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Short Communication

Nucleophilic Substitution Reactions of Azabenzanthrone Derivatives†

SUMMARY

Reaction of 1-cyano-2-substituted amino-3-azabenzanthrone with p-chloroaniline in the presence of potassium hydroxide in dimethyl sulphoxide gave a mixture of the 4- and 6-p-chloroanilino derivatives. Replacement of the cyano group by the hydroxyl group was observed when the reaction was carried out in the absence of the aromatic amine. Reaction of a 3,9-diazaperylene derivative with p-chloroaniline gave rise to a monoanilino derivative.

1. INTRODUCTION

In a recent communication[1] the arylamination of 3-bromo- and 3-nitro-benzanthrones in dimethyl sulphoxide in the presence of potassium hydroxide (DMSO/KOH) has been described. The present paper deals with the nucleophilic reaction of 3-azabenzanthrones with arylamines under similar conditions.

2. RESULTS

Reaction of 1-cyano-2-morpholino-3-azabenzanthrone (**Ia**) with *p*-chloroaniline (PCA) in DMSO/KOH gave rise to two products which were separated and identified as the 4- and 6-substituted compounds (**IIa** and **IIIa**). The structures were established by the difference in the

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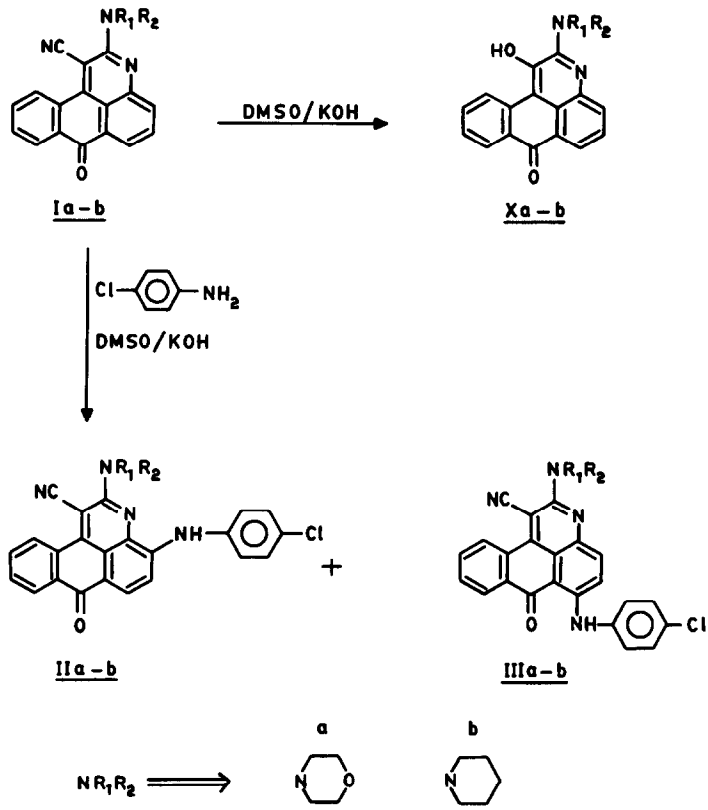
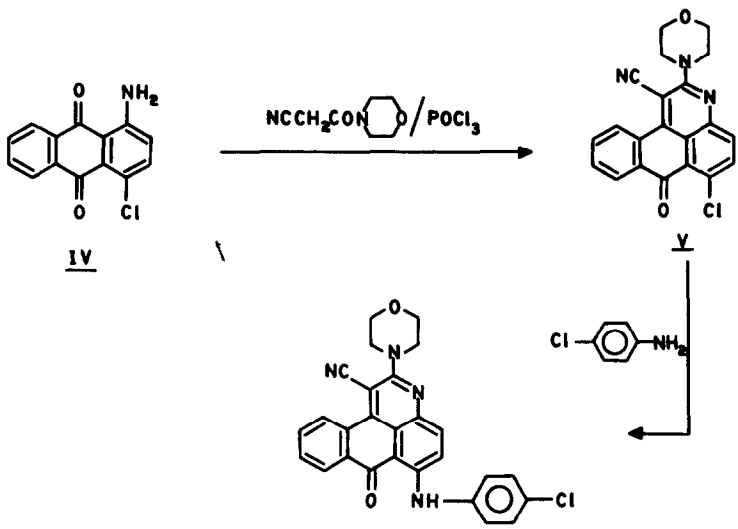


bathochromic shift in alkaline medium (130 nm for 4-substituted and 70 nm for 6-substituted compound). The structure of the 6-substituted product was also confirmed by its synthesis from 1-amino-4-chloro-anthraquinone (**IV**) cyanoacetyl morpholide and $POCl_3$ and subjecting the product **V** to nucleophilic displacement. Similarly, reaction of 1-cyano-2-piperidino-3-azabenzanthrone (**Ib**) with PCA in DMSO/KOH also gave a mixture of 4- and 6-substituted 3-azabenzanthrones (**IIb** and **IIIb**).

In a similar fashion, 8-benzamido-1-cyano-2-morpholino-3-azabenz-anthrone (**VIa**) was reacted with PCA in DMSO/KOH and again two products (**VIIa** and **VIIIa**) could be isolated. The structures were established on the basis of the greater polarity of the 4-substituted derivative (**VIIa**) as indicated during the chromatographic separation. This was similar to the behaviour of **IIa** as compared with **IIIa**. The distinction between the two structures on the basis of the shift in λ_{max}



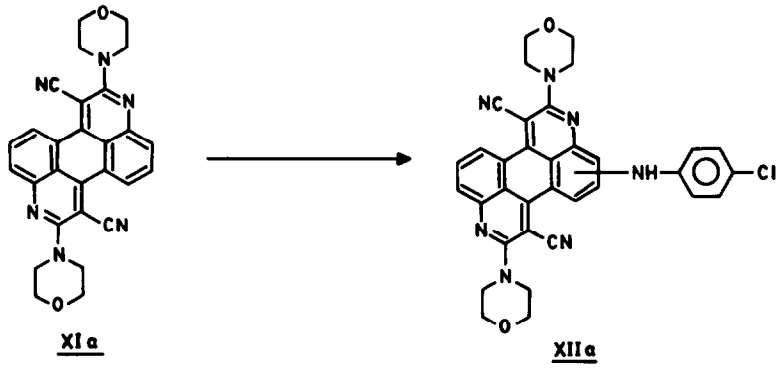
under alkaline conditions was not clearcut since the compound **VIIa** had twin peaks at 515 and 570 nm. On the other hand, the 6-benzamido derivative (**IXa**) did not undergo any reaction under these conditions. This can be attributed to the greater acidity of the N—H function of the 6-benzamido group as compared with the 8-benzamido group. This results in the ionisation of the 6-benzamido function and delocalisation of the anionic charge with the carbonyl function of the 3-azabenzanthrone which renders the nucleus inert to the nucleophilic attack.

Reaction of 1-cyano-2-morpholino-3-azabenzanthrone (**Ia**) with KOH in DMSO without any added nucleophile led to the displacement of the cyano group. This was indicated by the formation of the phenolic product which analysed for the structure (**Xa**) and showed the molecular ion peak M^+ at m/z 332.

Similar reaction of 1-cyano-2-piperidino-3-azabenzanthrone in DMSO/KOH gave the phenolic product (**Xb**) with displacement of the cyano group.

Finally, reaction of 1,7-dicyano-2,8-dimorpholino-3,9-diazaperylene (**XIa**) with PCA in DMSO/KOH gave a violet product which was found to be the mono-substituted product (**XIIa**) as indicated by elemental analysis. The position of substitution was not determined.

Some of the compounds described in this paper were applied to polyester but they did not possess good dyeing and fastness properties.



XIa XIIa

3. EXPERIMENTAL PROCEDURE

All melting points are uncorrected. The visible spectra were recorded on a Beckmann DK-2A spectrophotometer. The mass spectra were recorded on a Varian CH-7 instrument.

The various 1-cyano-2-substituted amino-3-azabenzanthrones were prepared by the reported procedure.[2]

3.1. General procedure for the arylamination of 3-azabenzanthrones

A mixture of powdered KOH (2·0 g) and PCA (0·015 mol) in DMSO (15 ml) was stirred for 15 min. The 3-azabenzanthrone derivative (0·003 mol) was added to this and the mixture stirred at room temperature overnight. The reaction mixture was poured into ice-cold water, acidified with conc. HCl and the product which separated was filtered. The solid was washed with Na_2CO_3 solution, then water, and dried. The yield, m.p., method of purification, molecular formula and absorption data of the various aminated products are given in Table 1.

3.2. Preparation of 1-hydroxy-2-substituted amino-3-azabenzanthrones (Xa and Xb)

The 1-cyano-2-substituted amino-3-azabenzanthrone (**Ia,b**) (1 g) was added to powdered KOH (2 g) in DMSO (15 ml) with stirring and the reaction mixture stirred overnight. The mixture was poured into ice-cold water, acidified with HCl (1:1) and the product which separated was

TABLE 1
Physical Data of the Various Arylamino-3-Azabenzanthrone Derivatives

Compound	*Substituent*	*Yield* (%)	*M.p.* (°C)	*Purification*[a] *eluent*	*Mol.*[b] *formula*	λ_{max} (*nm*) (*in DMF*)	*log E*	λ_{max} (*nm*) (*in DMF 2% aq.* NaOH)	*Shift in* λ_{max} (*nm*)
1-Chloro-2-morpholino									
IIa	4-(*p*-chloroanilino)	35	270	C_6H_6–EtOAc (95:5)	$C_{27}H_{19}ClN_4O_2$	536	3·93	666	130
IIIa	6-(*p*-chloroanilino)	32	250	C_6H_6		536	3·97	612	76
VIIa	8-benzamido-4-(*p*-chloroanilino)	33	266	C_6H_6–EtOAc	$C_{34}H_{24}ClN_5O_2$	570 515	4·11	625	
VIIIa	8-benzamido-6-(*p*-chloroanilino)	28	249	C_6H_6		590	4·06	650	60
XIIa	X-(*p*-chloroanilino) diazaperylene	62	300	C_6H_6–EtOAc (9:1)	$C_{34}H_{26}ClN_7O_2$	595	4·36	—	—
1-Cyano-2-piperidino									
IIb	4-(*p*-chloroanilino)	28	249	C_6H_6	$C_{34}H_{24}ClN_5O_2$	545	4·10	615	70
IIIb	6-(*p*-chloroanilino)	33	266	C_6H_6–EtOAc (95:5)		540	4·15	670	130

[a] Chromatographed over neutral alumina using chlorobenzene (minimum) as solvent.
[b] Satisfactory elemental analysis data were obtained.

chromatographed over neutral alumina using chlorobenzene as solvent and eluting with benzene–ethyl acetate (1:1). 1-Hydroxy-2-morpholino-3-azabenzanthrone (**Xa**) was obtained in 54% yield, m.p. 232–234°C (EtOAc). (Found: C, 71·9; H, 5·0; N, 8·2; $C_{20}H_{16}N_2O_3$ requires C, 72·3; H, 4·8; N, 8·4%.) 1-Hydroxy-2-piperidino-3-azabenzanthrone (**Xb**) was obtained in 48% yield, m.p. 201–202°C. (Found: N, 8·3; $C_{21}H_{18}N_2O_2$ requires N, 8·5%.)

3.3. Synthesis of 6-(*p*-chloroanilino)-1-cyano-2-morpholino-3-azabenzanthrone (IIIa)

A mixture of 6-chloro-1-cyano-2-morpholino-3-azabenzanthrone (**IIIa**)[3] (0·0015 mol) [obtained by the Vilsmeier reaction on 1-amino-4-chloroanthraquinone using cyanoacetylmorpholine and $POCl_3$ m.p. 258°C (EtOAc)], PCA (0·0018 mol) and anhydrous NaOAc (0·5 g) was refluxed in ethanediol (10 ml) for 30 min. The product, obtained in 68% yield on adding the reaction mixture to water, was crystallised from benzene, m.p. 251–252°C. It was found to be identical (m.p., TLC and IR) to the product obtained from the first fraction obtained during the chromatographic separation of the amination product of **Ia**.

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D. R. Tatke and S. Seshadri†
Dyes Research Laboratory,
Department of Chemical Technology,
University of Bombay,
Bombay 400 019, India

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† To whom all correspondence should be addressed.