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Method for Quaternization of Nitrogen-Containing Heterocyclic Azo Dyes

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ABSTRACT

A method is described for the quaternization of nitrogen-containing heterocyclic azo dyes using dimethyl sulphate and arylsulphonic acid methyl esters as alkylation agents in a two-phase liquid medium. The method is distinguished by fully competed quaternization at high reaction rates and moderate reaction temperatures.

1 INTRODUCTION

Various cationic azo dyes (C.T. Basic Blue 41, C.T. Basic Blue 54, C.T. Basic Red 22, etc.) containing heterocyclic diazo components currently find wide application in the dyeing of polyacrylic fibres. They are prepared by diazotization of the heterocyclic amine, coupling and subsequent quaternization of the heterocyclic nitrogen atom with alkylating agents such as dialkyl sulphates, benzene- and toluene-sulphonic acid esters, acrylamides, epoxy compounds and alkyl halides. Dimethyl sulphate, being cheap and readily available, finds wide commercial application.

Our results on the quaternization of nitrogen-containing heterocyclic azo dyes with dimethyl sulphate or methyl benzenesulphonate in a two-phase liquid system are reported in this present study.

2 RESULTS AND DISCUSSION

Two basic methods exist for the quaternization of nitrogen-containing heterocyclic azo dyes, i.e. quaternization in an organic solvent and

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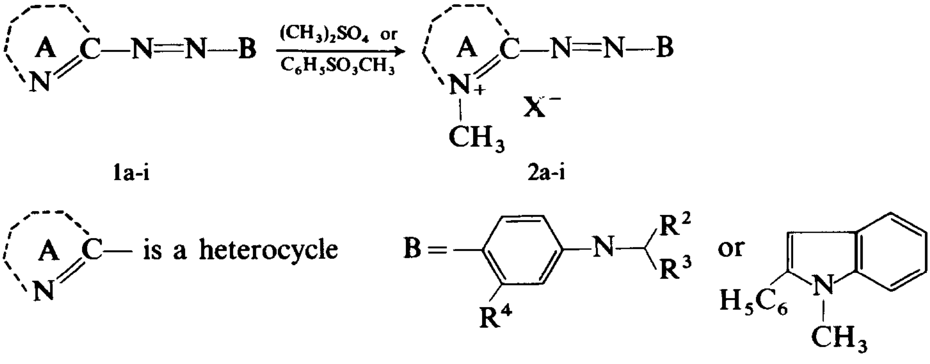


$R^2,R^3 = CH_3; C_2H_5; C_2H_4OH$
$R^4 = H, Cl; X^- = CH_3SO_4^-; C_6H_5SO_3^-$

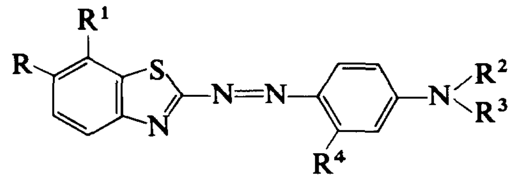
Scheme 1

quaternization in an aqueous medium. Quaternization in inert organic solvents using dialkyl sulphates and arylsulphonic acid alkyl esters was the basic method for the preparation of cationic dyes.[1-3] Later this method was further developed by the use of glacial acetic acid as inert medium.[4] Spiliadis[5] studied this type of quaternization in organic solvents and concluded that it proceeds according to an S_N1 mechanism.

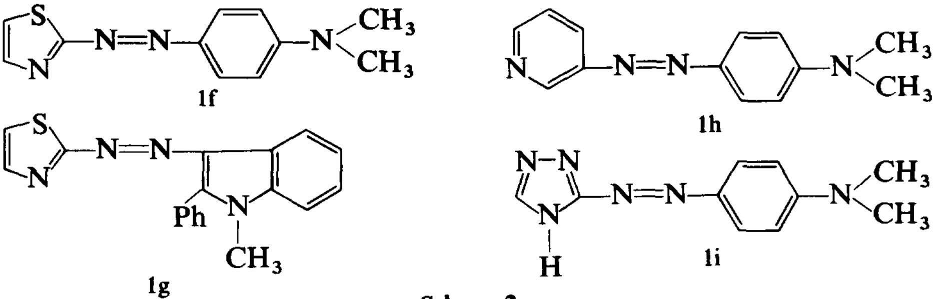
In a patent disclosure[6] a method is proposed for quaternization with dimethyl sulphate in an aqueous suspension in the presence of basic agents. Other workers have studied the same problem[7] using sodium sulphate as a means of preventing the decomposition of the dimethyl sulphate. Balta[8] studied the reaction path in aqueous medium, establishing a mechanism similar to S_N2.

Other methods combining quaternization in an organic solvent and aqueous medium[9] and using dextrin and sodium chloride as an inert medium for the quaternization[10] have been described. According to these methods, the quaternization is continued for several hours. A small amount of unreacted dye is generally present in the reaction mixture, especially in organic solvent medium. At temperatures over 100°C the duration of the reaction is considerably shortened, but these high temperatures cause an abrupt rise in the rates of side reactions and the resulting dyes are of lower purity.

We have found that quaternization in a two-phase system (water–organic solvent) can be carried out below 100°C at a rate considerably higher than those achieved in organic solvent or aqueous media. Furthermore, after completion of the reaction no chromatographically detectable traces of unreacted dye can be observed. A new, rapid and effective method for the quaternization of azo dyes (**1a**–**1i**; Scheme 2) derived from various nitrogen-containing heterocyclic compounds is thus developed.



1a $R = OC_2H_4OH$; $R^1 = H$; $R^2,R^3 = CH_3$; $R^4 = H$
1b $R = OC_2H_4Cl$; $R^1 = H$; $R^2,R^3 = C_2H_5$; $R^4 = Cl$
1c R,R^1 = benzo; $R^2,R^3 = CH_3$; $R^4 = H$
1d $R = CH_3O$; $R^1 = H$; $R^2,R^3 = CH_3$; $R^4 = H$
1e $R = CH_3O$; $R^1 = H$; $R^2 = C_2H_5$; $R^3 = C_2H_4OH$; $R^4 = H$


1f
1g
1h
1i

Scheme 2

Quaternization was carried out in various two-phase systems comprising water and a water-immiscible or partially miscible organic solvent such as dichloroethane, toluene, chlorobenzene, carbon tetrachloride, chloroform, tetrachloroethylene, etc., using dimethyl sulphate, diethyl sulphate or alkylaryl sulphonates as alkylating agents at temperatures within the range 20–100°C.

At the lower temperatures, the reaction rate was comparable with that observed in aqueous medium and the process required a duration of 1–2 h. Increase in the temperature results in the establishment of a temperature value at which the reaction rate increases abruptly and the reaction duration becomes 1–6 min. This temperature value depends on the starting dye and is within the range 55–75°C. The heat liberated by the exothermic reaction at the optimal temperature is enough to keep the reaction mixture boiling.

Preferred quaternizing agents are dimethyl sulphate and alkylaryl sulphonates, since they lead to completion of the reaction with no chromatographically detectable traces of non-quaternized dye in the reaction mixture. The use of diethyl sulphate under these conditions leads to partial quaternization of the starting dye. All above-mentioned two-phase systems are suitable, but the dichloroethane–water system is especially preferred since it offers a number of advantages. The amount of alkylating agent is of special importance, 1·5–4 mol per mol of the starting dye being

TABLE 1

Yields, Melting Points, Reaction Conditions and Elemental Analysis Data for **2a**–**2i**

Dye	X^-	*Yield* (%)	*M.p./Lit. m.p.* (°C)	*Reaction conditions*			*Molecular formula*	*Mol. wt*	*Analysis for N*	
				Optimum temp. (°C)	*Reaction time (min)*	*Alkylating agent/(mol)*			*Found* (%)	*Calcd* (%)
2a	CH_3SO_4	89	190–191/190[a]	70	5	DMS/4	$C_{19}H_{24}N_4O_6S_2$	468·5	—	—
2b	$C_6H_5SO_3$	91	171–173	70	5	MBS/4	$C_{26}H_{28}Cl_2N_4O_4S_2$	595·5	9·6	9·4
2c	CH_3SO_4	97	157–159	75	6	DMS/4	$C_{21}H_{22}N_4O_4S_2$	458·5	12·1	12·2
2d	CH_3SO_4	96	[b]	70	5	DMS/4	$C_{18}H_{22}N_4O_5S_2$	438·5	—	—
2e	CH_3SO_4	94	[c]	70	5	DMS/4	$C_{20}H_{26}N_4O_6S_2$	482·6	—	—
2f	CH_3SO_4	95	160–162	55	2	DMS/3·2	$C_{13}H_{18}N_4O_4S_2$	358·4	16·1	15·6
2g	CH_3SO_4	95	227–229	55	3	DMS/3	$C_{20}H_{20}N_4O_4S_2$	444·5	12·5	12·6
2h	CH_3SO_4	91	204–205/202[d]	70	1	DMS/1·5	$C_{15}H_{20}N_4O_4S$	352·4	—	—
2i	BF_4	64[e]	209–210	70	6	DMS/5	$C_{12}H_{17}BF_4N_6$	332·1	25·1	25·3

[a] Ref. 15.

[b,c] Liquid forms, chromatographically identical with Basacryl Blue GL and Basacryl Blue X-3GL.

[d] Ref. 16.

[e] Incompletely isolated due to high solubility. Yield 100%, established chromatographically.

required. In cases where two nitrogen atoms have to be alkylated (e.g. **1i**), this molar ratio should be corrected appropriately. Our observations suggest that the basicity of the nitrogen atom in the heterocycle influences the alkylating agent/starting dye molar ratio; viz. fewer basic nitrogen atoms require greater amounts of alkylating agent, e.g. 1·5:1 in the case of pyridine dyes and 4:1 for benzothiazole dyes (see Table 1).

Different volume ratios and quantities of water and organic solvents can be used; however, the range from 1:1 to 3:1 (v/v) is preferred for the organic solvent/alkylating agent ratio, whilst the water/dye ratio should be at least 1:1.

Dyes containing benzothiazole, naphthothiazole, thiazole, pyridine and triazole rings are quaternized according to the proposed method. Some of these dyes find commercial application.[1-3,11-14] The method has been applied successfully to the quaternization of *c*. 0·02 kg mol azo dye and the results obtained are similar to those reported above.

3 EXPERIMENTAL

The respective monoazo dye **1a–1i** (0·01 mol), 7 ml of water and 7 ml of dichloroethane were placed in a round-bottomed flask equipped with stirrer, thermometer, condenser and dropping funnel. The reaction mixture was heated to the optimal temperature (Table 1) with stirring, and 0·015–0·04 mol of the respective alkylating agent (dimethyl sulphate or arylsulphonic acid methyl ester) was then added immediately. The reaction was monitored by TLC and the quaternization was complete within 1–6 min. The reaction mixture was further treated according to one of the following procedures.

(a) Dichloroethane was distilled off, ethanol (20 ml) was added, the dye precipitated with ether and filtered.

(b) Water was removed azeotropically using additional quantities of dichloroethane. Chlorobenzene (60–80 ml) was then added and the precipitate filtered.

(c) Dichloroethane was distilled off, water (60–70 ml) added, the solution filtered while hot and, after cooling the filtrate, the dye was either precipitated, for example with sodium tetrafluoroborate or zinc chloride, as a slightly soluble salt, or was salted out with sodium chloride.

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