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A new method for the preparation of 1-amino-4-bromo-2-anthraquinonesulphonic acid (bromamine acid) directly from anthraquinone

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Abstract

Bromamine acid (1-amino-4-bromo-2-anthraquinonesulphonic acid) is one of the most important intermediates in the synthesis of acid dyes. Apart from quinizarin and leucoquinizarin, more acid dyes have been produced from bromamine acid by replacement of the bromine atom with aryl amino groups than from any other anthraquinone intermediate. This paper presents a new method for the preparation of 1-amino-4-bromo-2-anthraquinonesulphonic acid in high yield and good quality economically. In most of the methods of nitration of anthraquinone, about 30% anthraquinone is converted to by-product such as dinitroanthraquinones which can be separated only with great difficulty and used as a reagent of reaction and in the end must be discarded and these methods are not economical. Due to the formation of about 35–45% 1-nitroanthraquinone, diffusion of product such as 1-nitroanthraquinone in solvent of nitration is more than anthraquinone, consequently 1-nitroanthraquinone is quickly nitrated from anthraquinone, and the factor of diffusion in nitration is very important. With due attention to analyses of formation of nitroanthraquinones from anthraquinone which are obtainable by high pressure chromatography and from Ref. [Hohmann Walter, Wunderlich Klaus. Process for the mononitration of anthraquinone. U.S.Pat. 4203885; May 20, 1980], nitration of anthraquinone is stopped in about 35–45% conversion of anthraquinone to 1-nitroanthraquinone because the formation of by-product at this point is minimal, and at the end of manufacture of bromamine acid, the unreacted anthraquinone is returned to step of nitration.

Keywords: 1-Amino-4-bromo-2-anthraquinonesulphonic acid (bromamine acid); Anthraquinone acid dyes; Nitration and sulphonation of anthraquinone

1. Introduction

Most procedures for the manufacture of 1-amino-4-bromo-2-anthraquinonesulphonic acid require mononitration of anthraquinone, and all procedures developed for the mononitration of anthraquinone to 1-nitroanthraquinone give by-products such as 1,5-, 1,8-, 2,5-, 2,6-, 2,7-, 2,8-dinitroanthraquinone and 2-nitroanthraquinone [2]. Numerous new processes for nitrating anthraquinone, as well as techniques for purifying crude reaction products have been developed [3] because of the serious pollution problem associated with the purification of 1-nitroanthraquinone from crude nitroanthraquinones. Purification and nitrating methods have been studied extensively by our research group, for example Refs. [4–6]. It is to be noted that all of the procedures involving the nitration of the anthraquinone have been presented to give by-products and the purification of by-products is more difficult, and not economical. Even the best, most recent methodology permits preparation of only 75–80% of the theoretical amount of 1-nitroanthraquinone (see Table 1). Dinitration can be retarded significantly during nitration with mixed acids by increasing the water content. For example, according to Ref. [1] which indicated analyses of production after the start of the experiment (see Table 1):

At the end of nitration process in the best method [1], the reagent composition contains 2.1% of anthraquinone, 73.8% of 1-nitroanthraquinone, 8.3% of 2-nitroanthraquinone,

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Table 1
Hundred and fifty grams of mixture, in which the reaction was ended, the proportion of anthraquinone in which after 420 min had approximately the composition indicated in table, serve as the nitration mixture

Time after the start of the experiment (min)	Amount of A″non introduced	Temperature (°C)	Analyses (%)								
			A″non	1-NA	2-NA	1,6-DNA	1,7-DNA	1,5-DNA	1,8-DNA	2,6-, 2,7-DNA	Other
36	100	50	51.8	37.6	3.0	1.9	1.8	1.7	1.7	0.2	–
72	200	50	49.5	38.6	3.4	1.6	1.5	1.4	1.4	0.1	2.1
108	300	50	36.8	49.5	5.6	1.5	1.5	1.9	1.9	0.1	0.9
144	400	50	31.8	52.1	6.5	1.5	1.5	1.9	1.9	0.1	2.4
180	500	50	30.8	53.2	7.1	1.5	1.5	2.5	2.5	0.1	0.6
210	500	50	21.5	59.8	7.8	1.9	1.8	2.4	2.4	0.1	1.9
240	500	50	17.0	63.7	8.3	2.0	2.0	2.5	2.5	0.2	1.4
300	500	60	6.4	71.4	9.0	2.5	2.5	3.1	3.1	0.2	1.7
360	500	60	3.3	73.3	8.7	2.9	2.9	3.5	3.2	0.2	2.0
420	500	60	2.1	73.8	8.3	3.2	3.2	3.6	3.3	0.2	2.3

A″non = anthraquinone; 1-NA = 1-nitroanthraquinone; 1,6-DNA = 1,6-dinitroanthraquinone.

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-, 2,7-dinitroanthraquinone, 2.3% of others.

From analyses of products it can be concluded that 100% production contains 73.8% 1-nitroanthraquinone and 26.2% by-product, and pure 1-nitroanthraquinone may be obtained by treating the crude product of direct nitrations with dimethylformamide or *N*-methylpyrrolidinone in the presence of triethylamine or pyridine [2]; sodium sulphite in an aqueous solution of pyridine or dioxane [7,8]; dilute nitric acid and sulpholane or 1,2-dichloroethane [9] in 1,2-dichloroethane, having added sodium hydroxide, magnesium oxide, or sodium nitrite, and distilling the azeotropic water–dichloroethane [10]; and by adding a ketone or ester such as diethyl ketone, cyclohexanone, or diethylmalonate [11].

As indicated above, purification of crude nitroanthraquinones need material and long time, in addition 26.2% dinitroanthraquinones after purification are discarded and the method is not economical.

Consequently stage of nitration is stopped in 40–45% progressive reaction, and at the end of the preparation of 1-amino-4-bromo-2-anthraquinonesulphonic acid, the unreacted anthraquinone is precipitated by dilution and drying, it is recirculated as reclaimed quinine.

In this paper, 1-amino-4-bromo-2-anthraquinonesulphonic acid is obtained by five stages:

Step (1): nitration of anthraquinone, which has the following composition: 55.0% of anthraquinone, 36.6% of 1-nitroanthraquinone, 2.5% of 2-nitroanthraquinone, 1.5% of 1,6-dinitroanthraquinone, 1.5% of 1,7-dinitroanthraquinone, 1.4% of 1,5-dinitroanthraquinone, 1.4% of 1,8-dinitroanthraquinone, 0.1% of 2,6-, 2,7-dinitroanthraquinone, 0.0% of others.

Step (2): the crude nitroanthraquinones are converted into crude aminoanthraquinones by reduction with sodium sulphide.

Step (3): the crude aminoanthraquinones are first treated with oleum at temperature ranging from 90 to 150 °C, optionally in the presence of an alkali metal sulphate and the product is then treated with bromine.

Step (4): clarification in an acid medium, for example at pH 3, or an alkaline clarification, or at pH 9, has proven suitable for separating off the water-insoluble anthraquinone, and the recovery of some unreacted anthraquinone is returned to Step (1).

Step (5): the bromamine acid can be precipitated out of the filtrate of the clarification in the form of its alkali metal salt by salting out, for example with sodium chloride and/or potassium chloride or sodium sulphate and/or potassium sulphate.

Formation of bromamine acid directly from anthraquinone is indicated in Scheme 1.

2. Experimental

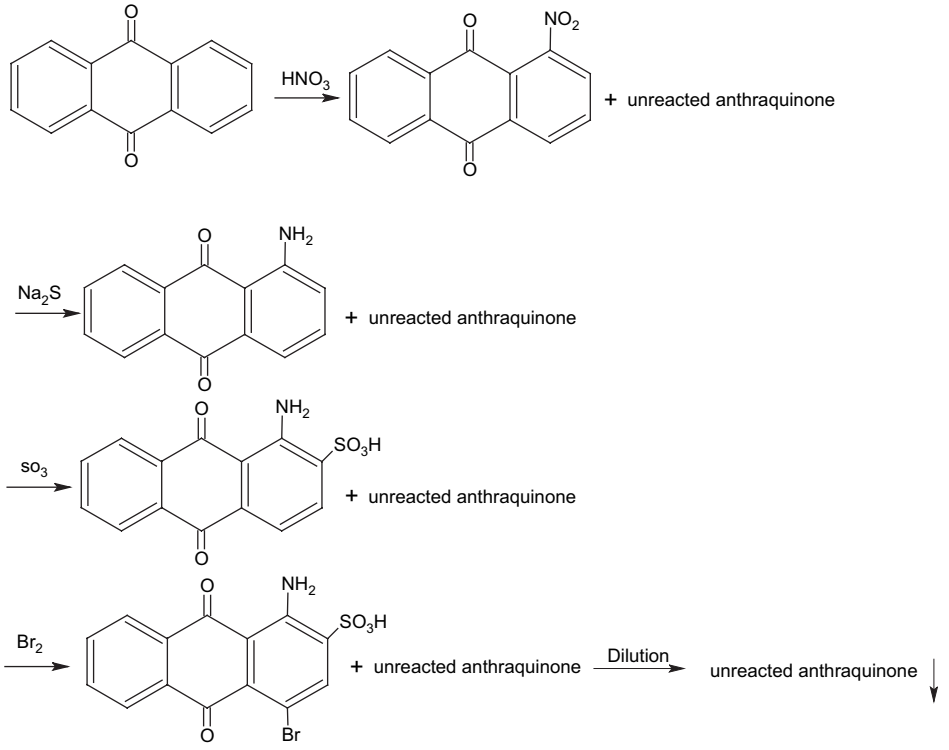
2.1. Apparatus

Melting points were determined by using a Gallenkamp heated block apparatus. All the anthraquinone intermediates synthesized were purified where necessary by column chromatography on Silica gel C.T. (Reeve A) and eluted with toluene. Analytical thin-layer chromatography (TLC) was done on 0.25-mm plates of $Kisselgel_{60}$ PF 244 + 365 (benzene/ethyl formate/formic acid, 75/24/1) for anthraquinone intermediates, and on 0.25-mm plates of Silica gel G or cellulose layer (*n*-butyl acetate–pyridine–water, 40/40/20) for acid dyes. Microanalyses were performed by Butterworth Microanalytical Consultancy, Teddington, Middlesex. ^{1}H NMR were recorded on a Bruker Avance DRX at 500 MHz. The progress of nitration was followed by high pressure chromatography.

2.2. Procedure

2.2.1. Preparation of crude nitroanthraquinones

A 250 ml flask is equipped with a dropping funnel and thermometer. The flask is charged with 80 g of 100% sulphuric



Scheme 1.

acid followed by 15 g *o*-benzoylbenzoic acid. The temperature is raised to 135 °C where it is held for 1/2 h. The mixture is cooled to 30–35 °C with 11 g of water being carefully added. Then 7.4 g of mixed acid (33% nitric acid, 67% sulphuric acid) is added from dropping funnel at a rate so as to maintain the temperature at 30–35 °C. The charge is then heated for 3 h at 65–70 °C and the reaction mass is blown into 150 ml of cold water subsequently stirred at 60 °C for 1/2 h and filtered and the residue is washed with hot water until neutral and dried in vacuo at 120 °C. Crude nitroanthraquinones (13.56 g) of the following composition are obtained: 7.46 g of anthraquinone; 4.96 g of 1-nitroanthraquinone; 0.34 g of 2-nitroanthraquinone; 0.2 g of 1,6-dinitroanthraquinone; 0.2 g of 1,7-dinitroanthraquinone; 0.19 g of 1,5-dinitroanthraquinone; 0.19 g of 1,8-dinitroanthraquinone; 0.014 g of 2,6-, 2,7-dinitroanthraquinone.

2.2.2. Preparation of crude aminoanthraquinone

A 250 ml three-necked flask is equipped with a stirrer, and a thermometer. The flask is charged with 60 ml of water and 24 g of $Na_2S \cdot 9H_2O$. The mixture is heated to 90–95 °C, 10 g of finely crude nitroanthraquinones (content 36.6% 1-nitroanthraquinone) is then stirred at the same temperature for a course of 15 min and finally stirred at 90–95 °C for 10 min. The reaction mixture is filtered and the residue is washed with hot water until neutral and dried at 60 °C. Crude aminoanthraquinone (9.37 g) of the following composition are obtained: 5.40 g of anthraquinone; 3.16 g of 1-aminoanthraquinone = 98% by theory; 0.21 g of 2-aminoanthraquinone; 0.12 g of 1,6-diaminoanthraquinone; 0.12 g of 1,7-diaminoanthraquinone; 0.11 g of 1,5-diaminoanthraquinone; 0.11 g of 1,8-diaminoanthraquinone; 0.011 g of 2,6-, 2,7-diaminoanthraquinone.

2.2.3. Preparation of bromamine acid

A 100 ml three-necked flask is equipped with a stirrer and thermometer and a dropping funnel. The flask is charged with 10 g of crude aminoanthraquinone (content: 36.6% 1-aminoanthraquinone) and 7 ml of oleum (20% strength) and 3.5 g of anhydrous Na_2SO_4. The temperature thereby raises to 130 °C. The mixture is kept at this temperature until less than 3% of 1-aminoanthraquinone can be detected in a sample which is removed (about 15 min). The mixture is the cooled to room temperature, 0.2 g of finely powdered iodine is added, 5 ml of bromine solution in glacial acetic acid (1 ml Br_2, 4 ml HoAC) is added dropwise from dropping funnel at room temperature in the course of 10 min, the mixture is warmed to 80 °C in the course of 10 min and kept at this temperature until only traces of 1-amino-4-bromo-2-anthraquinonesulphonic acid can be detected in sample which is removed (about 1–2 h are required), excess bromine is now stripped off in vacuo, reaction mixture which remained is stirred in 200 ml of water. Twenty-five grams of Na_2SO_4 is added in portions to the solution and the mixture is stirred at room temperature for 1 h. The precipitate is filtered off and washed with 10% strength Na_2SO_4 solution

until almost neutral. The precipitate contains anthraquinone and bromamine acid.

2.2.4. Clarification for separating off the unreacted anthraquinone

In order to separate off the non-sulphonated anthraquinone and aminoanthraquinone constituents, the material on the filter obtained from Section 2.2.3 is stirred in 70 ml of water at 95 °C, 0.5 g of active charcoal is added, the pH is adjusted to 9–10 by adding sodium carbonate and the mixture is filtered at 90 °C. The precipitate contains 5.30 g of anthraquinone which is returned to the stage of nitration. The Na salt of the bromamine acid is salted out of the clarified filtrate with 2 g of Na_2SO_4, the mixture is stirred in cold for 10 h and the product is filtered off, washed with 1% Na_2SO_4 solution and dried.

Bromamine acid of 6.65 g is obtained giving the following analyses:

1-Amino-4-bromo-2-anthraquinonesulphonic acid (6.11 g); 0.07 g 1-amino-2-anthraquinonesulphonic acid; 0.46 g of water. The yield is accordingly 95% by theory.

References

[1] Hohmann Walter, Wunderlich Klaus. Process for the mononitration of anthraquinone. U.S.Pat. 4203885; May 20, 1980.
[2] Hartwig G, Ackermann O, Eilingsfeld H. Manufacture of 1-nitroanthraquinone. U.S.Pat. 376622; October 16, 1973.
[3] Yamada Eiji, Yamada Mutuo. Process for preparing dinitroanthraquinone. U.S.Pat. 4076734; February 28, 1978.
[4] Thiem Karl-Werner, Auge Wolfgang. Process for the preparation of 1-nitroanthraquinone. U.S.Pat. 3959317; May 25, 1976.
[5] Istvan Szekely, Basel, Switzerland. Process for the nitration of anthraquinone. U.S.Pat. 3968130; July 6, 1976.
[6] Yamada Eiji, Takatsuki, Fukasawa Akira. Production of 1-nitroanthraquinone and 1-aminoanthraquinone. U.S.Pat. 4054454; August 30, 1977.
[7] Fukazaw K, Kawamura S, Yamada E. Purification of 1-nitroanthraquinone. Jpn.Pat. 74, 126729; Dec 4, 1974.
[8] Linhart Karl, Leverkusen, Reinold. Process for preparing 1-nitroanthraquinone. U.S.Pat. 3960903; June 1, 1976.
[9] Toth Istvan, Bottmingen, Switzerland. Purification of 1-nitroanthraquinone. U.S.Pat. 4012426; Mar 15, 1977.
[10] Toth I. Purification of 1-nitroanthraquinone. Ger.Pat. 2304233; August 16, 1973.
[11] Galinowski S. Process for the purification of 1-nitroanthraquinone. Fr.Pat. 1846803; June 30, 1967.