Dyes and Pigments 5 (1984) 431–436

Nucleophilic Substitution Reactions on 3-Bromo- and 3-Nitrobenzanthrones

T. Vaidyanathan and S. Seshadri†

Dyes Research Laboratory, University Department of Chemical Technology,
Matunga, Bombay 400019, India

(Received: 26 July, 1983)

SUMMARY

Nucleophilic substitution reactions of 3-bromobenzanthrone and 3-nitrobenzanthrone have been studied. Reaction of 3-bromobenzanthrone with different arylamines gave rise to 6-arylamino-3-bromobenzanthrones. Anomalous behaviour was observed with 2-aminobenzothiazole, when the bromine atom underwent displacement, and with thiourea, when 3-mercaptobenzanthrone was obtained. Reactions of 3-nitrobenzanthrone, on the other hand, gave rise to 4-substituted amino derivatives.

The nucleophilic substitution reactions of benzanthrone and its derivatives in dimethyl sulphoxide containing potassium hydroxide (DMSO/KOH) have been reported.[1–4] The present paper presents some of our findings with 3-bromo and 3-nitro-benzanthrones.

1. REACTIONS OF 3-BROMOBENZANTHRONE

The reactions of 3-bromobenzanthrone (I) with various nucleophiles such as aniline, 2-aminopyridine, 2-aminobenzothiazole, guanidine nitrate and thiourea in DMSO/KOH were studied (Schemes 1 and 2). The reaction of 3-bromobenzanthrone with aniline in DMSO/KOH gave a

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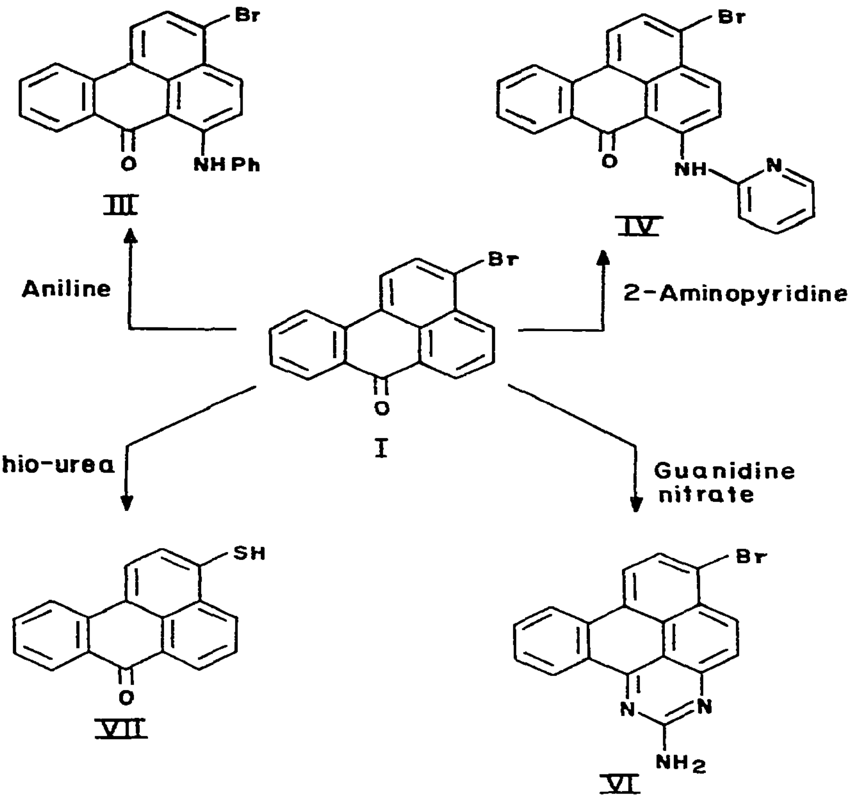
† To whom correspondence should be addressed.

Dyes and Pigments 0143-7208/84/$03·00

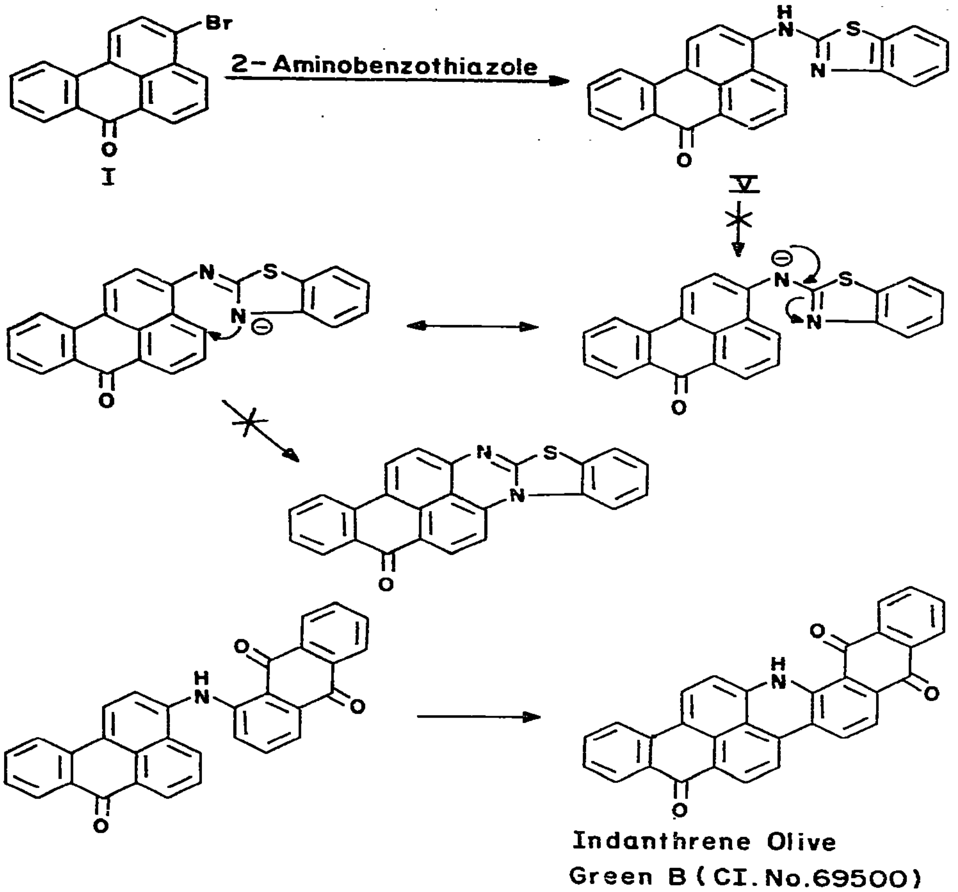


Scheme 1

product which was found to be 6-anilino-3-bromobenzanthrone (**III**). The product was characterised by elemental analysis, mass spectrum (*m/e* at 399 and 401) and the orientation was established by the very slight colour change with alkali (a shift of only 45 nm on addition of alkali). It is known that 4-aminobenzanthrones give a strong colour change in alkaline medium when compared with 6-aminobenzanthrones.[5]

A similar reaction occurred when 3-bromobenzanthrone was reacted with 2-aminopyridine. The product obtained was again the 6-substituted derivative (**IV**), characterised by elemental analysis and mass spectrum (*m/e* at 400 and 402).

Rather surprisingly, the reaction of 2-aminobenzothiazole with 3-bromobenzanthrone proceeded by nucleophilic attack at the 3-position with elimination of halogen to yield **V**. Elemental analysis and mass



Scheme 2

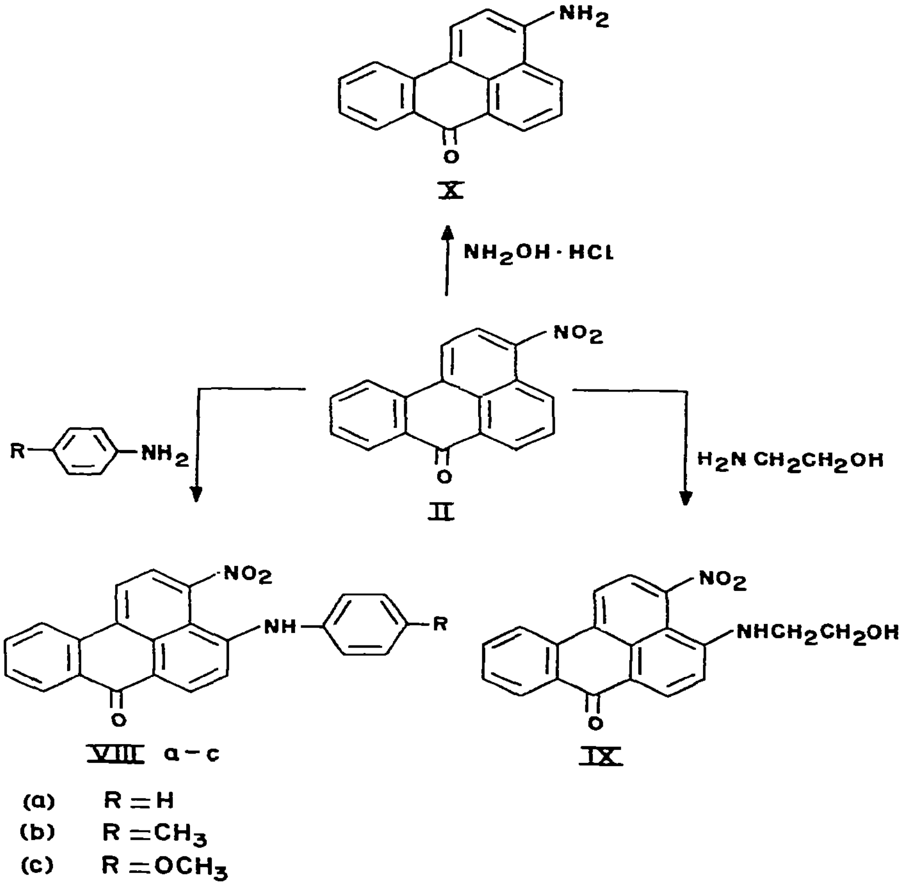
spectrum clearly established the nature of the reaction. This anomalous behaviour with 2-aminobenzothiazole is difficult to explain.

It was anticipated that the 3-(2-aminobenzothiazolyl) benzanthrone would undergo cyclisation in isobutanolic potassium hydroxide to yield a 3,4-fused heterocyclic derivative of benzanthrone in a manner similar to the formation of the vat dye Indanthrene Olive Green B. However, the attempted cyclisation did not occur and the starting material was recovered under various reaction conditions (Scheme 2).

Reaction of guanidine nitrate with 3-bromobenzanthrone in DMSO/KOH gave a product which analysed for VI and was further characterised by the mass spectrum (*m/e* at 347 and 349). Presumably, the initial reaction product obtained by attack at the 6-position underwent spontaneous cyclisation under the reaction conditions.

Reaction of thiourea with 3-bromobenzanthrone in DMSO/KOH led to the formation of 3-mercaptobenzanthrone (VII), characterised by its elemental analysis (C, H and S values and absence of Br).

Thus, the reaction of 3-bromobenzanthrone with different nucleophiles depends on the nature of the nucleophile but no satisfactory explanation can be offered for the different types of reaction with different nucleophiles.



Scheme 3

2. REACTIONS OF 3-NITROBENZANTHRONE

In view of the fact that 3-bromobenzanthrone showed such behaviour with different nucleophiles, it was of interest to study the nucleophilic reactions of 3-nitrobenzanthrone (Scheme 3). Reaction of 3-nitrobenzanthrone with aniline in DMSO/KOH gave rise to 4-anilino-3-nitrobenzanthrone (**VIIIa**) as shown by its elemental analysis; the orientation was confirmed by the strong colour change in alkaline medium (as expected of a 4-amino derivative[5]). Similar aminated products were obtained by reaction with *p*-toluidine, *p*-anisidine and ethanolamine. However, reaction of 3-nitrobenzanthrone with hydroxylamine hydrochloride led to the reduction of the nitro group and gave rise to 3-aminobenzanthrone (**X**) (which was found to be identical with a sample prepared as described elsewhere[16]).

3-Nitro-4-substituted anilinobenzanthrone derivatives were evaluated as disperse dyes on polyester but were found to have low tinctorial power and poor lightfastness.

3. EXPERIMENTAL PROCEDURE

All melting points are uncorrected. The infra-red spectra were recorded on Perkin-Elmer Model No. 21. The visible spectra were recorded on a Beckmann DK-2A spectrophotometer. Commercially available 3-bromobenzanthrone was crystallised from HOAc. 3-Nitrobenzanthrone was prepared by the reported procedure.[6]

3.1. General procedure for the nucleophilic substitution reaction on 3-bromo- and 3-nitro-benzanthrones

3-Bromobenzanthrone or 3-nitrobenzanthrone (0·0032 mol) was added to a stirred mixture of the nucleophile (0·01 mol) in DMSO (20 ml) containing powdered KOH (4 g). The mixture was stirred for 16 h at room temperature, during which time its colour changed from pale green to red and finally to blue–violet. The reaction mixture was diluted with ice-cold water (250 ml) and was adjusted to pH 4–5 using conc. HCl, when the product which separated was filtered, washed with water and dried. The yield, melting point, method of purification and molecular formula of the products are given in the table.

TABLE 1
Physical Data of the Substituted Products

Compound	*Yield (%)*	*m.p. (°C)*	*Purification*	*Mol. formula*[b]	*λ_{max} in DMF (nm)*	*Shift in DMF contg 2% NaOH (nm)*	*Shift in λ_{max} (nm)*
From 3-bromobenzanthrone							
III	77	172–174	C_6H_6/EtOAc[a] (80:20 by vol.)	$C_{23}H_{14}BrNO$	465	510	45
IV	70	247–249	C_6H_6/EtOAc[a] (80:20 by vol.)	$C_{22}H_{13}BrN_2O$	475	475	—
V	88	210–221	C_6H_6/EtOAc[a] (60:40 by vol.)	$C_{24}H_{14}N_2OS$	—	—	—
VI	85	165–169	EtOAc/EtOH[a] (80:20 by vol.)	$C_{18}H_{10}BrN_3$	—	—	—
VII	90	256–258	DMF (cryst.)	$C_{17}H_{10}OS$	—	—	—
From 3-nitrobenzanthrone							
VIIIa	73	138–140	C_6H_6 (cryst.)	$C_{23}H_{14}N_2O_3$	475	565	90
VIIIb	72	146–148	C_6H_6 (cryst.)	$C_{24}H_{16}N_2O_3$	485	575	90
VIIIc	80	150–151	C_6H_6 (cryst.)	$C_{24}H_{16}N_2O_4$	490	590	100
IX	75	150–152	C_6H_6 (cryst.)	$C_{10}H_{14}N_2O_4$	515	650	135
X	50	238–240	C_6H_6[a]	$C_{17}H_{11}NO$	—	—	—

[a] Chromatographed over neutral alumina using chlorobenzene as solvent (minimum).
[b] Satisfactory analyses obtained.

ACKNOWLEDGEMENTS

The authors thank Dr K. Nagarajan of Ciba Research Centre, Bombay, for the mass spectral data, Mr S. Y. Achrekar for the dye evaluations, and the micro-analytical section for the analyses. One of us (T.V.) is grateful to the U.G.C., New Delhi for the award of a junior research fellowship.

REFERENCES

1. C.F.M., DBP 1,171,441, June 4, 1964.
2. C.F.M., French Patent 1,376,198; British Patent 992,568, Oct. 23, 1964.
3. J. N. Dalal, Ph.D. thesis, University of Bombay, 1967.
4. A. S. Kaji, K. M. Shah and K. H. Shah, *Ind. J. Chem.*, **6**, 613 (1968).
5. W. Bradley, *J. Soc. Dyers Colourists*, **58**, 2 (1942).
6. A. Luttringhaus and H. Neresheimer, *Ann.*, **473**, 285 (1929).