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One-pot Synthesis of 1,3-Dimethyl-2-[4-N(N,N-disubstitutedamino)phenylazo]imidazolium Cationic Dyes

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ABSTRACT

Starting from 4-chloro- or 4-fluoroaniline, the four reaction steps — diazotization, coupling with imidazole, quaternization with dimethyl sulphate and substitution with dialkylamines, piperidine derivatives or hexamethyleneimine — were carried out as a one-pot preparation of 1,3-dimethyl-2-[4-(N,N-disubstitutedamino)phenylazo]imidazolium cationic dyes. The reaction procedure shortened considerably the overall reaction time and avoided some technical operations, such as filtration and drying. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The diazotization of an aromatic or a heteroaromatic primary amine followed by coupling reaction with electron donor substituted aromatic compounds are the two steps by which practically almost all azo dyes are produced.[1] For the preparation of basic heterocyclic azo dyes, quaternization of the heterocyclic nitrogen is then carried out.[2] Oxidative azo coupling, first reported by Hünig[3,4] is another method by which azo derivatives of heterocyclic compounds have become accessible. In this method, aromatic heterocycle hydrazones are converted oxidatively into a diazonium intermediate which reacts with a coupling component.

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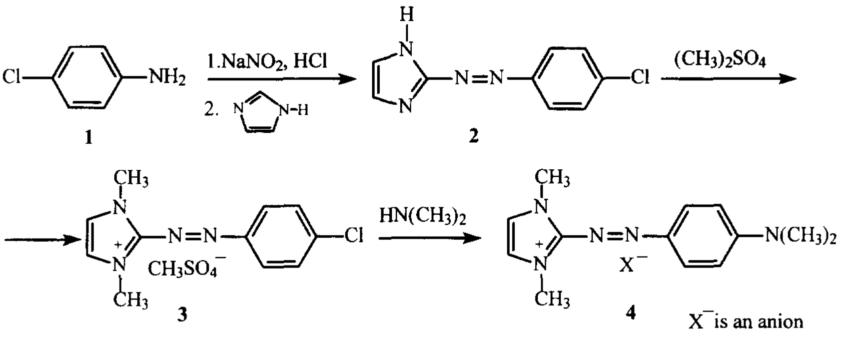
Baumann and Dehnert[5] reported a modified method for the preparation of cationic imidazolium azo dyes. Diazotization of 4-chloroaniline **1** followed by coupling with imidazole at the 2-position in the imidazole ring (Scheme 1)



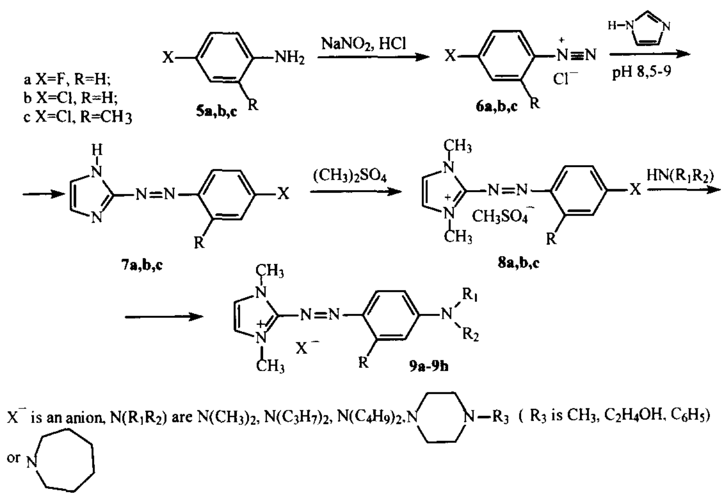
Scheme 1.

gives 2-(4-chlorophenylazo)imidazole **2**, which then is quaternized to give the cationic compound **3**, 1,3-dimethyl-2-(4-chlorophenylazo)imidazolium methosulphate. In compound **3** the chlorine atom is very labile and can be exchanged with nucleophiles, a reaction proceeding especially easily with dialkylamines. Thus, substitution of the chlorine atom in **3** with dimethylamine gives dye **4** which is produced by BASF as *Basacryl Red X-BL.*[6] This dye imparts a bright red color to acrylic fibres and is also marketed as *Remacryl Red 2BL, Maxilon Red M-4GL,* and *Sevron Rubin Y.*[6] CIBA-GEIGY introduced migrating cationic dyes for the level coloration of acrylic fibres.[7–9] Because of the small size of the dye cation (molecular weight is about 250), the dye molecule can migrate from one site to another in the fibre during the coloration process, thus giving very level dyeings; these dyes are commercialized under the trade name *Maxilon M*, including compound **4**, *Maxilon Red M-4GL.*

In this paper we report a one-pot preparation of 1,3-dimethyl-2-[4-(N,N-disubstitutedamino)phenylazo]imidazolium cationic dyes.

RESULTS AND DISCUSSION

The cationic imidazolium azo dyes were synthesized in a one-pot process without isolation of intermediates, avoiding operations such as filtration and drying at intermediate stages and thus shortening the overall reaction time. Starting from 4-chloro- or 4-fluoroaniline derivatives (Scheme 2),

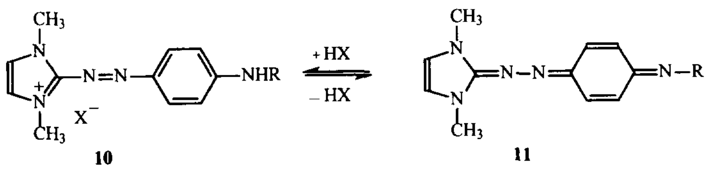


Scheme 2.

diazotization is complete within about 30 min. The coupling reaction of the diazonium salts with imidazole proceeds at pH 8.5–9 over 2 h, and the resulting dye **7** is then quaternized with dimethylsulphate in a two-phase system over about 1 min.[2] The quaternized azo compounds have very easily exchangeable halogen (Cl or F), which are replaceable by dialkylamines over 30–60 min at 50–60°C. The dyes **9a–9h** were isolated by precipitating as the perchlorates or as double zinc salts (Table 1).

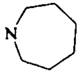
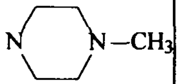
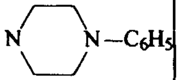
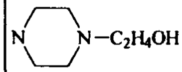
Dyes **9a–9h** absorb in the region 525–545 nm and have molar absorptivity 45,000–70,000 $\mathrm{mol}^{-1}\ \mathrm{cm}^{-1}$. They impart a bright red color to polyacrylonitrile fibres.

The reactive intermediates **8** (the most reactive compound is the fluoro derivative **8a**) have a considerable selectivity to secondary aliphatic amines and some saturated nitrogen heterocycles such as piperidine, pyrrolidine and morpholine. Aromatic amines can also be used but the replacement process is slow and is not complete even after boiling for several hours. With primary aliphatic amines, the required color is not developed because in alkaline media such dyes are in the uncharged form **11** (Scheme 3)



Scheme 3.

TABLE 1 Substituents, Anion, Melting Points, Yields, λ_{max}, Molar Absorptivity ϵ, and Elemental Analysis of **9a–9h**

Dye	R	NR_1R_2	X^-	m.p.^{0}C (yield %)	λ_{max}nm (ϵlmol^{-1}cm^{-1})	Molecular formulae	Analysis found/calc. %		
							C	H	N
9a	H	$N(CH_3)_2$	CH_3SO_4	300 (67)	540 (52100)	$C_{14}H_{21}N_5O_4S$	-	-	19,5/19,7
9b	CH_3	$N(CH_3)_2$	ClO_4	270-273 (70)	545 (52600)	$C_{14}H_{20}ClN_5O_4$	-	-	19,8/19,6
9c	H	$N(C_3H_7)_2$	ClO_4	181-182 (65)	540 (69500)	$C_{17}H_{26}ClN_5O_4$	51,2/51,1	6,8/6,5	17,6/17,5
9d	H	$N(C_4H_9)_2$	ClO_4	121-122 (60)	540 (55500)	$C_{19}H_{30}ClN_5O_4$	54,1/53,4	7,4/7,1	16,9/16,3
9e	H		ClO_4	234-235 (59)	540 (64000)	$C_{17}H_{23}ClN_5O_4$	51,2/51,3	6,1/6,1	17,1/17,6
9f	H		ClO_4	196-197 (65)	528 (44800)	$C_{16}H_{23}N_6O_4$	47,9/48,1	6,1/5,8	19,8/20,1
9g	H		ClO_4	266-267 (67)	524 (45300)	$C_{21}H_{35}ClN_6O_4$	55,3/54,7	5,4/5,6	18,2/18,2
9h	H		ClO_4	211-212 (58)	530 (48500)	$C_{17}H_{25}ClN_6O_5$	48,1/47,6	6,0/5,9	19,4/19,6

and their color is very close to that of the intermediate **8**. The difference in the absorption wavelength of **8** and dyes **9a–9h** is about 160 nm. We consider that the intermediates **8** (in their pure forms) could be of interest as selective derivatization reagents for secondary aliphatic amines.

The one-pot preparation of cationic imidazolium azo dyes has the following advantages:

- considerable shortening of the overall reaction time;
- avoidance of some technical operations such as filtration and drying;
- lower energy costs.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. The absorption spectra were recorded on a Carl Zeiss Jena Specord UV-VIS spectrophotometer (2×10^{-5} M/liter in methanol)

General procedure for preparation of 9a–9h[10]

The respective 4-chloro- or 4-fluoroaniline (0.02 m) was dissolved in acetic acid (2 ml), hydrochloric acid (5 ml) and water (25 ml). The resulting solution was cooled to 0°C and a solution of sodium nitrite (1.4 g, 0.02 m) in water (5 ml) was added dropwise at 0–5°C. After 30 min the diazotization was complete. Imidazole (1.55 g, 0.02 m) dissolved in water (25 ml) was added to the diazo solution and the reaction liquor adjusted to pH 8.5–9 by dropwise addition of 40% aq. sodium hydroxide. The coupling reaction was complete after 2 h stirring at 10–15°C. Dichloroethane (16 ml), sodium acetate (4.8 g, 0. 06 m) and dimethyl sulphate (10.6 g, 0.08 m) were then added to the reaction mixture and the liquor warmed to 70°C. At this temperature the quaternization proceeded over 1 min (TLC control). Dichloroethane was distilled off and the reaction mixture was cooled to 50°C. The appropriate dialkylamine, piperazine derivative or hexamethyleneimine (0.1 M) was added to the reaction solution (in the case of volatile dialkylamines, such as dimethylamine, the reaction was carried out in a closed vessel). The replacement of the halogen substituent by the dialkylamino group was complete at 50–60°C over 30–40 min (TLC control). After cooling to room temperature, the dye was salted out with sodium chloride and zinc chloride, or precipitated as the perchlorate with sodium perchlorate. The dye was then filtered and dried.

Data for dyes **9a–9h** are shown in Table 1.

REFERENCES

1. Zollinger, H., *Color Chemistry. Synthesis, Properties and Applications of Organic Dyes*. Verlag Chemie, Weincheim, 1987.
2. Simov, D., Deligeorgiev, T., Gadjev, N. & Penchev, A., *Dyes and Pigments*, **15** (1991) 83.
3. Hünig, S., Balli, H., Fritsch, K. H., Herrmann, H., Köbrich, G., Werner, H., Grigat, E., Müller, F. & Nöther, H., *Ayngew. Chem.*, **70** (1958) 215.
4. Hünig, S., Balli, H., Breither, E., Brühne, F., Geiger, H., Grigat, E., Müller, F. & Quast, H., *Angew. Chem.*, **74** (1962) 818.
5. Baumann, H. & Dehnert, J., *Chimia*, **15** (1961) 163.
6. Raue, R. & Riester, O., *Ullman's Encyclopedia of Chemical Technology*, Vol. 16. Verlag Chemie GmbH, Weinheim, 1978, p. 635.
7. Biedermann, W., *Rev. Prog. Coloration*, **10** (1979) 1.
8. Biedermann, W., Galafassi, P., Moser, P. & Scheidegger, H., *Textilveredlung*, **12** (1977) 122.
9. Galafassi, P., Biedermann, W., Horn, U., Moser, P. & Scheidegger, H., *Textilveredlung*, **12** (1977) 250.
10. Deligeorgiev, T., Ph.D. Thesis, University of Sofia, 1981.