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A convenient and efficient process for the manufacture of benzenesulfonic acid, 2-((4-amino-3-bromo-9,10-dihydro-9,10-dioxo-1-anthracenyl)amino)-5-methyl monosodium salt (C.I. Acid Blue 78) directly from anthraquinone

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Abstract

C.I. Acid Blue 78 is an important acid dye; its manufacture depends on 1-nitroanthraquinone and all procedures developed for the mononitration of anthraquinone give by-products such as dinitroanthraquinones. This paper presents a new method for the manufacture of C.I. Acid Blue 78 in high yield and good quality. HPLC was used to follow the formation of nitroanthraquinone from anthraquinone, which allowed the nitration of anthraquinone to be stopped at 35–45% conversion to 1-nitroanthraquinone, as the formation of by-products at this point was minimal. At the end of the formation of C.I. Acid Blue 78 from anthraquinone, residual, unreacted anthraquinone was reused for nitration after a single recrystallization stage from acetic acid.

Keywords: Anthraquinone acid dyes; C.I. Acid Blue 78; Nitration of anthraquinone; Aminoanthraquinones; Purification of nitroanthraquinones; Sulfonation of anthraquinone

1. Introduction

With the exception of azo dyes, the anthraquinonesulfonic acids constitute the most important group of dyes for wool and polyamide fibers and blend of both these fibers [1,2]. One of these acid dyes is C.I. Acid Blue 78 (benzenesulfonic acid, 2-((4-amino-3-bromo-9,10-dihydro-9,10-dioxo-1-anthracenyl) amino)-5-methyl monosodium salt), CA number [6424-75-5], C.I. constitution number 62105, discovered by O. Unger in 1899, and most procedures for its manufacture require mononitration of anthraquinone and all procedures developed for the preparation of 1-nitroanthraquinone give by-products such as dinitroanthraquinone [3]. Even the best methodologies permit preparation of only 75–80% of theoretical amount of 1-nitroanthraquinone, composition containing 2.1% of anthraquinone, 73.8% of 1-nitroanthraquinone, 8.3% of 2-nitroanthraquinone, 3.2% of 1,6-dinitroanthraquinone, 3.2% of 1,7-dinitroanthraquinone, 3.6% of 1,5-dinitroanthraquinone, 3.3% of 1,8-dinitroanthraquinone, 0.2% of 2,6- and 2,7-dinitroanthraquinones, 2.3% of others (see Table 1 [4]).

Because of the serious pollution problems associated with the purification of 1-nitroanthraquinone from crude nitroanthraquinones, numerous processes for purifying crude reaction products of nitration had been developed [5]. As indicated above about the nitration products, purification of crude nitroanthraquinones is costly and time consuming, and 26.2% dinitroanthraquinone is discarded after purification, consequently methods of purification are not economical.

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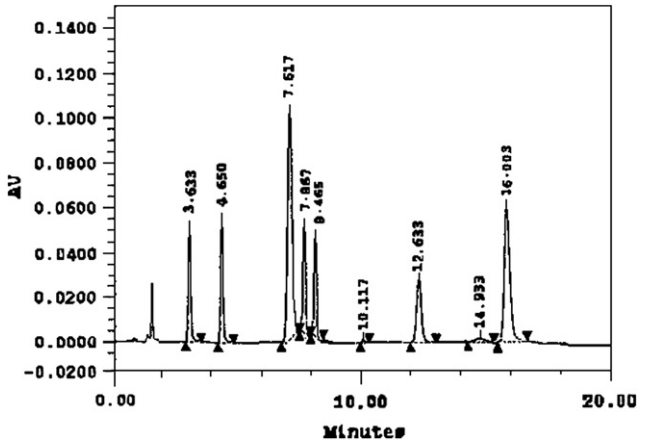


Fig. 1. Chromatogram of crude nitroanthraquinones after addition of 140 mol.% (relative to anthraquinone) of 87% nitric acid, composition: 2.45% 1,8-dinitroanthraquinone, 2.85% 1,5-dinitroanthraquinone, 75.92% 1-nitroanthraquinone, 4.10% 1,7-dinitroanthraquinone, 4.8% 1,6-dinitroanthraquinone, 3.6% anthraquinone, 5.26% 2-nitroanthraquinone, 1.01% of others.

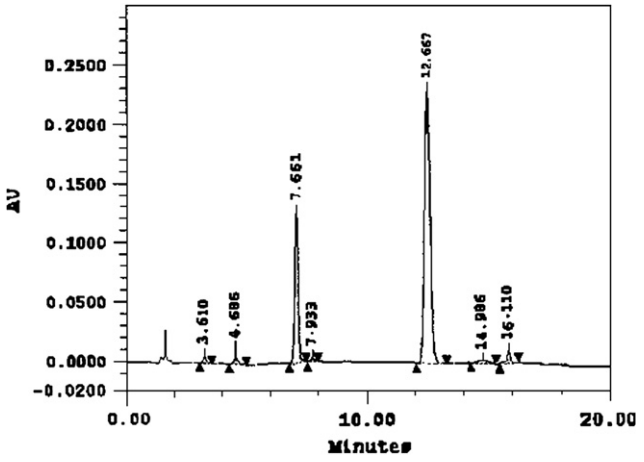


Fig. 2. Chromatogram of crude nitroanthraquinones after addition of 34 mol.% (relative to anthraquinone) of 87% nitric acid, composition: 62.00% anthraquinone, 36.82% 1-nitroanthraquinone, 1.18% of others.

In this work with the analyses of reaction products of nitration by HPLC (Fig. 1, Table 1, and Fig. 2, Table 2) and according to the results shown in Table 1 [4], we have found out that the formation of dinitroanthraquinone starts at 30–35% conversion of anthraquinone to 1-nitroanthraquinone, at this point addition of nitrating reagent to reaction medium was stopped and chromatogram of product formation is shown in Fig. 2. Other steps of reaction until preparation of C.I. Acid Blue 78 were proceeded; the unreacted anthraquinone was separated from C.I. Acid Blue 78 by dilution and filtration, and returned to the step of nitration after a recrystallization from acetic acid.

In this paper C.I. Acid Blue 78 was obtained through six stages: (1) partial nitration of anthraquinone, (2) converting the crude nitroanthraquinone to crude anthraquinon-1-amines by reduction with sodium sulfide, (3) converting the crude anthraquinonamines to 2,4-dibromoanthraquinon-1-amines with bromine in glacial acetic acid [6], (4) condensing *p*-toluidine with 2,4-dibromoanthraquinon-1-amines and formation of 2-bromo-4-*p*-toluidinoanthraquinon-1-amine, (5) formation of C.I. Acid Blue 78 with sulfonation [7], (6) separation of unreacted anthraquinone from C.I. Acid Blue 78 with dilution (Scheme 1).

Table 1
Analysis results of HPLC determination of crude nitroanthraquinone[a] (Fig. 1)

No.	Retention time (min)	Components	Content (%)
1	3.63	1,8-Dinitroanthraquinone	2.45
2	4.65	1,5-Dinitroanthraquinone	2.85
3	7.62	1-Nitroanthraquinone	75.92
4	7.87	1,7-Dinitroanthraquinone	4.1
5	8.13	1,6-Dinitroanthraquinone	4.6
6	10.12	Unknown-1	0.26
7	12.63	Anthraquinone	3.60
8	14.93	Unknown-2	0.75
9	16.00	2-Nitroanthraquinone	5.26

[a] Composition of crude nitroanthraquinones after addition of 140 mol.% (relative to anthraquinone) of 87% nitric acid.

2. Experimental

2.1. Apparatus

Melting points were determined by using a Buchi 450 apparatus. All of the anthraquinone acid dyes synthesized were purified whenever necessary by column chromatography on Silica gel C.T. (Reeve A) and eluted with *n*-butyl acetate/pyridine/water, 40:40:20 (volume ratio). Analytical thin-layer chromatography (TLC) was performed on 0.25-mm plates of $Kieselgel_{60}$ PF 244 + 365 (benzene/ethyl formate/formic acid, 75:24:1 (volume ratio)) for anthraquinone intermediates. Microanalyses were performed by Heraeus CHN Rapid Microanalyzer. Mass spectrum of final product was recorded by Agilent Technology Model No. 5973 Network Mass Selective Detector. ^{1}H NMR spectra were recorded on a Bruker Avance DRX at 500 MHz. Appropriate amount of synthetic samples was dissolved in dimethyl formamide/1,4-dioxane/dimethyl sulfoxide, 5:2:1 (volume ratio). The separation was performed with HPLC system containing Waters pump (model 600), Waters Novapak C_{18} column (150 × 4.6 mm), UV–vis detector (waters 486) at 254 nm and 1,4-dioxane/methanol/water, 15:45:40 (volume ratio) as mobile phase.

2.2. Procedure

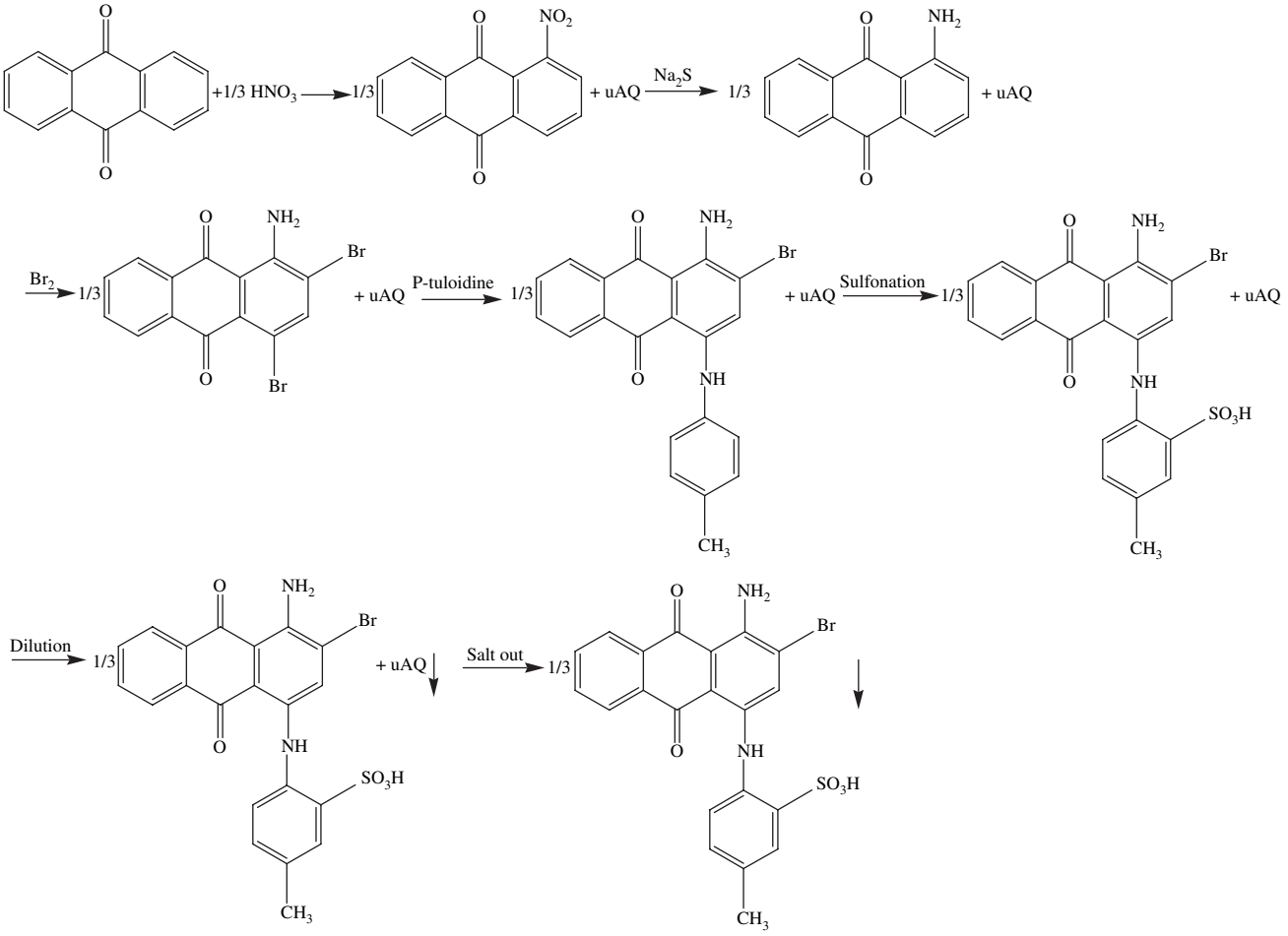
2.2.1. Preparation of crude nitroanthraquinones

Anthraquinone (8.50 g, 0.040 mol) was dissolved in sulfuric acid (50 g, 98%) and then 3 g of mixed acid [33% nitric acid

Table 2
Analysis results of HPLC determination of crude nitroanthraquinone[a] (Fig. 2)

No.	Retention time (min)	Components	Content (%)
1	7.66	1-Nitroanthraquinone	36.82
2	12.67	Anthraquinone	62.00
3	–	Others	1.18

[a] Composition of crude nitroanthraquinones after addition of 34 mol.% (relative to anthraquinone) of 87% nitric acid.



Scheme 1. Formation of C.I. Acid Blue 78 directly from anthraquinone.

(87%, 0.99 g, 0.0136 mol) and 67% sulfuric acid (98%, 1.97 g, 0.0201 mol)] was added from dropping funnel at a rate so as to maintain the temperature at 25–30 °C. The contents were then heated for 3 h at 65–70 °C and the reaction mass was poured into 80 ml of cold water subsequently stirred at 60 °C for 0.5 h and filtered, and the residues were washed with hot water until neutralization and dried in vacuo at 80 °C. Crude nitroanthraquinones of 8.72 g of the following composition were obtained: 5.27 g, 0.0253 mol of anthraquinone; 3.13 g, 0.0123 mol of 1-nitroanthraquinone, yield 90.44% relative to HNO_3; 0.32 g of others.

2.2.2. Preparation of crude aminoanthraquinone

$Na_2S \cdot 9H_2O$ (15.00 g, 0.0625 mol) was dissolved in water (40 ml) and stirred at 90–95 °C for 1.2 h, then finely crude nitroanthraquinones (8.00 g, containing 2.87 g of 1-nitroanthraquinone (0.0128 mol)) were added and stirred in the same temperature for 15 min, then stirred in the same temperature in the course of 15 min. The reaction mixture was filtered and the precipitates were washed with hot water until neutralization, and dried at 60 °C. Crude 1-aminoanthraquinone of 7.62 g of the following composition was obtained: 4.83 g, 0.234 mol of anthraquinone; 2.49 g, 0.0112 mol of anthraquinon-1-amine, yield 87.5% relative to 1-nitroanthraquinone component; 0.29 g of others.

2.2.3. Preparation of crude 1-amino-2,4-dibromoanthraquinone

Crude anthraquinon-1-amine (6 g, containing 1.96 g, 0.009 mol of anthraquinon-1-amine) was dissolved in glacial acetic acid (40 ml) and refluxed in a hood. Then, bromine (2.54 g, 0.016 mol) was added dropwise during 6 h. After completion of the reaction (as monitored by TLC), the reaction mixture was poured into bisulfite solution (50 ml, 0.05 N) to remove extra bromine, then filtered and the residues were washed with hot water until neutralization, and dried at 60 °C. Crude 2,4-dibromoanthraquinone-1-amine of 6.59 g of the following composition was obtained: 3.80 g, 0.0183 mol of anthraquinone; 2.56 g, 0.0067 mol of 2,4-dibromoanthraquinone-1-amine, yield 76.4% relative to 1-aminoanthraquinone; 0.23 g of others.

2.2.4. Preparation of crude 2-bromo-4-p-toluidinoanthraquinon-1-amine

Five grams of crude 2,4-dibromoanthraquinon-1-amine (containing 1.94 g, 0.0051 mol of 2,4-dibromoanthraquinon-1-amine) and sodium acetate (0.6 g, 0.0073 mol) were added to toluidine (5 g, 0.0467 mol), and heated with vigorous stirring at 150 °C for 0.5 h. The reaction mixture was diluted with ethanol (7.5 ml), filtered and the residues were washed with ethanol. Crude 2-bromo-4-*p*-toluidinoanthraquinon-1-amine of 5.46 g

of the following composition was obtained: 2.88 g, 0.014 mol of anthraquinone; 2.41 g, 0.006 mol of 1-amino-2-bromo-4-*p*-toluidinoanthraquinone, yield 97.2% relative to 2,4-dibromoanthraquinon-1-amine; 0.17 g of others.

2.2.5. Formation of C.I. Acid Blue 78

Five grams of crude 2-bromo-4-*p*-toluidinoanthraquinon-1-amine (containing 2.27 g, 0.0056 mol of 2-bromo-4-*p*-toluidinoanthraquinon-1-amine and 2.73 g, 0.0132 mol of anthraquinone) and 1.5 g of anhydrous Na_2SO_4 were added to oleum (4 ml, 20% strength) and stirred at 135 °C for 15 min, then the mixture was cooled to room temperature and diluted with water (1 ml), the unreacted anthraquinone was precipitated and filtered. The residues were washed with water until neutralization and after drying and recrystallization from acetic acid returned to step of nitration (2.63 g, 0.0127 mol of anthraquinone); the filtrate was saturated with NaCl and C.I. Acid Blue 78 was precipitated and filtered and dried at 80 °C. C.I. Acid Blue 78 (2.59 g, 0.0053 mol) was obtained (yield 89.2% relative to 2-bromo-4-*p*-toluidinoanthraquinon-1-amine).

^{1}H NMR (D_2O, 500 MHz): δ 2.35 (s, 3H), 7.14 (m, 2H, 2CH), 7.22 (m, 2H, 2CH), 7.42 (m, 2H, 2CH), 7.62 (m, 2H, 2CH), 8.036 (s, 1H, 1CH). MS: $m/z = 487$. Anal. Calcd for $C_{21}H_{15}BrN_2O_5S$: C, 51.74; H, 3.08; N, 5.74. Found: C, 51.44; H, 3.21; N, 5.62.

The colouristic properties of the final product are the same as the previously published data about C.I. Acid Blue 78 [8,9].

3. Results and discussion

Considering the results, it can be seen that the method disclosed in this paper has some advantages over the previous synthetic methods for C.I. Acid Blue 78. First of all, we have found that the reason for separation of C.I. Acid Blue 78 from anthraquinone was that sulfonation of aryl residue in 2-bromo-4-*p*-toluidinoanthraquinon-1-amine (unsulfonated C.I. Acid Blue 78) is faster than anthraquinone. Unsulfonated C.I. Acid Blue 78 was sulfonated at arylamino moiety and anthraquinone was not sulfonated and separated with dilution and returned to the step of nitration after recrystallization from acetic acid.

C.I. Acid Blue 78 can be obtained by this method in high quality. More importantly than that, without need to additional purification of intermediate byproducts such as dinitroanthraquinones and anthraquinonediamines, the products of any stage can be transferred to the next stage of production. This is essentially an advantage for this process. Finally, it has to be mentioned that only with a simple step of recrystallization at the end of this process, we can reuse the unreacted anthraquinone in the first stage of another process of nitration toward C.I. Acid Blue 78. So, as a result of these advantages, we have found out that this process can be economical and can be used in industry.

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