

Synthesis and Characterisation of Azo Disperse Dyes Containing Terminal Aziridinyl Group

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1. Introduction

The introduction of an aziridinyl group into dyes based on 4-aminoazobenzene and related heterocyclic compounds has been the subject of intense research activity for many years.

The ring-opening reaction of the terminal aziridine ring, involved in the dyeing mechanism, leads to substantial bathochromic effects¹. For example, the nitro derivative (Figure 1) undergoes rapid solvolysis², resulting in the ring-opened azonium ion which shows a bathochromic shift of 68.4 nm in acetone.

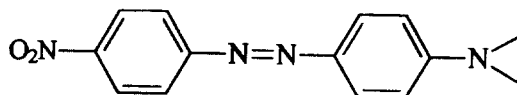


Figure 1

In the case of transfer printing, the conditions used result in fission of the heterocyclic ring and interaction with the adjacent substrate, with the effect that aziridine dyes on polyester and other fabrics display a significant bathochromic shift³. Thus, disperse dyes containing terminal aziridinyl groups are capable of exploitation as reactive dyes⁴. It is apparent that the yield in aziridine ring formation is low when K_2CO_3 was used via 2-arylaminoethanol and hydrogen bromide compared to the use of $NaNH_3$, via methanesulphonyl derivatives and lithium bromide. There is thus the possibility of increasing the yield by removing the bromination step and employing direct cyclisation from methanesulphonyl derivatives to obtain the aziridinyl ring⁵.

¹. S M Burkinshaw and G Hallas, *JSDC.*, **109** (1993) 78.

². G Cerichelli and L. Luchetti, *J. Chem. Soc., Chem. Commun.*, (1985) 339.

³. J Morgan, MSc Thesis, University of Leeds, 1987.

⁴. G Hallas, J F Dawson and S M Burkinshaw, UK Patent GB 2,221,693 B (13 November 1991).

⁵. J H Choi, *The synthesis of novel aziridinyl azo disperse dye*, PhD Thesis, University of Leeds, 1995

2. Synthesis of Azo Disperse Dyes Containing Terminal Aziridinyl Group

The parent amine was first synthesised in 1953 by cyclisation of *N*- β -bromoethylaniline hydrobromide⁶ and the resultant product is extremely sensitive to nucleophilic attack in the presence of acid. Consequently, aziridine ring formation must be the final step of the dye synthesis. Numerous methods have been used for the formation of aziridine rings⁷, those of most relevance to this work are based on the conversion of β -hydroxyethyl aniline into arylaziridine via β -methanesulphonylethylaniline⁸.

The reaction between a primary aromatic amine and 2-chloroethyl chloroformate to give the corresponding 2-chloroethyl carbanilide forms the basis of a convenient method of synthesis of 2-arylaminoethanols. Treatment of the carbanilide with sodium hydroxide produces the 2-hydroxyethyl compound via the *N*-aryl-2-oxazolidone⁹.

Conversion of the 2-hydroxyethyl derivatives into the required 2-bromoethylamines can be achieved by using hydrobromic acid¹⁰; the resulting hydrobromide salts are suitable for use as coupling components.

As mentioned before, cyclisation of methanesulphonyloxyethyl dyes is also suitable to give the desired coupling components. Cyclisation of the bromoethyl dyes to form the corresponding aziridines takes place under basic conditions.

Hydrolysis also occurs to some extent in aqueous media and by-products include 2-hydroxyethyl azo dyes as well as derivatives of *N,N'*-diphenylpiperazine. Hydrolysis can also be expected from methanesulphonyl derivatives¹¹ which are unstable in the presence of water^{12, 13}.

⁶ H W Heine, B J Kapur and C S Mitch, *J. Amer. Chem. Soc.*, **76** (1954) 1173; 2503.

⁷ J A Deyrup, in *The chemistry of heterocyclic compounds*, Ed. A Hassner, Vol. 42, Part 1, Wiley-Interscience, New York (1983) p.1.

⁸ V R Gaertner, *J. Org. Chem.*, **35** (1970) 3952.

⁹ R Adams and J B Segur, *J. Am. Chem. Soc.*, **45** (1923) 785.

¹⁰ W M Pearlman, *J. Amer. Chem. Soc.*, **70** (1948) 871.

¹¹ B Helfrich and P Papalambrou, *Ann.*, **551** (1942) 235.

¹² P W C Barnard and R E Robertson, *Can. J. Chem.*, **39** (1961) 881.

¹³ R K Crossland and K L Servis, *J. Org. Chem.*, **35** (1970) 3195.

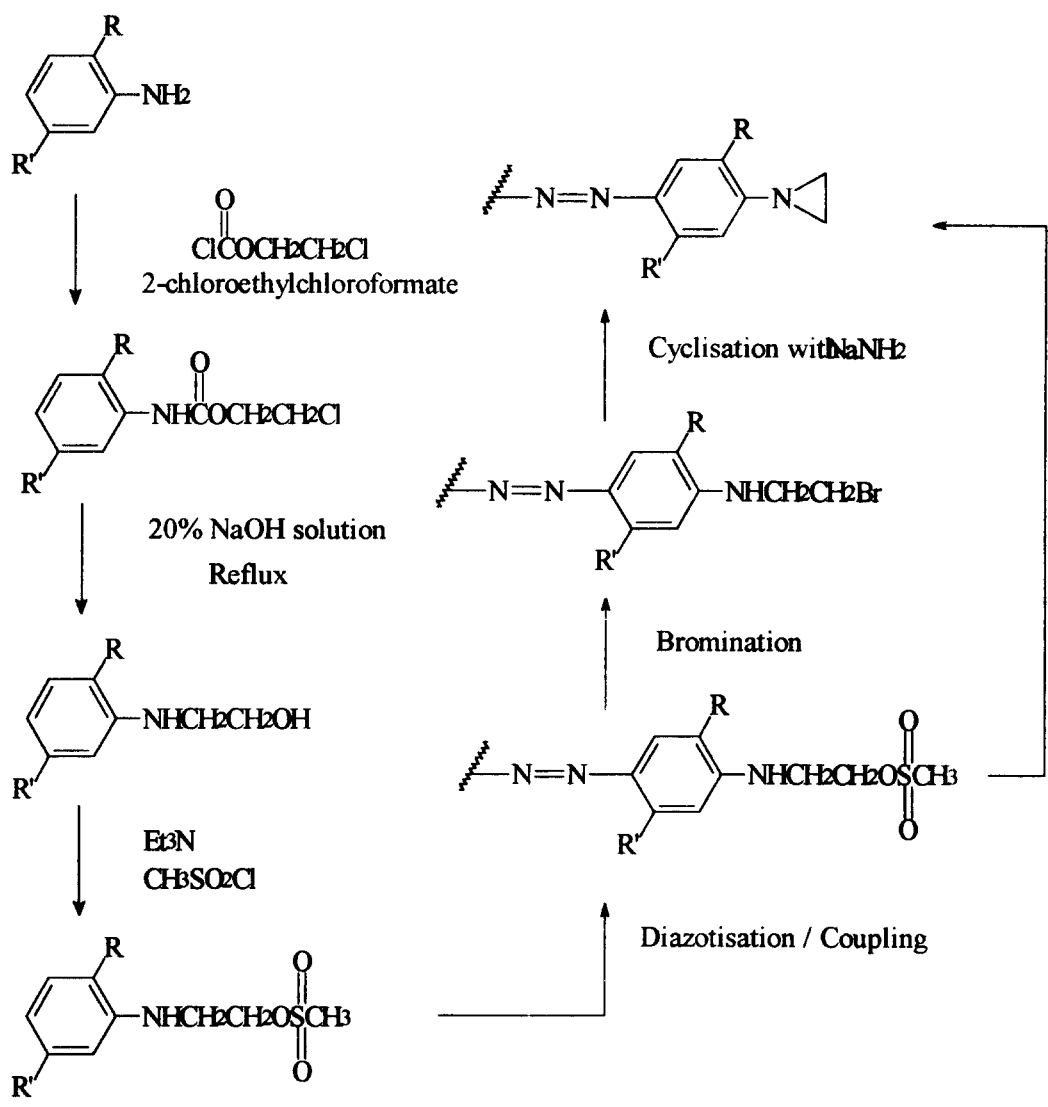
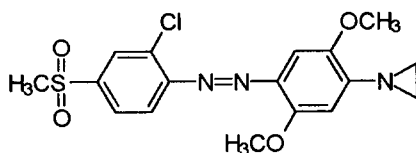


Figure 2 Synthesis of aziridinyl azobenzene dye

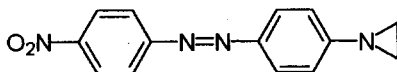
2.1. Aziridinyl azo dyes

Four aziridinyl azo dyes were obtained using procedure shown above as follows

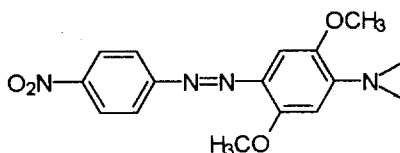
2-chloro-4-methanesulphonylaniline \rightarrow 1-(2,5-dimethoxyphenyl) aziridine (Dye A-1)



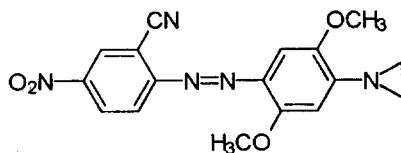
4-nitroaniline → 1-phenylaziridine (Dye C-1)



4-nitroaniline → 1-(2,5-dimethoxyphenyl) aziridine (Dye D-1)



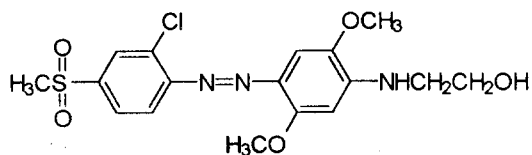
2-cyano-4-nitroaniline → 1-(2,5-dimethoxyphenyl) aziridine (Dye E-1)



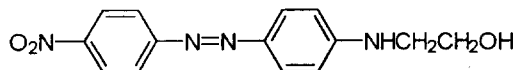
2.2. 2-hydroxyethyl azo disperse dyes

Aziridinyl azo dyes, susceptible to hydrolyse in aqueous dyeing condition, produce *N*, β -hydroxyethylaniline azo dyes during dyeing procedure. Four 2-hydroxyethylaniline azo dyes were produced as a hydrolysed form of the aziridinyl azo dyes

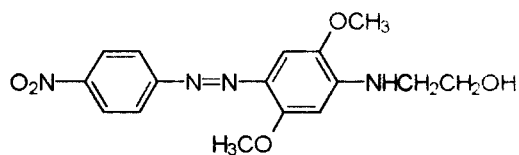
2-chloro-4-methanesulfonylaniline → 2,5-dimethoxy-*N*, β -hydroxyethylaniline (Dye A-2)



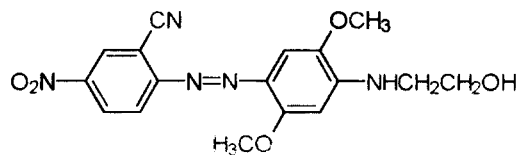
4-nitroaniline → *N*, β -hydroxyethylaniline (Dye C-2)



4-nitroaniline → 2,5 dimethoxy-*N*, β -hydroxyethylaniline (Dye D-2)



2-cyano-4-nitroaniline → 2,5 dimethoxy-*N*- β -hydroxyethylaniline (Dye E-2)



3. Conclusion

- Direct cyclisation to aziridinyl ring from the *N*, β -methanesulphonylester aniline precursor resulted in excellent yields.
- The λ_{\max} of the aziridinyl dye displayed hypsochromic shifts compared with the analogous *N*, β -hydroxyethylaniline azo dyes.
- In the NMR spectrum of aziridinyl dyes, the peak for the aziridinyl ring appeared at δ 2.23 (dye A-1), 2.21 (dye C-1) and 2.22 (dye D-1) as a singlet respectively.
- In the DSC analysis, the smaller exothermic peak for ring opening observed soon after melting.