RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

April 1963

ADVANCES IN THE PREPARATION, INVESTIGATION, AND USE OF QUINOLINIUM COMPOUNDS

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CONTENTS

I. Introduction 167

II. Preparation of quinolinium salts 167

1. Production of quaternary salts by alkylation 167

2. Preparation of quinolinium salts by cyclisation of secondary arylamines 168

III. Chemical properties of quinolinium salts 169

1. Addition reactions 169

2. Substitution reactions 170

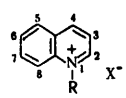
3. Reactions forming quinolinium dyes 172

4. Other reactions 181

IV. Uses of quinolinium compounds 181

I. INTRODUCTION

Quinolinium compounds are quaternary salts of quinoline in which the radical R can vary from methyl to complex aliphatic and aromatic radicals:



Positions 2–8 may also have any substituents; X is an acid residue. Quinolinium compounds are intermediates in the production of dyestuffs for sensitising photographic emulsions, for dyeing natural and synthetic fibres, and for biological preparations. They have a number of interesting biological properties, of which their cancerostatic, photodynamic, mutagenic, and plant growth regulating properties are only just beginning to be studied. Quinolinium compounds are widely studied for antiseptic, chemotherapeutic, hypotensive, and ganglion-blocking properties, and a number of very valuable substances have been found.

Because of the electrophilic nitrogen atom in the ring and the consequent reduction of electron density on the carbon atoms, quinolinium salts are good models for studying nucleophilic reactions, which they undergo fairly readily. Quinaldinium and lepidinium salts, which have a labile methyl-group, are extremely reactive, and readily condense with organic carbonyl-compounds, ortho-esters, diazonium salts, nitroso-compounds, etc., to form various types of dyestuff.

Cyanine dyes are good models for studying the relationship between structure and colour, and possess interesting photoelectric properties[1].

Quinolinium compounds are also used as surface-active substances and analytical reagents.

This review will consider in some detail work of the last 25–30 years, which have seen the most interesting studies in the field of quinolinium compounds. We shall not touch upon matters covered sufficiently in other reviews (*e.g.* the relationship between colour and structure, structure and photographic properties, etc.).

II. PREPARATION OF QUINOLINIUM SALTS

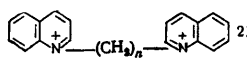
1. Production of Quaternary Salts by Alkylation

The simplest quinolinium salt, *N*-methylquinolinium iodide, was first prepared by Williams[2] by heating quinoline with methyl iodide; *N*-methylquinaldinium and *N*-methyllepidinium halides were obtained similarly[3,4]. The rate of reaction depends on the alkylating agent and the substituents in the quinoline nucleus. Some quinoline derivatives, *e.g.* 8-nitroquinoline, do not react with alkyl halides:

Decker[5] used dimethyl sulphate to obtain the 8-nitroquinolinium salt. Aralkyl halides also react with quinolines to form the quaternary salts.

A considerable number of substituted quaternary salts derived from quinoline, its homologues, and derivatives are known.

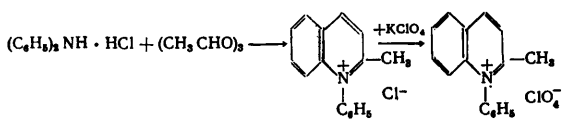
This reaction can be carried out in various ways, in the presence of a solvent (ether, alcohols, benzene, nitrobenzene, etc.) or in its absence. Alkyl and aralkyl halides are used as alkylating agents there as well as alkyl esters of sulphuric or various aromatic sulphonic acids. If dihalogenoalkanes are used bis-quarternary salts are obtained[6-8]:



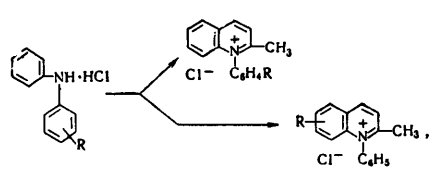
The kinetics of the alkylation of quinoline with alkyl halides were first investigated by Menschutkin[9]. Winkler and Hinshelwood[10] used Menschutkin's method to study the rate of reaction between quinoline and methyl iodide in benzene. The influence of the alkyl radical, the halogen, and the heterocyclic base on the rate of formation of the quaternary salts has also been studied[11], using equimolar amounts of quinoline and alkyl halide in methanol. The rate of reaction, measured conductimetrically, decreases with increasing number of carbon atoms in the alkyl radical, but increases in the series I > Br > Cl.

2. Preparation of Quinolinium Salts by Cyclisation of Secondary Arylamines

The principal new method for the preparation of quinolinium salts is the cyclisation of secondary aromatic amines with organic carbonyl compounds. This is a general method, and can be used to prepare quaternary salts with aliphatic, aliphatic-aromatic or aromatic radicals on the nitrogen. These last have not yet been prepared by other methods, since the direct arylation of quinoline does not produce *N*-arylquinolinium salts[12]; aryl halides and aryl esters of aromatic sulphonic acids do not form quaternary salts on heating with quinoline or its derivatives, because of their low reactivity. This was one of the reasons why until recently no such quarternary salts, or derivatives with aryl radicals on the nitrogen, were known. Pilyugin and Krainer[13,14] applied the Doebner–Miller reaction to diarylamines, and developed a general method for the preparation of *N*-arylquinaldinium salts:



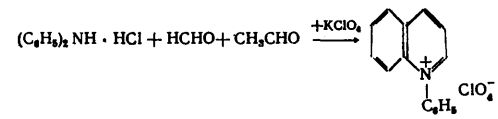
Symmetrical secondary aromatic amines can condense with paraldehyde to form only one compound; an asymmetrical amine can form two isomers with equal probability[15]:



but in the overwhelming majority of cases only one of the two possible isomers has been isolated.

It was later shown[16] that in acid medium secondary arylamines react with vinyl ethers to form *N*-arylquinaldinium salts. The use of butyl vinyl ether instead of paraldehyde considerably reduces the period of reaction and increases the yield of quinaldinium salts. Acetal, which is converted into acetaldehyde by hydrolysis, can also be used in this reaction[17]. Higher saturated aldehydes can also be used as the carbonyl component; *e.g.* propionaldehyde and butyraldehyde give respectively 2-ethyl-3-methyl- and 2-propyl-3-ethyl-*N*-arylquinolinium salts[18]. *N*-Phenylquinaldinium salts can also be prepared by heating diphenylamine in solution in isobutyl alcohol with sodium isobutoxide, the reaction mixture then being heated in acid solution[17]. Ferric chloride and zinc chloride have been suggested as condensing agents for the preparation of quinaldinium salts by cyclising secondary arylamines with acetaldehyde, paraldehyde, aldol, or crotonaldehyde in anhydrous alcohol[19].

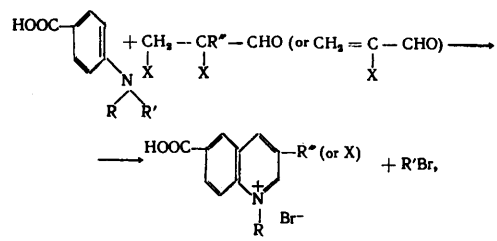
Aliphatic aromatic amines, *e.g.* ethylaniline, react with paraldehyde to form *N*-alkylquinaldinium salts. Applying Beyer's reaction[20] to secondary amines, Pilyugin and Gutsulyak prepared a number of *N*-aryllepidinium salts[21-25]. The preparation of certain aryllepidinium salts has been described in the patent literature[26,27]. Ardashev and Tertov[28] prepared 1-phenyl-3-methyllepidinium perchlorate by using ethyl methyl ketone in place of acetone. The use of acetaldehyde instead of acetone produces an *N*-arylquinolinium salt[29]:



N-Phenylquinolinium salts are also obtained by the reaction of β-hydroxypropionaldehyde with diphenylamine in the presence of nitrobenzene and sulphuric acid: the perchlorate has been isolated[30].

Unsaturated carbonyl compounds react with diarylamines to form *N*-aryl quaternary salts of quinoline and its homologues[26,27,31]. Heterocyclic secondary amines also produce quinolinium derivatives[26,32]. Replacing the aldehydes by methyl vinyl ketone gives the corresponding lepidinium salts.

Weygand and coworkers[33,34] have developed an interesting method for the preparation of quaternary salts of 3-substituted quinoline-carboxylic acids, by boiling halogenoaldehydes with *N*-substituted aminobenzoic acids in dioxan:

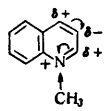


where R = $C_6H_5CH_2$, R′ = H, CH_3, or $C_6H_5CH_2$, R″ = H, Br, CH_3, or C_2H_5, and X = Br.

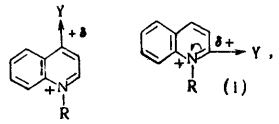
Other material on the preparation of *N*-arylquinolinium salts has also been published[35-41].

III. CHEMICAL PROPERTIES OF QUINOLINIUM SALTS

Because of the electron-accepting quaternary nitrogen atom in quinolinium salts, the electron density on the carbon atoms of the pyridine ring is less than in the base, particularly in positions 2 and 4:



Quinolinium compounds are therefore particularly prone to nucleophilic addition and substitution reactions at positions 2 and 4, and electrophilic reactions proceed with difficulty at position 3. If the quinolinium ring is 2- or 4-substituted by one of the electron-withdrawing groups I, SR, OAr, or CN, nucleophilic substitution becomes easier, these groups being split off; this is explained by the increased positive charge on the 2- or 4-carbon atom:

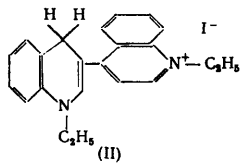


(I)

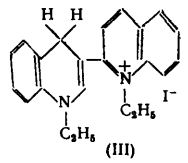
where Y = I, SR, OAr, or CN.

Nucleophilic reactions proceed more readily at the 4-position than at the 2-position, although some, *e.g.* addition of the OH-group and reactions with organometallic compounds, take place exclusively at the 2-position.

The electron distribution given above for the quinolinium ring (I) is supported by the experimental fact that heating a concentrated alcoholic solution of an *N*-alkylquinolinium iodide with alkali produces two isomeric red and yellow dyes which have been named erythroapocyanine (II) and xanthoapocyanine (III):[45-47]



(II)



(III)

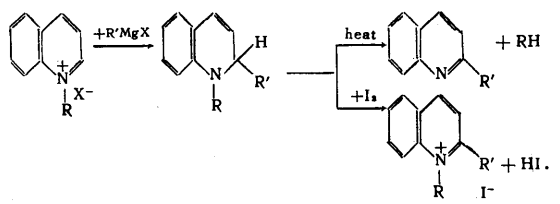
1. Addition Reactions

(a) Addition of hydrogen. Addition of 1 mole of hydrogen to a quinolinium salt can produce an *N*-substituted 1,2- or 1,4-dihydroquinoline derivative. Ishii[48] found that in some cases the reduction of 1-ethylquinolinium, quinaldinium, and lepidinium iodides with $Na_2S_2O_4$ in 5% $NaHCO_3$ could lead to the isolation of the dihydro-derivatives. The lithium tetrahydroaluminate reduction of *N*-alkylquinolinium salts can produce the unstable 1,2-dihydro-derivatives[49], which are isolated only with difficulty when $Na_2S_2O_4$ is used as reducing agent.

De Mayo and Rigby[50] obtained 1-methylquinolinium, identified as the chloroplatinate, by the $LiAlH_4$ reduction of 1-methylquinolone in ether; however, it was later shown[51] that the $LiAlH_4$ reduction of 1-methylquinolinium iodide and 1-methylquinol-2-one produces 1-methyl-1,2-dihydroquinoline in each case. The reduction of 1-(2,6-dichlorobenzyl)-3-carbamoylquinolinium bromide with $Na_2S_2O_4$ and with $NaBH_4$ produces the same product, a 1-(2,6-dichlorobenzyl)-1,*x*-dihydroquinoline carboxylic acid amide[52]; its chemical properties (stability to acids) and ultraviolet spectrum indicate it to be the 1,4-dihydro-derivative.

With more vigorous reduction of quinolinium compounds, 2 moles of hydrogen are added, forming 1,2,3,4-tetrahydroquinolines. These show all the properties of tertiary amines: they distil with steam, form salts with acids, produce quaternary salts on alkylation, and couple with aromatic diazo-compounds to produce valuable dyes. Nitrous acid produces the nitroso-compounds. Tetrahydroquinolines are also intermediates in the production of valuable pharmaceuticals, and their preparation has accordingly received much attention[53-57].

(b) Other addition reactions. Addition in the 2-position. Freund[58,59] studied the action of CH_3MgBr and C_6H_5MgBr on *N*-methylquinolinium iodide; in each case he obtained the corresponding 1-alkyl-2-alkyl-(or -aryl-)1,2-dihydro-quinoline or -quinaldine, which were readily reduced to the 1-alkyl-1,2,3,4-tetrahydroquinolines. Oxidation produced acylanthranilic acids. In 1954 Bradley and Jeffrey[60] studied the reaction between organometallic compounds and quinolinium salts in more detail, and found that methyl-, ethyl-, propyl-, and butyl-magnesium iodides and bromides, irrespective of structure, react with quinolinium salts to form 2-substituted 1-alkyl-1,2-dihydroquinolines, which on heating give the 2-substituted quinolines. Oxidation of the dihydro-compounds with iodine in alcoholic solution produces the 1,2-disubstituted quinolinium iodides:

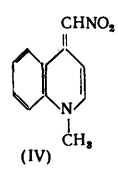


Bradley and Jeffrey were the first to study the reaction between quinolinium salts and dialkylcadmiums.

Boiling an aqueous solution of a quinolinium salt with piperidine produces the 2-addition product[61].

(c) Addition in the 3-position. ω-Chloroacetophenone reacts with the quaternary salts in alcoholic alkali solution to form the 3-phenacyl-derivatives[62].

(d) Addition in the 4-position. The reaction of quinolinium salts with nitromethane was studied by Leonard and coworkers[63], who found that the reaction product, despite Kaufmann's statement[64], has the structure (IV):

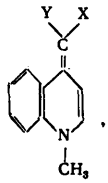


(IV)

This was shown by reducing (IV) over Raney nickel to the amine, the benzoyl derivative of which was found to be

identical with the benzoyl derivative of 1-methyl-4-aminomethyltetrahydroquinoline prepared from 1-methyl-4--cyanodihydroquinoline. Nitromethane also adds to *N*-methylquinaldinium iodide, but *N*-methyllepidinium iodide does not give a crystalline product.

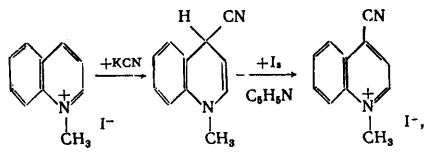
Malononitrile and cyanoacetic ester add in the 4-position of quinolinium compounds in the same way as nitromethane (V):[65]



(V)

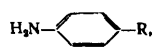
where X = Y = CN, or X = $COOC_2H_5$, and Y = CN. Thus the condensation of *N*-(2,4-dichlorobenzyl)quinolinium bromide with malononitrile produced *N*-(2,4-dichlorobenzyl)-4--dicyanomethylene-1,4-dihydroquinoline in 90% yield[62]; under the same conditions ethyl cyanoacetate produces *N*-(2,4-dichlorobenzyl)-4-ethoxycarbonylcyanomethylene--1,4-dihydroquinoline. Leonard and Foster[66] showed that the reaction between *N*-methylquinolinium iodide and phenylacetonitrile produces 1-methyl-4-(α-cyanobenzyl)-1,4-dihydroquinoline, and not *o*-$CH_3NHC_6H_5CH{=}CHCH_2C_6H_4CN$ or 1-methyl-2-(α-cyanobenzyl)-1,2-dihydroquinoline, which Kaufmann[64] had earlier considered to be the product of condensation of *N*-methylquinaldinium sulphate with phenylacetonitrile.

With potassium cyanide, quinolinium salts give the 1,4-addition products:



which are converted into the quaternary salts by the action of iodine in the presence of pyridine[67].

(e) Addition to form adducts. Quinolinium salts tend to form coloured adducts with aromatic diamines and phenols[68-70]. Izmail'skii and Solodkov[71] showed that quinolinium compounds react with secondary and tertiary monoamines to form intensely coloured complexes which are decomposed by water; by choosing a suitable solvent, however, they can sometimes be isolated in the crystalline form. By reaction with hydroquinone or 1- or 2-naphthol, quinolinium salts give products of various shades of yellow. Mikhailenko and Minaf'ev[72] reported the formation of red products by the reaction of *N*-benzylquinolinium chloride with aniline, *p*-toluidine, diphenylamine, *p*-nitraniline, and piperidine, but incorrectly ascribed to them the structure of polymethine dyestuffs. Vompe[73] studied the reaction of *N*-benzylquinolinium chloride with primary amines of the formula:



where R = CH_3, Cl, Br, I, NO_2, OCH_3, or OC_2H_5; he obtained products of the formula:

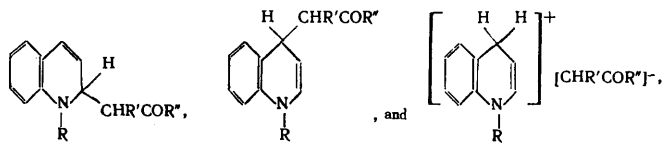
$$C_9H_7\overset{+}{N}CH_2C_6H_5 \cdot H_2NC_6H_4R\text{-}n \quad Cl^-,$$

which were shown to be of complex structure, but crystalline adducts could not be isolated. The reaction of the same quinolinium salt with benzidine gave a crystalline product of formula:

$$(C_9H_7\overset{+}{N}CH_2C_6H_5, Cl^-)_2 \cdot (H_2NC_6H_4C_6H_4NH_2)_3.$$

The structure of the complexes remains an open question. Vompe considers that the bonding and the state of colour are due to intermolecular interaction of the type discussed by Izmail'skii[74,75]. Later the optical properties of the complexes of 2-*p*-dimethylaminostyrylquinoline with ethyl-2-styrylquinolinium iodide, etc. were studied[76], and it was suggested that there is here a special type of π bond, the *exo-bond*, differing from a normal π bond in that there is no accompanying σ bond.

Kröhnke and Vogt[61] have shown that quinolinium salts form adducts with methyl- or methylene-ketones. Of the three possible structures for the adducts:



the last is the most probable. Oxidation of the adducts with $AgNO_3$, benzoquinone, or *p*-nitrosodimethylaniline produces 4-acetonylidene- or 4-benzal-1,4-dihydroquinolines; oxidation with $KMnO_4$ gives 2-acetonylidene- or 2-benzal-1,2-dihydroquinolines[77]. Under mild conditions bromine reacts with the adducts to form the 3-bromoquinolinium salts.

2. Substitution Reactions

The direct nitration, sulphonation, and halogenation of quinolinium salts have hardly been studied, since the desired groups (NO_2, SO_3H, halogen, etc.) can be introduced into the tertiary base (quinoline) before its quaternisation, or, even earlier, into the aromatic amine (or amine precursor) before its conversion into the quinoline. In the former case the substituting group can enter either the pyridine or the benzene ring of the quinoline nucleus, and in the latter case only the benzene ring.

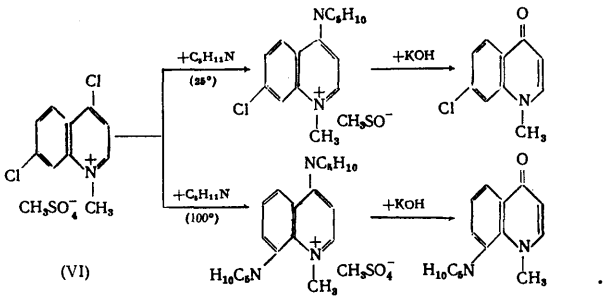
There is, however, an indication that nitration of *N*-ethylquinolinium nitrate produces the 5-nitro-derivative[78].

Halogen atoms present in the 2- or 4-position in quinolinium salts are labile and are easily replaced by other atoms or groups. This can be used to obtain cyanine dyes, which are valuable photographic emulsion sensitisers, or to obtain intermediates from which cyanine dyes can be produced. This type of reaction has been most studied.

An iodine atom in the 2-position of quinolinium salts is readily replaced by various thioether groups in the presence of triethylamine[79].

4-Halogenoquinolinium compounds are used to determine the structure of isocyanines[80], and 2-iodo- and 2-alkylthioquinolinium salts are used in the production of pseudocyanines. The hydrolysis of 4,7-dichloro-1-methylquinolinium methyl sulphate with aqueous alkali produces a mixture of 4,7-dichloro-1-methylquinol-2-one and 7-chloro-1-methylquinol-4-one[81]. The corresponding

iodide does not give quinolones on oxidation[82]. With aliphatic and aromatic amines and their hydrochlorides[81] the 4-chloro-atom is replaced by the amino-group even at room temperature, and the 7-chloro-atom is similarly replaced at elevated temperature:

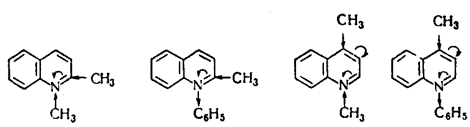


(VI)

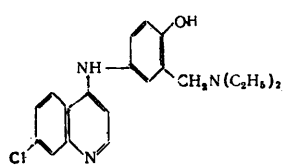
The reaction of (VI) with 4-amino-2-diethylaminomethylphenol dihydrochloride produces the quaternary salt (VII) of the antimalarial drug "Amodiaquin".†

When boiled with alcohol in the presence of triethylamine, 4-alkoxyquinolinium salts can exchange the alkoxy-radical for the alcohol residue[83].

Substitution reactions at 2- and 4-methyl groups. The hydrogen atoms of methyl groups in the 2- and 4-positions of quinolinium salts are highly labile, and can be replaced by various groups; with longer alkyl chains the hydrogen atoms on the α-carbon atom are labile. Replacement of an electron-donating group, *e.g.* methyl, on the ring nitrogen atom by an electron-withdrawing group, *e.g.* the phenyl radical, increases the lability of the hydrogen atoms, and hence the activity of these compounds

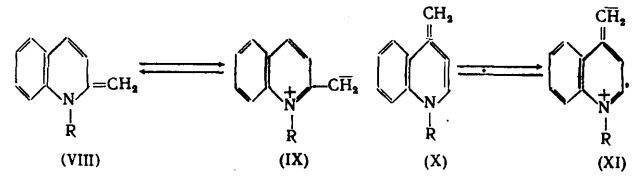


† Equation omitted from Russian text. Amodiaquin (VII) is:



(Ed. of Translation).

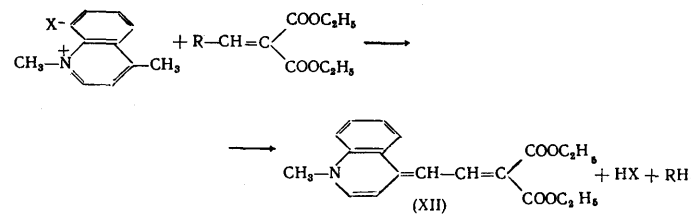
Under the action of bases, quinaldinium and lepidinium salts lose hydrogen to form the so-called methylene bases (VIII) and (X):



(VIII) (IX) (X) (XI)

which were isolated at low temperatures[84]. Compounds (VIII) and (X) can be presented as the bipolar ions (IX) and (XI), *i.e.* as betaines, which are typical nucleophilic reagents, and because of this Kharkharov[85] put forward an expanded form of the Porai–Koshits rule[86] for the activity of the methyl group.

Quinaldinium and lepidinium salts react with alkylidenemalonic esters to give the corresponding 4-methylene-1,4-dihydroquinoline derivatives (XII):[87,88]

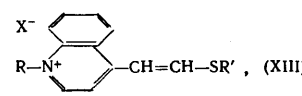


(XII)

where R = OH, OAlk, or NHAr.

Quinaldinium and lepidinium toluenesulphonates react with the acetal of β-ethylthioacrolein to form 1-methyl-4(2)-ω-ethylthiobutadienylquinolinium salts[89]. Ketomethylene compounds containing a thioether group react with lepidinium and quinaldinium salts to give cyanine dye intermediates[90]

Lepidinium salts react with trithioorthoformic ester to produce compounds of type (XIII):[91]

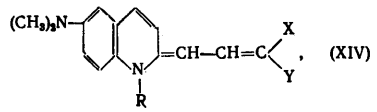


(XIII)

and as a consequence it was shown that trithioacetals react with the quaternary salts to form intermediates and symmetrical trimethinecyanines[92,93]. Halogenation of quinaldinium and lepidinium salts replaces all three hydrogen atoms of the active methyl group by halogen[94,95].

Nitroalkenes add on to the active methyl group of *N*-methylquinaldinium iodide[96,97]. Reduction of the resulting condensation products gives the corresponding amines, and hydrolysis with hydrochloric acid gives the carboxylic acids. The quaternary salts condense with mono-, di-, and tri-bromoacetaldehyde, chloral, and compounds containing

an active methylene group; thus 1-alkyl-6-dimethylaminoquinaldinium salts react with unsaturated esters and ketones to form compounds (XIV):[98,99]



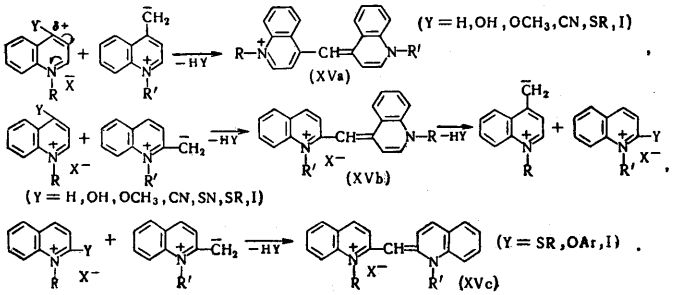
(XIV)

where R = CH_3, X = OCH_3, and Y = $COOC_2H_5$; R = C_2H_5, X = $COCH_3$, and Y = $COOC_2H_5$; and R = CH_3, X = Y = = $COCH_3$.

3. Reactions Forming Quinolinium Dyes

Quinocyanine dyes. Reactions of quinolinium salts, which lead to the formation of cyanine dyes, have been the most widely studied, because the cyanine dyes are used as sensitisers for photographic emulsions. Many reviews on the chemistry of all types of cyanines have been published[100-105].

(a) Monomethinecyanine dyes. As stated above, quinolinium compounds containing a methyl group in the 2- or 4-position readily lose a proton in the presence of bases, forming the bipolar ions (IX) and (XI), which readily react with quinolinium compounds in the 2- or 4-position. Unsubstituted quinolinium salts add the nucleophilic reagent (IX) or (XI), always in the 4-position. If the quinoline ring is substituted in the 2-position by I, OAr, SR, or CN, the addition takes place at this position; with such groups in the 4-position, reaction proceeds more readily than with the unsubstituted compounds. The reactions can be shown thus:



(Y = H, OH, OCH_3, CN, SR, I)

(XVa)

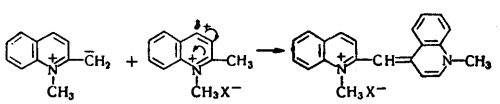
(XVb)

(Y = H, OH, OCH_3, CN, SN, SR, I)

(Y = SR, OAr, I)

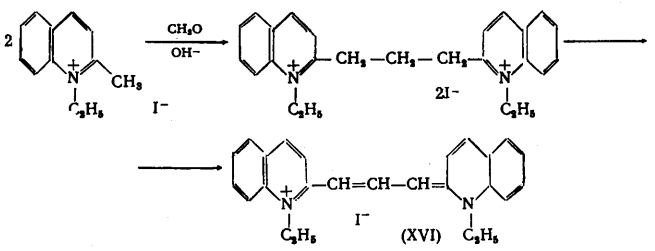
(XVc)

Quinaldinium compounds react as follows[4,106,107]:



The first dye of type (XVa) was obtained by Williams[108], and named cyanine because of its blue colour. The dyes of type (XVb), named isocyanines, were discovered simultaneously by Spalteholz[109] and Hoogewerff and van Dorp[4,106]. The pseudocyanines (XVc) were first prepared by Kaufmann and Wonderwahl[107], and their structure proved by Scheibe and Rossner[110]. All these compounds contain a single methine group and are called monomethinecyanines. They are prepared by heating alcoholic solutions of the reactants with bases such as KOH, K_2CO_3, CH_3COONa, diethylamine, triethylamine, and piperidine. This method can also be used to obtain asymmetric quinocyanines in which the second heterocyclic ring is not a quinoline ring; thus a series of thiaquinomonomethinecyanines has been prepared by reacting *N*-methylthiobenzothiazolium salts with quinaldinium or lepidinium salts in the presence of sodium acetate[111]. Monomethinequinocyanines have been prepared containing benzothiazole[112], diazole, pyrimidine[113], and other rings[114-139].

(b) Trimethinequinocyanines (carbocyanines). Quinolinium dyes containing two quinoline nuclei joined at the 2- or 4-position by a bridge of three methine groups are known as trimethinecyanine or carbocyanine dyes. The first dye of this type (XVI) was prepared by condensing *N*-ethylquinaldinium iodide with formaldehyde in alkaline medium[140]. The formation of (XVI) (which is known as pinacyanol or sensitol red) is shown by the equation:



(XVI)

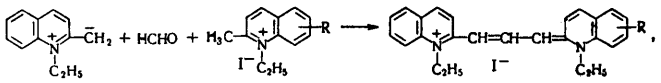
Of other methods for obtaining carbocyanines, Hamer's method[141] has found practical application. Dyes derived from lepidinium salts, where the bridge is at the 4-position, are known as cryptocyanines[142]. The trimethinecyanine dye containing one quinaldinium and one lepidinium ring can be obtained from the corresponding salts and di-*o*-(formylmethylamino)diphenyl disulphide in pyridine[143]. The reaction of 2- or 4-methylquinolinium salts with chloroform and Na_2S produces a dicyanine, pinacyanol, and cryptocyanine[144-146].

The preparation of trimethinecyanines by condensing the quaternary salts with thioformanilide, thioformamide, or formamidoxime has been suggested[147], using as condensing agents organic bases (triethylamine or pyridine), sodium acetate, acetic anhydride, or alkali metal hydroxides or carbonates[148]. Zenno[149,150] used 2-aminothiazole, formanilide, diphenylmethane, phenylacetonitrile, 2-amino-4-methylthiazole, acetamide, acetanilide, etc., as condensing agents for the production of trimethinecyanines from quinaldinium salts and orthoformate; best results were obtained with acetamide and acetanilide[150]. Brooker and Heseltine[151] prepared a number of trimethinequinocyanines with *N*-carbamoylmethyl groups; these are of use for sensitising silver halide emulsions.

Al'perovich and Ushenko[152] prepared a series of symmetrical quinocyanines containing unsaturated substituents at the 5- and 6-positions.

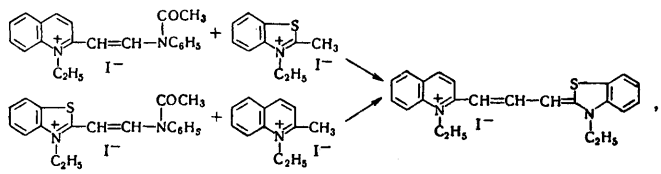
Symmetrical carbocyanines derived from lepidine having hydroxy-groups in the 6- and 7-positions have been prepared[153]. The reaction of hydroxyquinaldinium salts with diphenylformamidine in the presence of carboxylic acid anhydrides produces intermediates suitable for the production of asymmetrical dyes, the hydroxy-groups being acylated[154]. Takahashi and Satake[155] have prepared dimethylamino-substituted quinocarbocyanines, and also other analogous dyes[156,157]. Pailer and Kuhn[158] obtained trimethinecyanines from 7-acetamido-1-ethyl-2,4-dimethylquinaldinium iodide and ortho-esters of monocarboxylic

acids; a mixture of the 2,2'-, 2,4'-, and 4,4'-trimethinecyanine dyes would be expected, but chromatography showed that the product was mainly the 2,2'-derivative, with two dyes absorbing at longer wavelengths (the 2,4'- and 4,4'--derivatives). Asymmetrical quinocarbocyanines were first prepared by Mills and Raper[159]:

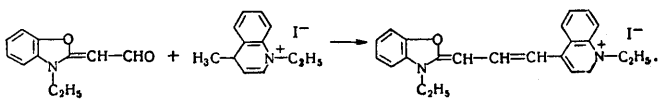


where R = 6-CH_3 or 5,6-benzo.

The most widely used method for obtaining asymmetrical carbocyanines is that of Piggott and Rodd[160], in which aminovinyl derivatives of quaternary salts are heated with other heterocyclic *N*-containing quaternary salts containing an active methyl group:

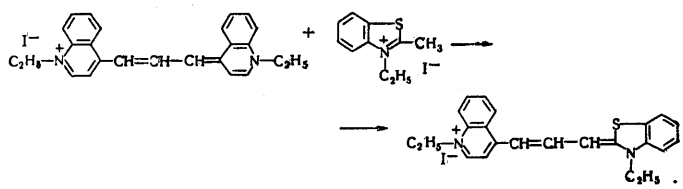


Somewhat later it was suggested that asymmetrical carbocyanines could be prepared from lepidinium or quinaldinium salts and formylmethylene compounds[161].

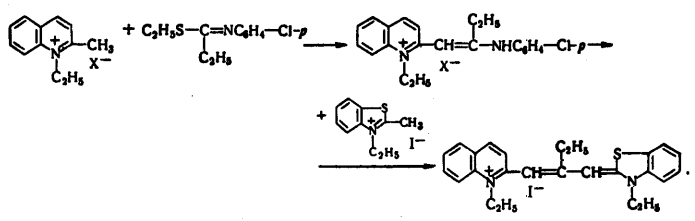


Other work which should be mentioned is that of Kiprianov and Stetsenko[162,163] on the preparation of carbocyanines with the quinone nucleus, and the preparation of quinobenzimidazolecarbocyanines[164] and quinothiadiazolecarbocyanines[165,166].

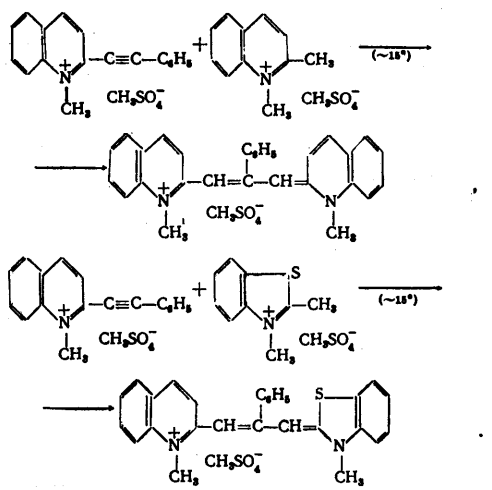
A new method for the production of asymmetrical carbocyanines, proposed by Ogata and Noguchi[167], is illustrated by the reaction:



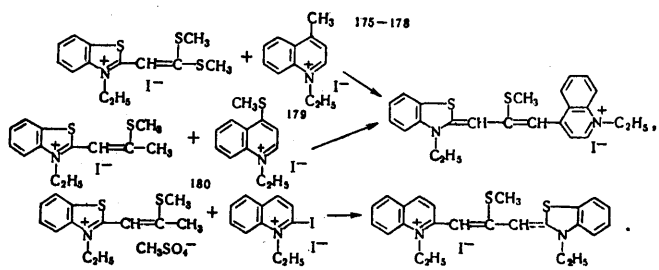
Symmetrical carbocyanines with an alkyl group on the trimethine chain can be obtained by using homologues of orthoformic ester, *e.g.* orthoacetic and orthopropionic esters, in place of the orthoformic ester. Symmetrical and asymmetrical trimethinecyanines with an alkyl radical in the *meso*-position can be prepared from acylmethylene compounds[168,169]; other asymmetrical quinocarbocyanines, derivatives of benzothiazole and benzoselenazole with *meso*-substituents, are prepared similarly[170]. Nawiasky and Speer[171] developed another method for the production of such dyes, which may be illustrated as follows:



When quinaldinium and lepidinium salts react with methyl dithioacetate, symmetrical 10-methyl trimethinecyanines are obtained as by-products. A method for the simultaneous production of *meso*-alkyl carbocyanines and thioketones has been found[172]. Kiprianov and Dyadyusha[173] have proposed an interesting method for obtaining *meso*--phenylquinocarbocyanine dyes of symmetrical or asymmetrical structure:

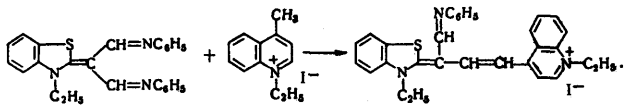


Schultz[174] prepared 1,1'-diethyl-6,6'-dimethylquinoline--*meso*-(ethylthio)trimethinecyanine iodide by condensing ethyliminodithiocarboxylic acid diethyl ester with 1-ethyl--2,6-dimethylquinolinium iodide. Other methods for the production of *meso*-(alkylthio)carbocyanines are illustrated by the following:



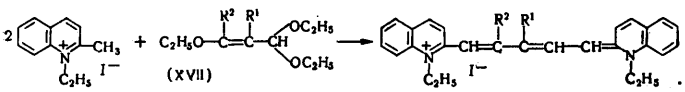
When these dyes are boiled with ammonia or primary or secondary amines, the SCH_3 group is replaced by the amino--group; OR and SeR groups on the polymethine chain are similarly replaced by the amino-group[177].

These dyes are useful for sensitising photographic emulsions, as filter dyes, etc. They differ from the dyes with an SR group on the polymethine chain in that the absorption maximum occurs at shorter wavelengths; they are also stable to aqueous alkalis. Hamer and coworkers[181] prepared trimethinecyanine dyes with an anilinomethyl group in the *meso*-position‡; these are used as intermediates for preparing trinuclear dyes. The method can be illustrated as follows:

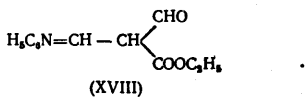


N-Ethylquinaldinium iodide reacts with $C_6H_5NHCCl_2$ to form a *meso*-substituted trimethinecyanine with the anilino-group in the 10-position[182]. Methods have been developed for the preparation of carbocyanines with the CN group in the polymethine chain[183,194].

(c) Pentamethinequinocyanines (dicarbocyanines). Pentamethine dyes are the vinyl analogues of the trimethines, and are used as sensitisers for photographic emulsions in the infrared region. They were first obtained by König[185] by condensing the quaternary salts with β-ethoxyacrolein acetal (XVII), the vinyl analogue of orthoformic ester. The acetal may be substituted in the α- or β-position, when chain-substituted pentamethinecyanine dyes are obtained[186]:

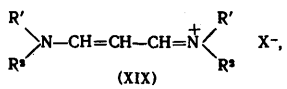


Kendall and Edwards[187] replaced compound (XVII) by its thio-analogue $C_2H_5SCH{=}CHCH(SC_2H_5)_2$. Compound (XVIII) reacts with quinaldinium salts to form dicarbocyanines with the ethoxycarbonyl group in the methylene chain[188].



(XVIII)

β-Formyl-β-chloro-α-phenoxyacrylic acid reacts with 1-ethylquinaldinium iodide in ethanol in the presence of triethylamine, giving off CO_2 and forming a dye[189]. The use of β-anilinoacrolein anil can give symmetrical or asymmetrical pentamethinequinocyanines[190-192]. The anil can be replaced by its derivative:

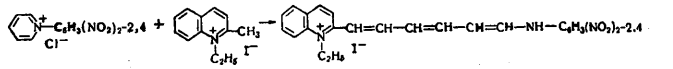


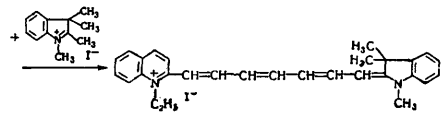
(XIX)

in which case the reaction is carried out in alcoholic solution in the presence of pyridine or piperidine[193]. Asymmetrical dicarbocyanines can be obtained from (XIX) in acetic acid[194] or β-anilinoacrolein anil hydrochloride in pyridine solution[195]; this last method can provide dicarbocyanines with an alkyl group on the polymethine chain[196].

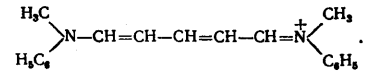
Quinaldinium and lepidinium salts also form dicarbocyanines with 1,1,3,3-tetraalkoxypropane or 1,1,3,3-tetraacyloxypropane in pyridine[197]; good yields are obtained. Methods are also known for preparing dicarbocyanines with a CN group in the *meso*-position[183,184].

(d) Heptamethinecyanine dyes (tricarbocyanines) of the quinoline series can be prepared by condensing quinaldinium or lepidinium salts with compounds containing five methine groups and having, at the ends of the chain, groups which are readily split out; or with compounds which can react during the condensation to form a pentamethine group. Wahl[198] used pyridine salts which can decompose to form derivatives of glutaconic aldehyde; symmetrical and asymmetrical dyes can be produced, since the reaction takes place in two stages:





Best results are given by using, instead of the pyridinium salts, their amine reaction products, *e.g.* (XX):[191]



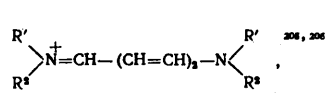
(XX)

The condensation is carried out in alcoholic solution in the presence of inorganic[199] or organic[200] bases.

4,4′-Tricarbocyanines (xenocyanines) are said to be obtained by condensing 2 moles of a lepidinium salt with 1 mole of glutaconic aldehyde hydrohalide in the presence of an organic base stronger than pyridine[201]. The dianilide may be substituted in the polymethine chain[202]. Dyes of this type, and also their 2,2′-analogues, have been prepared from lepidinium or quinaldinium salts and benzoxazolepyridinium chloride[203], which decomposes during the reaction to produce the polymethine chain.

Tricarbocyanines can also be formed by the action of quinaldinium or lepidinium salts on the reaction product of 1-ethyl-2-iodoquinolinium iodide with pyridine, 1-ethyl-2-(1-pyridinium)quinolinium diiodide[204].

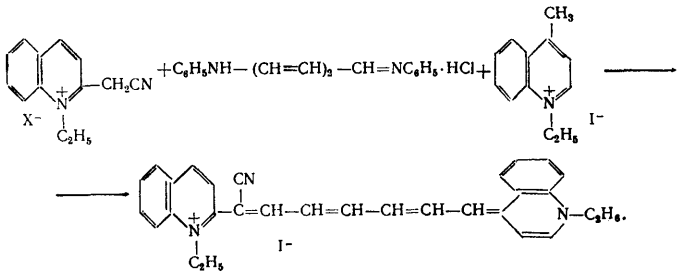
Asymmetrical heptamethinecyanines can be obtained analogously to the pentamethinecyanines by condensing a quinaldinium salt and another heterocyclic quaternary salt in two stages with



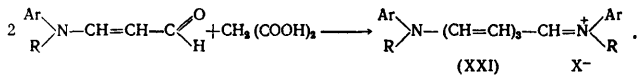
pyridylpyridinium chloride[205], glutaconic aldehyde tetraacetal[206], or a salt thereof[209]. Similar dyes can be obtained by condensing a heterocyclic pentamethine aldehyde with a heterocyclic quaternary salt containing a methyl group[210].

‡ Presumably the authors are referring to the 3-ethyl-2-(dianilinoisopropylidene)benzothiozoline at this point (Ed. of Translation).

Kendall and Doyle[183,184] prepared tricarbocyanines with a CN group on the polymethine chain:

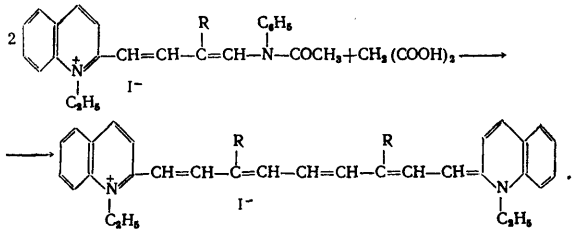


Tetra- and penta-carboquinocyanines, which show a sensitisation maximum at 940 and 1120 mμ respectively, have also been prepared, using a compound of type (XXI) for forming the bridge[212-214]:

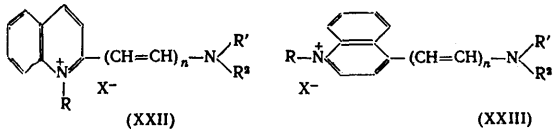


(XXI)

Ogata[215] developed a method for preparing nonamethine-quinocyanines:

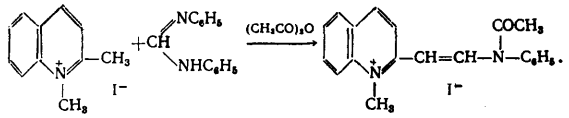


(e) Hemiquinocyanine dyes have structure (XXII) or (XXIII):



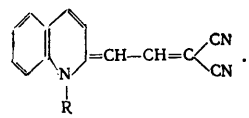
(XXII) (XXIII)

A special case is when $n = 1$, *i.e.* the aminovinyl derivatives, which are intermediates in the production of asymmetrical carbocyanines. They were first obtained by heating a quinaldinium salt with diphenylformamidine in acetic anhydride[216,217]:



Takahashi and coworkers[218-221] prepared a series of aminovinyl compounds by fusing quinaldinium salts with formamidine; the products have been used as pharmaceutical dyes. Heating quinaldinium or lepidinium salts with a diarylformamidine in the presence of orthoformic ester in an alcoholic medium produces the aminovinyl derivatives in higher yields[222,223]. Analogous aminovinyl compounds can be obtained by heating the quaternary salts with orthoformic ester and a primary or secondary amine[224-227]. The production and investigation of a number of aminovinylquinolinium derivatives have been reported[228-230]. Similar studies by Japanese chemists were carried out to find the optimum conditions for preparing these compounds and to investigate their pharmacological properties[156,231-233].

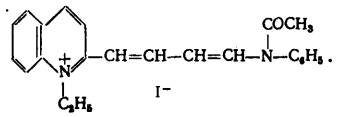
The condensation of phenylhydrazine or *N*-ethylphenylhydrazine with ethyl orthoformate and quinolinium salts produces the phenylhydrazinovinyl derivatives. Pilyugin and coworkers[234] obtained the anilinovinyl derivatives of *N*-arylquinolinium salts by reacting diphenylformamidine with *N*-phenylquinaldinium perchlorate and with *N*-phenyl-5,6-benzoquinaldinium iodide. The acetanilidovinyl derivatives react with malononitrile in the presence of an organic base to form (XXIIIa), which is used as a supersensitiser for silver halide emulsions[235]:



(XXIIIa)

The arylamino- and acylarylamino-vinyl derivatives are hydrolysed in aqueous alcohol to the formylmethylene compounds[236-238].

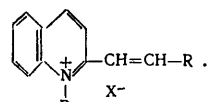
By replacing diphenylformamidine by its vinyl analogues (*e.g.* $C_6H_5NH-CH=CH-CH=NC_6H_5$), quinolinium compounds with a longer chain in the 2- or 4-position can be obtained[190-192]:



To obtain a hexamethine chain, the quaternary salts are condensed with the product obtained by first condensing the salt with *N*-dinitrophenylpyridinium chloride[198].

(f) Styrylquinolines. Quinostyryl dyes can be considered as derivatives of styrene, from which they are in fact named.

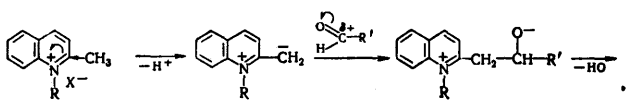
Quinostyryl compounds with a quaternary nitrogen atom (XXIV) are cyanine dyes:



(XXIV)

They were first obtained by Kaufmann and Vallette[239] from quinolinium salts containing an active methylene group and aromatic aldehydes in alcoholic solution in the presence of piperidine; pyridine or acetic anhydride can also be used

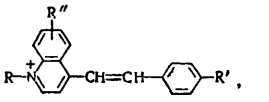
as reaction medium. Mills and coworkers[159] have studied the mechanism of this reaction. Electronically, the reaction can be represented:



(XXIV)

The preparation of these dyes has been much studied, since they are used as sensitisers, supersensitisers, and desensitisers for photographic emulsions, and are also physiologically active. In 1934 Atabekova *et al.*[240] prepared 6-ethoxy-1-methyl-2-(*m*-nitrostyryl)quinolinium methyl sulphate (Pinakryptol Yellow), which has a desensitising action. Mikhailov and Pryanishnikov[241] proposed the production of analogous compounds by condensing various quinaldinium salts with 3-nitrobenzaldehyde or 4-dimethylamino-3-nitrobenzaldehyde in the presence of alcohols containing more than two carbon atoms; there is also an analogous American patent[242]. Maurin[243] showed that *N*-methyl- and *N*-ethyl-4-hydroxyquinaldinium iodide forms styryl dyes with *p*-dimethylaminobenzaldehyde, cinnamaldehyde, vanillin, and anisaldehyde in the presence of piperidine; benzaldehyde does not react. Meyer and coworkers[244] carried out a similar condensation of 6- and 8-methyl-4-hydroxyquinaldinium salts and the corresponding 4-alkoxy- and 4-chloro-derivatives with salicylic, cinnamic, and anisic aldehydes, and with piperonal, vanillin, and dimethylaminobenzaldehyde in the presence of traces of piperidine or diethylamine, but in the absence of a solvent. 3-Dialkylaminostyrylquinolinium salts have been obtained by condensing 3-dialkylaminobenzaldehydes with quinaldinium salts in piperidine[245].

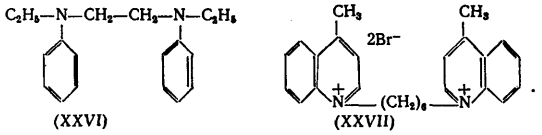
The condensation of 1-methyl-4-phenoxyquinaldinium iodide with piperonal in the presence of triethylamine produces 1-methyl-2-(3,4-methylenedioxystyryl)-4-phenoxyquinolinium iodide[246]. If a secondary amine, *e.g.* piperidine, is used as catalyst, the phenoxy-group is replaced by the amino-group. 2-Amino-4-styrylquinolinium compounds have been prepared and their pharmacological properties studied[247]. Stanek and Zvěřina[248] showed that 1-methylquinaldinium iodide reacts with benzaldehyde in the presence of piperidine or morpholine to form 1-methylstyrylquinolinium iodide. Doja and Sinha[249,250] prepared styryl compounds by condensing *p*-dimethylamino- and *p*-diethylamino-benzaldehyde with 6-amino-, 6-formamide-, 6-acetamido-, 6-chloro-, 6-bromo-, and 6-iodo-1-ethylquinaldinium iodides; the 1-ethyl-6-formamido- and -acetamido-styrylquinaldinium iodides were found to be very good sensitisers. *cis*- and *trans*-isomers of 2-styrylquinolinium compounds have been prepared[251]: condensing quinaldinium salts with aromatic aldehydes in the presence of piperidine gave the *trans*-isomers; reacting the quinaldines with the aldehydes in acetic anhydride gave the *cis*-2-styrylquinolines, which were then quaternated. Ito and Matsumura[252] obtained a high yield of the iodide of *trans*-1-(1′-ethylquinol-2′-yl)-2-(8″-hydroxyquinol-5″-yl)ethylene by heating an equimolar mixture of 5-formyl-8-hydroxyquinoline and 1-ethylquinaldinium iodide in acetic anhydride or propan-2-ol in the presence of piperidine. Heating quinaldine with 5-formyl-8-hydroxyquinoline in acetic anhydride gives 1-(8-hydroxyquinolyl)-2-(quinol-2-yl)ethylene, which with an alcoholic solution of ethyl iodide produces the *cis*-isomer, which is not converted into the *trans*-isomer by boiling with acetic anhydride. The *cis*- and *trans*-isomers of 1-ethyl-2-(3′-methoxy-4′-hydroxystyryl)quinolinium iodide were obtained similarly from vanillin and 1-ethylquinaldinium iodide or quinaldine. The condensation of 1-methylquinaldinium iodide with veratryl aldehyde in the presence of morpholine gives 1-methyl-(3,4-dimethoxybenzylidene)-quinaldinium iodide, which is hydrogenated to *d,l*-cuspareine in the presence of platinum[253]. Bahner and coworkers[254] prepared a number of 1-alkyl-4-(*p*-dimethylaminostyryl)quinolinium iodides (XXV) to study their anti-tumour activity:



(XXV)

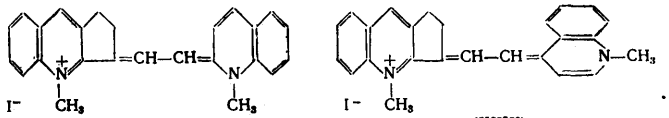
where R′ = $(CH_3)_2N$, CH_3CONH, NO_2, or F, and R″ = H, 6-I, 3-CH_3, 8-CH_3, or 8-C_6H_5.

Styrylquinolinium compounds containing two or more styryl groups have been prepared by condensing compounds of type (XXVI) with 2- or 4-methylquinolinium salts[255], or condensing substituted monoarylaldehydes with alkylene-bis-quinolinium salts of type (XXVII):[256]



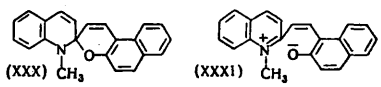
(XXVI) (XXVII)

Lal and Petrow[257] condensed 2,3-dihydroquinindene ethyl iodide with 2- or 4-(2-anilinovinyl)-1-methylquinolinium iodide to obtain the quinostyryl analogues (XXVIII) and (XXIX):



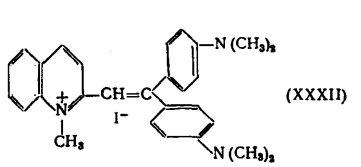
(XXVIII) (XXIX)

The reaction between *N*-methylquinaldinium methyl sulphate and 2-hydroxy-1-naphthaldehyde in the presence of piperidine has produced 1-methyl-α-(2-hydroxy-1-naphthylidene)quinaldinium perchlorate, which is converted by ammonia into the compound of structure (XXX) or (XXXI):[258]



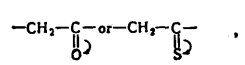
(XXX) (XXXI)

Philips[259] prepared styrylquinolinium analogues by condensing cinchoninic aldehyde with 2- or 4-methylquinolinium salts. Michler's ketone does not react with quinaldinium salts in acetic anhydride, but the methyl sulphate salt of the *N*-methyl derivative of the corresponding thioketone has given the dye (XXXII) with maximum absorption at 538 mμ:[260]



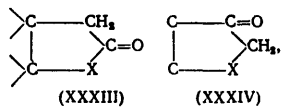
(XXXII)

(g) Non-ionic dyes. Meroquinocyanines. Cyclic (including heterocyclic) compounds containing the group



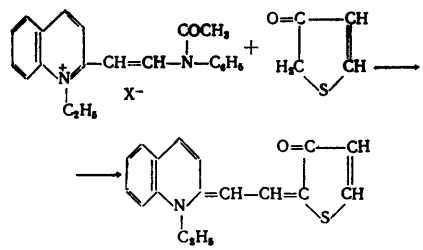
possess labile hydrogen atoms and therefore readily react with quinolinium compounds containing active groups, to form non-ionic polymethine dyes known as merocyanines. These are highly soluble in non-polar solvents and exhibit solvatochromism[261].

Kendall[262] first prepared a number of meroquinocyanine dyes in 1933 by reacting organic compounds of the formula (XXXIII) or (XXXIV):

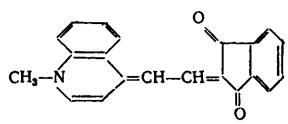


(XXXIII) (XXXIV)

where X = C, S, or O, with quinolinium salts substituted in the 2- or 4-position by halogen atoms or thioether, seleno-ether, aminovinyl, or methyl groups, usually in the presence of basic catalysts:



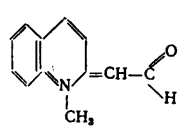
Heating acetanilidomethenylindane-1,3-dione with 1-methyllepidinium iodide in pyridine gave the dye (XXXV):



(XXXV).

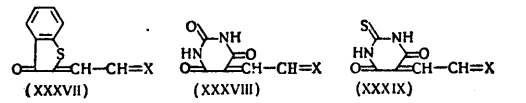
As ketomethylene component there may also be used rhodanine, thiohydantoin, etc.[263] Quinolinium salts substituted in the 2- or 4-position by halogeno-, cyano-, or thio--ether groups react with keto- or thioketo-methylene compounds to form dyes not containing methine groups[264-268].

Formylmethylene bases such as (XXXVI) also form merocyanines with ketomethylene-substituted cyclic compounds[269]:

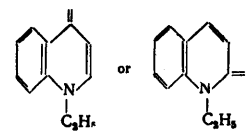


(XXXVI).

Brooker[270] has prepared a series of dimethinerhodanines (XXXVII)–(XXXIX) by reacting quinolinium salts 2- or 4-substituted by an *N*-arylaminovinyl group, with 2(1)-thionaphthenone, thioindoxylic acid, or barbituric acid or its derivatives:

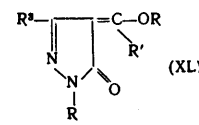


(XXXVII) (XXXVIII) (XXXIX)

where X =  or

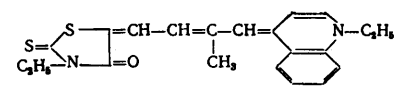
Improved yields are obtained by using alkali metal hydroxides, carbonates, or alkoxides as condensing agents[271].

Compounds (XL), obtained by boiling the pyrazolone derivative with the ortho-ester of a monocarboxylic acid, react with *N*-ethylquinaldinium iodide to form dimethine-merocyanines substituted on the methine chain[272]:

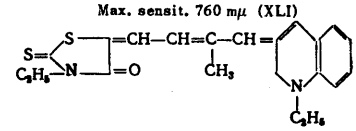


(XL)

The patent literature also refers to the preparation of the tetramethinemeroquinocyanines (XLI) and (XLII), which show maximum sensitising activity in the infrared[273]:

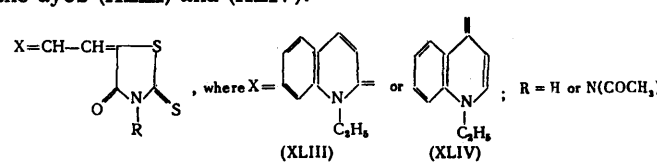


Max. sensit. 760 mμ (XLI)



Max. sensit. 730 mμ (XLII)

The production of oxazolone dyes is described in another patent[274]. Reacting ethylrhodanine with the product obtained from diphenylformamidine and 7-acetamido-1-ethyl--2,4-dimethylquinolinium iodide produces a mixture of isomers, the relative proportions of which depend on the condensation conditions[158]. Sytnik *et al.*[275] have prepared the dyes (XLIII) and (XLIV):



(XLIII) (XLIV)

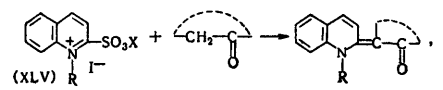
A number of di-, tetra-, and hexa-methinemeroquinocyanines in which the second ring is a rhodanine ring have also been prepared[276]. Similar quinomerocyanines, imidazoline-2-thione-4-one derivatives, were prepared by Jeffreys[277].

Zenno[278] obtained meroquinocyanines by reacting 3-phenyloxazol-5-one, 3-ethylrhodanine, 3-phenylrhodanine, 1-methyl-3-phenylpyrazolone, and 3-hydroxythionaphthenone with 2,2-(*NN'*-diphenylhydrazino)divinylquinoline dimethiodide or diethiodide. The reaction of barbituric acid, thiobarbituric acid, 1,2-diaryl-3,5-dihydroxypyrazolidines, or other heterocyclic diketomethylene compounds

with orthoformic ester and quinaldinium salts also produces meroquinocyanine dyes[279,280]. With malonic ester only symmetrical quinocarbocyanines are obtained[279]. Using acetic or benzoic anhydride instead of the orthoformic ester produces merocyanines methyl- or phenyl--substituted on the polymethine chain[280]. Merocyanines are also obtained if orthoformic ester is condensed with barbituric or thiobarbituric acid, and the resulting dye reacted with 1-methyl- or 1-ethyl-quinaldinium salts[281].

If merocarbocyanines are heated with quinaldinium salts, there is an exchange of heterocyclic nuclei and quinomerocyanines are produced[282].

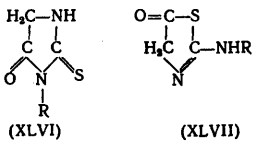
Compounds of type (XLV) react fairly readily with cyclic ketomethylene or thioketomethylene compounds to form merocyanines[283]:



(XLV)

where X = H or Na.

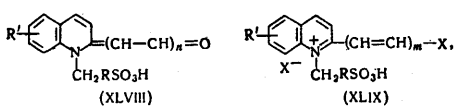
Jeffreys[284] prepared merocyanines from quinolinium salts and (XLVI) or (XLVII):



(XLVI) (XLVII)

Meroquinocyanines with an alkoxy-group on the methine chain are known[285].

Quinomerocyanines with an acylamino-group in the ketomethylene ring have also been prepared[286]. Brooker and Heseltine[287] have obtained merocyanines containing the sulphonic acid group by condensing quinolinium salts having active groups which are readily split out, with a ketomethylene compound $H_2C-SO_2-X-C=O$ (where X represents the atoms making up a five-membered ketomethylene ring). Bach and Brunken[288] prepared merocyanines containing the sulphonic acid group by condensing a quinolinium compound (XLVIII) or (XLIX):

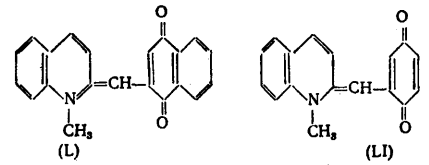


(XLVIII) (XLIX)

where X = alkyl, halogen, SR", or OR", with the five- or six-membered heterocyclic ketomethylene compounds rhodanine, 2-thiohydantoin, 2-thiooxazolid-4-one, pyrazol-5-one, 3-hydroxythionaphthene, barbituric acid, or 2-thiobarbituric acid.

Sytnik and others[289,290] prepared di- and tetra-methinequinomerocyanines containing an electropositive substituent in the α-position, in order to study their optical properties.

(h) Other types of non-ionic dyes. In 1937 Kröhnke[291] described the reaction of *N*-methylquinaldinium iodide with 2,3-dichloro-1,4-naphthoquinone in alkaline medium. Gates[292,293] mixed benzene solutions of 1,4-naphthoquinone and the methylene base derived from *N*-methylquinaldinium iodide to obtain (L):

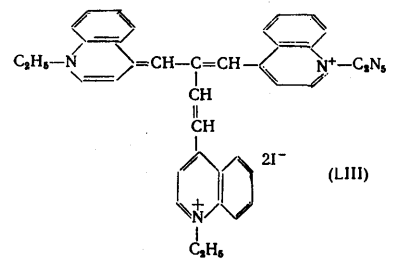


(L) (LI)

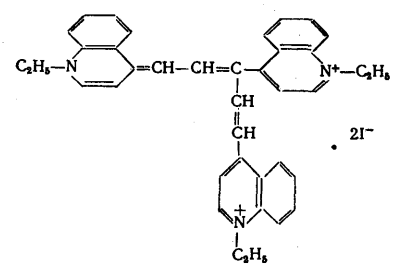
Kiprianov[294] showed that in the presence of alkalis quinaldinium salts react with benzo- and naphtho-quinones to form dyes such as (L) and (LI); the reaction mechanism was given.

Zenno[295] showed that quinaldinium and lepidinium salts react readily with alloxan and 5,5-dibromobarbituric acid to form dyes; with acetylisation, isatin β-anilide and *NN'*-diphenyl-3,5-dioxopyrazolidine, indigo dyes are formed.

(i) Trinuclear quinocyanine dyes. In the production of bis(1-ethylquinol-4-yl)trimethinecyanine iodide from *N*-ethyllepidinium iodide and triethyl orthoformate, small amounts of another dye were formed; this was named Neocyanine[296]. Its structure was investigated by Hamer[297] and König[298], who suggested formulae (LIII) and (LIV):



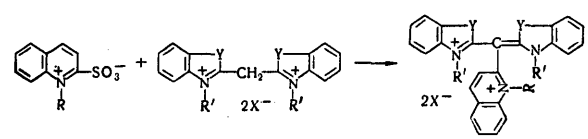
(LIII)



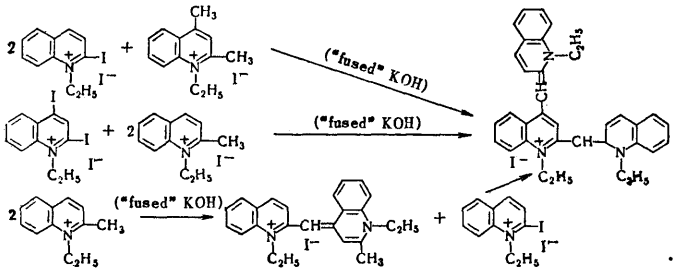
(LIV)

Neocyanine was found to be a very effective infrared sensitising agent for photographic emulsions and to be physiologically active, and it has accordingly been much studied to find optimum conditions for its formation and for the preparation of related dyes with three heterocyclic nuclei[299-317].

Larivé and Collet[318] prepared trinuclear quinocyanine dyes by the reaction:

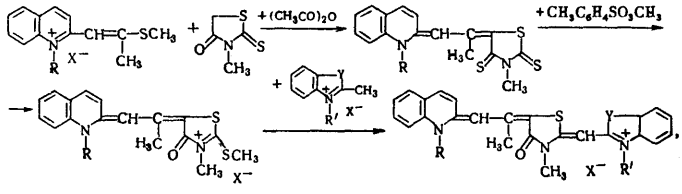


Trinuclear cyanine dyes have been prepared in which the polymethine chain is substituted in the *meso*-position by a pyrrole, pyrrocoline, or indoline nucleus[319]. Trinuclear pentamethinecyanines can be obtained by using the 2-acetanilidovinylquinolinium compound instead of the 2-methylmercapto-derivative. Brooker and Smith[320,321] prepared trinuclear dyes by the reactions§:



It is interesting that the absorption spectra and sensitising action of these compounds consist of two bands separated by a region of full transmission.

A number of trinuclear quinocyanine dyes have been prepared by condensing lepidinium or quinaldinium salts with five-membered heterocyclic thioketomethylene compounds, followed by methylation of the resulting merocyanine and condensation with a quaternary salt, in accordance with the reactions[322,323]:

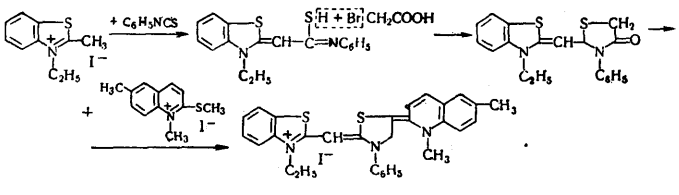


where Y = S, Se, O, or $-CH=CH-$.

Similar dyes are obtained by condensing 5-anilinomethylene-substituted monomethinecyanine derivatives of thiazolin-4-one or pyrazolone with quinaldinium or lepidinium salts[324,325].

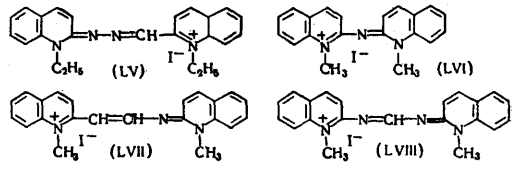
Dyes with a central thiohydantoin nucleus have been prepared[326], and are used in colour photography. Dyes with a central oxadiazole, thiadiazole, or triazole nucleus have also been proposed as sensitisers for colour photography[327-329].

Thompson[330] has prepared a series of trinuclear dyes by the interesting method:

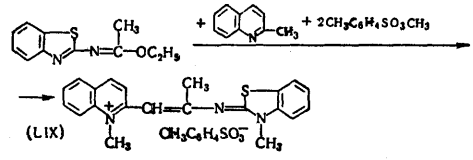


The reaction of thiazolone cyanine dyes with diphenylformamidine, β-anilinoacrolein anil hydrochloride, or glutaconic aldehyde dianil hydrochloride gives anilino- (or acetanilido-) methine derivatives, which produce trinuclear dyes with quinaldinium and lepidinium salts[331]. The optical and photographic properties of such trinuclear dyes (merocyaninecarbocyanines) have been studied by Levkoev and coworkers[332,333].

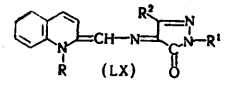
(j) Quinolinium dyes with hetero-atoms in the polymethine chain. Fuchs and Grauaug[334] obtained quinolinium dyes (of the cyanine type) in which the $-CH=CH-$ group is replaced by nitrogen, *e.g.* (LV), by reacting quinolinium hydrazines with appropriate heterocyclic 2-aldehydes. Kendall[335,336] and Hamer[337] prepared the similar dyes (LVI), (LVII), and (LVIII):



Kendall and Fry[338] developed a method for the production of the asymmetrical *meso*-substituted dyes (LIX) by reacting the amino-compounds with ortho-esters and condensation of the intermediates with quinaldine with simultaneous quaternation:

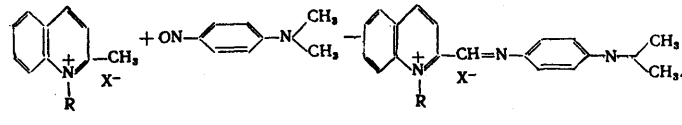


The preparation of the azamerocarbocyanine dyes of the quinolinium series (LX) has been described[339]:



where R^1 and R^2 are H, alkyl, or aryl and R is *n*-alkyl of 1–4 carbon atoms.

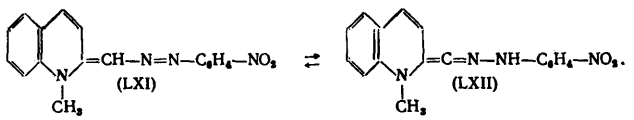
(k) Styryl analogues (azomethines). Hamer[340] obtained a styryl analogue with a nitrogen atom in place of a methine group by reacting a quinaldinium salt with *p*-nitrosodimethylaniline:



The formation of azomethine dyes has been studied in more detail by Katayanagi[341]; they are also produced by condensing quinaldinium or lepidinium salts with 1-ethyl-2-phenyl-3-nitrosoindole[342].

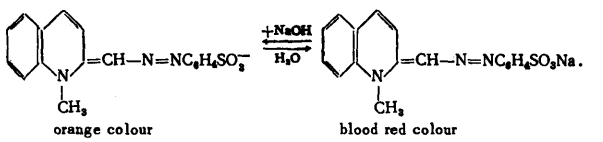
§ "Fused" KOH is not mentioned in either of the papers cited, although one[320] refers to powdered KOH (Ed. of Translation).

Monoazo-compounds of quinaldinium salts, such as (LXI), are obtained by the reaction of diazonium salts with the methylene bases (derived from quinaldinium salts) in neutral ether[343]:



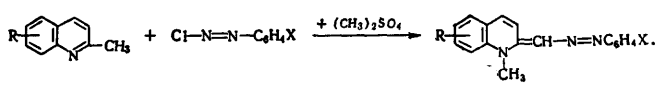
This dye was found to be identical with (LXII), which was prepared from 1-methyl-ω-bromoquinaldinium bromide and *p*-nitrophenylhydrazine[344]. The existence of a tautomeric equilibrium is indicated.

N-Methylquinaldinium iodide and phenyldiazonium chloride react analogously. Under analogous conditions diazotised sulphanilic acid also forms a dye:

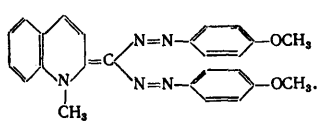


Good yields of the dyes are obtained in each case.

Humphries[345] prepared monoazo-compounds by the action of *p*-nitrophenylnitrosamine or the anti-diazotate on quinaldinium or lepidinium salts. Königs and Büren[346] obtained 1-methylphenylazomethylene-1,2-dihydroquinoline and certain of its derivatives by reacting a quinaldine with a diazo-compound in the presence of dimethyl sulphate in an alkaline medium; there is simultaneous alkylation and azo-coupling:



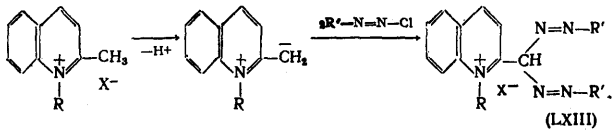
Lepidine reacts analogously. The reaction of 1-methylquinaldinium methyl sulphate with a *p*-methoxyphenyldiazonium salt produces the bis-azo-dye:



These azo-dyes have shown *in vitro* bactericidal activity against staphylococci. It is of interest that 1-methyl-2-methoxylepidinium and 1-methyl-4-methoxyquinaldinium methyl sulphates do not couple with phenyldiazonium chloride in alkaline medium.

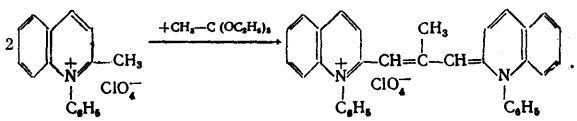
Seyhan[347] prepared the two methylene-azo-dyes of the quinoline series 4-(4-nitrophenylazomethylene)- and 4-(2,4-dinitrophenylazomethylene)-1-ethyl-dihydroquinoline, by the action of concentrated potassium hydroxide solution on the 4-nitro- and 2,4-dinitro-phenylhydrazones of quinoline-4-aldehyde. In solution the colour of both dyes depends on the solvent used.

Wahl and Le Bris[348] showed that in alkaline medium quinaldinium and diazonium salts react to form the bis-azo-dyes (LXIII). They suggest that both diazo-groups couple simultaneously, since no monoazo-dye could be isolated.

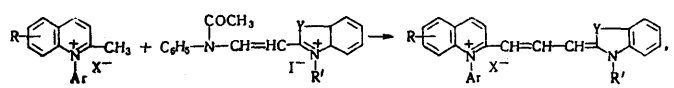


A simple method for the production of methyleneazo-dyes has been proposed, by the reaction of quinaldinium or lepidinium salts with antidiazotate in aqueous or alcoholic solution[349].

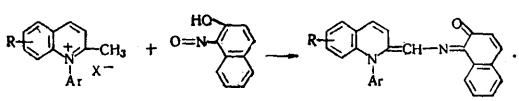
(1) *N*-Arylquinocyanines. The preparation and study of quinocyanines containing aryl radicals on the nitrogen heteroatom have become possible only by the development of general methods for the production of *N*-aryl-quinolinium, -quinaldinium, and -lepidinium salts. The presence of the electron-withdrawing aromatic radical on the nitrogen in conjugation with a methyl group in the 2- or 4-position renders the methyl group more active than in the corresponding *N*-alkyl compounds. Thus even *N*-aryl-benzoquinaldinium iodides react with orthoformic ester, and not just the sulphonates, as is the case with the *N*-alkyl analogues. Also reaction occurs with orthoacetic ester, which is not the case with the *N*-alkyl compounds[350]:



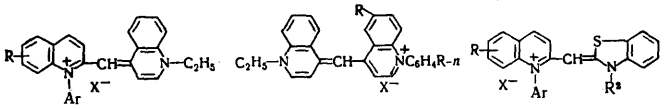
N-Aryl-quinaldinium and -lepidinium salts, as already stated, react with orthoformic and orthoacetic ester to produce symmetrical quinocarbocyanines[14,22,37,41-47,350,351]; they also react with acetanilidovinyl-substituted heterocyclic compounds to produce asymmetrical carbocyanines[14,23,24,41-46,234,351,354]:



where Y = $-C-(CH_3)_2$, $-S-$, or $-CH=CH-$; with aromatic aldehydes to produce styrylquinolinium dyes[14,22-24,37,41,44-46,351,355]; with nitroso-compounds to produce azomethines, the styryl analogues[350,351,356,357]; and with nitrosophenols to produce non-ionic azomethines which exhibit solvatochromism[353]:

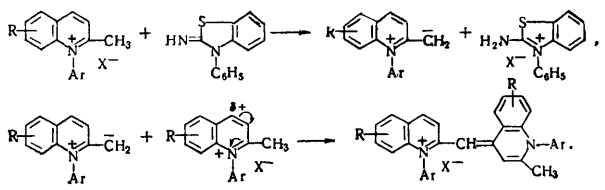


N-Aryl-quinaldinium and -lepidinium salts have also been used[22-24,37,42-44,46,358,359] to prepare monomethinecyanines of the types:

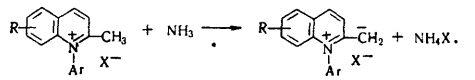


where R = C_2H_5 or C_6H_5.

In the preparation of monomethinecyanines containing the benzothiazole ring, isocyanines are obtained as by-products, possibly by the reactions:



The first stage of methylene base formation can also be effected by ammonia:

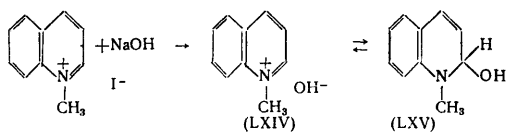


5,6-Benzoquinaldinium salts do not form isocyanines in this reaction, because of steric hindrance; this can presumably be used to prove the structure of the arylquinaldinium salts obtained by cyclisation of asymmetrical diarylamines such as phenylnaphthylamine.

Mono-[360] and bis-azo-dyes[361] have been obtained from *N*-arylquinaldinium salts.

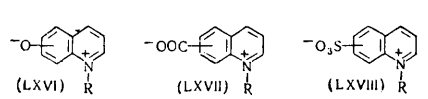
4. Other Reactions

(a) Ion exchange reactions. Quinolinium salts, like ammonium salts, are ionic; they are readily soluble in water, dissociating into an organic cation and, usually, an inorganic anion. The aqueous and alcoholic solutions are fairly good conductors of electricity. In addition to normal ion-exchange reactions, these salts also exhibit certain specific reactions; thus when caustic alkalis react with quinolinium salts, there is first an exchange of ions, with the formation of the ammonium base (LXIV), which is as strong as caustic alkalis; on standing, however, the conductivity of the aqueous solutions falls (LXIV) changing into the pseudobase (LXV):



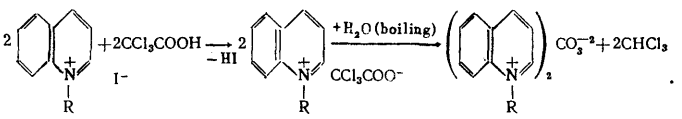
This effect was first studied by Hantzsch and Kalb[362]; Aston and Lasselle[363] studied the kinetics of this reaction.

As stated, the reaction of quinaldinium and lepidinium salts with alkali produces the so-called methylene bases (VIII) and (X), which are bipolar ions of the betaine type. The action of caustic alkalis on quinolinium salts containing OH, COOH, or SO_3H groups produces the betaine-like compounds (LXVI), (LXVII), and (LXVIII)[364-366]:



Simonov[367] has studied in detail the conversion of 6-amino-substituted 1-alkylquinolinium salts in the presence of bases. Harris[368] has shown that mixing boiling acetone solutions of $NaCu_2I_3$ and methylquinolinium iodide produces *N*-methylquinolinium cupriodide, which is also obtained by treating *N*-methylquinolinium iodide with solutions of NaI and Cu_2I_2. Alkali metal salts of complex acids, *e.g.* $K_4[Fe(CN)_6]$, $K[HgI_3]$, $Na_3[Co(CN)_6]$, $Na_3[Co(NO_2)_6]$, $K[BiI_4]$, and $K_4[Mo(CN)_8]$, in aqueous solution react with quinolinium salts to precipitate the corresponding quinolinium salts of the complex acids[369-376]. The colour of these precipitates and of quinolinium salts with other anions has been discussed[377,378]. Treatment of an aqueous solution of a quinolinium salt with hydrochloric acid (1 : 1) and ferric chloride precipitates the chloroferrates, which may be used instead of the picrates, chloroaurates, and chloroplatinates for the identification of the quaternary salts[379].

With thionyl chloride in acetic anhydride at 0° quinolinium salts produce dichloroiodides, a 2-iodo-atom being replaced by chlorine[380]. Vilsmeier[381] formed quaternary ammonium (including quinolinium) carbonates as follows:



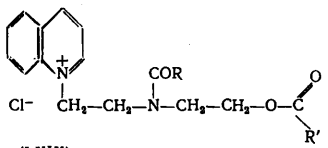
The products are valuable as additives when dyeing with indigo dyes, and as intermediates for the production of other salts, *e.g.* tartrates and citrates of the quaternary bases. Knowing that certain aliphatic amine nicotinates are therapeutically active, Simon[382] prepared *N*-methyl-*N*-ethyl-, and *N*-propyl-quinolinium nicotinates by reacting the corresponding halide with an aqueous suspension of silver nicotinate.

(b) Elimination reactions. When quinolinium salts with an alkyl or aralkyl radical on the nitrogen atom are heated above their melting point, the substituting radical is split out as the halide, leaving the quinoline; this has been used to separate mixtures of quinoline and pyridine bases having very similar boiling points, *e.g.* quinoline, isoquinoline, and methylquinolines, the decomposition temperatures of the corresponding quaternary salts being relatively far apart. The method can also be used to separate mixtures of halides otherwise difficult to separate, *e.g.* *o*- and *p*-chlorobenzyl chloride[383]. Later Menzl[384] developed a method for the decomposition of the quaternary salts by heating with ethanolamines or other alkanolamines, which again produces the quinoline and the alkyl halide. Kursanov and coworkers[385-387] investigated the reaction of 1-alkoxymethylquinolinium salts with alcohols and carboxylic acids and their salts and esters; in each case the alkoxymethyl radical is split out. Raison[388,389] found that of *m*- and *p*-aminobenzyl-substituted quinolinium salts, only the former are stable; the *p*-isomers are readily decomposed to form quinoline, and are stable only in the presence of mineral acid or as the acyl derivatives.

IV. USES OF QUINOLINIUM COMPOUNDS

(a) Quinolinium salts. Quaternary ammonium salts, including quinolinium salts, form the main type of cationic surface-active substance, and are employed in washing, disinfecting, and stabilising compositions used in the food and medicinal industries[235,390-399]. They are efficient emulsifying, dispersing, and wetting agents[400], and are used as textile treatment additives[381,401-405].

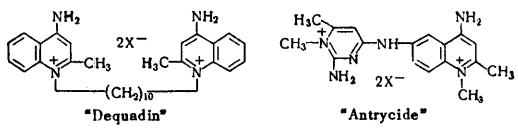
Compounds (LXIX) are used to break oil emulsions and as wetting agents when filling exhausted oil-bearing strata with water[406]:



(LXIX)

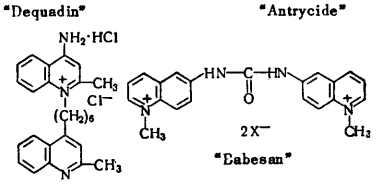
where RCO is an acyl radical containing not more than five carbon atoms, and R'CO is an acyl radical containing not more than 18–32 carbon atoms.

Some quinolinium salts have been recommended as additives in bright nickel plating[407-409], and others as bactericides and fungicides, especially against agricultural plant pests[397,410-419]. Good antibacterial and chemotherapeutic properties are possessed by "Dequadin"[419-425], "Antrycide" (Pyraldin)[426-430], "Tosocide"[428], and "Babesan"[431], which are used for treating various illnesses of domestic animals.



"Dequadin"

"Antrycide"



"Tosocide"

"Babesan"

Bis-quinolinium salts of some types exhibit a strong ganglio-blocking and hypotensive activity[6,7,432,433].

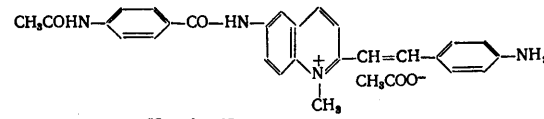
Quinaldinium salts have been suggested as azo-coupling agents for diazotype light-sensitive paper[434]. Quinolinium salts are very sensitive reagents for the micro-determination of bismuth[370,371] and persulphate ion[435].

(b) Quinolinium dyes. The use of quinocyanine dyes in the cinematographic industry as sensitisers, desensitisers, and supersensitisers for photographic emulsions and filter and antifogging dyes is well known[101-105]. Although ordinary cyanine dyes are fairly sensitive to light, with certain inorganic heteropoly-acids, such as tungsto-molybdophosphoric acid, they form very light-stable lakes suitable for use in dyeing[436,437]. Some types of quinocyanine and azo-dyes have been recommended for stable dyeing of fibres[438-448].

The quino-azo-dyes are particularly interesting. They have a high affinity for polyacrylonitrile fibre, give very deep shades of yellow, red, claret, violet, and blue colours, are very stable to light, and are unaffected by change of pH. Because of these properties, investigations have been started to develop convenient methods for the production of these dyes and their use in dyeing[447-449].

Quinocyanine dyes have been successfully used in fine histochemical investigations[450-452] and also for studying the mechanism of action of antibiotics on microbes[453]. Pinacyanol[454], Cyanine (Quinoline Blue)[455], and Neocyanine[456,457] are strong bactericides and have been recommended for clinical use.

Certain quinocyanines, derivatives of pyrrole and pyrimidine, are effective anthelminthics[458-463]. Quinostyryls, lepidinium derivatives, possess anti-tumour activity towards lymphoma 8 and some types of sarcoma[464-468]. "Styryl 430" has interesting radiomimetic properties, but they have not yet been sufficiently investigated[469-471]:



"Styryl 430"

Quinocyanines and quinostyryls have been recommended as plant growth regulants[472-478]. Hirshberg[479,480] suggests the use of the quinospirans (XXX) and their analogues as a photochemical memory unit in cybernetic machines.

Cyanines, particularly 1,3'-diethyl-6'-nitro-2-quinothiacyanine iodide, increase the sensitivity of certain light-sensitive polymers which become insoluble when irradiated and are used for obtaining linogravures by an optical method[481]. Cyanine dyes of the quinolinium series can be used to determine Hg^{2+}, Ag^{+},[482,483] and Mg^{2+},[484,485] to detect primary and secondary amines in tertiary amines[486], and for other analytical purposes[487].

A method has been suggested for the analysis of mixtures of anionic and cationic soaps, using Pinacyanol as indicator[488,489]. Particular attention is directed to the use of cyanine dyes, including quinolinium derivatives, as good models for studying the relationship between the structure and colour of a dye, and so to their importance in developing a theory of colour[22-25,35,37,40-47,102,105,350-359,490-506].

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MECHANISM OF THE CATALYTIC REDISTRIBUTION OF HYDROGEN IN UNSATURATED CYCLIC HYDROCARBONS

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CONTENTS

1. Introduction 188
2. Redistribution of hydrogen as a combination of dehydrogenation and hydrogenation 189
3. Direct intermolecular transfer of hydrogen atoms 190
4. New data on changes undergone by six-membered cyclic hydrocarbons on palladium and platinum films 191
5. Dependence of catalytic activity towards hydrogen redistribution on ability of metal to absorb hydrogen 194
6. Peculiarities of hydrogen redistribution on oxide catalysts 195
7. Redistribution of hydrogen on aluminosilicate catalysts 197

1. INTRODUCTION

The catalytic redistribution of hydrogen in hydrocarbons has been studied for more than half a century. The interest taken in these reactions is due to the important part they play in many processes, both in the chemical and petroleum-processing industries and in Nature, for example, in any enzymic oxidation.

The amount of work done on simultaneous hydrogenation and dehydrogenation on metal catalysts has been especially large. The redistribution of hydrogen among molecules of the same substance, going practically to completion without the evolution of gaseous hydrogen, was discovered by Zelinskii and Glinka[1]. Such changes undergone by various hydrocarbons on palladium catalysts were subsequently investigated by Wieland[2] and by Zelinskii and his school[3-10]. On nickel catalysts the conversion was less complete[11] than on palladium catalysts, and it was usually accompanied by hydrogen evolution. With platinum catalysts higher temperatures are required for the redistribution of hydrogen than with palladium catalysts. In many cases this process is accompanied by isomerisation. For example, copper and iron catalysts[12] behave similarly to oxide catalysts[13] towards cyclohexene. Conversion into benzene and cyclohexane has been observed only when a mixture of cyclohexene and hydrogen is used[12]. On metallic rhenium[14] the conversion of cyclohexene at certain temperatures is not accompanied by the evolution of hydrogen, the ratio of benzene to cyclohexane in the products corresponding to that found on palladium catalysts. However, the proportion of cyclohexene which has undergone such reaction on rhenium does not exceed 32% at 300°, whereas on palladium catalysts this process goes to completion at far lower temperatures.

Comparison of these results shows that hydrogen redistribution in unsaturated hydrocarbons takes place differently on different metal catalysts. Insufficient attention has been paid in the literature to the reasons for this, and a possible explanation is suggested below for the decrease in activity, with respect to the redistribution of hydrogen, for the series: palladium, nickel, platinum.

The mechanism of hydrogen redistribution in cyclohexadiene, cyclohexene, and decalin hydrocarbons having an unsaturated bond in the side-chain has been elucidated by Levina[15,16], but the changes undergone by hydrocarbons having an unsaturated bond in the ring are interpreted in two different ways.

Balandin[17] suggested models in which transformations of cyclohexene or cyclohexadiene are effected by direct intermolecular transfer of hydrogen atoms. This scheme is examined in detail in Section 3, as also the closely similar views of Linstead and his collaborators[18,19].

A different view of the mechanism of catalytic hydrogen redistribution was held by Zelinskii[1,3] and Wieland[2], who