

Condensation and Cellulosic Derivatization of Bromamine Acid.

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ABSTRACT

A reaction pathway was proposed to the synthesis of an anthraquinone dye for cellulose. The Ullmann condensation of sodium 1-amino-4-bromoanthraquinone-2-sulphonate (bromamine acid) with 1, 4- phenylenediamine (PD) gave a blue intermediate product which was subsequently diazotized. This product was coupled with pre-mercerized wood cellulose, ethylcellulose, and cellulose acetate, respectively.

Reaction-progress at each stage was monitored by thin layer chromatography (TLC) and Ultraviolet-Visible spectrophotometry analyses. Fourier-Transform infrared (FT-IR) spectroscopic analysis was used in the partial characterization of the derivatized compound. The proton-NMR spectroscopic analysis carried out on the ethyl cellulose derivative supports the proposed structure.

The results may be summarized as follows: 1) The Ullmann condensation reaction is evoked by the application of copper sulphate, 2) No side reaction was observed, 3) The presence of electron releasing substituent, para to the diazotized amine end enhanced the electrophilic substitution reaction, 4) The condensation reaction was possible when the temperature of the reaction medium was maintained between 60 – 65°C, 5) The extent of the mercerization of the cellulose and cellulose derivatives determines the extent of the diazo coupling, and 6) Final product obtained possesses good leveling, milling, shade, light fastness properties, etc. The possible reaction schemes are discussed in this paper. The success of the coupling reaction provides a novel alternative application of vat dyes to textile materials.

(Keywords: Fourier transform infrared, Ullmann condensation, bromamine acid, chemisorption)

INTRODUCTION

Sodium-1-amino-4-bromoanthraquinone-2-sulphonate also called bromamine acid is an important aminoanthraquinone derivative widely used in the dyeing and colouring industries. It is produced by the sulphonation of 1-aminoanthraquinone with subsequent bromination at a controlled temperature (Lee and Klein, 1938). The reaction of bromamine acid with an arylamine has been carried out following the Ullmann synthesis technique (Fanta 1994). The Ullmann condensation reaction is carried out at a controlled temperature in the presence of copper sulphate acting as the catalyst (Reynold and Cleveland, 1955).

A new trend in the pursuit of dyes by manufacturers is to obtain dyes produced by coupling diazo compounds with tanning condensation products (Eital, 1994). The condensed products of Bromamine acid with arylamine are usually applied to wool materials directly.

Naoki, et al. (1994) prepared a highly soluble reactive dye and applied it on cellulose fibers. An Anthraquinone reactive dye (Figure 1) was used with monoethylnaphthalene sulphuric acid formaldehyde condensate sodium salt for dyeing cotton-cellulose. A level deep blue coloration was obtained.

On the other hand, wood cellulose has been dyed with acid dye at initial pH of 5-13 in the presence of a pH sliding agent which gradually hydrolyzed in the acid for controlling the dyeing pace. A dyed veneer with minimum color fluctuation was obtained (Sakamoto and Masakazu 1993)/

Moreover the photoamination of bromamine acid to produce sodium 1, 4-diaminoanthraquinone-2-sulphonate was also reported (Inoue et al., 1971).

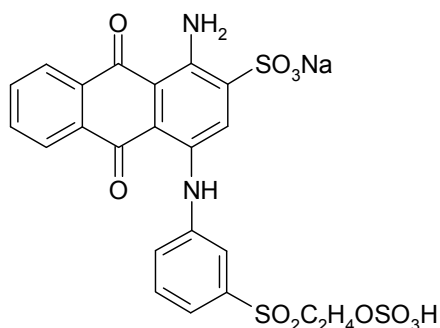


Fig 1

Likewise, cellulose and cellulose derivatives of azo compounds have been reported (Ibrahim, 2002).

It was discovered that exhaust dyeing of cellulose material with reactive dyestuffs in the presence of an alkaline reagent and significant amount of sodium salt improved the quality of absorption on fibers (Trotman, 1970).

The objective of this work was to synthesis a new anthraquinone dye by arylamination of bromamine acid (BA) and coupling it with cellulose derivatives by diazo-coupling. This novel method is expected to give products that are brightly colored viz-a-viz a good milling and leveling, in addition to improved color retention and fastness.

Maha's analytical techniques of preparation of cellulose derivative azo compounds (Ibrahim, 2002) was selected to monitorize the reactions, based on the reported excellent coupling products obtained.

EXPERIMENTAL MATERIALS

The sodium-1-amino-4-bromoanthraquinone-2-sulphonate (BA) was obtained in pure form from "ACROSS" chemical company in Taiwan, and used without further purification. The 1,4-phenylenediamine (PD) was obtained from a natural rock sample in Ghana, and recrystallized using diethyl ether as reported (Adebayo 2006). The sodium hydroxide solution used was prepared from analytical grade sodium hydroxide pellets obtained from a reputable chemical store in Ilorin, Nigeria. The wood cellulose used was obtained by applying the non-destructive wood-free extractive method (Paech and Tracey 1963). The diethyl ether, chloroform, hexane, heptanol,

benzene, hydrochloric acid, ammonia and sodium nitrite were also obtained in Ilorin in analytical grade and used without further purification.

MEASUREMENTS

A Shimadzu recording spectrophotometer, AQUAMATE® V4.60 in the Chemistry Department of the University of Ilorin, Nigeria, was used for the measurements of the visible absorption spectra. The Infrared (IR) spectra were recorded as film on sodium chloride disks using a NICOLET AVATAR® 330FT-IR (Thermal Electron Corporation Spectrum Instrument) available in central research laboratory of LAUTECH University, Ogbomosho, Nigeria, while Proton NMR spectrum was recorded on a mercury 200BB spectrometer (Obafemi Awolowo University, Ile Ife, Nigeria), operating at a basic frequency of 199.966 MHz. Deuterated methanol was used as the solvent.

CONDENSATION REACTION OF BROMAMINE ACID WITH 1,4-PHENYLENEDIAMINE

6.0g (15mMol) of sodium-1-amino-4-bromoanthraquinone-2-sulphonate (BA) was dissolved in 60mL ethanol in a 250mL conical flask. 20mL H₂O was added and stirred well. Thereafter 1.50g (15mMol) 1, 4-phenylenediamine (PD) was added and a pinch of sodium carbonate. The mixture was homogenized and the temperature was raised to 65°C and maintained by the use of an electric thermostat with magnetic stirrer. The addition of copper sulphate catalyst at this temperature hastened the formation of the blue synthesized product.

The blue color product (BAPD), was separated by salting out using a cold saturated solution of sodium chloride and Buckner filtering. The blue product obtained was dried at room temperature to prevent thermal decomposition at higher temperature.

DIAZOTIZATION OF BAPD

The product BA-PD was diazotized at the free amino end of the PD. This was achieved by dissolving 18g (40mMol) of BA-PD in 60ml H₂O and 64ml conc. HCl, in a 250ml conical flask. The mixture was then cooled (0°-3°C) and continuously stirred in a calorimeter packed with

ice block. 16g NaNO_2 dissolved in 80ml H_2O cooled in ice/salt bath was added in portions to the cooled mixture containing BA-PD with the medium temperature constantly kept below 5°C by adding a some grams of ice block to the mixture.

COUPLING

The Wood Cellulose was mercerized in 40% sodium hydroxide solution for about an hour to enhance adequate chemisorption (8). The diazonium salt was added in portions to the mercerized Wood Cellulose (WC) until saturation with the temperature kept below 5°C . The reaction mixture was kept in the refrigerator overnight to allow the coupling to be completed. The product was isolated by filtration and washing with saturated brine solution. It was allowed to dry in a petri dish. The coupling was repeated for ethyl cellulose (EC) and cellulose acetate (CA).

ANALYTICAL TESTS

Solubility tests using diethyether, chloroform, ethanol, ethanol, methanol and water were carried out on the three final products; Bromamine acid-1, 4-phenylenediamine-wood cellulose (BAPDWC), Bromamine acid-1, 4-phenylenediamine ethyl cellulose (BAPDEC) and Bromamine acid-1, 4-phenylenediamine-ethylcellulose acetate (BAPDCA)

CHROMATOGRAPHIC ANALYSIS

The intermediate product BAPD and the three final products were subjected to thin layer chromatography (TLC). The solvent system, propanol/hexane/ammonia ratio 4:2:1 was used.

RESULTS AND DISCUSSION

The intermediate and the final products were subjected to UV/Visible and infrared spectroscopic analyses.

BAPD: The blue intermediate BAPD ($R_f=0.55$) in Scheme 1 below, showed absorption intensity at 589 nm (λ_{max}) and 624 nm (λ_{max}) with 0.548 and 0.610 intensities respectively in the UV/Visible spectrum (Figure 2).

A red shift was observed when compared with the UV spectrum of BA which has absorption at 489nm (λ_{max}) with an intensity of 0.77. The shift to a longer wavelength confirms that BA was successfully condensed with PD and the conjugation has actually increased as expected.

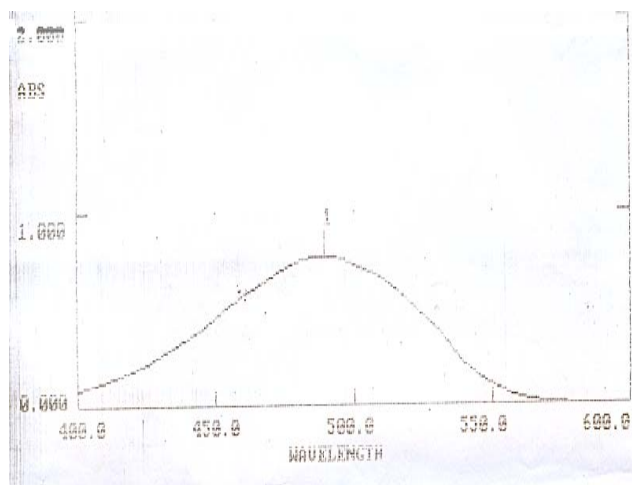


Figure 2: UV Spectrum of BA.

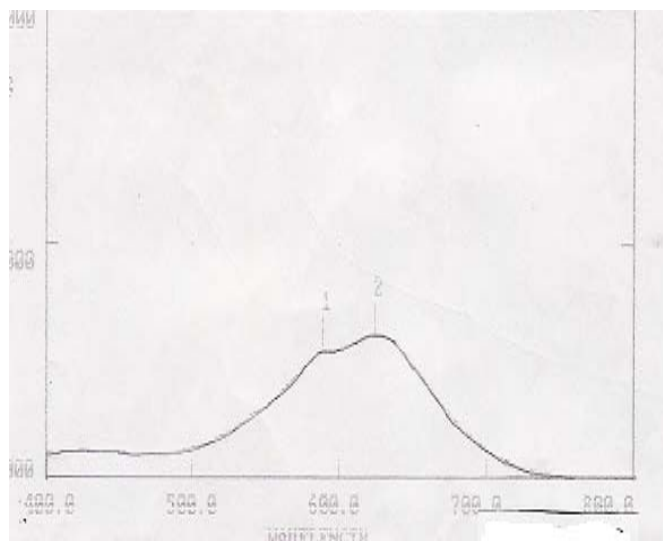
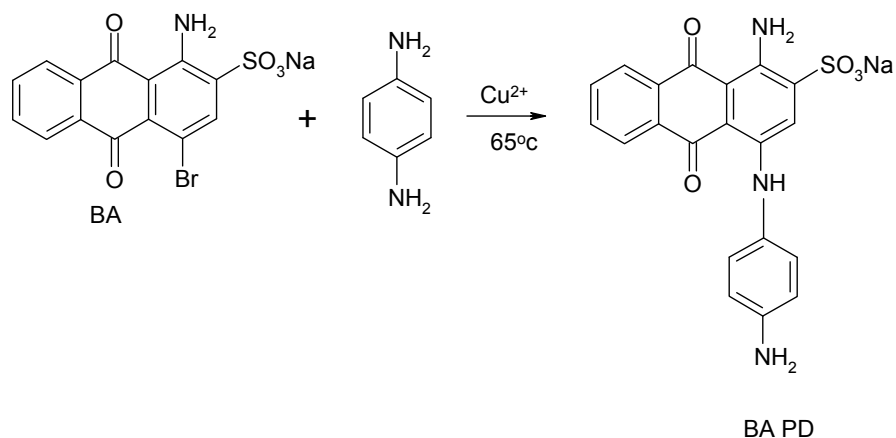
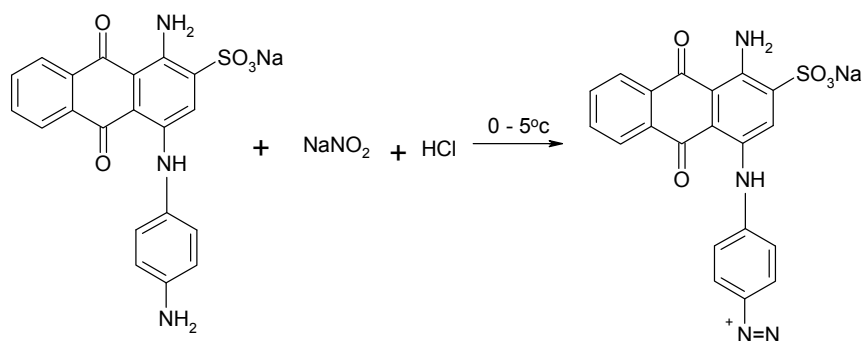


Figure 3: UV Spectrum of BAPD.

The IR spectrum of the blue product (BAPD) and the TLC chromatogram also supported this suggestion.



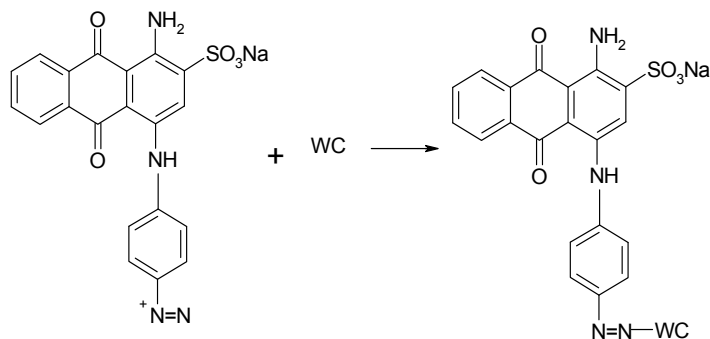
Diazotization of the precursor followed the equation below; (scheme 2).



The dark brown BAPDWC ($R_f = 0.60$) was insoluble in acetone, methanol and water. The deep blue BAPDEC ($R_f = 0.70$) is soluble in methanol, acetone and sparingly soluble in diethylether, while the black BAPDCA ($R_f = 0.65$) is insoluble in acetone, methanol and water. The products are not decomposable at 300°C .

1.010, (fig. 4). Hypsochromic shift was observed compared to that of the precursor BAPD. The reason for the hypsochromic shift is not fully comprehended. A similar observation was made in the synthesis of new dyes obtained by coupling 3-amino-carbazole with isomers of chloroanthraquinone using Buchwald –type reaction (Ashok, 2006).

BAPDWC: BAPDWC (Scheme 3) showed UV absorption maximum at 455nm with the intensity



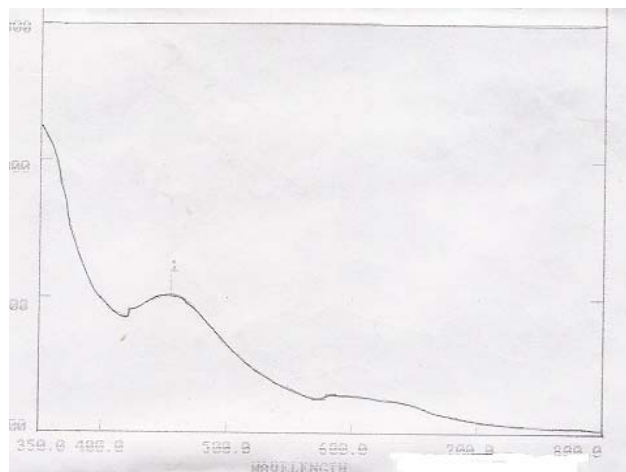


Figure 4: UV Spectrum of BAPDWC.

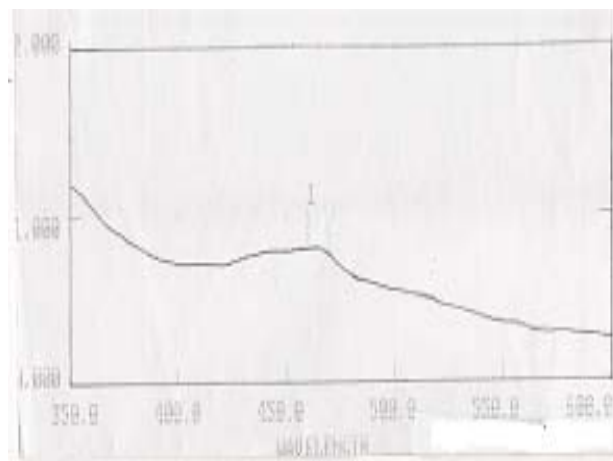


Figure 6: UV Spectrum of BAPDCA.

The IR spectrum of BAPDWC (Figure 5) registered -NH stretching vibration band of both the primary and secondary amine at 3859 and 3755 cm^{-1} . The -OH absorption band at 3441 cm^{-1} was very prominent due to numerous number of -OH group present in the cellulose portion. The peaks at 1154-1044 cm^{-1} are attributed to the ether linkage of the cellulose. A similar ether linkage was reported by Ibrahim 2002. Other peaks in the spectrum occurred at 2923, 2853, 2724, 1939, 1460, 1376, 722 cm^{-1} .

The IR spectrum (Figure 7) uniquely exhibited a peak at 1738 cm^{-1} representing the vibrational stretching of the carbonyl functional group in the cellulose acetate derivative. The stretching at 1154 cm^{-1} is attributed to the ether linkage of the cellulose. 1557 cm^{-1} is attributed to the azo dye functionality. Oftentimes, azo group stretching appears very weak or not IR active as reported by Ejila et al 2004. Other observable peaks include 3418, 2923, 2853, 1633, 1589, 1460, 1376, 972, 722, 625 cm^{-1} .

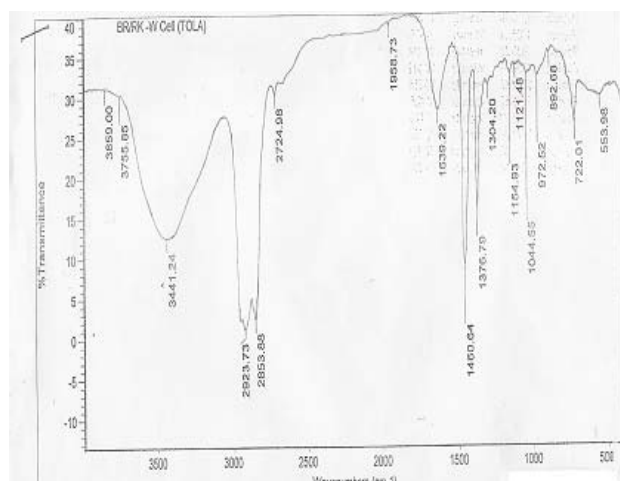


Figure 5: FTIR Spectrum of BAPDWC.

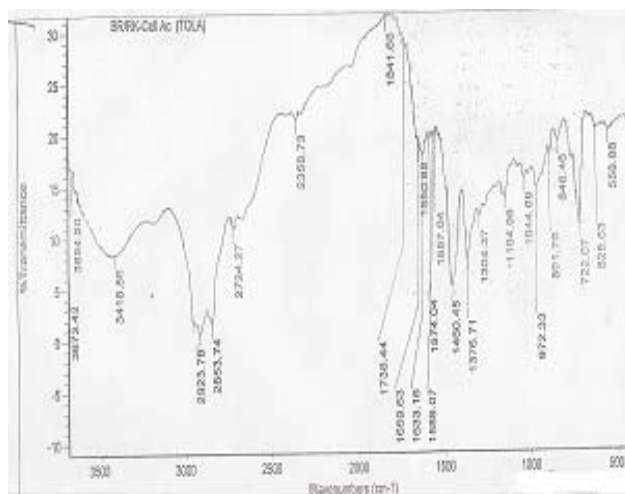


Figure 7: FTIR Spectrum of BAPDCA.

BAPDCA: BAPDCA showed only a flat peak at 460 nm (0.814) in UV-spectrum (Figure 6). Hypsochromic shift was observed due to the reason stated for BAPDWC above.

BAPDEC: The UV spectrum of BAPDEC (Figure 8) shows peaks at 483 nm (0.162) and between 389-500 nm. (William et al 1980) reported that peaks at 400-500nm region are not of much significance. In the IR spectrum (Figure 9), the -

OH band was registered at 3427cm^{-1} . The ether linkage of the ethyl cellulose is assumed to have its absorption at 1040 cm^{-1} .



Figure 8: UV Spectrum of BAPDEC.

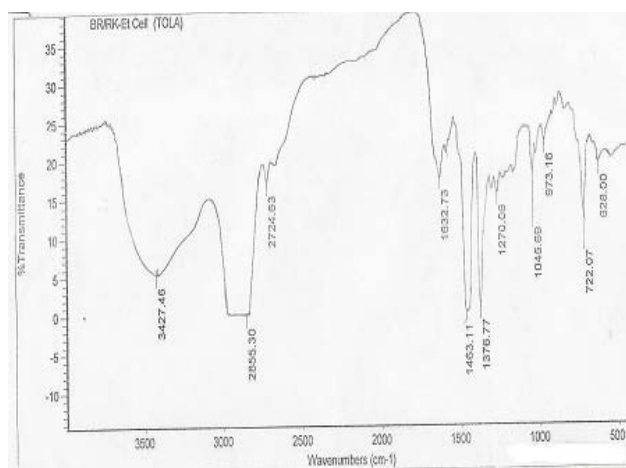


Figure 9: FTIR Spectrum of BAPDEC.

Proton NMR spectrum of BAPDEC (Figure 10) shows prominent signals at 5.0, 4.8, 4.1, 3.3, and 3.0 ppm. The aromatic proton of the anthraquinone segment appeared at 8.3 ppm, while the aromatic proton of "PD" portion was observed at 7.8 ppm. The aromatic proton integral ratio was understandably lower compared to that of the ethyl cellulose to which BAPD was coupled.

CONCLUSION

The results presented in this paper are evidences of the possibility of producing in situ cotton (cellulose) dyes from bromamine acid, an anthraquinone derivative.

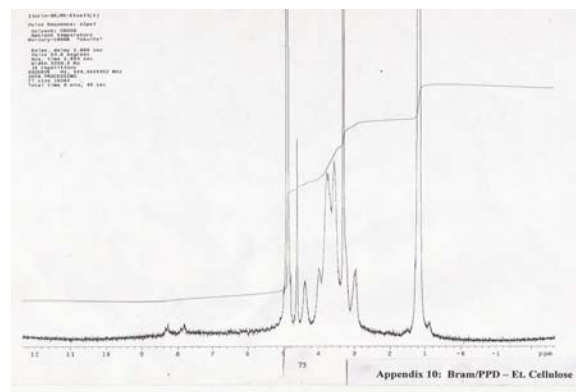


Figure 10: NMR spectrum of BAPDEC.

The method prescribed a good technique for coloring cellulosic materials to obtain a good hue. The authenticity of the first intermediate product (BAPD) was affirmed by TLC, physical properties, UV/Vis, and IR spectral data. The three products obtained have good hue amidst other valuable properties. The ^1H NMR spectroscopic study of BAPDEC derivative shows that the compound was not diazotized at the free amino group on the anthraquinone as no by-product was formed (or formed insignificantly), as also evident from the TLC. This novel method is expected to enhance the production cellulosic material that have improved color retention and fastness.

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