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A new method for the preparation of 1-amino-2,4-dibromoanthra-9,10-quinone

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Abstract

1-Amino-2,4-dibromoanthra-9,10-quinone is an important intermediate in the preparation of anthra-9,10-quinone dyes, manufacture of which has been patented. Various methods of brominating aminoanthraquinone have been studied extensively by our research group. It is to be noted that all the procedures involving the bromination of the aminoanthraquinone have been presented to give mixture of isomers and purification of isomers is more difficult, and doesn't readily lend itself to economic separation. This paper presents a new procedure for brominating 1-aminoanthra-9,10-quinone to produce 1-amino-2,4-dibromoanthra-9,10-quinone in high yield and purity.

Keywords: Anthraquinone dyes; Bromination of aminoanthraquinone; Purification of aminobromoanthraquinones

1. Introduction

The halogenations of aminoanthraquinone are more difficult, when α-aminoanthraquinone is halogenated in glacial acetic acid, the first halogen enters at the *ortho* position; further halogenations lead to 1-amino-2,4-dihaloanthra-9,10-quinone [1]. The α-alkylaminoanthraquinones, however, differ from primary derivatives in that the *para* position is attacked first [2]. This paper deals with the process of economically brominating 1-aminoanthra-9,10-quinone to produce 1-amino-2,4-dibromoanthra-9,10-quinone in high yields and purity.

Brominating methods of 1-aminoanthra-9,10-quinone are patented. Several such methods have been extensively studied by our research group. For example 1-aminoanthra-9,10-quinone is brominated in 20% sulfuric acid at 70–80 °C [3]. In the other method, bromination is carried out in 70–95% sulfuric acid at elevated temperature to obtain 1-amino-2,4-dibromoanthra-9,10-quinone with or without catalyst [4].

Further more to Ref. [5] 1-amino-2,4-dibromoanthra-9,10-quinone may be obtainable by bromination of 1-aminoanthra-9,10-quinone in a suspension of chloroform.

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 (toluene/ethylacetate/glacial acetic acid, 8:2:1). Microanalyses were performed by Butterworth Microanalytical Consultancy, Teddington, Middlesex. ^{1}H NMR spectra were recorded on a Bruker Avance DRX at 500 MHz.

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2.2. Procedure

Procedures for the preparation of 1-amino-2,4-dibromoanthra-9,10-quinone are as follows (Fig. 1).

2.2.1. Method A

A 250-ml flask equipped with a Begasungsruhrer stirrer, a reflux condenser, a dropping funnel, and a thermometer is used. The flask is charged with 40 ml of methanol, 10 ml chlorobenzene with 6 g 1-aminoanthra-9,10-quinone. A solution of 3 ml of bromine in 1 ml of methanol is added drop by drop to the flask at 35 °C. The mixture is heated to 60 °C for 5 h and held at this temperature for 19 h. The reaction mixture is poured into 250 ml bisulfite solution, to destroy the excess bromine. The mixture precipitates as a red colored solid which is collected on a large Büchner funnel. After thorough washing with 250 ml of water, the filtrate is dried in an oven at 70 °C for 12 h. Purification of the products with column chromatography yields two products.

Product **II**: 1-amino-2-bromoanthra-9,10-quinone; m.p.: 172 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.40 (s, 2H, NH_2), 7.21 (d, 1H, CH), 7.42 (d, 1H, CH), 7.67 (m, 2H, 2CH), 8.17 (m, 2H, 2CH).

Product **III**: 1-amino-2,4-dibromoanthra-9,10-quinone; m.p.: 223 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.56 (s, 2H, NH_2), 7.77 (m, 2H, 2CH), 8.07 (s, 1H, CH), 8.23 (m, 2H, 2CH).

2.2.2. Method B

A 250-ml flask equipped with a Begasungsruhrer stirrer, a reflux condenser, dropping funnel, and a thermometer is used. The flask is charged with 50 ml of 90% sulfuric acid and 15 g of 1-aminoanthra-9, 10-quinone is added to flask at 30 °C. Bromine (7.5 ml) is introduced drop by drop from a dropping funnel and the mixture is heated to 50 °C for 4 h and then heated to 80 °C, after stirring for 2 h at 80 °C. The reaction mixture is cooled to 50 °C and additional 1.5 ml bromine is introduced from a dropping funnel.

After stirring for 2 h at 50 °C, the reaction mixture is heated to 100 °C for 16 h. The reaction mixture is poured into 250 ml bisulfite solution, to destroy the excess bromine. The mixture precipitates as a red colored solid which is collected on a large Büchner funnel. After thorough washing with 250 ml of water, the filtrate is dried in an oven at 70 °C for 12 h. Purification of the products with column chromatography yields two products.

Product **II**: 1-amino-2-bromoanthra-9,10-quinone; m.p.: 172 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.40 (s, 2H, NH_2), 7.21 (d, 1H, CH), 7.42 (d, 1H, CH), 7.67 (m, 2H, 2CH), 8.17 (m, 2H, 2CH).

Product **III**: 1-amino-2,4-dibromoanthra-9,10-quinone; m.p.: 223 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.56 (s, 2H, NH_2), 7.77 (m, 2H, 2CH), 8.07 (s, 1H, CH), 8.23 (m, 2H, 2CH).

2.2.3. Method C

A 250-ml flask equipped with a Begasungsruhrer stirrer, a reflux condenser, a dropping funnel, and a thermometer is used. The flask is charged with 25 ml of 98% sulfuric acid and 10 g of 1-aminoanthra-9, 10-quinone and 0.05 g of iodine are added to flask at 35–45 °C. Five milliliters of bromine is introduced drop by drop from a dropping funnel and the mixture is heated to 60 °C with stirring and held at 60 °C for 5 h. The reaction mixture is then heated to 100 °C, and held at this temperature for 19 h. The reaction mixture is poured into 250 ml bisulfite solution, to destroy the excess bromine. The mixture precipitates as a red

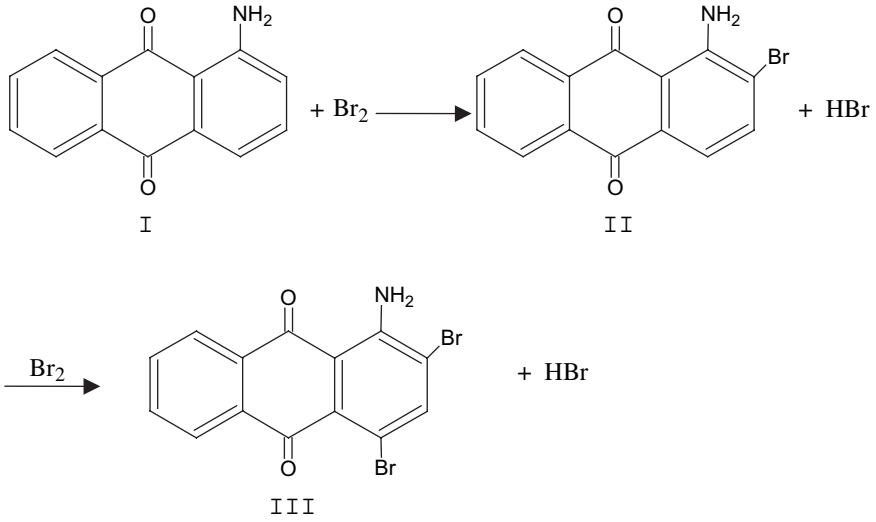

Fig. 1. Preparation of 1-amino-2,4-dibromoanthraquinone.

colored solid which is collected on a large Büchner funnel. After thorough washing with 250 ml of water, the filtrate is dried in an oven at 70 °C for 12 h. Purification of the products with column chromatography yields two product.

Product **II**: 1-amino-2-bromoanthra-9,10-quinone; m.p.: 172 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.40 (s, 2H, NH_2), 7.21 (d, 1H, CH), 7.42 (d, 1H, CH), 7.67 (m, 2H, 2CH), 8.17 (m, 2H, 2CH).

Product **III**: 1-amino-2,4-dibromoanthra-9,10-quinone; m.p.: 223 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.56 (s, 2H, NH_2), 7.77 (m, 2H, 2CH), 8.07 (s, 1H, CH), 8.23 (m, 2H, 2CH).

2.2.4. Method D

A 250-ml flask equipped with a Begasungsruhrer stirrer, a reflux condenser, a dropping funnel, and a thermometer is used. The flask is charged with 15 ml of 98% sulfuric acid and 20 ml of glacial acetic acid and 10 g 1-aminoanthra-9,10-quinone is added to flask at 35–45 °C. Five milliliters of bromine is introduced drop by drop from a dropping funnel and the mixture is heated to 60 °C for 5 h and then heated to 70–75 °C and held at this temperature for 6 h, then heated to 100 °C and held at this temperature for 9 h. The reaction mixture is poured into 250 ml bisulfite solution, to destroy the excess bromine. The mixture precipitates as a red colored solid which is collected on a large Büchner funnel. After thorough washing with 250 ml of water, the filtrate is dried in an oven at 70 °C for 12 h. Purification of the products with column chromatography yields two products.

Product **II**: 1-amino-2-bromoanthra-9,10-quinone; m.p.: 172 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.47 (s, 2H, NH_2), 7.87 (d, 1H), 7.67 (d, 1H), 7.77 (m, 2H), 8.13 (m, 2H).

Product **III**: 1-amino-2,4-dibromoanthra-9,10-quinone; m.p.: 223 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.56 (s, 2H, NH_2), 7.77 (m, 2H, 2CH), 8.07 (s, 1H, CH), 8.23 (m, 2H, 2CH).

2.2.5. Method E

We use a 250-ml flask equipped with a Begasungsruhrer stirrer, a reflux condenser, a dropping funnel, and a thermometer. The flask is charged with 40 ml glacial acetic acid and 10 g 1-aminoanthra-9,10-quinone is added to flask at 35–45 °C. Five milliliters of bromine is introduced drop by drop from a dropping funnel and the mixture is heated to 60 °C for 5 h and then heated to 70–75 °C and held at this temperature for 6 h, then heated to 100 °C and held at this temperature for 9 h. The reaction mixture is poured into 250 ml bisulfite solution, to destroy the excess bromine. The mixture precipitates as a red colored solid which is collected on a large Büchner funnel. After thorough washing with 250 ml of water, the filtrate is dried in an oven at 70 °C for 12 h. Purification of the products with column chromatography doesn't yield two products.

Product **III**: 1-amino-2,4-dibromoanthra-9,10-quinone; m.p.: 223 °C; ^{1}H NMR ($CDCL_3$, 500 MHz): δ 1.56 (s, 2H, NH_2), 7.77 (m, 2H, 2CH), 8.07 (s, 1H, CH), 8.23 (m, 2H, 2CH).

3. Result and discussion

We have found that 1-aminoanthra-9,10-quinone cannot be brominated in 20–98% sulfuric acid, at temperature between 50 and 100 °C, for over 24 h, with or without catalyzer (methods B, C), and with solvents such as methanol and chlorobenzene (method A). Investigations and studies characterized that bromination is accomplished by holding bromine in medium of reaction, for example in method D it is carried out in 98% sulfuric acid: glacial acetic acid, 1:1 at 100 °C for 24 h, to obtain 1-amino-2,4-dibromoanthra-9,10-quinone in high yield. In method E, we changed the solvent from 98% sulfuric acid: glacial acetic acid, 1:1 to glacial acetic acid and bromination is carried out in glacial acetic acid at 100 °C for 2 h, consequently 1-amino-2,4-dibromoanthra-9,10-quinone is produced in high yield and quality. As indicated above, it is an objective of the present paper to provide new and improved process of brominating 1-aminoanthra-9,10-quinone which doesn't produce mixture of isomers and yet at the same time produces a high yield of 1-amino-2,4-dibromoanthra-9,10-quinone of excellent quality and time of reaction becomes as shorter as other reactions indicated in methods A–D (Table 1).

Table 1
Condition for brominating 1-aminoanthra-9,10-quinone

Methods	Solvent	T (°C)	Catalyzer	Time (h)	By-product	1-aminoanthra-9,10-quinone	
						2-Bromo	2,4-Dibromo
A	Methanol–chlorobenzene	60	KI	24	–	+	+
B	90% Sulfuric acid	100	–	24	–	+	+
C	98% Sulfuric acid	100	I_2	24	+	+	+
D	98% Sulfuric:glacial acetic acid 1:1	100	–	24	–	–	+
E	Glacial acetic acid	100	–	2	–	–	+

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