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A Novel Synthesis of Anthraquinone[1,2-*b*]pyrroles and Their Conversion to 1-Amino-2-benzoylanthraquinone Derivatives†

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SUMMARY

Reaction of 1-aminoanthraquinone derivatives with benzyl cyanide under alkaline conditions has been shown to lead to the formation of 2-amino-3-phenylanthraquinone [1,2-b]pyrrole derivatives in moderate to good yields. Oxidation of these fused anthraquinone derivatives has been utilised to evolve a new synthetic approach to 1-amino-2-benzoyl-anthraquinones which are useful disperse dye structures.

1. INTRODUCTION

The nucleophilic substitution of 1-amino-2,4-dibromoanthraquinone with amines at the 4-position has been frequently employed to obtain commercially important dyes. It was therefore expected that 1-amino-2,4-dibromoanthraquinone would react with benzyl cyanide under alkaline conditions to yield an intermediate (**I**) which would cyclise to yield the furanthrone (**II**) (Scheme 1). However, contrary to our expectations the reaction took an entirely different course and gave rise to the anthraquinone[1,2-*b*]pyrrole derivative (**III**). The structures of these derivatives were confirmed by elemental analysis, i.r. spectra and mass spectra. The condensed anthraquinone structure was also evidenced by

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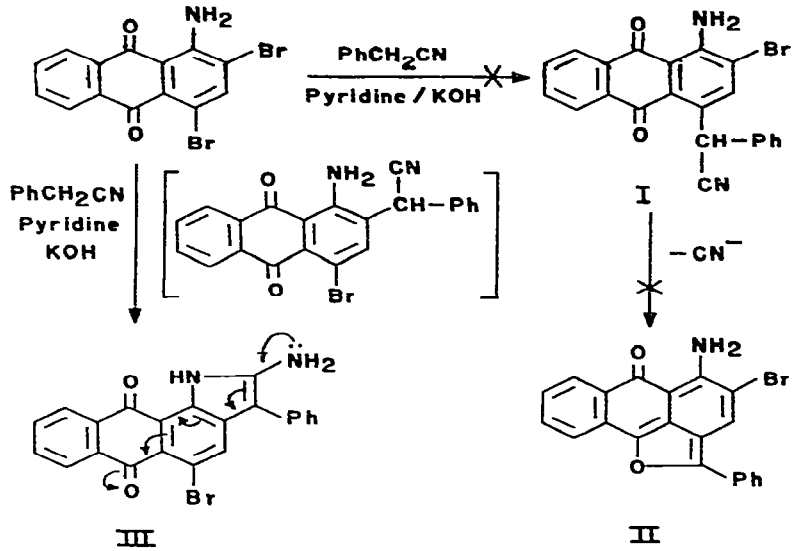


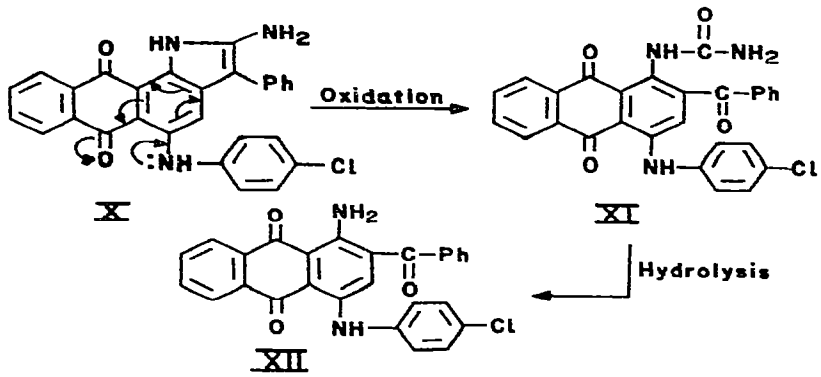
Scheme 1

the deep violet colour of the product which definitely ruled out the furanthrone structure and also the acyclic structures (**I**). Obviously, under the reaction conditions the cyclisation of the 1-amino group on the nitrile function occurs readily to yield the fused heterocyclic system. The deep colour of the anthraquinone[1,2-*b*]pyrrole system is due to the presence of the amino group in the pyrrole ring and this is established by the hypsochromic shift in concentrated hydrochloric acid (bluish violet to brownish red). Further, benzoylation of the amino compound also gave a product which is brownish in colour.

When the reaction was carried out on 1-amino-2-bromo-anthraquinone, the anthraquinonepyrrole (**IV**) was obtained much purer and in high yields, showing that the presence of a bromine atom at the 4-position leads to side reactions and therefore to lower yields.

It is curious to note that although there is an extensive literature on anthraquinones fused with a wide variety of heterocycles, the literature on compounds containing an anthraquinone ring with a fused pyrrole ring is very scanty. In view of the ease of the synthesis of anthraquinonepyrroles by the present method and in view of the deep colour of the product obtained, we were interested in studying this reaction in greater detail.

Accordingly, 1-amino-2-bromoanthraquinones with various substituents at the 4-position were similarly reacted with benzyl cyanide and the products obtained characterised. Rather surprisingly all the



Scheme 2

compounds proved to be different shades of violet, thus showing that the auxochromic substitutent at the 5-position of the condensed anthraquinonepyrrole system had only a minor influence on the colour. This unexpected behaviour may be explained on the basis that the colour of the 5-anilino derivatives (**IX** and **X**) is due to the supply of electrons from the anilino nitrogen atom to the adjacent keto group (Scheme 2), thereby decreasing the effective interaction of the keto group with the amino group at the 2-position. This argument is substantiated by the observation that the benzoylation of the *p*-chloro anilino derivative (**X**) effects only a small hypsochromic shift (27 nm) as compared with the large shift (89 nm) produced by the benzoylation of (**IV**). However, when a benzamido group is present in the 7-position of anthraquinonepyrrole system **V**, the colour changes to a green.

The yields of the products were found to be fairly high except in the case of the mercapto derivatives **VI** and **VII**. The reaction was particularly efficient in the case of 1-amino-4-nitroanthraquinone, which gave good yields of a pure product even in the absence of a 2-bromo substituent. This is in contrast to the poor yields obtained in the reactions of 1-aminoanthraquinone and 1-amino-5-benzamidoanthraquinone which gave very low yields of highly impure products.

Obviously the electron-withdrawing effect of the nitro group is responsible for the high reactivity of 1-amino-4-nitroanthraquinone.

The absorption characteristics of the different products are given in Table 1. The compounds were applied on polyester fibre as disperse dyes. It will be noted that the shades obtained were tinctorially weak and the lightfastness was also poor.

TABLE 1

Anthraquinonepyrrole				*Benzoyl derivative*				
No.	*Colour*	λ_{max} (*nm*)	*log E*	*No.*	*Colour*	λ_{max} (*nm*)	*log E*	*M.p.* (°C)
IV	Bluish violet	574	3·91	XIII	Brownish	485	3·66	275–7
III	Violet	562	3·97	—				
IX	Bright violet	563	4·15	—				
X	Bright violet	564·5	4·25	XIV	Reddish violet	537	4·07	360
VI	Dull violet	575	3·94	—				
VII	Dull violet	561	4·02	—				
VIII	Violet	571	3·94	—				
V	Dull green	603	4·05	—				

1.1. Synthesis of 1-amino-2-benzoylanthraquinone derivatives

It was expected that the anthraquinone[1,2-*b*]pyrroles would undergo oxidative cleavage of the pyrrole ring in a manner similar to indole derivatives. Such an oxidation would yield a product (**XI**) which could be easily converted to 1-amino-2-benzoylanthraquinone derivatives (**XII**).

The oxidation of the anthraquinone[1,2-*b*]pyrrole was carried out using a variety of oxidising agents and different reaction conditions. The best results were obtained when chromium trioxide in acetic acid was used. The oxidation gave rise to a yellow product which, however, could not be obtained in pure form. Hydrolysis of the crude oxidation product yielded the 1-amino-2-benzoylanthraquinone derivative contaminated with other impurities which were difficult to remove. It could only be purified by chromatography. The structures of 1-amino-2-benzoylanthraquinone derivatives were established by melting point and elemental analysis. Further confirmation was obtained in the case of the 1-amino-2-benzoyl-4-(*p*-chloroanilino)anthraquinone (**XII**) by mass spectrum (M^+/e peaks at 452 and 454).

2. EXPERIMENTAL PROCEDURE

Commercially available 1-aminoanthraquinone, 1-amino-2,4-dibromoanthraquinone and 1-amino-5-benzamidoanthraquinone were used for

the reactions. The other starting materials, such as 1-amino-2-bromo anthraquinone,[1] 1-amino-4-bromoanthraquinone,[2,3] 1-amino-4-nitro-anthraquinone,[4,5] 1-benzoylamino-2-bromoanthraquinone[6] and 1-amino-5-benzoylamino-2-bromoanthraquinone,[7] were prepared by the known methods with slight modifications for better yields.

Various 1-amino-4-substituted-2-bromoanthraquinones were prepared by the following general procedure developed in our laboratory by Sunthankar and co-workers.[8]

To a cooled solution (15–20 °C) of aluminium chloride (5M) in nitrobenzene (8 ml per g of the anthraquinone derivative) was added under stirring 1-amino-2,4-dibromoanthraquinone (1M). After 15 min the required nucleophile (6M) was added in portions during 30 min, keeping the temperature below 35 °C. The mixture was stirred at room temperature for 4–5 h and then poured into ice cold water containing a little hydrochloric acid. The nitrobenzene was removed by steam distillation and the product that separated was filtered, washed well and dried. These compounds were crystallised from chlorobenzene in 90–95 % yield.

All the i.r. spectra were recorded on a Perkin-Elmer 397 spectrophotometer. The u.v. spectra were recorded on a Hitachi-200 spectrophotometer or a Beckmann DK-2 ratio recording spectrophotometer. Room temperature wherever mentioned corresponds to 30 °C and all melting points are uncorrected.

2.1. General method of preparation of various 2-amino-3-phenyl anthraquinone[1,2-*b*]pyrroles

To a mixture of powdered potassium hydroxide (3M) and pyridine (8 ml per g of aminoanthraquinone) benzyl cyanide (1·2M or 1·7M; see Table 2) was added under stirring. The mixture was stirred for 20 min at room temperature and then the respective aminoanthraquinone (1M) was added with stirring. The mixture was stirred at 60 °C for 4–6 h (see Table 2) and then poured into ice-cold dilute acetic acid (10 ml per ml of pyridine); the thick precipitate of the product was filtered, washed well and dried. The reaction conditions and other details are listed in Table 2. The structures of these 2-amino-3-phenylanthraquinone[1,2-*b*]pyrroles were confirmed by elemental analysis and mass spectra.

TABLE 2

Anthraquinone derivative	*Benzyl cyanide concn* (M)	*Temp.* (°C)	*Time* (h)	*Mol. formula of product*[a]	*No.*	*M.p.* (°C)	*Yield* (%)
1-Amino-2-bromo	1·7	60	6	$C_{22}H_{14}N_2O_2$	IV	310–12[b]	89
1-Amino	1·2	60	6	$C_{22}H_{14}N_2O_2$	IV	310–12[c]	10
1-Amino-2,4-dibromo	1·7	60	4	$C_{22}H_{13}BrN_2O_2$	III	279[c]	57
1-Amino-4-anilino-2-bromo	1·2	60	4	$C_{28}H_{19}N_3O_2$	IX	290[b]	92
1-Amino-2-bromo-4-(*p*-chloroanilino)	1·2	60	4	$C_{28}H_{18}ClN_3O_2$	X	297[b]	92
1-Amino-2-bromo-4-(2-mercaptobenzothiazolyl)	1·2	45	6	$C_{29}H_{17}N_3O_2S_2$	VI	321–3[c]	58
1-Amino-2-bromo-4-thiophenoxy	1·2	50	4	$C_{28}H_{18}N_2O_2S$	VII	308[c]	60
1-Amino-4-nitro	1·2	30	6	$C_{22}H_{13}N_3O_4$	VIII	315[b]	85
1-Amino-5-benzoylamino-2-bromo	1·2	60	6	$C_{29}H_{19}N_3O_3$	V	301[b]	80
1-Amino-5-benzoylamino	1·2	60	6	$C_{29}H_{19}N_3O_3$	V	301–2[c]	12

[a] All compounds showed correct elemental analysis.
[b] Crystallised from chlorobenzene.
[c] Purified by column chromatography on neutral alumina by dissolving the compound in *o*-dichlorobenzene and elution with a mixture of benzene and ethyl acetate (7·5:1 by vol.).

2.2. General procedure for the synthesis of 1-amino-2-benzoylanthraquinones

(a) *Oxidation.* The 2-amino-3-phenylanthraquinone[1,2-*b*]pyrrole derivatives (0·01M) were suspended in aqueous acetic acid (1:1 by vol., 35 ml) and cooled to 0–5 °C. Chromium trioxide (0·04M) was added in portions under stirring, keeping the temperature between 0 and 5 °C. The reaction mixture was stirred at room temperature for 6 h during which the colour changed from violet to brownish yellow. The reaction mass was diluted to 80 ml with water and heated at 85–90 °C for 1 h. On cooling it was further diluted to 100 ml and filtered to obtain yellow intermediate (Scheme 2).

(b) *Hydrolysis.* The wet cake from (a) was refluxed in 5% NaOH

(30 ml) for 2 h. The resulting red-coloured mixture was then poured into excess of ice-cold aqueous acetic acid and filtered to get a red product which was treated with 20 % H_2SO_4 at 50 ° for 30 min and cooled. The red compound **XII** (Scheme 2) so obtained was filtered, washed well and dried. Various 1-amino-2-benzoylanthraquinone derivatives so obtained are listed in Table 3. They were purified by column chromatography using neutral alumina. Their structures were confirmed by elemental analysis and mass spectrum of one typical example from the series.

TABLE 3

Anthraquinone-[1,2-b]pyrrole	*Oxidation product*			*1-Amino-2-benzoyl-anthraquinone derivative*	
	No.	*Yield (%)*	*M.p. (°C)*	λ_{max} *(nm)*	*log E*
IV	**XV**	53	189	495	4·240
V	**XVI**	21	260–1	512	4·182
VIII	**XVII**	20	270	492	4·150
IX	**XVIII**	21	172–4	640	4·275
X	**XI**	24	192	642	4·336

(c) *Synthesis of 1,5-diamino-2-benzoylanthraquinone* (**XX**). In sulphuric acid (6 ml, 90 %), **XVI** (1 g) was stirred at 60 °C for 1–1·5 h. On cooling, it was poured into ice with stirring to get the red compound (**XX**), which was filtered, washed well, dried and purified by column chromatography; m.p. 297–9 °C.

2.3. Benzoylation of 2-amino-3-phenylanthraquinone[1,2-*b*]pyrrole derivatives

The anthraquinonepyrrole derivatives **IV** and **X** were refluxed in chlorobenzene with equimolar amounts of benzoyl chloride for 1 h, cooled, filtered and washed first with chlorobenzene and then with petroleum ether to get a benzoyl derivative which was brown in the case of **IV**, but a reddish violet in the case of **X**. These were crystallised from chlorobenzene almost quantitatively. The spectral data of these compounds are given in Table 2.

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