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Preparation of 2-(*N*-Alkyl-*N*-arylamino)ethyl trimethylammonium Salts

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ABSTRACT

The N-*alkylation of 2-(*N-*arylamino)ethyl trimethylammonium salts with allyl chloride, benzyl chloride, epichlorohydrin, ethylene chlorohydrin and acrylonitrile was studied and the preparation of 2-(*N-*allyl-, -benzyl-, -2-hydroxyethyl-, 3-chloro-2-hydroxypropyl-and 2-cyanoethyl-*N-*arylamino)-ethyl trimethylammonium salts is described. A method is proposed for obtaining a series of differently* N-*substituted derivatives of these salts from the same 2-(*N-*arylamino)ethyl trimethylammonium salts.*

1 INTRODUCTION

N-substituted 2-(*N*-arylamino)ethyl trimethylammonium salts are used as coupling components in the synthesis of cationic azo dyes.[1] During our investigations we have established that they inhibit the corrosion of ferrous metals in mineral acids. This practically important property provides possibilities for their application as inhibitors in the etching of ferrous metals.[2]

2 RESULTS AND DISCUSSION

Several methods[3–8] have been used for the preparation of these salts and we have concluded that the method described in Ref. 8 has substantial

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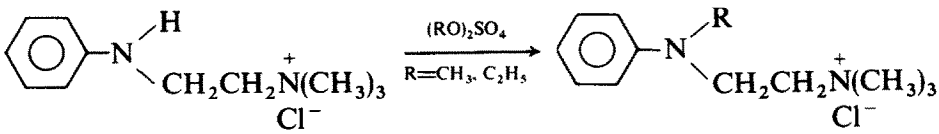


Scheme 1

advantages over the other routes mainly because relatively simple starting materials are used, i.e. primary aromatic amines which are alkylated successively with chlorocholine chloride and dialkyl sulphates.

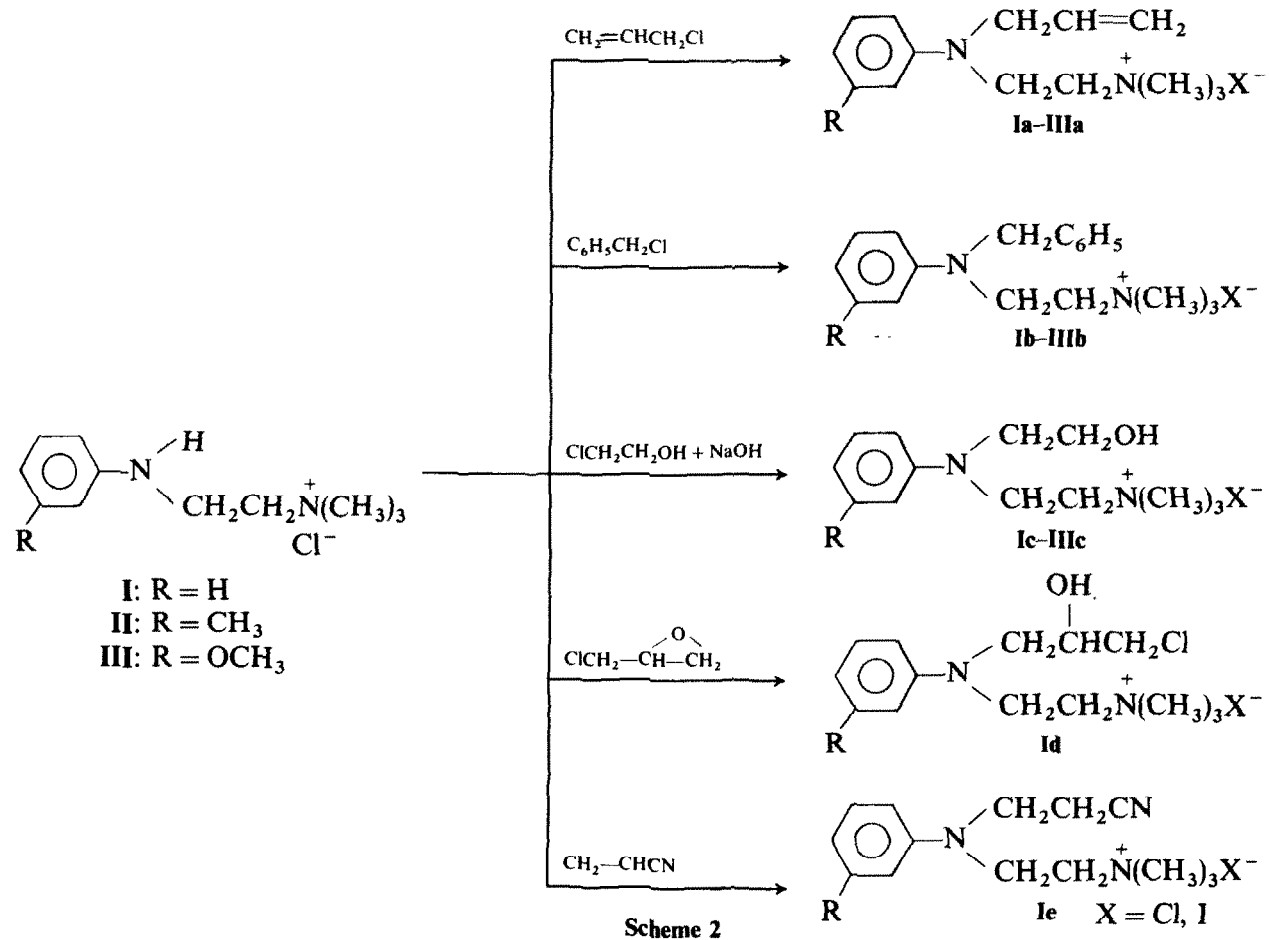
The application of this method is to a large extent practically restricted to the preparation of *N*-methyl- and *N*-ethyl derivatives (Scheme 1) since higher dialkyl sulphates are less available. The preparation of 2-(*N*-alkyl-*N*-arylamino)ethyl trimethylammonium salts is outside the scope of this method. These compounds, however, are of practical importance as intermediates for the preparation of cationic dyes, and by varying the substituent at the nitrogen atom the rate of exhaustion of the dye can be altered considerably without greatly influencing the colour and stability of the dye. The object of this study was to prepare *N*-substituted-2-(*N*-arylamino)ethyl trimethylammonium salts by alkylation of 2-(*N*-arylamino)ethyl trimethylammonium salts obtained according to the procedure described in Ref. 8, with different alkylating agents, viz. (1): compounds with a labile halogen atom, such as allyl chloride and benzyl chloride, (ii) epoxy compounds such as epichlorohydrin, (iii) compounds which are transformed into epoxy compounds in the course of the reaction, such as ethylene chlorohydrin in alkaline medium and (iv) compounds having a polar double bond, e.g. acrylonitrile. Thus the synthetic possibilities of the known method are considerably broadened.

The starting 2-(*N*-arylamino)ethyl trimethylammonium salts and the synthesised *N*-substituted derivatives are shown in Scheme 2.

Compounds **Ia–IIIa** and **Id** are new. Data concerning the preparation of compounds **Ib–IIIb**, **Ic–IIIc** and **Ie** have not been published, but dyes based on these compounds are included in the general formulae of patent-protected substances.[9,10]

The alkylation with allyl chloride and with benzyl chloride proceeded smoothly by refluxing in an aqueous–alcoholic medium with excess of alkylating agent at pH 7–10 (addition of sodium carbonates). Under these conditions a conversion of 89–94% was achieved of compounds **I–III** into the *N*-allyl and *N*-benzyl derivatives.

Hydroxyethylation with ethylene chlorohydrin (in 2·5–3-fold excess) was carried out at 55–65°C and pH 9–10 (NaOH) in aqueous medium. At higher temperatures a considerably larger excess of ethylene chlorohydrin was required due to the rapid hydrolysis of this reagent. A conversion of 87–95%


CH2=CHCH2Cl
C6H5CH2Cl
ClCH2CH2OH + NaOH
ClCH2—CH—CH2
CH2—CHCN
CH2CH=CH2
CH2CH2N(CH3)3X−
Ia–IIIa
CH2C6H5
Ib–IIIb
CH2CH2OH
Ic–IIIc
OH
CH2CHCH2Cl
Id
CH2CH2CN
Ie X = Cl, I
I: R = H
II: R = CH3
III: R = OCH3

Scheme 2

was achieved. Under these conditions, the actual hydroxyethylating agent was ethylene oxide, formed by dehydrochlorination of ethylene chlorohydrin. Epichlorohydrin interacts with compound **I** both in neutral and in slightly acidic or slightly alkaline medium. The appropriate temperature range is 40–50°C, requiring a reaction duration of more than 10 h. Higher temperatures lead to the formation of a viscous oligomeric product. A conversion of 92–94% was achieved.

Studies on the *N*-cyanoethylation of compound **I** showed that the reaction proceeded slowly and was difficult to complete. The best results (conversion of 68–69%) were obtained in acetic acid in presence of $ZnCl_2$ as a catalyst by refluxing for 50–60 h. Under these conditions polymerisation of acrylonitrile was observed and for this reason it should be present in excess.

The identity of the salts **Ia–IIIa**, **Ib–IIIb** and **Ic–IIIc** was confirmed by elemental analysis of the respective iodides (Tables 1–3). The salts **Id** and **Ie** were also identified by the dyes obtained through coupling with *p*-nitrobenzenediazonium chloride. The characteristic frequency of the imino group observed in the IR spectra of the starting compounds is lacking in the IR spectra of the new salts. The band characteristic of the hydroxy group in the salts having a hydroxyethyl moiety (**Ic–IIIc**) appears in the range 3370–3420 cm^{-1}. Their electronic spectra in the range 200–400 nm are characterised by three absorption bands at 207–214, 249–254 and 293–297 nm, respectively, which are analogous to those of benzene. For the compounds studied, these bands are bathochromically shifted and more

TABLE 1
Yields, Melting Points, Elemental Analysis Data and UV Spectra of Salts **Ia–IIIa**

Compound	*Yield* (%)	*M.p.* (°C)	*Molecular formula*	*Analysis*[a] (%)			*UV absorption spectra*	
				C	*H*	*N*	λ_{max} (*nm*)	*log* ε
Ia	90	184–185	$C_{14}H_{23}N_2I$	49·0	6·7	7·8	206	4·01
				48·6	6·7	8·1	219sh	3·87
							250	3·78
							296	3·10
IIa	92	141–143	$C_{15}H_{25}N_2I$	50·1	7·1	7·6	211	4·28
				50·0	7·0	7·8	252	3·79
							296	3·02
IIIa	91	149–150	$C_{15}H_{25}N_2OI$	47·8	6·6	7·1	214	4·26
				47·9	6·7	7·4	251	3·73
							293	3·27

[a] Upper line, Found; lower line, Calculated.

TABLE 2
Yield, Melting Points, Elemental Analysis Data and UV Spectra of Salts **Ib–IIIb**

Compound	*Yield* (%)	*M.p.* (°C)	*Molecular formula*	*Analysis*[a] (%)			*UV absorption spectra*	
				C	*H*	*N*	λ_{max} (*nm*)	*log ε*
Ib	92	151–152	$C_{18}H_{25}N_2I$	54·9	6·6	6·85	206	4·05
				54·55	6·4	7·1	219sh	3·90
							250	3·87
							296	3·18
IIb	92	188–190	$C_{19}H_{27}N_2I$	55·4	6·9	6·9	210	4·25
				55·6	6·6	6·8	251	3·80
							294	3·16
IIIb	94	194–195	$C_{19}H_{27}N_2OI$	53·8	6·4	7·0	213	4·35
				53·5	6·4	6·6	249	3·75
							293	3·39

[a] Upper line, Found; lower line, Calculated.

intense due to conjugation and disturbances in the symmetry of the molecule.

Our results suggest that the scheme for the preparation of 2-(*N*-alkyl-*N*-arylamino)ethyl trimethylammonium salts starting from primary aromatic amines and chlorocholine chloride[8] can be applied to the preparation of their *N*-alkylated derivatives, thus avoiding some of the above-mentioned restrictions.

TABLE 3
Yield, Melting Points, Elemental Analysis Data, IR Absorption Maxima and UV Spectra of Salts **Ic–IIIc**

Compound	*Yield* (%)	*M.p.* (°C)	*Molecular formula*	*Analysis*[a] (%)			*IR absorption maxima* $\nu_{(OH)}$ (cm^{-1})	*UV absorption spectra*	
				C	*H*	*N*		λ_{max} (*nm*)	*log ε*
Ic	87	145–146	$C_{13}H_{23}N_2OI$	44·7	6·9	7·6	3370	207	3·95
				44·6	6·6	8·0		219sh	3·87
								252	3·85
								293	3·18
IIc	95	145–146	$C_{14}H_{25}N_2OI$	46·4	6·8	7·8	3300–3370	211	4·09
				46·2	6·9	7·7		254	3·80
								296	3·15
IIIc	93	144–146	$C_{14}H_{25}N_2O_2I$	44·2	6·7	7·0	3430	213	4·18
				44·2	6·6	7·4		252	3·73
								297	3·24

[a] Upper line, Found; lower line, Calculated.

The proposed method has the advantage that a series of various *N*-substituted derivatives can be prepared starting from the same 2-arylaminoethyl trimethylammonium salt. The latter can be readily synthesised from a primary amine and chlorocholine chloride[8] in almost quantitative yield, so that the use of the respective secondary or tertiary aromatic amine as the starting material for each *N*-substituted derivative can be avoided.

The possibility of the synthesis of a series of various *N*-substituted coupling components for cationic dyes starting from the same compound allows the relatively easy preparation of dyes of a given colour with the same structure and almost the same stability but with different dyeing behaviour depending on the substituent in the alkyl moiety at the nitrogen atom, i.e. with different compatibility to acrylic fibres.

3 EXPERIMENTAL

3.1 General

The melting points were determined on a Kofler apparatus and were not corrected. IR spectra were recorded on a Specord 71 IR spectrophotometer (Carl-Zeiss, Jena) in Nujol. UV spectra were recorded on a Specord UV–VIS spectrophotometer in 95% ethanol at concentration of 1×10^{-4} mol litre^{-1} and $3{\cdot}33 \times 10^{-5}$ mol litre^{-1}.

The starting salts **I–III** were obtained according to the described procedure[8] and used as prepared in the form of solutions without isolation. In order to establish the completion of the reactions, the method of nitrosation[11] was applied, by which the residual quantity of the starting salt **I–III** in the reaction mixture was determined as a secondary amine and the quantity of the prepared *N*-substituted derivative could be calculated from the difference between the initial and final content of the starting reagent. The prepared salts can be isolated from the aqueous solutions by converting them into less soluble salts, e.g. iodides, tetrafluoroborates, double salts with $ZnCl_2$, etc. They were identified as iodides except for **Id** and **Ie**, for which dyes from *p*-nitrobenzenediazonium chloride were obtained. The salts were purified by recrystallisation from ethanol. They could be used in the synthesis of dyes as prepared in the form of solutions, without subsequent isolation.

3.2 Preparation of compounds Ia–IIIa

An aqueous solution of **I** (10·7 g, 0·05 mol), **II** (11·5 g, 0·05 mol) or **III** (12·2 g, 0·05 mol) was prepared and ethanol (about one-half of the initial volume),

$NaHCO_3$ (5 g, 0·06 mol) and allyl chloride (8 ml, 7·5 g, 0·098 mol) were added. The reaction mixture was refluxed with stirring for 1·5–2 h, after which time the reflux temperature became constant. A sample was then taken to check the completion of the reaction. The solvent and excess allyl chloride were distilled off. The respective yields and some constants of the compounds thus prepared are given in Table 1.

3.3 Preparation of compounds Ib–IIIb

Each of the above aqueous solutions of the salts **I–III** was diluted with ethanol (one-third of the initial volume) and Na_2CO_3 (4·25 g, 0·04 mol) and benzyl chloride (7·8 ml, 8·6 g, 0·068 mol) were added. The reaction mixture was refluxed with stirring for 5 h. Following completion of the reaction, the solvent was distilled off and the residue was extracted with ether to remove excess benzyl chloride. The respective yields and some constants of the compounds prepared are given in Table 2.

3.4 Preparation of compounds Ic–IIIc

Ethylene chlorohydrin (11·8 ml, 14·1 g, 0·175 mol) was added to an aqueous solution containing one of the salts **I–III** (in the amounts stated above) and sodium hydroxide (8 g NaOH in 20 ml H_2O) was added dropwise to the stirred reaction mixture so that pH was maintained in the range of 9–10, maintaining a temperature of 55°C. Stirring was continued at 55–65°C until the reaction was complete. The respective yields and some constants of the compounds prepared are given in Table 3.

3.5 Preparation of compound Id

Epichlorohydrin (9·4 ml, 11·1 g, 0·12 mol) was added dropwise to a stirred aqueous solution containing the salt **I** (10·7 g, 0·05 mol) and Na_2CO_3 (0·2 g) at 40°C. Stirring was continued at 40°C for 12 h and the reaction mixture was then extracted with ether and the aqueous layer treated with charcoal. The yield was 94%. Compound **Id** was converted to the dye 2-{*N*-(3-chloro-2-hydroxypropyl)-*N*-[4-(4-nitrophenyl)azophenyl]amino}ethyl trimethylammonium iodide.

3.6 Preparation of compound Ie

An aqueous solution of the salt **I** (11·6 g, 0·54 mol) was evaporated in vacuum almost to dryness and acetic acid (8 ml), $ZnCl_2$ (0·7 g) and acrylonitrile (9 ml, 7·2 g, 0·1 mol) were added to the residue. The reaction mixture was refluxed

with stirring for 50–60 h, then diluted with water and treated with charcoal. The yield was 64%. Compound **Ie** was converted to the dye 2-{*N*-(2-cyanoethyl)-*N*-[4-(4-nitrophenyl)azophenyl]amino}ethyl trimethylammonium iodide.

3.7 Preparation of the azo dye 2-{*N*-(3-chloro-2-hydroxypropyl)-*N*-[4-(4-nitrophenyl)-azophenyl]amino}ethyl trimethylammonium iodide

4-Nitroaniline (1·38 g, 0·01 mol) was diazotised as described in Ref. 12. The suspension of 4-nitrophenyldiazonium chloride was poured with stirring into an aqueous solution of **Id** (0·01 mol) prepared as described above. Crystalline sodium acetate (3 g) was added and the reaction mixture was stirred for 2–3 h below 10°C until completion of the coupling reaction. The dye was isolated by the addition of potassium iodide. The product (91%, m.p. 144–147°C) was recrystallised from acetone to give the pure dye, m.p. 162–163°C.

Calcd for $C_{20}H_{27}N_5O_3ClI$: N, 12·55. Found: N, 12·8%. IR: ν_{OH} 3380 cm^{-1}.

3.8 Preparation of the azo dye 2-{*N*-(2-cyanoethyl)-*N*-[4-(4-nitrophenyl)azophenyl]amino}ethyl trimethylammonium iodide

The procedure used was similar to the above. The starting materials were 4-nitroaniline (0·1 mol) and compound **Ie** (0·1 mol) as an aqueous solution. The yield of the product, melting at 229–233°C, was 93%. After recrystallisation from an ethanol–water mixture, the pure substance had a melting point of 244–246°C.

Calcd for $C_{20}H_{25}N_6O_2I$: C, 47·25; H, 5·0; N, 16·5. Found: C, 47·0; H, 5·2; N, 16·2%. IR: ν_{CN} 2230 cm^{-1}, very weak.

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