol) was added under stirring. After about 2 min, a cold solution of naphthol (1.0 mmol) in aqueous sodium hydroxide (5.0 mL; 0.2 M) was added. The formation of a solid coloured azo compound was observed, this mixture was stirred for about 10 min and then it was filtered in vacuum and dried under air. The yield was calculated from the weight of solid recovered and the initial naphthol quantity. The product purity was analyzed by <sup>1</sup>H NMR.

#### 2.1.2. Alternative synthesis of azo compounds

2.1.2.1. *With HCl solution and ferric nitrate.* This synthesis was performed in acetonitrile, ACN, as solvent. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.4 mmol) was dissolved in ACN (1.0 mL), the amine (2.0 mmol) was dissolved in ACN (5.0 mL) and this solution was cooled in ice, later a concentrate

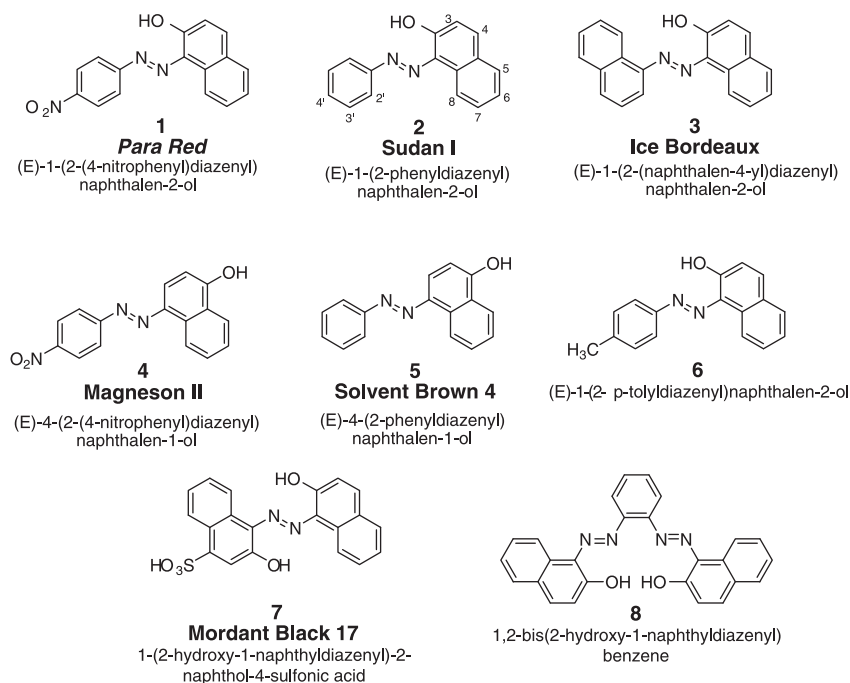


Fig. 1. Azo compounds synthesized.

HCl solution (4.6 mL in 5.0 mL ACN) was added dropwise for a 30 min. The solution temperature was maintained at (0–5)°C and under stirring. After about 10 min, a solution of naphthol (1.0 mmol) and sodium hydroxide (5.0 mmol) in ACN/water (3.0 mL/2.0 mL) was added.

**2.1.2.2. With HCl solution and nitric acid solution.** The amine (2.0 mmol) was dissolved in ACN (5.0 mL) and this solution was cooled in ice, later a concentrate HCl solution (6.2 mL in 5.0 mL ACN) was added dropwise for a 30 min. The temperature was maintained at (0–5)°C and concentrate solution of HNO<sub>3</sub> (2.5 mmol, 0.2 mL) was added to this mixture under stirring. After about 2 min, a solution of naphthol (1.0 mmol) and sodium hydroxide (4.5 mmol) in ACN/water (5.0 mL/1.0 mL) was added.

**2.1.2.3. With HCl gaseous and nitric acid solution.** The amine (2.0 mmol) was dissolved in ACN (5.0 mL) at room temperature and a concentrate solution of HNO<sub>3</sub> (2.0 mmol) was added dropwise under stirring (solution1). The gaseous HCl, generated by addition of concentrated sulphuric acid to dry sodium chloride, was bubbled in excess into the solution 1 and, simultaneously, a solution of naphthol (1.0 mmol) and sodium hydroxide (4.5 mmol) in ACN/water (5.0 mL/1.0 mL) was added.

In all methods described in 2.1.2, the reactions were analyzed from time to time by thin layer chromatography with chloroform : ethyl ether 1:1 as solvent system. The coloured azo compound was observed, this mixture was stirred for about 24 h and then the solid was filtered under vacuum and it was dried under air. A minimum quantity of dichloromethane (10.0 mL) was added to the liquid face

(H2'); 7.60(H3'); 7.81(H4'); 7.91(H5'); 7.57(H6'); 7.66(H7'); 8.33(H8'). m.p. decomp. above 96 °C.

**Magneson II, 4.**- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 12.01(OH); 6.83(H2); 8.32(H3); 8.54(H5); 7.82(H6); 7.64(H7); 8.32(H8); 7.74(H2'); 8.32(H3').

**Solvent Brown 4, 5.**- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 11.22(OH); 7.07(H2); 7.93(H3); 8.94(H5); 7.65(H3'); 8.94(H5); 7.65(H6); 7.76(H7); 8.29(H8); 8.03(H2'); 7.65(H3'); 7.53(H4'). m.p. 115.8–116.7 °C.

**Compound, 6.**- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 15.00(NH); 7.74(H3); 6.97(H4); 7.65(H5); 7.41(H6); 7.57(H7); 8.63(H8); 7.70(H2'); 7.31(H3').

**Mordant Black 17, 7.**- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 6.53(H3); 7.50(H4); 7.70(H9); 7.33(H3'); 8.36(H9'); 7.20–7.6(H6,H7,H8,H6',H7',H8').

**Compound, 8.**- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 17.53(NH); 6.6(H3); 7.47(H8); 7.72(H7); 7.90(H6,H4); 8.34(H9); 7.44–7.58(H2',H3',H4'). HS-MS Found (Calcd): *m/z* = 418,10 (418.14) [M<sup>+</sup>]. m.p. 205.6–207.0 °C.

The NH in the HNMR data correspond to the hydrazone isomer [39,40]

In all azo compounds obtained, the IR spectra show a signal at 1630–1575 cm<sup>-1</sup> corresponding at N=N stretching.

### 2.3. Green metric calculations

The green metrics were calculated using the procedures reported in the literature [41]. They are defined as follows:

$$\text{Reaction mass efficiency (RME)} = \frac{\sum \text{mass of products}}{\sum \text{mass of reactants}} \times 100$$

$$\text{Carbon efficiency (CE)} = \frac{N^{\circ} \text{ of moles of product} \times N^{\circ} \text{ of carbons in product}}{\sum (N^{\circ} \text{ of moles of reactant} \times N^{\circ} \text{ of carbons in reactant})} \times 100$$

to extract the product. The organic layer was washed with distilled water (3 × 10.0 mL) to remove any inorganic residue. Then, it was dried with MgSO<sub>4</sub> and the solvent was evaporated and collected to be reused. The solid obtained from liquid face was analysed by different spectroscopic methods too. The yield was calculated considering the amount of product recovered from the reaction and the initial naphthol quantity. The product purity was analyzed by <sup>1</sup>H NMR.

The products obtained are shown in Fig. 1. The starting materials were 4-(nitro)aniline and β-naphthol for **1**; aniline and β-naphthol for **2**; 1-naphthylamine and β-naphthol for **3**; 4-(nitro)aniline and α-naphthol for **4**; aniline and α-naphthol for **5**; 4-(methyl)aniline and β-naphthol for **6**; 4-(amine)-3-(hydroxy)naphthalensulphonic acid and β-naphthol for **7**; 1,2-phenyldiamine and β-naphthol for **8**.

### 2.2. Products characterization

DEPT, COSY, ROESY, HMBC and/or HSQC experiments were performed for signal assignments of all products.

**Para red, 1** [36].- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 16.14(NH); 7.69(H3); 6.70(H4); 7.54(H5); 7.44(H6); 7.56(H7); 8.42(H8); 7.69(H2'); 8.32(H3'). m.p.(reported) 249.2–251.3 °C (250–252 °C) [37].

**Sudan I, 2.**- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 16.26(NH); 7.71(H3); 6.86(H4); 7.59(H5); 7.40(H6); 7.55(H7); 8.57(H8); 7.70(H2'); 7.48(H3'); 7.28(H4').

**Ice Bordeaux, 3** [38].- <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 17.24(NH); 6.92(H3); 7.74(H4); 7.61(H5); 7.41(H6); 7.57(H7); 8.64(H8); 8.21

$$\text{Atom economy (AE)} = \frac{\text{molecular weight of product}}{\sum \text{molecular weight of reactant}} \times 100$$

An example of a typical calculation follows: β-naphthol (0.144 g, 1.0 mmol, FW 144.17) react with 4-(nitro)aniline (0.414 g, 3.0 mmol, FW 138.12), and the sodium nitrite (0.345 g, 5.0 mmol, FW 69.00) in presence of HCl aqueous solution to give *para red* (FW 293.28) in 26% yield (0.26 mmol, 0.076 g) as determined by <sup>1</sup>H NMR.

$$\begin{aligned} \text{Reaction Mass Efficiency} &= [0.076 / (0.144 + 0.414 + 0.345)] \times 100 \\ &= 8.4\% \end{aligned}$$

$$\begin{aligned} \text{Atom Economy} &= [293.28 / (144.17 + 138.12 + 69.00)] \times 100 \\ &= 83.5\% \end{aligned}$$

$$\begin{aligned} \text{Carbon Efficiency} &= [0.26 \times 16 / (1 \times 10) + (3 \times 6)] \times 100 \\ &= 14.9\% \end{aligned}$$

### 3. Results and discussion

We studied three synthetic alternatives to obtain azo compounds. The yields obtained were approximately equal to traditional synthesis and, in some cases better, Table 1. Moreover, our synthetic methods have additional advantages. One is the lower

**Table 1**  
Percent yields of azo compounds synthesized by different sources of nitrosonium ion.<sup>a</sup>

Entry	Product	NaNO <sub>2</sub> /HCl (aq) <sup>b</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl (aq) <sup>c</sup>	HNO <sub>3</sub> (aq)/HCl (aq) <sup>d</sup>	HNO <sub>3</sub> (aq)/HCl (g) <sup>e</sup>
1	<b>1</b>	26	47	53	60
2	<b>2</b>	39	35	Traces <sup>f</sup>	Traces <sup>f</sup>
3	<b>3</b>	26	19	30	27 <sup>g</sup>
4	<b>4</b>	31	20	60	60
5	<b>5</b>	27	18	Traces <sup>f</sup>	20
6	<b>8</b>	11	43	52	47

<sup>a</sup> Percent yield of product determined by <sup>1</sup>H NMR analysis of the reaction crude and calculated from the product recovered of reaction and the initial naphthol quantity.

<sup>b</sup> Classical synthesis [35], aqueous media.

<sup>c</sup> Solvent acetonitrile, nitrosonium ion source Fe(NO<sub>3</sub>)<sub>3</sub>/HCl<sub>(aq)</sub>.

<sup>d</sup> Solvent acetonitrile, nitrosonium ion source HNO<sub>3(aq)</sub>/HCl<sub>(aq)</sub>.

<sup>e</sup> Solvent acetonitrile, nitrosonium ion source HNO<sub>3(aq)</sub>/HCl<sub>(g)</sub>.

<sup>f</sup> Only product traces are detected (<2%).

<sup>g</sup> Some unidentified by products were detected.

amine : naphthol ratio. In traditional synthesis it is 3:1 and in our alternative methodology was 2:1. Also nitrosonium ion source : naphthol ratio is smaller leading to a reactants mass reduction, Table 2, and by-products are not observed in the most cases, in fact by-products were formed only in one case, Table 1, entry 3. It is also noteworthy that the remaining substrates can be recovered and reused. These aspects give to our synthetic methodology better Green Chemistry metrics than the traditional.

For diazonium salts generation, we used as nitrosonium ion sources Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O<sub>(s)</sub>/HCl<sub>(aq)</sub> or HNO<sub>3(aq)</sub>/HCl<sub>(aq)</sub> or HNO<sub>3(aq)</sub>/HCl<sub>(g)</sub> in acetonitrile. In these media, nitrosonium ions are generated *in situ* by the different mechanisms, for example, decomposition of nitric acid and subsequently generation of nitrous acid and/or disproportionation of the inorganic nitrogen species and/or by reaction between nitric and hydrochloric acids [42]. Equation 1; the ClNO has been used as nitrosating agent [43]. Moreover, previous electrochemical studies showed that nitric acid can oxidize bromide into bromine while it reduces to nitrous acid [44], Scheme 2. Simultaneously we synthesized the same azo compounds by the traditional methodology. The cation, whichever way it is formed, can react with different arylamines to produce the desired aryldiazonium salt by classic diazotation mechanism. The obtained yields are summarized in the Table 1 and the molar ratios between all of reactants used in the synthesis are shown in Table 2.

In the case of Para Red, compound **1** (Table 1, entry 1), best yield was obtained with HNO<sub>3(ac)</sub>/HCl<sub>(g)</sub> as nitrosonium ion source. When the product was Sudan I, compound **2** (Table 1, entry 2), the yield obtained with Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O/HCl<sub>(aq)</sub> as nitrosonium ion source was similar to that obtained in traditional synthesis. In this case, other synthetic alternatives only produced traces of the product of interest.

In the case of Ice Bordeaux, compound **3** (Table 1, entry 3) the yields were similar with all methods but our methodology gave less

**Table 2**  
Relative molar amount of reactants in the different synthetic methods used.<sup>a</sup>

	NaNO <sub>2</sub> /HCl (aq) <sup>b</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl (aq) <sup>c</sup>	HNO <sub>3(aq)</sub> /HCl (aq) <sup>d</sup>	HNO <sub>3(aq)</sub> /HCl (g) <sup>e</sup>
Amine	3.0	2.0	2.0	2.0
Naphthol	1.0	1.0	1.0	1.0
NaNO <sub>2(s)</sub>	5.0	—	—	—
HNO <sub>3</sub> (aq)	—	—	2.5	2.0
Fe(NO <sub>3</sub> ) <sub>3(s)</sub>	—	0.4	—	—

<sup>a</sup> HCl, gaseous or aqueous, was added in excess in all cases.

<sup>b</sup> Classical synthesis [35], aqueous media.

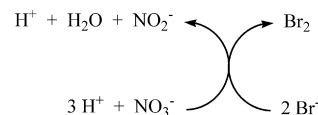
<sup>c</sup> Solvent acetonitrile, nitrosonium ion source Fe(NO<sub>3</sub>)<sub>3</sub>/HCl<sub>(aq)</sub>.

<sup>d</sup> Solvent acetonitrile, nitrosonium ion source HNO<sub>3(aq)</sub>/HCl<sub>(aq)</sub>.

<sup>e</sup> Solvent acetonitrile, nitrosonium ion source HNO<sub>3(aq)</sub>/HCl<sub>(g)</sub>.



**Equation 1.** ClNO generation in *aqua regia*.



**Scheme 2.** HNO<sub>2</sub> generation in presence of nitric acid and bromide anions.

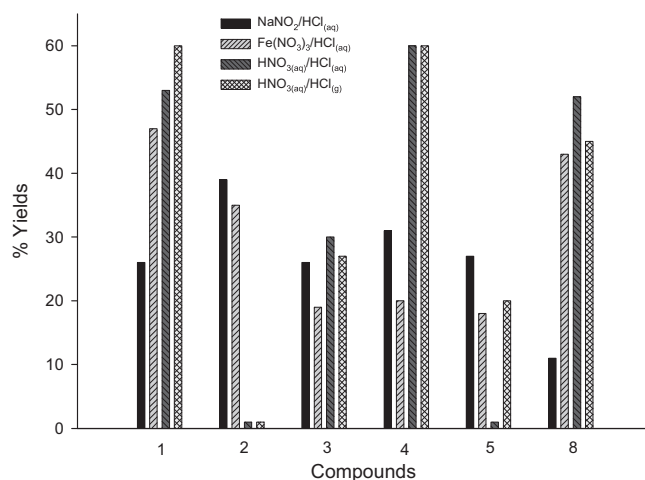
amount of by-products. On the other hand, the yields of compound **8** (Table 1, entry 6) was significantly improved with our methodology.

For the synthesis of compounds **4 y 5**,  $\alpha$ -naphthol is used as nucleophile where *ortho* and *para* positions are both activated for the reaction; and usually both colorants are equally obtained in a mixture. We focused on the *para* substituted compound due to the fact that our alternative synthetic method showed selectivity for this product. The yields of compound **4** (Table 1, entry 4) were bigger in two of our synthetic methods than in the traditional synthesis, these were the nitrosonium ion source HNO<sub>3(ac)</sub> with HCl<sub>(aq)</sub> or HCl<sub>(aq)</sub>

On the other hand, compound **5**, Solvent Brown 4, showed lower yields under all synthetic conditions and corresponding *ortho* isomer was detected in our synthetic methods. (Table 1, entry 5).

Compound **6** was synthesized and detected, but better reaction condition must be searched for amines bearing electron donor substituents. Finally, Mordant Black 17, compound **7**, presented problems in the recuperation and quantification of product because of their high solubility in water that made its isolation difficult.

In the Graph 1, it can quickly be observed that the 4-nitroaniline and diaminobenzene produce more azo compound by our alternative synthetic methods (compounds **1, 4** and **8**), whereas aniline produce more azo compound by traditional synthesis (compounds **2** and **5**), naphthylamine produce about the same by various methods. These facts can be attributed to the solubility of the used amines [45], since the synthesis in the organic media is more effective when the amine solubility in water is low. This behaviour can be of interest for the synthesis of new azo compounds starting from amines which usually do not react due to water solubility problems.



**Graph 1.** Percent yields of azo compounds synthesized from different sources of nitrosonium ion.

**Table 3**  
Green metrics calculated for the synthetic reactions of azo compounds.<sup>a</sup>

Product	Synthetic methods	% RME	% CE	% AE
1	NaNO <sub>2</sub> /HCl <sub>(aq)</sub> <sup>b</sup>	8.41	14.9	83.49
1	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl <sub>(aq)</sub> <sup>c</sup>	23.7	34.2	42.73
1	HNO <sub>3</sub> (aq)/HCl <sub>(aq)</sub> <sup>d</sup>	23.4	38.5	84.93
1	HNO <sub>3</sub> (aq)/HCl <sub>(g)</sub> <sup>e</sup>	28.7	43.6	84.93
2	NaNO <sub>2</sub> /HCl <sub>(aq)</sub> <sup>b</sup>	12.6	22.3	81.06
2	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl <sub>(aq)</sub> <sup>c</sup>	17.7	25.5	38.72
3	NaNO <sub>2</sub> /HCl <sub>(aq)</sub>	8.5	13.0	83.72
3	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl <sub>(aq)</sub> <sup>c</sup>	9.6	12.7	43.15
3	HNO <sub>3</sub> (aq)/HCl <sub>(aq)</sub> <sup>d</sup>	13.4	20.0	85.15
3	HNO <sub>3</sub> (aq)/HCl <sub>(g)</sub> <sup>e</sup>	13.0	18.0	85.15
4	NaNO <sub>2</sub> /HCl <sub>(aq)</sub> <sup>b</sup>	10.1	17.7	83.49
4	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl <sub>(aq)</sub> <sup>c</sup>	10.1	14.5	42.73
4	HNO <sub>3</sub> (aq)/HCl <sub>(aq)</sub> <sup>d</sup>	26.6	43.6	84.93
4	HNO <sub>3</sub> (aq)/HCl <sub>(g)</sub> <sup>e</sup>	28.7	43.6	84.93
5	NaNO <sub>2</sub> /HCl <sub>(aq)</sub> <sup>b</sup>	8.7	15.4	81.06
5	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl <sub>(aq)</sub> <sup>c</sup>	9.1	13.1	38.72
5	HNO <sub>3</sub> (aq)/HCl <sub>(g)</sub> <sup>e</sup>	9.5	14.5	82.67
8	NaNO <sub>2</sub> /HCl <sub>(aq)</sub> <sup>b</sup>	5.7	10.2	130.25
8	Fe(NO <sub>3</sub> ) <sub>3</sub> /HCl <sub>(aq)</sub> <sup>c</sup>	34.5	50.8	63.76
8	HNO <sub>3</sub> (aq)/HCl <sub>(aq)</sub> <sup>d</sup>	36.2	61.5	132.72
8	HNO <sub>3</sub> (aq)/HCl <sub>(g)</sub> <sup>e</sup>	35.6	88.5	132.72

<sup>a</sup> % RME: percentage reaction mass efficiency. % CE: percentage carbon efficiency. % AE: percentage atom economy.

<sup>b</sup> Classical synthesis [35], aqueous media.

<sup>c</sup> Solvent acetonitrile, nitrosonium ion source Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O/HCl<sub>(aq)</sub>.

<sup>d</sup> Solvent acetonitrile, nitrosonium ion source HNO<sub>3</sub>(aq)/HCl<sub>(aq)</sub>.

<sup>e</sup> Solvent acetonitrile, nitrosonium ion source HNO<sub>3</sub>(aq)/HCl<sub>(g)</sub>.

In the last decade, atom economy (AE), reaction mass efficiency (RME) and the carbon efficiency (CE) have been proposed as measures of environmental sustainability in terms of minimisation theoretical waste amount [41]. AE was introduced by Trost [46] and is a theoretical measure of the chemical and environmental efficiency of a chemical reaction based on stoichiometric equation; it does not consider solvents, possible excess of reagents, formation of unwanted products, etc. RME is a more sophisticated measure of greenness which allows for the effect of yield and the excess or catalytic amount of reactants used, but it does not account for solvent use. Finally, CE is the percentage of carbon in the reactants that remain in the final product. In an ideal situation % AE ~ 100, % RME ~ 100, % CE ~ 100.

In the Table 3, the green metrics calculated for our alternative method and traditional synthesis are summarized. The results show that our synthetic methods have good RME values and, in all cases, better than the classical synthesis. In addition, the other values show the same tendency.

#### 4. Conclusions

It can be concluded that the new proposed methods are excellent synthetic alternative procedures to obtain known azo compounds and they would permit to synthesize new azo compounds. The nitrosonium ion source HNO<sub>3</sub>(ac)/HCl<sub>(g)</sub> is the best because it gave very good yields in most of the cases. Except for the synthesis of Ice Bordeaux, no by-products were formed which is very important because there are no washed material and the purification of the desired azo dye is easier.

Our reaction conditions are agreement with some the Green Chemistry principles and they gave very good values of the green metrics.

In summary, we report herein efficient and greener methods for the synthesis of azo compounds with good yields and excellent prospect to obtain new azo compounds.

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