# THE CYANINE DYES

M. Q. DOJA

*Department of Chemistry, Patna University, Patna, India*

*Received November 16, 1931*

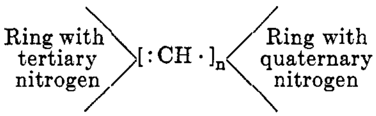
It is now more than seventy years since Greville Williams (6a) discovered the first member of the cyanine dyes. During the intervening years, particularly in the last decade, great advances have been made, chiefly by Mills and his collaborators, in the technique of the preparation of these compounds, the elucidation of their chemical constitution, and the examination of their photographic properties. Excluding the scores of derivatives which have been prepared and examined, there are no less than thirty-seven different types of cyanine dyes known at the present time. This review attempts a general survey (80a–d) of the methods of preparation, general properties (89), and structural formulas of these compounds.[1] The general arrangement of the subject will be evident from table 1 which is also designed to bring out clearly the relationship between the various types of cyanine dyes.

The great commercial value of the cyanines lies in their power of conferring (93) extra-sensitiveness on silver halide photographic plates. Ordinarily such plates are sensitive only to the violet and blue regions of the spectrum, but by adding suitable cyanine dyes to the liquid emulsion or by bathing the dried emulsion film in the dye solutions, the plates may be rendered remarkably sensitive to green, yellow, orange, red, and even to the invisible infra-red portions of the spectrum.

The sensitizing property of these dyes is probably dependent on the presence in their molecules of the characteristic grouping

---

[1] On account of limitations of space, certain aspects of the subject, particularly the non-chemical ones, have been either entirely omitted or only briefly mentioned.



$$\text{Ring with tertiary nitrogen} \rangle [:CH\cdot]_n \langle \text{Ring with quaternary nitrogen}$$

where n = 0, 1, 2, 3, ......

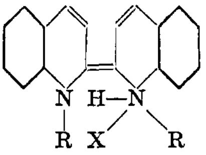
(one equivalent of an acid radical and two nitrogen atoms of basic function joined together by a chain of conjugated double bonds), which is universally present in all kinds of sensitizing cyanine dyes. Why and how the cyanine dyes sensitize (33e, 80a, 81) are questions yet to be answered. The only thing which we know with any certainty is that the dyestuff is adsorbed by the silver halide. All beyond this is speculation.

## CYANINE DYES WITH NO METHENYL GROUP BETWEEN THE TWO RINGS

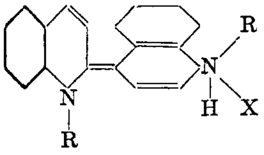
### *Apocyanines*

When a highly concentrated methyl alcoholic solution of a quinoline alkyl halide or of one of its derivatives is boiled with some caustic potash dissolved in the same solvent, two isomeric red and yellow dyes are produced (1, 2, 5), which have been called by Kaufmann and Strübin (2) the erythroapocyanines [1][2] and the xanthoapocyanines [**2**], respectively. Unlike those of the other cyanines, the aqueous solutions of apocyanines are not instantly decolorized by mineral acids They share, however, the sensitizing property of the cyanines, being good sensitizers (3) for the gelatino-bromide plate.

An investigation into the constitution (2, 4, 5, 19) of these dyes was undertaken by Kaufmann and Strübin (2), who assigned formula I to the erythroapocyanines and formula II to the xan-



I

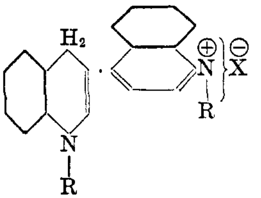


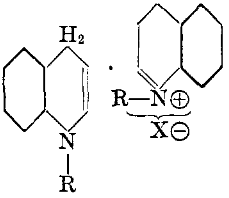
II

---

[2] These numerals refer to table 1.

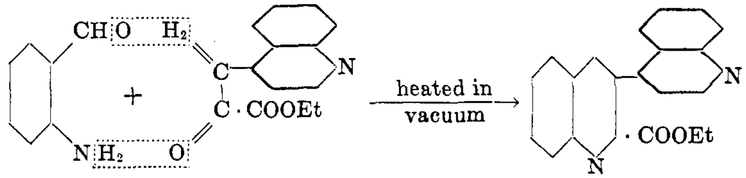
thoapocyanines. Eleven years later König (4) suggested, without any experimental support, formulas corresponding to formulas III and IV for the two series of compounds.


III


IV [3]

A more detailed examination of the problem was made by Mills and Ordish (5), who used the potassium permanganate oxidation method, which has proved so useful in elucidating the constitution of the cyanine dyes, and who supported König's views. The nature of the oxidation products pointed towards the existence of a diquinolyl skeleton in the apocyanines, and since the latter are so similar to the cyanines in general, it was surmised that of the two nitrogen atoms, one must be quaternary and the other tertiary, the two being joined by the usual conjugated chain of carbon and hydrogen atoms. For this condition to be satisfied the 3-position of one quinoline residue must be linked to either the 2- or the 4-position of the other. Consistent with their deeper color the erythroapocyanines were given the formula with a longer chain between the two nitrogen atoms (III), while the xanthoapocyanines received the other (IV).

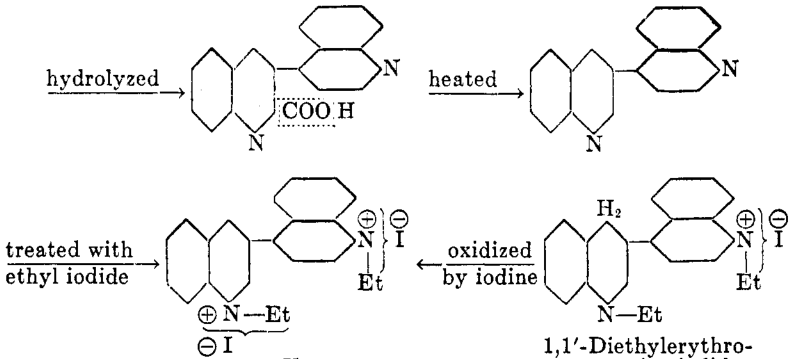
That the apocyanines do possess this constitution has been further established (5) by the following synthesis of 3,4′-diquinolyl diethiodide (V) identical with that obtained by oxidizing erythroapocyanine by iodine:



o-Amino-benzaldehyde + Ethyl 4-quinolyl pyruvate

---

[3] In view of the electronic conception of valence it is better to represent the fifth valency of nitrogen by an electrovalent bond.



V

1,1'-Diethylerythro-apocyanine iodide

### CYANINE DYES WITH ONE METHENYL GROUP BETWEEN THE TWO RINGS

#### *True cyanines*

Early in the second half of the last century Williams (6) on treating the quinoline obtained from cinchonine with amyl iodide and subsequently treating the brown oil thus formed with ammonia, obtained a beautiful blue substance called cyanine. About the same time von Babo (7), who was working on the decomposition products of cinchonine, prepared an exactly similar type of compound which he named irisin. He treated the quinoline with methyl sulfate and the product with caustic potash, when a very pretty blue compound was formed. He purified it and made a careful examination of its properties, including its optical characteristics; he noted in particular the discharge of its color on the addition of acids and the reappearance of color on treatment with alkalies. He also succeeded in preparing the corresponding ethyl derivative (ethylirisin) by using ethyl sulfate instead of the methyl compound. The preparation of these substances from the quinoline obtained from coal-tar was accomplished by Schnitzer (8), who published a detailed method for the purpose in 1861, his "chinolinblau" being identical with Williams' cyanine.

Some time later Hoogewerff and Van Dorp (9) found that the said cyanine could be very easily prepared by treating a mixture of quinoline and lepidine alkyl iodides in equal molecular proportions with caustic potash, provided an excess of the quinoline compound were present. Not only did they show (10) that pure quinoline cannot be used for preparing the dye and that the presence of a certain proportion of lepidine is essential, but they also demonstrated that amyl iodide can be replaced by any other suitable alkyl halide (11).

Providing himself with a sample of cyanine manufactured by the firm of Von Menier in Paris, Hofmann (12) undertook an investigation into the nature of this compound, and came to the conclusion that lepidine alone is concerned in its formation.

$$\underset{\text{Lepidine}}{C_{10}H_9N} + \underset{\substack{\text{Amyl}\\ \text{iodide}}}{C_5H_{11}I} \longrightarrow \underset{\substack{\text{Amyl lepidyl}\\ \text{ammonium iodide}}}{C_{15}H_{20}NI} \tag{1}$$

$$2\,(C_{15}H_{20}NI) + KOH \longrightarrow \underset{\text{Cyanine}}{C_{30}H_{39}N_2I} + KI + H_2O \tag{2}$$

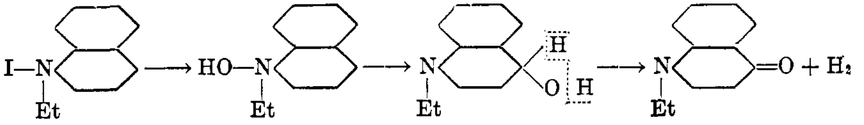
Nadler and Merz (13), on the other hand, on the basis of the preparation and analysis of a large number of different salts of cyanine (sulfate, borate, oxalate, nitrate, etc.), considered quinoline to be the all-important compound.

$$\underset{\substack{\text{Quinoline amyl}\\ \text{iodide}}}{2\,[C_9H_7N \cdot C_5H_{11}I]} + KOH \longrightarrow \underset{\text{Cyanine}}{C_{28}H_{35}N_2I} + KI + H_2O$$

Much nearer the mark was the suggestion put forward by Hoogewerff and Van Dorp (9), who as a result of their investigations regarded both quinoline and lepidine to be necessary for the preparation of the compound and formulated the reaction as follows:

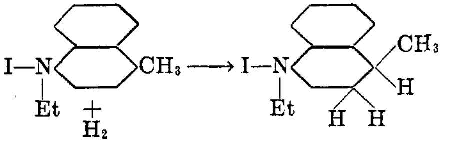
$$\underset{\substack{\text{Quinoline}\\ \text{methiodide}}}{C_9H_7N \cdot CH_3I} + \underset{\substack{\text{Lepidine}\\ \text{methiodide}}}{C_{10}H_9N \cdot CH_3I} \longrightarrow \underset{\text{Cyanine}}{C_{21}H_{19}N_2I} + HI + H_2$$

A more rational interpretation of the reaction and one which also threw some light on the constitution of the compound was suggested by Miethe and Book (14), who thought that in the first stage the quinoline alkyl halide was converted into the corresponding $\alpha$-quinolone (VI). The hydrogen thus liberated then reduced the lepidine alkyl halide to its dihydro derivative (VII), which finally condensed with the quinolone to give the cyanine (VIII).



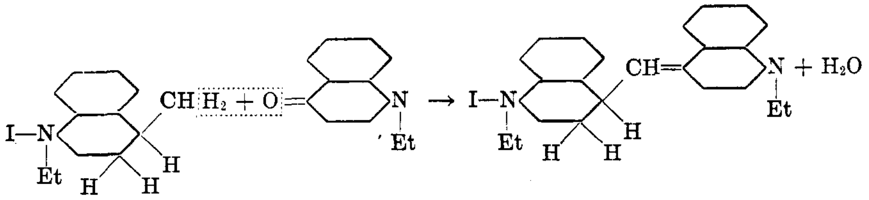
(1)

VI



VII

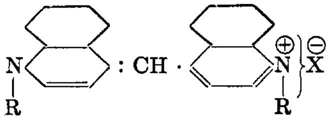
(2)



(3)

VIII

Since a methyl group in a quinoline ring is known to lose its power of condensation with ketones or aldehydes when the ring is partially or wholly reduced, König (15) thought it more probable that the cyanine had two atoms of hydrogen less than that shown in Miethe and Book's formula (VIII)—a view quite in conformity with the constitution of blue cyanines (IX), [**3**], which follows from the now well-established formula of isocyanines (see below).



IX

### *Isocyanines*

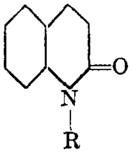
The credit of discovering the isocyanines goes jointly to Spalteholtz (16) and to the Dutch investigators Hoogewerff and Van Dorp (17), both of whom, independently, observed the formation of a purplish red dye when a mixture of quinoline and quinaldine alkyl halides was heated with caustic potash. In harmony with their views on the mechanism of the formation of the blue cyanine, the latter investigators regarded the isocyanine as formed in the following manner:

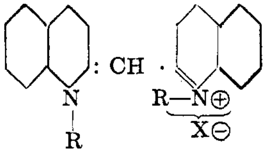
$$\underset{\substack{\text{Quinaldine}\\ \text{ethiodide}}}{C_{12}H_{14}NI} + \underset{\substack{\text{Quinoline}\\ \text{ethiodide}}}{C_{11}H_{12}NI} \rightarrow \underset{\text{Isocyanine}}{C_{23}H_{23}N_2I} + HI + H_2$$

whereas Spalteholtz, relying on his analytical figures, gave the dye two atoms of hydrogen more.

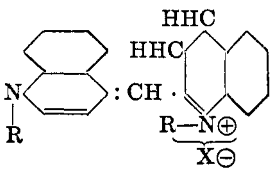
$$\underset{\substack{\text{Isocyanine}\\ \text{(Spalteholtz)}}}{C_{23}H_{25}N_2I}$$

Decker (18) was of the opinion that the production of these dyes was dependent on the oxidation of a molecule of the alkyl halide through its pseudo base to the corresponding 1-alkyl-2-quinolone (X), and the latter's subsequent condensation with another molecule of the unchanged quinaldine alkyl halide. On the basis of this view of the mechanism of the isocyanine condensation, he proposed a formula of type XI for the isocyanines.


X

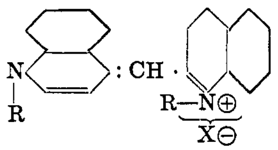

XI

Views very similar to the above were put forward by Miethe and Book (20), except that in their interpretation a 1-alkyl-4-quinolone was supposed to condense with a partially reduced quinaldine alkyl halide, giving the isocyanine (XII).

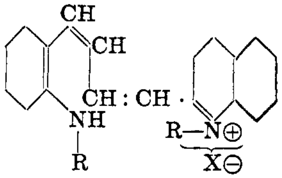


XII

Two years later, König (15) suggested a modification (XIII) of this formula, which he regarded more probable on general grounds. He did not adhere to this, however, but in 1912 proposed (21) a different constitution (XIV) for the isocyanines

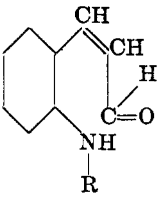


XIII



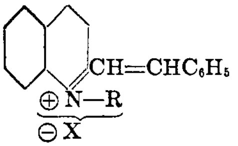
XIV

based on the view that the pseudo bases derived from quinoline alkyl halides are aldehyde-amines (XV), and that the isocyanines are the normal condensation products of these with quinaldine alkyl halides.



XV

Great support has been given to König's first formula (XIII) by the combined researches of Vongerichten and Höfchen (22) and of Kaufmann and Vonderwahl (23a). The former have definitely proved that the 2-methyl group of quinaldine alkyl halide is concerned in the isocyanine condensation, because compounds in which this is engaged, such as benzylidine quinaldine alkyl halides (XVI),

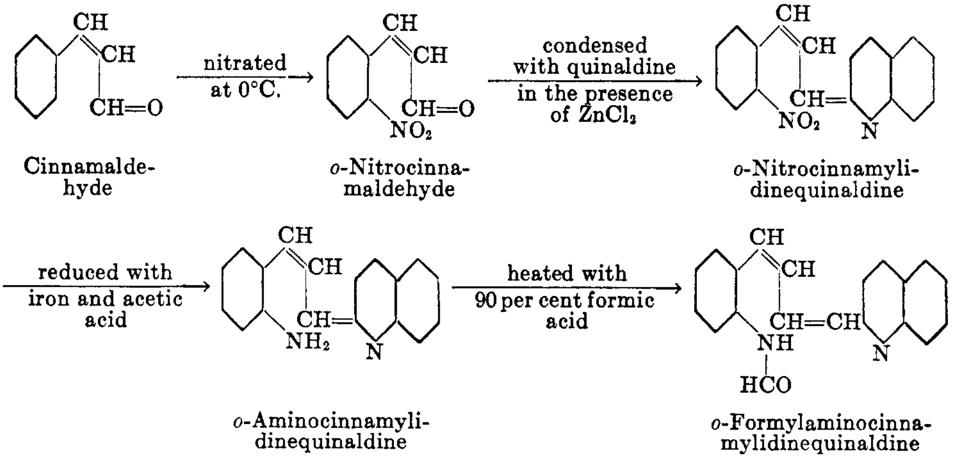


XVI

cannot take part in the formation of isocyanines.[4] Again, when diethylisocyanine chloride is oxidized with alkaline potassium ferricyanide, 1-ethyl-2-quinolone is found in the products of oxidation; this fact also points in the same direction.

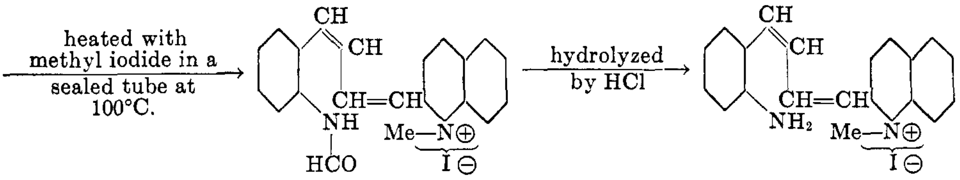
The position of attachment of the quinoline ring in the isocyanine molecule has been fixed by the very important observations of Kaufmann and Vonderwahl (23a) that 4-chloroquinoline alkyl iodide combines with quinaldine alkyl iodide in the presence of alkali with the elimination of *hydrogen chloride as well as of hydrogen iodide* to give the same isocyanine as is produced when unsubstituted quinoline alkyl iodide is used, and that if the 4-position is appropriated by non-reactive groups, such as phenyl, no condensation takes place at all.

The problem of the constitution of these dyes has been finally settled by the work of Mills and his coworkers. The synthesis of *o*-aminocinnamylidenequinaldine methiodide (XVII) by Mills and Evans (24),



---

[4] Mills and Wishart (26) do not consider such arguments conclusive, as the formation of these compounds is very much influenced by steric hindrance.

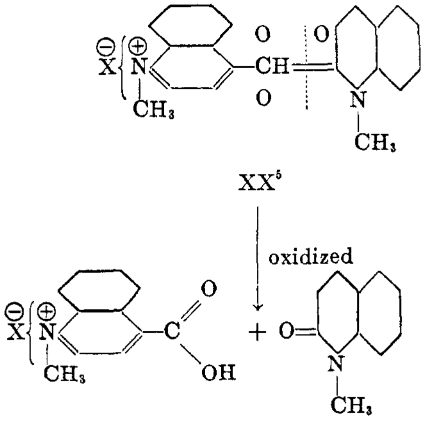


o-Formylaminocinnamylidinequinaldine methiodide

XVII

and the demonstration that it possesses properties entirely different from those of isocyanines, removed König's (21) "chain" formula (XIV) from the field—a constitution which König himself abandoned (25) a year later after the comparison of the ultra-violet absorption spectra of solutions of p-dimethylaminocinnamylidinequinaldine methoperchlorate and isocyanines decolorized by hydrochloric acid.

The last word on the subject came (26) when an ice-cold aqueous solution of dimethylisocyanine acetate was oxidized smoothly by potassium permanganate to 1-methyl-2-quinolone (XVIII) and a cinchonic acid methosalt (XIX), fixing once for all the constitution of the dye as given in formula XX, [4].



XX[5]

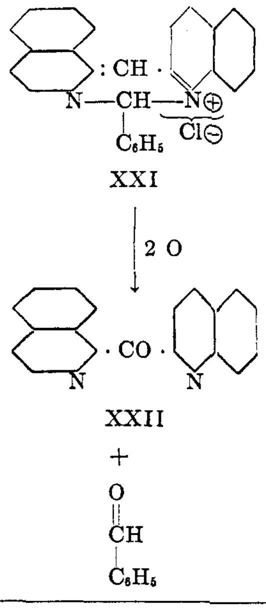
XIX XVIII

---

[5] The possibility of the existence of the other tautomeric form of isocyanines where the acid radical is attached to the quinaldine ring should not be overlooked; as a matter of fact, it has been shown to exist in some cases (26).

Owing to the great commercial importance of the isocyanines, a very large number of different derivatives of this series of dyes have been prepared and examined (27a–k).[6]

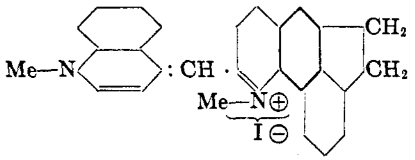
A novel kind of isocyanine dye called isoquinoline red (XXI) was obtained by E. Jacobson (28) by heating a mixture of commercial quinoline, benzotrichloride, and zinc chloride to 130°C.; a better yield is obtained, however, by using molecular proportions of quinaldine and isoquinoline instead of the crude quinoline (29). The dye forms reddish brown crystals, and gives a beautiful crimson-colored solution in water and alcohol. It is a good sensitizer (30) and like the other isocyanines shows two narrow bands in its absorption spectrum. It is of no value as a dye, the color imparted to silk and wool being fugitive. When oxidized by potassium dichromate and dilute sulfuric acid, isoquinoline red gives quinolylisoquinolyl ketone (XXII) and benzaldehyde. It has therefore been assigned (31a–c) the constitution given in formula XXI.



---

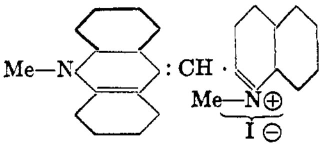
[6] It is interesting to note in this connection that the presence of a nitro group either in the quinoline or in the quinaldine ring prevents isocyanine formation (27j).

In an attempt to prepare dyes sensitizing farther into the red end of the spectrum by increasing their molecular weights, which is known to produce a shift of the maxima of extra-sensitization towards the red, F. M. Hamer (32) has succeeded in preparing two new and very interesting dyes of the isocyanine type.[7] The first of these (XXIII) was prepared by boiling a solution of 2-methylacenaphthpyridine methiodide and quinoline methiodide with sodium dissolved in alcohol in the usual manner. It is green in color and shows a very uniform band of extra-sensitization extending to the red.



XXIII

By the interaction of 5-methylacridine methiodide and 2-iodoquinoline methiodide in the presence of caustic potash, with water as the solvent, the second compound (XXIV) was obtained. It differs from the simpler isocyanines both in optical and photographic properties, being entirely devoid of all sensitizing characteristics.

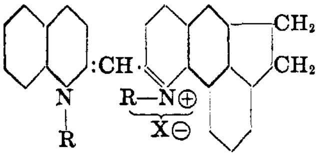


XXIV

---

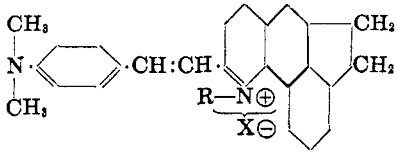
[7] In the course of the same investigation dyes of the following types have also been isolated:

(1)



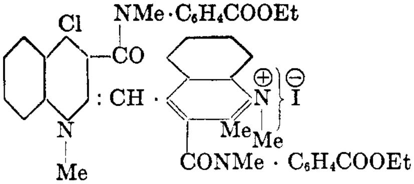
ψ-Cyanine derivative

(2)



Styryl derivative

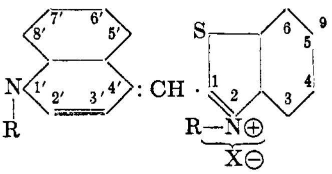
An isocyanine dye (88) which in spite of its great complexity retains the general characteristics of the dyes of this class is



exemplified in 4′-chloro-3,3′-di(*o*-carbethoxyphenylmethylcarbamyl)-1,2,1′-trimethylisocyanine iodide.

Most of the isocyanines are powerful sensitizers (33a–i) for the photographic plate; the well-known commercial products, ethyl red (1, 1′-diethylisocyanine iodide), pinaverdol (63c, 34) (1,1′,6-trimethylisocyanine iodide)[8], pinachrome (1,1′-diethyl-6-ethoxy-6′-methoxyisocyanine iodide), are all dyes of the isocyanine type. It is of interest to mention that the introduction of alkoxyl groups into the nuclei greatly enhances the sensitizing power of these dyes.

*Thioisocyanines.* The thioisocyanines (XXV), [6], which contain in their molecule one quinoline and one benzothiazole nucleus joined together by a methenyl group, are prepared (35a) by the action of caustic soda in alcoholic solution on a mixture of quinoline alkyl salt and a 1-methylbenzothiazole alkyl salt. The great similarity between the isocyanines and the thioisocyanines, in their methods of preparation, in their



XXV

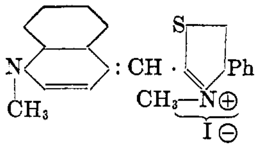
---

[8] Apart from being a powerful sensitizer, pinaverdol (in English, sensitol green) is also a very good antiseptic for *Bacillus coli* (87).

[9] The positions of substituting atoms and radicals in the cyanine dyes are usually indicated by the above scheme, namely, by affixing plain numerals to the positions in the nucleus carrying the acid radical and primed numerals to the positions in the other nucleus.

optical, photosensitizing, and chemical properties, and in the fact that the thioisocyanines can also be obtained, although indirectly[10], by the interaction of a lepidine alkyl salt and a benzothiazole alkyl salt (36), lead one to believe that they are formed in the same way as the isocyanines, and possess a similar constitution (XXV), which differs from that of the isocyanines only in having a sulfur atom in place of the (—CH═CH—) group.

A dye representing type [7] was prepared by Mills and Smith (37) in the form of 4-phenyl-3-methyl-2-thiazolenyl-4-quinolylmethane methiodide (XXVI) by the standard method of heating a solution of 4-phenyl-2-methylthiazole methiodide and quinoline methiodide and caustic soda in absolute alcohol. When recrystallized from methyl alcohol it is obtained in red crystals with a bluish-green metallic lustre, which exhibit the general characteristics of the isocyanines.



XXVI

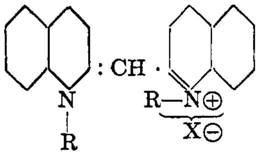
*Pseudocyanines*

The slow formation of a red dye by the action of caustic potash on an alcoholic solution of 2-iodoquinoline ethiodide and quinaldine ethiodide was first observed by Kaufmann and Vonderwahl (23a). Fischer and his coworkers, a few years afterwards (38a–b), isolated several of these dyes by treating the pseudo bases from 2-methylquinolyl alkyl halides, and their substitution products, in ethereal solution, with air and carbon dioxide. For this series of dyes they chose the name "pseudoisocyanines,"

---

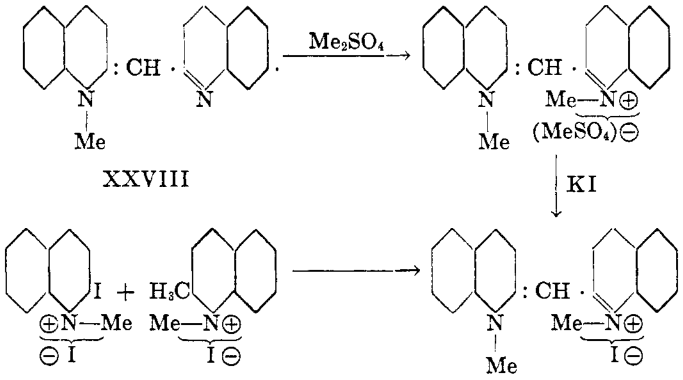
[10] Owing to the peculiar behavior of the benzothiazolonium base, which, as shown by Mills, Clark, and Aeschlimann (44), is converted by alkalies into the comparatively non-reactive metallic salts of *o*-formylmethylaminophenyl mercaptan, in the isocyanine condensation only the alkyl halide of quinaldine and not that of quinoline can be replaced by the corresponding benzothiazole derivative.

which was changed by Mills and Odams (36) to "pseudocyanines;" they gave the dyes a constitution similar to XXVII, [**5**].



XXVII

Great support has been lent to this formula by an observation of Scheibe and Rossner (39), that the ψ-cyanine (XXIX), obtained by heating *N*-methyl-2-quinolylenequinaldine (XXVIII) with an excess of methyl sulfate and isolation of the dye through the iodide, is identical with the ψ-cyanine prepared in the usual manner.



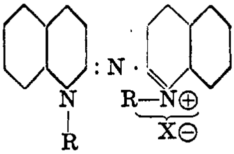
XXVIII

XXIX

The formation of the ψ-cyanines has been further investigated by Hamer (40), who, contrary to the views of Fischer and Scheibe (38b), has come to the conclusion that absolute alcohol is the best solvent to use in the ψ-cyanine condensation; by this method Hamer has succeeded in preparing a number of new ψ-cyanines in yields upwards of 30 per cent.

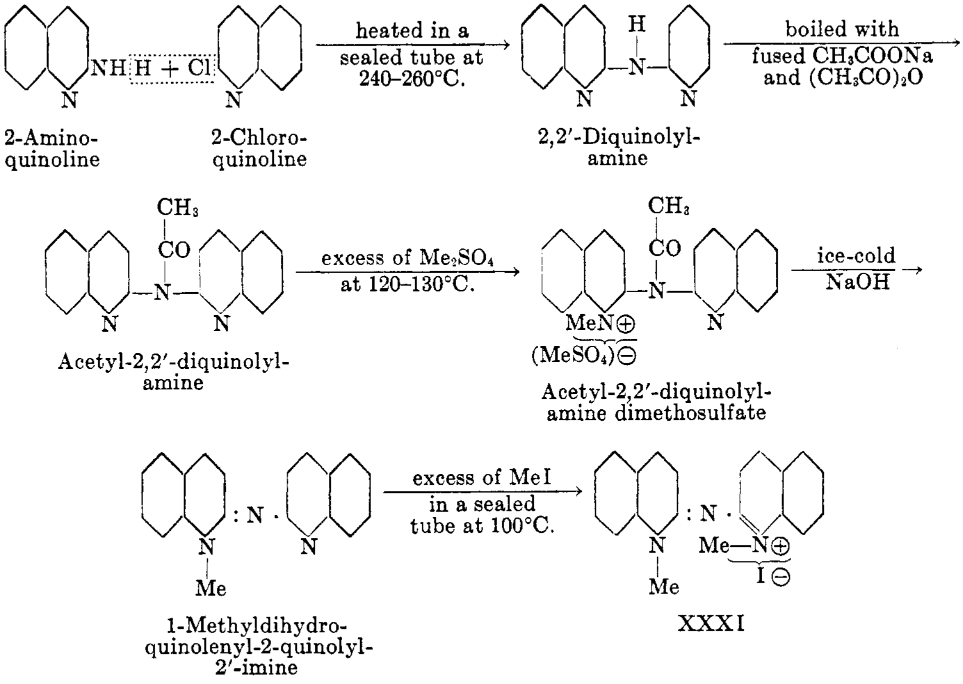
Some of the ψ-cyanines are of practical value in photography, exerting a sensitizing action in the bluish-green region of the visible spectrum (40).

No description of the ψ-cyanines could be complete without a reference to the azocyanines (XXX), a group of dyes which may



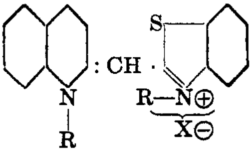
XXX

be regarded as ψ-cyanines in which the methenyl group (=CH—) joining the two nuclei has been replaced by an imino group (=N—). 1,1′-Dimethyl-2,2′-azocyanine iodide (XXXI), (a synthesis of which has been effected by Hamer (41), the discoverer of the azocyanines), although so similar to 1,1′-dimethyl-ψ-cyanine iodide (XXIX) in constitution, has nothing in common with it in either chemical or photographic properties.



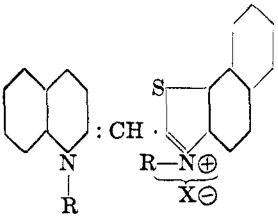
The dye is pale yellow in color, and its solution is not decolorized by acids. The absorption spectrum possesses three bands instead of the usual two, and a photographic plate bathed in the dye remains unaffected.

*Thiopseudocyanines.* The thio-ψ-cyanines [8], as was first shown by Mills and Braunholtz (42), result from the interaction of quinaldine alkyl salts and di-*o*-formylethylaminodiphenyl disulfide, $S_2(C_6H_4NEtCHO)_2$, in hot pyridine solution.

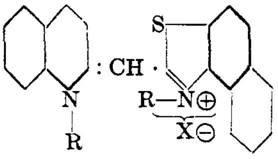


Thio-ψ-cyanine

A method of formation which resembled more the general method for the preparation of ψ-cyanines, was employed by Hamer (43) in synthesizing several different thio-ψ-cyanines of the general formula XXXII and XXXIII, by condensing methylnaphthothiazoles and 2-iodoquinoline alkyl halides in the presence of alcoholic caustic potash. All the thio-ψ-cyanines exhibit the general behavior of the cyanine dyes.

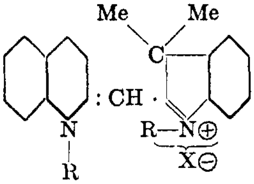


XXXII



XXXIII

*Indopseudocyanines.* The general method for the preparation of ψ-cyanines has been extended to the synthesis of dyes of a new type (XXXIV), [9], for which the name "indopseudocyanines" has been proposed (40).



XXXIV

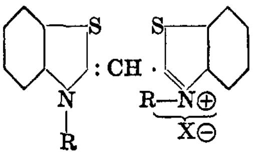
For the preparation of these dyes, 2-iodoquinoline alkyl halide is condensed with a substituted indolenine quaternary salt containing a reactive 2-methyl group. The dyes so obtained are brick-red in color but possess an extremely feeble sensitizing power.

*Thiocyanines.* Observing a great resemblance between the bases of the benzothiazole and the quinoline series, Hofmann (35b) attempted to prepare dyes analogous to the cyanines from the former. He actually succeeded in doing so, and the formation of one, which was produced by the condensation of benzothiazole amyl iodide and 1-methylbenzothiazole amyl iodide, he represented by the following equation:

$$C_7H_5NS \cdot C_5H_{11}I + C_8H_7NS \cdot C_5H_{11}I \rightarrow C_{25}H_{31}N_2IS_2 + HI + H_2$$

| | | |
|---|---|---|
| Benzothiazole amyl iodide | 1-Methylbenzothiazole amyl iodide | Cyanine dye of the benzothiazole series |

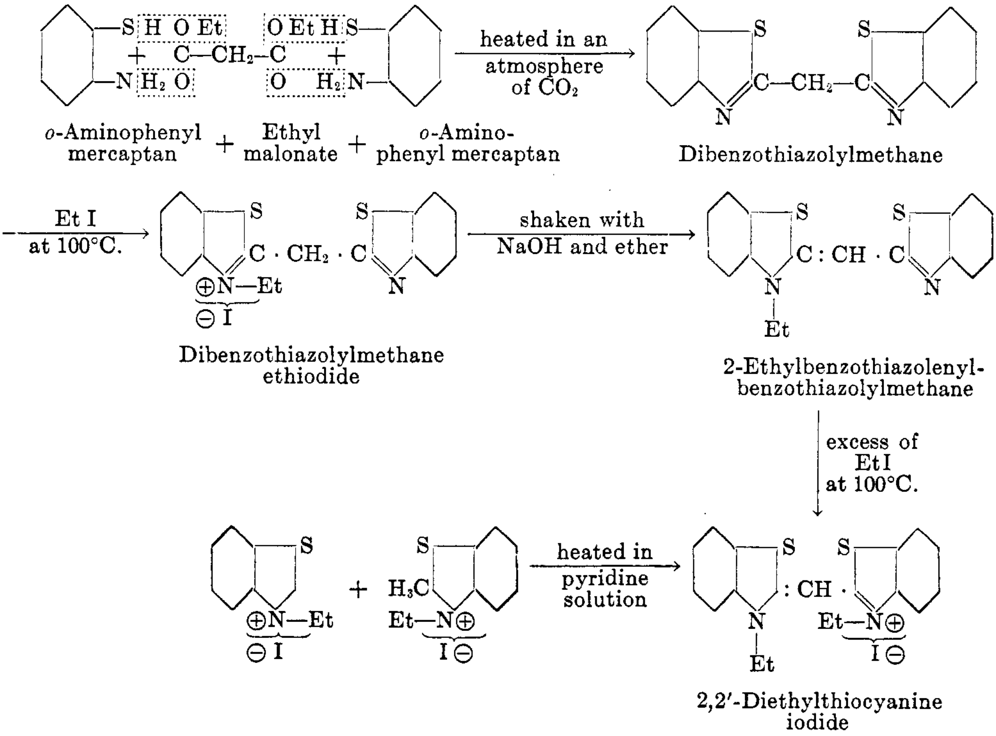
The yield of the dye obtained by Hofmann's method was so poor that Mills (45) undertook a reëxamination of these compounds, and soon discovered that the condensation could be carried out much more conveniently with pyridine, giving rise to bright yellow compounds, the thiocyanines (XXXV), [**10**], as *he called them; these proved to be powerful photographic* sensitizers, conferring sensitiveness on the green, yellow, and orange regions of the spectrum.



XXXV

The thiocyanines can also be prepared (42) by heating 1-methylbenzothiazole alkyl halide with di-*o*-formylethylaminodiphenyl disulfide. Both these methods, however, possess the disadvantage that the dye is always accompanied by the corresponding thiocarbocyanine. Quite recently Fisher and Hamer (46) have evolved a general method for the preparation of thiocyanines, which is free from this drawback and is also claimed to give better yields. The method consists in heating a benzothiazolinium chloride, containing a reactive methyl group, with amyl nitrite in the presence of acetic anhydride.[11]

The constitution of the thiocyanines has been established by an independent synthesis of the dye proving it to be identical with one prepared from benzothiazole alkyl halide and 1-methylbenzothiazole alkyl halide.

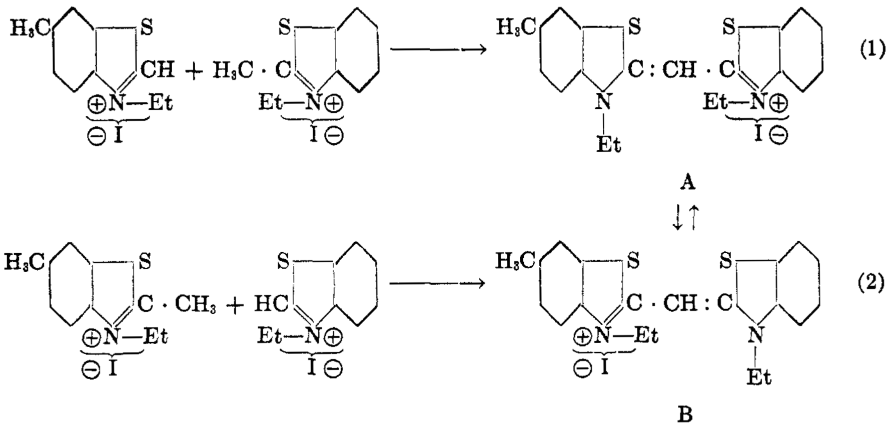


The existence of virtual tautomerism in the cyanine dyes, which has been inferred in other cases, has been experimentally demonstrated by Mills and Braunholtz (83) in the case of the thio-

---

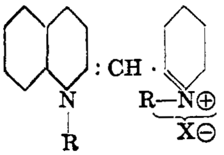
[11] In view of the well-known difficulty of synthesizing simpler cyanines, it is important to note that thiocyanines could not be prepared from 2,4-dimethylthiazole etho- or metho-chloride even by this method.

cyanines. They have synthesized the two compounds, A and B, which, according to their methods of formation, should be isomeric, differing in the nitrogen atoms to which the acid radical

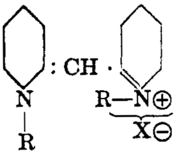


is attached; actually they were found to be identical. Not only was there exact correspondence in the general characters, the melting points, and the melting point of the mixture, but it was also found that neither would dissolve in the saturated solution of the other; thus the identity of the two products was fully established.[12]

*Meso-and proto-cyanines.* Both the mesocyanines (XXXVI), [**11**], and the protocyanines (XXXVII), [**14**], were prepared by



XXXVI



XXXVII

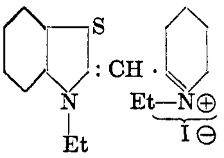
Moir (47) in connection with his work on color and molecular geometry, as applied to the dyes of the cyanine and related types.

*Thiopseudopyridocyanines.* The synthesis of a thio-ψ-pyrido-

---

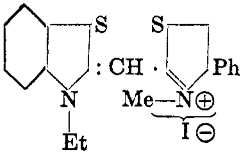
[12] A similar demonstration in the case of the ψ-cyanines has been made by Hamer (40).

cyanine was effected (42) by heating a solution of 2-picoline ethonitrate and di-*o*-formylethylaminodiphenyl disulfide in pyridine, and pouring the resulting deep red solution into an aqueous solution of potassium iodide, when 1′,2-diethylthio-ψ-pyridocyanine iodide (XXXVIII), [**12**], was produced.



XXXVIII

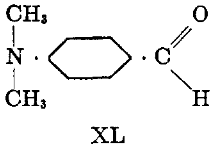
In the above reaction if the α-picoline compound is replaced by 4-phenyl-2-methylthiazole methiodide, a dye of type [**13**], (XXXIX), is produced (42).



XXXIX

## CYANINE DYES WITH TWO METHENYL GROUPS BETWEEN THE TWO RINGS

Heterocyclic bases containing a reactive methyl group, and particularly their quaternary salts[13] condense readily with *p*-dimethylaminobenzaldehyde (XL), to yield *p*-dimethylaminostyryl derivatives (21, 11a, 25, 37, 43, 53) identical with some of the cyanines of division III. The reaction is a very general one and

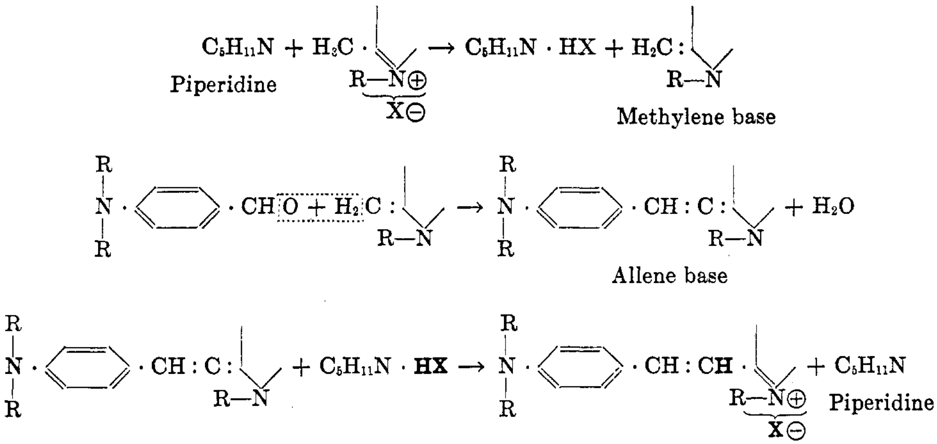


XL

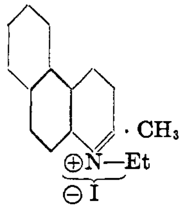
---

[13] The reactivity of the methyl group in bases like quinaldine, lepidine, picoline, etc., is greatly enhanced on their conversion into the corresponding quaternary salts (37); in the case of the methylquinolines it is greater in the 2- than in the 4-position (84).

can be best carried out in absolute alcohol with piperidine as a catalyst. It has been shown (48) to take place in the following manner:



The truth of this mechanism has been fully established by Mills and Raper (48) by the isolation in a typical case of all the intermediate compounds postulated in the above scheme. They chose for this purpose β-naphthoquinaldine ethiodide (XLI), which, when treated with caustic soda in ice-cold solution, gave the methylene base as bright yellow platelets turning green on



XLI

exposure to air. *p*-Dimethylaminobenzaldehyde condensed with this base, *without the addition of any catalyst,* to yield the corresponding allene derivative, which on treatment with piperidine hydroiodide produced 2-*p*-dimethylaminostyryl-β-naphthoquinaldine ethiodide, identical with the one obtained on boiling an alcoholic solution of β-naphthoquinaldine ethiodide and *p*-dimethylaminobenzaldehyde with a few drops of piperidine.[14]

With a few exceptions, all the *p*-dimethylaminostyryl derivatives are highly colored, lustrous, crystalline compounds, useless as dyestuffs owing to the fugitive character of the shades they impart. The discharge of color by mineral acids and its reappearance on the addition of alkali is characteristic of all these compounds. They all possess (33f, 52, 54) photosensitizing properties, some of them being pronounced sensitizers for the gelatino-bromide plate. Their absorption bands (54), however, are usually single and broad in contrast to the narrow double bands of the other cyanines.

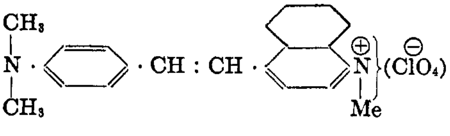
A series of compounds very similar to the *p*-dimethylaminostyryl derivatives, from the point of view of both constitution and general behavior, are the so-called *p*-dimethylaminoanils of heterocyclic ammonium compounds (XLII), formed (52, 54) in the same manner and under a similar set of conditions, by using *p*-nitrosodimethylaniline instead of *p*-dimethylaminobenzaldehyde. Like the styryl compounds they are highly colored and of no value as dyes; their color in solution is discharged by mineral acids and restored by alkalies. In photosensitizing properties, however, they differ in a marked degree from the styryl derivatives, being powerful desensitizers for the photographic plate(55), although not of much technical use.

XLII

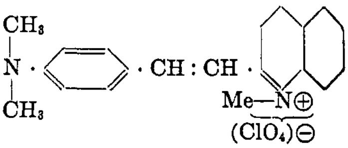
The condensation of *p*-dimethylaminobenzaldehyde with 2- and 4-methylquinoline salts was effected by Walter König (21, 25; also cf. 54) who, in addition to other salts, synthesized 4-*p*-dimethylaminostyrylquinoline methoperchlorate (XLIII), [15], and 2-*p*-dimethylaminostyrylquinoline methoperchlorate, (XLIV), [16], in the usual manner.

---

[14] It has been suggested (22, 49) that in the formation of the other types of cyanine dyes, too, the methylene bases play a very important part.



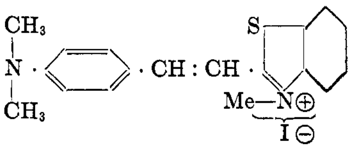
XLIII



XLIV

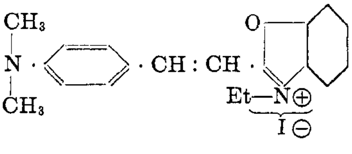
The anils corresponding to the quinaldinium and lepidinium salts were first isolated by Kaufmann and Vallette (56; cf. 54 and 57), who also noted the greater ease with which the quaternary salts react with *p*-nitrosodimethylaniline, as compared with the bases themselves.

J. L. B. Smith (52) has prepared 1-*p*-dimethylaminostyrylbenzothiazole methiodide (XLV), [**18**], the methoperchlorate of which was obtained by König and Treichel (25) and the ethiodide by Bloch and Hamer (54), who also synthesized the corresponding anils and investigated their photographic properties.

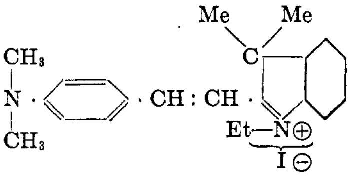


XLV

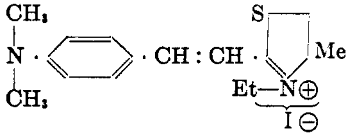
By the interaction of the appropriate quaternary salt with *p*-dimethylaminobenzaldehyde, Bloch and Hamer (54) have succeeded in preparing 1-*p*-dimethylaminostyrylbenzoxazole ethiodide (XLVI), [**19**], 2-*p*-dimethylaminostyryl-3,3-dimethylindolenine ethiodide (cf. 52) (XLVII), [**21**], and 4-methyl-2-*p*-dimethylaminostyrylthiazole ethiodide (cf. 37, 52) (XLVIII), [**23**], together with the anils corresponding to these compounds.



XLVI

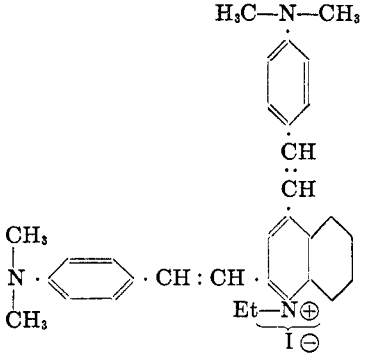


XLVII



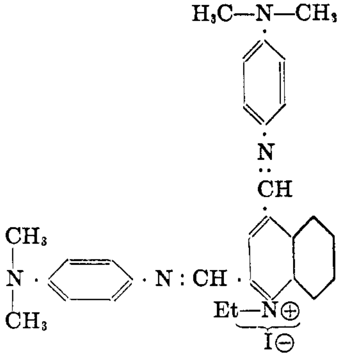
XLVIII

The same investigators have also prepared a novel compound (XLIX) in which two *p*-dimethylaminobenzylidine groups are attached to the same heterocyclic ammonium salt. A similar condensation with *p*-nitrosodimethylaniline gave the anil (L).



XLIX

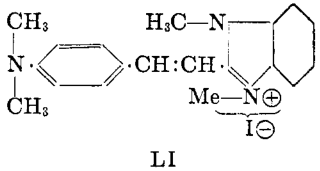
Tetramethyl-*p*, *p*′-diamino-2,4-distyrylquinoline ethiodide



L

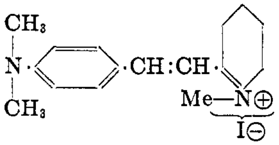
Quinoline-2,4-dialdehyde-di-*p*-dimethylaminoanil ethiodide

When the general method for the preparation of *p*-dimethylaminostyryl compounds is applied to a solution of 2,3-dimethylbenzimidazole methiodide, it gives 2-*p*-dimethylaminostyryl-3-methylbenziminazole methiodide (52) (LI), [**20**], as light yellow crystals. The color in solution is lemon-yellow and the dyestuff is a weak sensitizer.



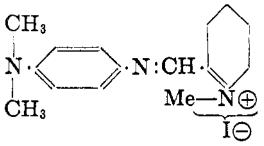
LI

Mills and Pope (58) have described the formation of a dye (LII), [**22**], by the condensation of *α*-picoline methiodide and *p*-dimethylaminobenzaldehyde, which has proved to be one of the most powerful sensitizers for green light for gelatino-silver bromide photographic plates. On recrystallization from methyl alcohol the dyestuff is obtained in bright red prisms which show a blue lustre and which dye silk a bright orange-yellow color which is not fast to light. It is noteworthy that the failure to sensitize photographic plates for a short region in the bluish-green part of the spectrum, which occurs so frequently with sensitizers for the yellow and red regions, does not occur with this compound.



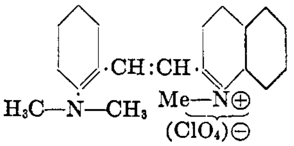
LII

It is curious to find that the anil (LIII) corresponding to the above compound was prepared as early as 1912 by Kaufmann and Vallette (56), but the analogous styryl compound (LII) did not attract the attention of chemists till the year 1922, when it was synthesized by Mills and Pope.

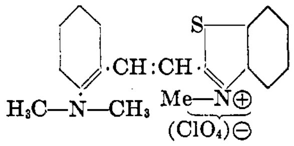


LIII

Like the *para* compound *o*-dimethylaminobenzaldehyde also condenses with methyl cycloammonium salts to yield the very similar *o*-dimethylaminostyryl compounds. It was in this way that König and Treichel (25) effected the syntheses of the methoperchlorates of 2-*o*-dimethylaminostyrylquinoline (LIV), **[17]**, and of 1-*o*-dimethylaminostyrylbenzothiazole, (LV), **[24]**. In the opinion of these authors the *o*-dimethylamino compounds are not



LIV



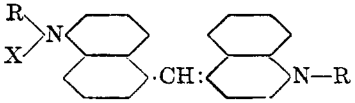
LV

true dyes to the same extent as are the corresponding *p*-derivatives.

### CYANINE DYES WITH THREE METHENYL GROUPS BETWEEN THE TWO RINGS

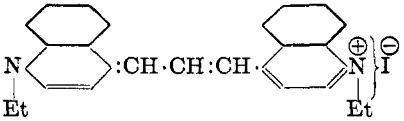
#### *Kryptocyanines*

When lepidine ethiodide is dissolved in boiling alcohol and slowly treated with a solution of sodium ethoxide and formalin, air being excluded, a purple black dye of a new type is produced (59), which has been designated as kryptocyanine by its discoverers. They have also suggested tentatively the constitution given in formula LVI for this group of dyes.



LVI

Two years later Mills and Braunholtz (42) isolated the same compound from the solution obtained by heating lepidine ethonitrate and di-*o*-formylethylaminodiphenyl disulfide in pyridine. The dye so produced forms beautiful pleochroic prisms, with a double green and golden lustre. It is a powerful photographic sensitizer, the band of extra-sensitization extending far into the red. As the new dye is isomeric with pinacyanole (see below), is formed in a similar manner, and bears to it the closest resemblance in general characters, Mills and Braunholtz have assigned to it the formula LVII[15] **[25]**, in preference to the one (LVI) proposed by Adams and Haller (59).



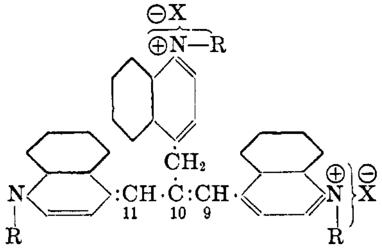
LVII

Neocyanine is the isolated example of a kryptocyanine with a substituent attached to the three-carbon chain. It was isolated

---

[15] Soon after their discovery, J. Kenner (59b) predicted this constitution for the kryptocyanines.

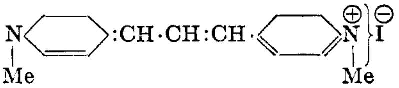
by Dundon, Schoen, and Briggs (72), as a less soluble by-product in the preparation of kryptocyanine. Since then Hamer (73) has found that the dyes of the neocyanine type can be prepared in very good yields by the condensation of lepidine alkyl-*p*-toluenesulfonate with orthoformic ester in a *small amount* of pyridine, and the subsequent conversion of the sulfonate into bromide by treatment with sodium bromide. Since the neocyanine is in each case less soluble than the corresponding kryptocyanine, it is readily purified by boiling the mixture of dyes with successive quantities of spirit insufficient for complete solution; as soon as the color of the filtrate shows the absence of kryptocyanine, the residue is recrystallized. All the dyes of this type are powerful sensitizers for the infra-red. The constitution of the neocyanines has not yet been fully established, but in all probability they may be regarded as kryptocyanines in which the hydrogen atom attached to the carbon atom 10 has been replaced by a lepidyl alkyl halide (LVIII).



LVIII

This formula accords with the method of synthesis of these compounds, agrees reasonably well with the analytical results, accounts for their optical and photographic properties, and also explains the slight solubility and high melting point of the neocyanines.

The action of chloroform on a solution of 4-methylpyridine methiodide in boiling alcohol in the presence of a large excess of potassium hydroxide gives (79) 1,1′-dimethyl-4,4′-pyridocarbocyanine iodide (LIX), [28].



LIX

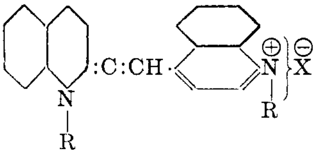
The dyestuff is a sensitizer, although not a very pronounced one, and shows the general behavior of the cyanines.

### *Dicyanines*

These are dyes which are formed (10b) by the action of an oxidizing agent on the quaternary salts of 2,4-dimethylquinoline or its substitution product, and are useful as sensitizers (60, 61, 92) for infra-red photography. Detailed methods for the preparation of these compounds have been given by Fischer (38a), and in an improved form by Mikeska, Haller, and Adams (60), whose method is based on the action of sodium methylate or ethylate on the substituted quinoline quaternary salt in a medium of absolute methyl or ethyl alcohol in the presence of air. The conditions affecting the synthesis of one of these dyes (dicyanine A) have been fully investigated by Palkin (61), who recommends the use of chloroform as a catalyst, sodium sulfide as the alkaline salt, and 95 per cent alcohol as the best medium.

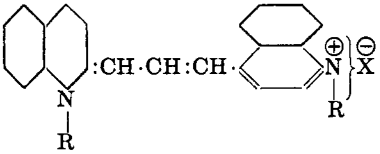
Finally Mills and Odams (36) have obtained dicyanines by the condensation of di-*o*-formylmethylaminodiphenyl disulfide with a mixture of quinaldine and lepidine ethonitrates dissolved in pyridine. The formation of the dicyanine, under these conditions, in preference to pinacyanole and kryptocyanine, demonstrates that the condensation of the methenyl residue derived from the disulfide takes place more readily with two dissimilar molecules than with two similar molecules of the two quaternary salts.

The problem of the constitution of these dyes has been investigated by O. Fischer (38a), who suggested for the parent substance of the group the formula LX. Mills and Odams (36), however, on the grounds of the great similarity which exists between the



LX

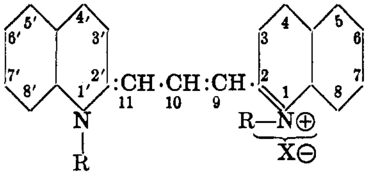
kryptocyanines, the dicyanines, and the true carbocyanines, not only with regard to their chemical composition and properties but also with regard to their absorption spectra, which in the case of the dicyanines are intermediate in character between those of the kryptocyanines and the true carbocyanines, have shown that the new dyes must have the constitution given in LXI, [**26**].



LXI

### *True carbocyanines*

Under the influence of alkalies, a series of blue dyes is produced (63a–d) by the condensation of two molecules of quinaldine alkyl salts or of their derivatives with one molecule of formaldehyde.[16] As will be shown later, these are the true carbocyanines, to be represented by the general formula LXII, [**27**].



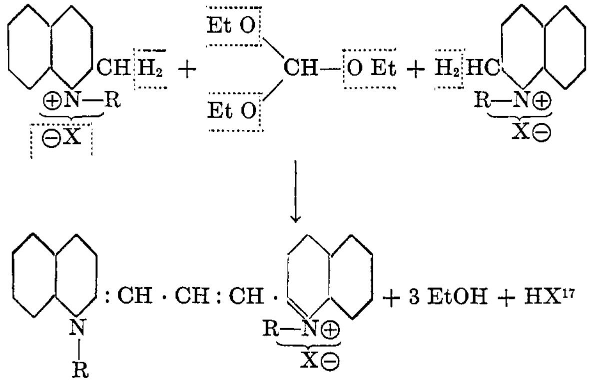
LXII

In the carbocyanine condensation, the part played by formaldehyde can also be taken by a trihalogenomethane (64, 62), glyoxylic acid (65), trioxymethylene (66), di-*o*-formylethylaminodiphenyl disulfide (42) (pyridine solvent), or by ethyl orthoformate (49) when the reaction takes place best in boiling acetic anhydride solution. A very general method for the preparation of these dyes, which gives better yields and purer products, has been discovered by Hamer (67). The method consists in boil-

---

[16] The yield of these dyes is considerably improved (63d) by the presence of a quinolinium alkyl salt in solution.

ing the quaternary salts of the heterocyclic bases with orthoformic ester in dry pyridine. The only precaution necessary is that of drying the solvent, while about four times the calculated quantity of ester should be taken. The reaction taking place is represented by the following equation:



The carbocyanines usually crystallize very well from methyl alcohol, often with solvent of crystallization which is difficult to remove. The crystals are beautiful and of various shades of blue and bluish-green. Owing to the decomposition of the molten salts, the melting point varies according to the rate of heating. The color of solutions[18] containing an excess of water is readily discharged by the addition of mineral acids; pure alcoholic solutions, on the other hand, are very resistant to this change and the decolorization does not take place until a considerable amount of the acid has been added.

The solutions of these dyes in methyl alcohol show characteristic absorption spectra distinguished by two well-marked bands which correspond roughly in position with the two maxima of photographic sensitization conferred by them.

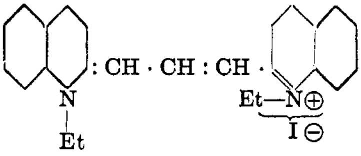
Most of the carbocyanines are powerful photographic sensitizers

---

[17] The formation of HX in the reaction suggested the use of a basic solvent, such as pyridine.

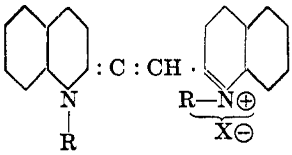
[18] It has been suggested (82) that in aqueous solution the dyes are present partially or wholly in the colloidal state.

(63d, 67, 59a). Pinacyanole[19] (LXIII), the well-known commercial sensitizer, is 1,1′-diethyl-2,2′-carbocyanine iodide.

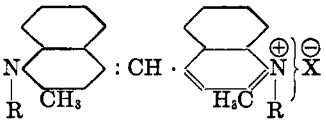


LXIII

Previous to the publication of Mills and Hamer's paper (68), which finally settled the constitution of the true carbocyanines, two different views were being held on the subject. The first of these, postulated by O. Fischer (38a), represented the carbocyanines by formula LXIV, and the second, sponsored by Wise, Adams, Stewart, and Lund (63c), suggested for them the constitution LXV.



LXIV



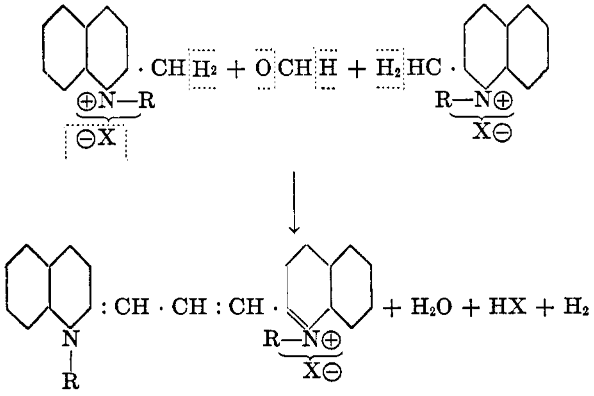
LXV

Fischer's formula is at variance with the analytical data and is also inconsistent with the intense blue color of these substances, while the substituted true cyanine structure proposed by the American investigators does not seem to accord with their photosensitizing action, nor does it agree with their behavior on oxidation. Mills and Hamer (68) have carefully analyzed pinacyanole, and by its oxidative degradation have isolated quinaldinic acid ethonitrate and 1-ethyl-2-quinolone in almost theoretical yield. These results, together with the fact that both the quinoline rings present in pinacyanole are derived from quinaldine ethiodide, and none from quinoline ethiodide, have led them to the conclusion that the true carbocyanines must possess the consti-

---

[19] Pinacyanole (in English, sensitol red) is also an extremely potent antiseptic for Staphylococci (87).

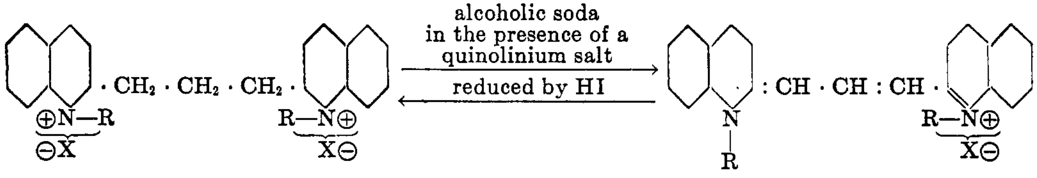
tution given by formula LXVI and must be formed in the following manner:



LXVI

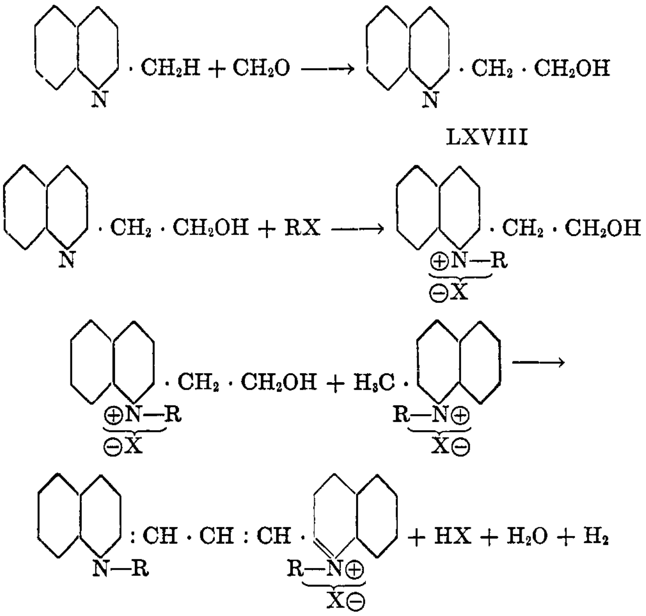
Confirmatory evidence in favor of this constitution has been brought by König (49) by a comparison of the absorption spectra of 1,1′-dimethyl-2,2′-carbocyanine iodide, and 1,1′-dimethyl-ψ-cyanine iodide, which show the same differences as are to be expected from two dyes which differ only by two methenyl groups in the conjugated chain.

Further support has been lent to this formula by the observation of Hamer that the dialkyl halides of methylenediquinaldine (LXVII) can be converted (69), under certain circumstances, into the corresponding carbocyanines, and the reverse transformation of a carbocyanine into methylenediquinaldine dialkyl halide can also be achieved (70).



LXVII

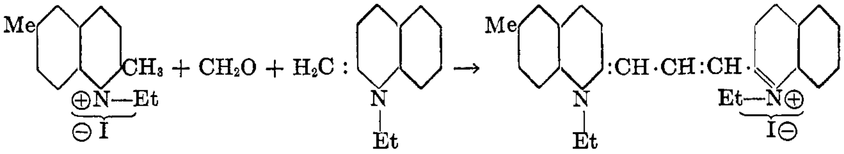
The fact that the central methenyl residue in the carbocyanines is provided by formaldehyde has received experimental confirmation at the hands of Ogata (66) who has shown that 2-methylquinoline and its substitution products combine with formaldehyde in the presence of alcohol to give 2-$\beta$-hydroxyethylquinoline derivatives (LXVIII), the alkyl halides of which react with quinaldine alkyl halides and their derivatives to yield true carbocyanine dyes.



The observation of Rosenhauer and his coworkers (71d) that pinacyanole can be synthesized by treating an alcoholic suspension of 1-methyl-2-methylene-1,2-dihydroquinoline with iodoform is additional important evidence in favor of the constitution proposed by Mills and Hamer. It also confirms the view that in the formation of the cyanine dyes the methylene bases and not the quaternary salts are the actual reactants.

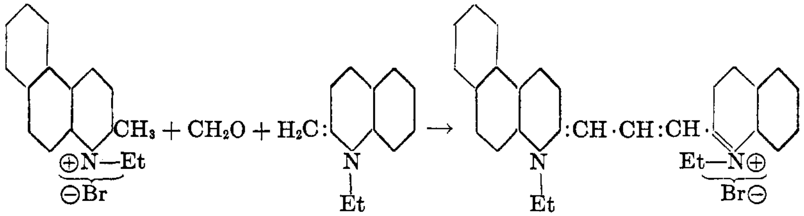
The true carbocyanines are very important chemical products, and on this account a considerable number of their derivatives have been prepared and examined (71a–d). Among these the unsymmetrical carbocyanines, synthesized by Mills and Raper (48), and the true carbocyanines having a substituent attached to the three-carbon chain deserve special consideration.

The synthesis of unsymmetrical carbocyanines,which has removed the presumption that carbocyanines can be prepared *only* when the two heterocyclic nuclei are similar in all respects (71a), has been accomplished by the condensation of the methylene base obtained from quinaldine ethiodide with *p*-toluquinaldine ethiodide and formaldehyde in one case (LXIX), and with β-naphthoquinaldine ethobromide and formaldehyde in the other (LXX). The first of these products (LXIX) is an exceedingly powerful photographic sensitizer for the red.



6′-Methyl-1,1′-diethyl-2, 2′-carbocyanine iodide

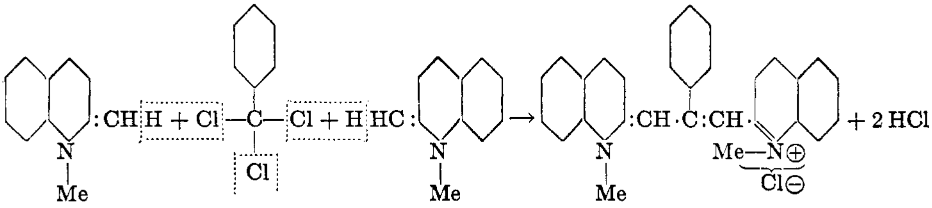
LXIX



5′,6′-Benzo-1,1′-diethyl-carbocyanine bromide

LXX

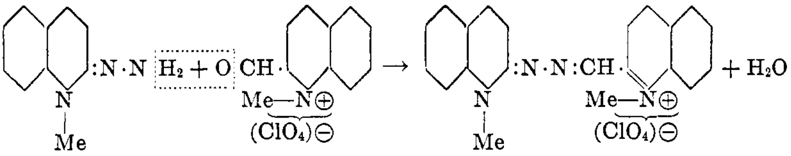
Two instances of true carbocyanines with substituents in the three-carbon chain seem to have been recorded in the literature. The first is that of the red dinitro derivative prepared by Mills and Hamer (68) by treatment of pinacyanole with nitric acid; the second is the particularly interesting compound, 1,1′-dimethyl-10-phenyl-2,2′-carbocyanine chloride (LXXI), obtained by Rosenhauer, Schmidt, and Unger (71d) by the action of benzotrichloride on 1-methyl-2-methylene-1,2-dihydroquinoline.



LXXI

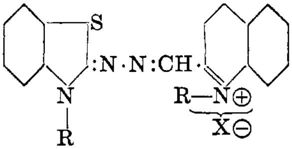
From methyl alcohol the above dyestuff crystallizes in green prisms. It dissolves in alcohol with a greenish-blue color which is discharged by the addition of acids and is restored by ammonia.

Of considerable interest is the preparation by Fuchs and Grauaug (74) of dyes which differ from the carbocyanines in having the grouping (=CH—N=N—) in place of the usual three-carbon chain (=CH—CH=CH—). The synthesis of these compounds has been achieved by a process which ultimately involves the condensation of a hydrazone with an aldehyde. Thus 1-methyl-2-quinolone hydrazone (LXXII) reacts with quinoline-2-aldehyde methoperchlorate (LXXIII) giving 1-methyl-2-quinolenyl hydrazone of quinoline-2-aldehyde methoperchlorate (LXXIV).

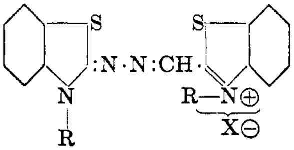


LXXII LXXIII LXXIV

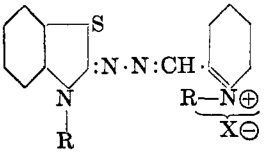
The same investigators, by a similar condensation of the appropriate aldehyde and hydrazone, have isolated compounds of the following different types.



(1)



(2)

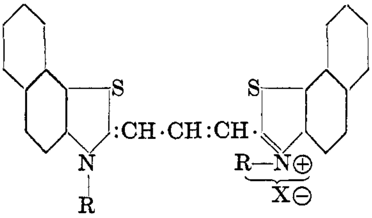


(3)

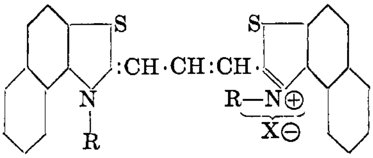
All these dyes crystallize in colored needles, and act as powerful desensitizers towards the photographic plate, whether in pretreatment or as an addition to the developer.

*Thiocarbocyanines.* The thiocarbocyanines, [29], which are the analogs of the true carbocyanines in the benzothiazole series, were first prepared by Mills (45) by the interaction of the alkyl halides of benzothiazole and 1-methylbenzothiazole and their substitution products in hot pyridine. The dye so formed usually contains a large proportion of thiocyanine, simultaneously produced, from which it is separated in a very ingenious manner by taking advantage of the difference in density of the two compounds. On treating the mixture with carbon tetrachloride the thiocarbocyanine floats, while the thiocyanine sinks; the former is thus easily obtained pure.

The general method (67) for the preparation of carbocyanines can also be extended to the preparation of thiocarbocyanines, and it was in this way that Hamer (43; cf. 53 and 77) obtained dyes of the types LXXV and LXXVI, by the condensation of the alkyl halides of methyl α- and methyl β-naphthothiazoles with orthoformic ester.

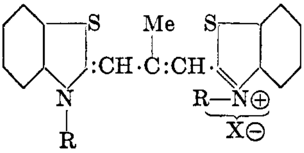


LXXV



LXXVI

When ethyl orthoacetate is used in place of ethylorthoformate, thiocarbocyanines (LXXVII) are produced (75, 43) with a methyl group attached to the central carbon atom of the three-carbon chain.[20]



LXXVII

The thiocarbocyanines are, as a rule, lighter in color than the corresponding carbocyanines. This, however, is not quite unexpected, for the benzothiazole derivatives are in general less deeply colored than the corresponding derivatives of quinoline. For instance, the alkyl iodides of the quinoline bases are yellow, while those of the benzothiazole bases are colorless or nearly so. Again the ψ-cyanines are red but the corresponding thio-ψ-cyanines are yellow.

In optical and photographic properties the thiocarbocyanines are very similar to the true carbocyanines. They act as powerful sensitizers for the gelatino-bromide photographic plate. In some cases (43), however, the methiodide possesses a very feeble sensitizing action as compared with the corresponding ethiodide. Such a difference between the methiodide and the ethiodide has also been observed among the true carbocyanines. Thus 1,1′-diethyl-2,2′-carbocyanine iodide (pinacyanole) is one of the most powerful sensitizers known, but the corresponding methiodide, namely, 1,1′-dimethyl-2,2′-carbocyanine iodide, is valueless.

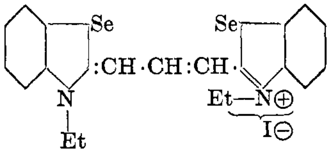
That the thiocarbocyanines are, from the constitutional viewpoint, true carbocyanines in which the quinoline nuclei have been replaced by the benzothiazole nuclei follows from their method of formation and the close agreement in general physical and chemical characteristics which exists between these two series of dyes.

*Selenocarbocyanines.* Bearing in mind the similarity between the alkyl halides of 1-methylbenzothiazole and 1-methylbenzoselenazole, Clark (76) attempted to synthesize selenocarbocya-

---

[20] In cases other than that of the thiocarbocyanines, no condensation takes place (75) when orthoacetic ester is used instead of orthoformic ester.

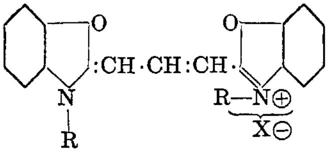
nines in the manner of the thiocarbocyanines, and succeeded in obtaining good yields of 2,2′-diethylselenocarbocyanine iodide (LXXVIII), [**30**], and the corresponding methiodide by boiling the appropriate alkyl halide of 1-methylbenzoselenazole with orthoformic ester in dry pyridine solution (Hamer's method).



LXXVIII

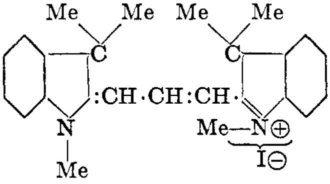
Like the thiocarbocyanines the selenocarbocyanines are powerful photographic sensitizers.

*Oxocarbocyanines.* When the quaternary salts of 1-methylbenzoxazole are treated with ethyl orthoformate in boiling acetic anhydride solution, oxocarbocyanines (LXXIX), [**31**], are produced (77), which are more resistant to acids than the corresponding sulfur analogs.



LXXIX

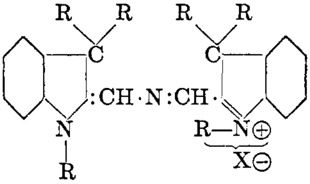
*Indocarbocyanines.* The above reaction when carried out with 1,2,3,3-tetramethylindolenine iodide in place of the oxazole derivative gives rise (78) to the indocarbocyanine (LXXX), [**32**].



LXXX

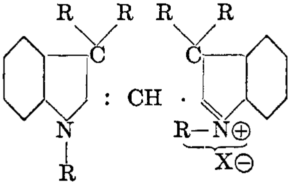
The indocarbocyanines are remarkable on account of their relatively great stability towards mineral acids.

Quite recently (90) a very interesting series of indocarbocyanine derivatives having the formula LXXXI has been prepared



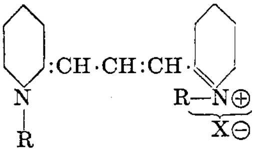
LXXXI

by the treatment of 2-methylene-1,3,3-trialkylindolenine or the corresponding indoleninium salt with an ester or salt of nitrous acid in the presence of an acid anhydride. This constitution (LXXXI), however, has been disputed by Kuhn, Winterstein, and Balser (91), who assign to these compounds a symmetrical indocyanine formula (LXXXII) and entirely dissociate themselves from any claim of novelty about them.



LXXXII

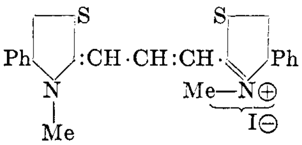
*Pyridocarbocyanines.* Curiously enough the quaternary salts of methylpyridine, in spite of the presence of a reactive methyl group, do not condense (67; cf. 79) with orthoformic ester to give the pyridocarbocyanines (LXXXIII), [33].



LXXXIII

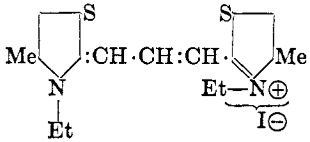
The synthesis of these compounds, however, has recently been achieved by Rosenhauer and Barlet (79), by the interaction of α-picoline alkyl halides and their derivatives with chloroform in the presence of a *large excess* of hot alcoholic caustic potash. The dyes are photographic sensitizers and the color of their solutions is discharged by mineral acids and restored by alkalies.

A dye of the type [**34**], (LXXXIV), is obtained together with the corresponding pseudocyanine, by the condensation of 4-phenyl-2-methylthiazolemethiodide with di-*o*-formylmethylaminodiphenyl disulfide in pyridine, as red needles with a brassy lustre.



4,4′-Diphenyl-3,3′-dimethylthiazole carbocyanine iodide
LXXXIV

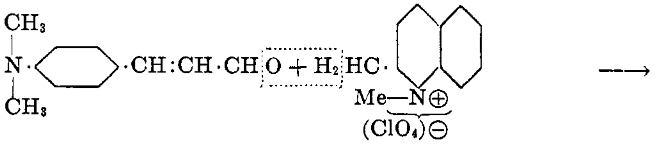
A much simpler (85) derivative (LXXXV) has been synthesized by Fisher and Hamer (46) by the orthoformic ester method, but the yield is extremely poor and the dye shows abnormal optical properties.



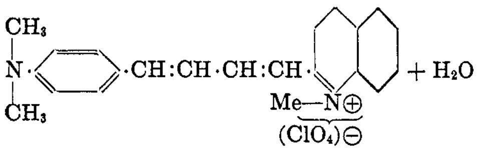
LXXXV

CYANINE DYES WITH FOUR METHENYL GROUPS BETWEEN THE TWO RINGS

Cyanine dyes having four methenyl groups between the two nuclei are comparatively scarce. König and Treichel (25), by the condensation of *p*-dimethylaminocinnamaldehyde (LXXXVI) with 2-methylquinoline methoperchlorate, obtained *p*-dimethylaminocinnamylidine-2-methylquinoline methoperchlorate (LXXXVII), [**35**], in lustrous green crystals.

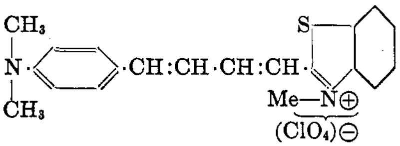


LXXXVI



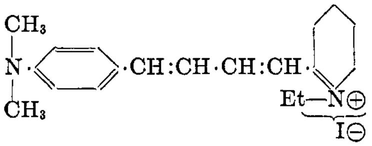
LXXXVII

In a similar manner the benzothiazole derivative (LXXXVIII), [36], was isolated. Bloch and Hamer (54) have prepared the



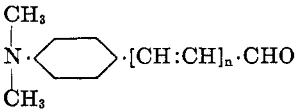
LXXXVIII

ethiodide corresponding to LXXXVIII, and also *p*-dimethylaminocinnamylidine-*α*-picoline ethiodide (LXXXIX), [37]. An examination (54) of their photographic properties has revealed that the cinnamylidine derivatives have but little photographic activity.



LXXXIX

So far no dye has been prepared which has more than four methenyl groups between the two rings, but considering the work of König, Rösch, and Schramek (86), which has culminated in the successful preparation of higher vinylene homologs of *p*-dimethylaminobenzaldehyde (XC), such a synthesis is not quite improbable.



XC

## REFERENCES

(1) German patent 154,448; Chem. Zentr. **1904,** II, 967; Brit. Chem. Abstracts **1904,** I, 1048.

(2) Kaufmann, A., and Strübin, P.: Ber. **44,** 690 (1911); Chem. Zentr. **1911,** I, 1140; Brit. Chem. Abstracts **1911,** I, 328.
See also Popper, N.: Sur la constitution des cyanines. Thése, Genéve, 1909. Sznajder, L.: Sur la constitution des apocyanines. Thése, Grenoble, 1910. Anastachewitch, A.: Sur les colorants de quinoline. Thése, Genéve, 1911. Strübin, P.: Sur les cyanines. Thése, Genéve, 1911.

(3) Bloch, O., and Hamer, F. M.: Phot. J. **68,** 21 (1928); Chem. Zentr. **1928,** I, 874; Brit. Chem. Abstracts **1928,** B, 285.

(4) König, W.: Ber. **55,** 3293 (1922); Chem. Zentr. **1923,** I, 443; Brit. Chem. Abstracts **1922,** I, 1188.

(5) Mills, W. H., and Ordish, H. G.: J. Chem. Soc. **1928,** 81; Chem. Zentr. **1928,** I, 1662; Brit. Chem. Abstracts **1928,** A, 308. See also Ann. Reports **25,** 180 (1928).

(6) Williams, G.: Dingler's polytech. J. **155,** 208; Chem. Zentr. **1860,** 359, 384; Chem. News. **2,** 15 (1860); Jahresber. **1860,** 361, 735. For earlier work see reference 6a.

(6a) Williams, G.: Trans. Roy. Soc. Edinburgh **31,** Pt. III, 377 (1856); Jahresber. **1856,** 532.

(7) von Babo: J. prakt. Chem. **72,** 73 (1857); Chem. Zentr. **1858,** 218.

(8) Gewerbebl. aus Württemberg **1861,** No. 19; Chem. Zentr. **1861,** 637.

(9) Hoogewerff, S., and Van Dorp, W. A.: Rec. trav. chim. **2,** 317 (1883); Chem. Zentr. **1884,** 138; Brit. Chem. Abstracts **1885,** 673. See also reference 27a.

(10) Hoogerwerff, S., and Van Dorp, W. A.: Rec. trav. chim. **1,** 1 (1882); Chem. Zentr. **1882,** 724; Brit. Chem. Abstracts **1883,** 89. See also references 10a–b.

(10a) Fischer, O.: Ber. **16,** 721 (1883).

(10b) German patent 155,541; Chem. Zentr. **1904,** II, 1527; Brit. Chem. Abstracts **1905,** I, 149.

(11) Hoogerwerff S., and Van Dorp, W. A.: Rec. trav. chim. **2,** 41 (1883); Chem. Zentr. **1883,** 434. For the preparation of the derivatives of true cyanines see reference 10b.

(11a) Barbier, H.: Bull. soc. chim. **28,** 427 (1920); Chem. Zentr. **1920,** III, 252; Brit. Chem. Abstracts **1920,** I, 568; J. Soc. Chem. Ind. **39,** 528A (1920). In regard to the photographic properties of true cyanines see references 30, 10b, 27f, 33b.

(12) Hofmann, A. W.: Compt. rend. **55,** 849 (1862); Chem. Zentr. **1863,** 353.

(12a) Hofmann, A. W.: Proc. Roy. Soc. London **12,** 410 (1863); Chem. News **7,** 85 (1863); Jahresber. **1862,** 351.

(13) Nadler, G., and Merz, V.: J. prakt. Chem. **100,** 129 (1867); Chem. Zentr. **1867,** 497.

(14) Miethe, A., and Book, G.: Ber. **37,** 2821 (1904); Chem. Zentr. **1904,** II, 661; Brit. Chem. Abstracts **1904,** I, 776.

(15) König, W.: J. prakt. Chem. **73**, 100 (1906); Chem. Zentr. **1906**, I, 763; Brit. Chem. Abstracts **1906**, I, 207.
(16) Spalteholtz, W.: Ber. **16**, 1847 (1883); Chem. Zentr. **1884**, 472; Brit. Chem. Abstracts **1883**, 1150.
(17) Hoogewerff, S., and Van Dorp, W. A.: Rec. trav. chim. **3**, 344 (1884). See also reference 11.
(18) Decker, H.: Ber. **24**, 692 (1891).
(19) Decker, H., and Kaufmann, A.: J. prakt. Chem. **84**, 235 (1911); Chem. Zentr. **1911**, II, 959; Brit. Chem. Abstracts **1911**, I, 807.
(20) Miethe, A., and Book, G.: Ber. **37**, 2008 (1904); Chem. Zentr. **1904**, II, 124; Brit. Chem. Abstracts **1904**, I, 622. See also references 20a–b.
(20a) Phot. Corresp. **1905**, 135; Chem. Zentr. **1905**, I, 1564.
(20b) Book, G.: Ber. **38**, 3804 (1905); Chem. Zentr. **1906**, I, 50; Brit. Chem. Abstracts **1906**, I, 42.
(21) König, W.: J. prakt. Chem. **86**, 166 (1912); Chem. Zentr. **1912**, II, 1219; Brit. Chem. Abstracts **1912**, I, 729.
(22) Vongerichten, E., and Höfchen, C.: Ber. **41**, 3054 (1908); Chem. Zentr. **1908**, II, 1606; Brit. Chem. Abstracts **1908**, I, 914.
(23a) Kaufmann, A., and Vonderwahl, E.: Ber. **45**, 1404 (1912); Chem. Zentr. **1912**, I, 2028; Brit. Chem. Abstracts **1912**, I, 502. Compare reference 23b.
(23b) Adams, E. Q., and Haller, H. L.: J. Am. Chem. Soc. **42**, 2389 (1920); Chem. Zentr. **1921**, I, 368; Brit. Chem. Abstracts **1921**, I, 53; J. Soc. Chem. Ind. **40**, 75A (1921).
(24) Mills, W. H., and Evans, P. E.: J. Chem. Soc. **117**, 1035 (1920); Chem. Zentr. **1921**, I, 28. See also Ann. Reports **17**, 121 (1920).
(25) König, W., and Treichel, O.: J. prakt. Chem. **102**, 63 (1921); Chem. Zentr. **1921**, III, 876; Brit. Chem. Abstracts **1921**, I, 738.
(26) Mills, W. H., and Wishart, R. S.: J. Chem. Soc. **117**, 579 (1920); Chem. Zentr. **1920**, III, 413. See also references 27j and 40.
(27a) de Coninck, O.: Rec. trav. chim. **4**, 58 (1885); Brit. Chem. Abstracts **1886**, 82.
(27b) British patent 9598; J. Soc. Chem. Ind. **23**, 384A (1904).
(27c) German patent 154,475; Chem. Zentr. **1904**, II, 1015.
(27d) German patent 158,078; Chem. Zentr. **1905**, I, 486; Brit. Chem. Abstracts **1905**, I, 548. See also reference 10b.
(27e) German patent 167,159; Chem. Zentr. **1906**, I, 799.
(27f) German patent 167,770; Chem. Zentr. **1906**, I, 1127; Brit. Chem. Abstracts **1906**, I, 716.
(27g) German patent 170,048; 170,049; Chem. Zentr. **1906**, I, 1857; Brit. Chem. Abstracts **1906**, I, 885.
(27h) U. S. patent 805,143; J. Soc. Chem. Ind. **25**, 13A (1906).
(27i) Mills, W. H., and Pope, W. J.; Phot. J. **60**, 183 (1920); J. Soc. Chem. Ind. **39**, 468A (1920). See also reference 11a.
(27j) Hamer, F. M.: J. Chem. Soc. **119**, 1432 (1921); Chem. Zentr. **1922**, I, 137; J. Soc. Chem. Ind. **40**, 791A (1921). See also references 23a and 33g.
(27k) Moudgill, K. L.: J. Chem. Soc. **121**, 1509 (1922); Chem. Zentr. **1923**, I, 88.

(28) Jacobson, E.: German patent 19,306; Ber. (Referate) **15,** 2646 (1882).

(29) Hofmann, A. W.: Ber. **20,** 4 (1887); Chem. Zentr. **1887,** 189; Brit. Chem. Abstracts **1887,** 380. See also Pope, W. J., and Harris, J. E. G.: J. Chem. Soc. **121,** 1029 (1922); Chem. Zentr. **1922,** III, 620; J. Soc. Chem. Ind. **41,** 581A (1922).

(30) Vogel, H. W.: German patent 19,306; Ber. (Referate) **20,** 620 (1887).

(31a) Vongerichten, E., and Krantz, L.: Ber. **43,** 128 (1910); Chem. Zentr. **1910,** I, 839; Brit. Chem. Abstracts **1910,** I, 201.

(31b) Vongerichten, E., and Homann, W.: Ber. **45,** 3446 (1912); Chem. Zentr. **1913,** I, 298; Brit. Chem. Abstracts **1913,** I, 99.

(31c) Krantz, L. P.: Chem. Weekblad **11,** 364 (1914); Chem. Zentr. **1914,** I, 2182; Brit. Chem. Abstracts **1914,** I, 740. Compare reference 39.

(32) Hamer, F. M.: J. Chem. Soc. **1930,** 995; Brit. Chem. Abstracts **1930,** A, 930.

(33a) Valenta, E.: Phot. Corresp. **1903,** 6S; Chem. Zentr. **1903,** II, 267.
See also Newton, A. J., and Bull, A. J.: Phot. J. **45,** 15 (1905).

(33b) Miethe, A.: Die Chemische Industrie **26,** 54 (1903); Chem. Zentr. **1903,** I, 553; J. Soc. Chem. Ind. **22,** 318 (1903). See also references 27f, 27e, 27j, 27k, 10b.

(33c) König, E.: Phot. Mitt. **41,** 81 (1904); J. Soc. Chem. Ind. **23,** 383 (1904).

(33d) Sheppard, S. E.: Brit. J. Phot. **55,** 679 (1908).

(33e) Sheppard, S. E.: J. Chem. Soc. **95,** 15 (1909); Chem. Zentr. **1909,** I, 85; J. Soc. Chem. Ind. **27,** 876 (1908).

(33f) Lumière, A. and L., and Barbier, H.: Bull. soc. franç. phot. **7,** 182 (1920); J. Soc. Chem. Ind. **40,** 27A (1921).

(33g) Adams, E. Q., and Haller, H. L.: U. S. patent 1,374,871; 1,374,872; Chem. Zentr. **1922,** IV, 248; J. Soc. Chem. Ind. **40,** 413A (1921).

(33h) Hamer, F. M.: Phot. J. **62,** 8 (1922); J. Soc. Chem. Ind. **41,** 120A (1922).

(34) In regard to the crystallography and optical properties of pinaverdol, see Wherry, E. T., and Adams, E. Q.: J. Wash. Acad. Sci. **9,** 396 (1919); Chem. Zentr. **1920,** III, 416; J. Soc. Chem. Ind. **38,** 756A (1919).

(35a) Brauholtz, W. T. K., and Mills, W. H.: J. Chem. Soc. **121,** 2004 (1922); Chem. Zentr. **1923,** I, 935; J. Soc. Chem. Ind. **41,** 997A (1922). Compare reference 35b.

(35b) Hofmann, A. W.: Ber. **20,** 2264 (1887); Chem. Zentr. **1887,** 1137; Brit. Chem. Abstracts **52,** 1039 (1887).

(36) Mills, W. H., and Odams, R. C.: J. Chem. Soc. **125,** 1919 (1924); Chem. Zentr. **1924,** II, 2483; J. Soc. Chem. Ind. **43,** B934 (1924). See also reference 42.

(37) Mills, W. H., and Smith, J. L. B.: J. Chem. Soc. **121,** 2736 (1922); Chem. Zentr. **1923,** I, 760.

(38a) Fischer, O., Bauer, C., Merkel, P., Scheibe, G., and Müller, R.: J. prakt. Chem. **98,** 204 (1918); Chem. Zentr. **1919,** I, 465; Brit. Chem. Abstracts **1919,** I, 172; J. Soc. Chem. Ind. **38,** 199A (1919).

(38b) Fischer, O., and Scheibe, G.: J. prakt. Chem. **100,** 86 (1919); Chem. Zentr. **1920,** III, 515; Brit. Chem. Abstracts **1921,** I, 56; J. Soc. Chem. Ind. **40,** 41A (1921).

(39) Scheibe, G., and Rossner, E.: Ber. **54,** 786 (1921); Chem. Zentr. **1921,** I, 903; Brit. Chem. Abstracts **1921,** I, 451.

(40) Hamer, F. M.: J. Chem. Soc. **1928,** 206; Chem. Zentr. **1928,** I, 1773; Brit. Chem. Abstracts **1928,** A, 307.

(41) Hamer, F. M.: J. Chem. Soc. **125,** 1348 (1924); Chem. Zentr. **1924,** II, 845; J. Soc. Chem. Ind. **43,** B667 (1924).

(42) Mills, W. H., and Braunholtz, W. T. K.: J. Chem. Soc. **123,** 2804 (1923); Chem. Zentr. **1924,** I, 1383; J. Soc. Chem. Ind. **43,** B155 (1924). Compare reference 36.

(43) Hamer, F. M.: J. Chem. Soc. **1929,** 2598; Chem. Zentr. **1930,** I, 2100. See also reference 40.

(44) Mills, W. H., Clark, L. M., and Aeschlimann, J. A.: J. Chem. Soc. **123,** 2353 (1923); Chem. Zentr. **1923,** III, 1617; J. Soc. Chem. Ind. **42,** 1063A (1923).

(45) Mills, W. H.: J. Chem. Soc. **121,** 455 (1922); Chem. Zentr. **1922,** III, 1227; J. Soc. Chem. Ind. **41,** 365A (1922). See also Ann. Reports **19,** 154 (1922).

(46) Fisher, N. I., and Hamer, F. M.: J. Chem. Soc. **1930,** 2502.

(47) Moir, J.: J. Chem. Soc. **127,** 2338 (1925); Chem. Zentr. **1926,** I, 946.

(48) Mills, W. H., and Raper, R.: J. Chem. Soc. **127,** 2466 (1925): Chem. Zentr. **1926,** I, 1578; Brit. Chem. Abstracts **1926,** A, 77. See also Ann. Reports **22,** 143 (1925).

(49) König, W.: Ber. **55,** 3293 (1922); Chem. Zentr. **1923,** I, 443; Brit. Chem. Abstracts **1922,** I, 1188; J. Soc. Chem. Ind. **41,** 934A (1922). Compare references 50 and 51.

(50) Vongerichten, E., and Rotta, W.: Ber. **44,** 1419 (1911); Chem. Zentr. **1911,** II, 472; Brit. Chem. Abstracts **1911,** I, 677.

(51) Fischer, O., Diepolder, E., and Wölfel, E. W.: J. prakt. Chem. **109,** 59, 69 (1925); Chem. Zentr. **1925,** I, 1315, 1316; Brit. Chem. Abstracts **1925,** I, 438, 439.

(52) Smith, J. L. B.: J. Chem. Soc. **123,** 2288 (1923); Chem. Zentr. **1924,** I, 186; J. Soc. Chem. Ind. **42,** 1102A (1923).

(53) König, W.: Ber. **61,** 2065 (1928); Chem. Zentr. **1928,** II, 2250; Brit. Chem. Abstracts **1928,** A, 1385.

(54) Bloch, O., and Hamer, F. M.: Phot. J. **70,** 374 (1930); Brit. Chem. Abstracts **1930,** B, 928.

(55) Hamer, F. M.: Phot. J. **69,** 409 (1929); Brit. Chem. Abstracts **1929,** B, 1032. See also German patent 396,402; J. Soc. Chem. Ind. **43,** B902 (1924).

(56) Kaufmann, A., and Vallette, L. G.: Ber. **45,** 1736 (1912); Chem. Zentr. **1912,** II, 358; Brit. Chem. Abstracts **1912,** I, 655.

(57) Rosenhauer, E., Schmidt, A., and Schleifenbaum, W.: J. prakt. Chem. **107,** 232 (1924); Chem. Zentr. **1924,** II, 338; Brit. Chem. Abstracts **1924,** I, 768; J. Soc. Chem. Ind. **43,** B551 (1924).

(58) Mills, W. H., and Pope, W. J.: J. Chem. Soc. **121,** 946 (1922); Chem. Zentr. **1922,** IV, 1024; J. Soc. Chem. Ind. **41,** 524A, 293R (1922).

(59) Adams, E. Q., and Haller, H. L.: J. Am. Chem. Soc. **42,** 2661 (1920); Chem. Zentr. **1921,** I, 574; Brit. Chem. Abstracts **1921,** I, 129; J. Soc. Chem. Ind. **40,** 75A (1921). Compare references 62 and 59a-b.

(59a) Mees, C. E. K., and Gutekunst, G.: Ind. Eng. Chem. **14,** 1060 (1922); Brit. J. Phot. **69,** 474 (1922); J. Soc. Chem. Ind. **41,** 689A (1922).

(59b) Ann. Reports **18,** 139 (1921).

(60) Mikeska, L. A., Haller, H. L., and Adams, E. Q.: J. Am. Chem. Soc. **42,** 2392 (1920); Chem. Zentr. **1921,** I, 368; J. Soc. Chem. Ind. **40,** 75A (1921). See also reference 60a.

(60a) Wise, L. E., and Adams, E. Q.: Ind. Eng. Chem. **10,** 801 (1918); Chem. Zentr. **1919,** II, 213.

(61) Palkin, S.: Ind. Eng. Chem. **15,** 379 (1923); Chem. Zentr. **1923,** III, 853; J. Soc. Chem. Ind. **42,** 544A (1923). See also reference 61a.

(61a) U. S. patent 1,437,674; J. Soc. Chem. Ind. **42,** 119A (1923).

(62) British patent 292,374; Brit. Chem. Abstracts **1928,** B, 625.

(63a) German patent 172,118; Chem. Zentr. **1906,** II, 650; Brit. Chem. Abstracts **1906,** I, 886. Compare reference 38a.

(63b) German patent 175,034; Chem. Zentr. **1906,** II, 1095.

(63c) Wise, L. E., Adams, E. Q., Stewart, J. K., and Lund, C. H.: Ind. Eng. Chem. **11,** 460 (1919); Chem. Zentr. **1920,** I, 754; J. Soc. Chem. Ind. **38,** 456A (1919).

(63d) Mills, W. H., and Pope, W. J.: Phot. J. **60,** 253 (1920); J. Soc. Chem. Ind. **39,** 802A, 235R (1920).

(64) German patent 200,207; Chem. Zentr. **1908,** II, 367.

(65) German patent 189,942; Chem. Zentr. **1907,** II, 2011. See also reference 65a.

(65a) German patent 178,688; Chem. Zentr. **1907,** I, 779.

(66) Ogata, T.: Proc. Imp. Acad. Tokyo **3,** 334 (1927); Chem. Zentr. **1927,** II, 1961–2; Brit. Chem. Abstracts **1927,** A, 1089.

(67) Hamer, F. M.: J. Chem. Soc. **1927,** 2796; Chem. Zentr. **1928,** I, 703; Brit. Chem. Abstracts **1928,** A, 76. See also reference 67a.

(67a) Ann. Reports **24,** 165 (1927).

(68) Mills, W. H., and Hamer, F. M.: J. Chem. Soc. **117,** 1550 (1920); Chem. Zentr. **1921,** I, 735; J. Soc. Chem. Ind. **40,** 41A (1921).

(69) Hamer, F. M.: J. Chem. Soc. **123,** 246 (1923); Chem. Zentr. **1923,** I, 1233; J. Soc. Chem. Ind. **42,** 646A (1923). See also reference 69a.

(69a) Ann. Reports **20,** 151 (1923).

(70) Hamer, F. M.: J. Chem. Soc. **127,** 211 (1925); Chem. Zentr. **1925,** I, 2378; J. Soc. Chem. Ind. **44,** B164 (1925).

(71a) Braunholtz, W. T. K.: J. Chem. Soc. **121,** 169 (1922); Chem. Zentr. **1922,** III, 378; J. Soc. Chem. Ind. **41,** 198A (1922).

(71b) Hamer, F. M.: J. Chem. Soc. **123,** 2333 (1923); Chem. Zentr. **1923,** III, 1619; J. Soc. Chem. Ind. **42,** 1103A (1923). Compare reference 59a.

(71c) U. S. patent 1,568,667; Chem. Zentr. **1926,** I, 2851; Brit. Chem. Abstracts **1926,** B, 265.

(71d) Schmidt, A., and Unger, H.: Ber. **59,** 2356 (1926); Chem. Zentr. **1926,** II, 2723; Brit. Chem. Abstracts **1926,** A, 1260. See also Rosenhauer, E., and Fischer, O.: Z. angew. Chem. **36,** 330 (1923). Compare reference 69.

(72) Dundon, M. L., Schoen, A. L., and Briggs, R. M.: J. Optical Soc. Am. **12,** 397 (1926); Chem. Zentr. **1926,** II, 318; Brit. Chem. Abstracts **1926,** B, 566. Compare Blunck: Astr. Nachr. **231,** 338 (1928).

(73) Hamer, F. M.: J. Chem. Soc. **1928,** 1472; Chem. Zentr. **1928,** II, 896; Brit. Chem. Abstracts **1928,** A, 901.

(74) Fuchs, K., and Grauaug, E.: Ber. **61,** 57 (1928); Chem. Zentr. **1928,** I, 1045; Brit. Chem. Abstracts **1928,** A, 430.

(75) Hamer, F. M.: J. Chem. Soc. **1928,** 3160; Chem. Zentr. **1929,** I, 897; Brit. Chem. Abstracts **1929,** A, 197. See also reference 75a.

(75a) Ann. Reports **26,** 164 (1929).

(76) Clark, L. M.: J. Chem. Soc. **1928,** 2314; Chem. Zentr. **1928,** II, 2145; Brit. Chem. Abstracts **1928,** A, 1264.

(77) König, W., and Meier, W.: J. prakt. Chem. **109,** 324 (1925); Chem. Zentr. **1925,** I, 2695; Brit. Chem. Abstracts **1925,** I, 705; J. Soc. Chem. Ind. **44,** B392 (1925).

(78) König, W., and Wagner, E.: Ber. **57,** 685 (1924); Chem. Zentr. **1924,** I, 2597; Brit. Chem. Abstracts **1924,** I, 685.

(79) Rosenhauer, E., and Barlet, F.: Ber. **62,** 2724 (1929); Chem. Zentr. **1930,** I, 385; Brit. Chem. Abstracts **1930,** A, 95.

(80a) Pope, W. J.: J. Soc. Chem. Ind. **39,** 369R (1920).

(80b) Pope, W. J.: Bull. soc. chim. Belg. **30,** 169 (1921); Chem. Zentr. **1921,** IV, 1050.

(80c) Meyer, V., and Jacobson, P.: Lehrbuch der organischen Chemie, Vol. II, part III, pp. 934 and 999. Vereinigung Wissenschaftlicher Verleger, Walter de Pruyter and Co., Berlin and Leipzig (1920).

(80d) Science Progress **23,** 585 (1929).

(81) Renwick, E. F.: J. Soc. Chem. Ind. **42,** 46T (1923).

(82) Sheppard, S. E.: Proc. Roy. Soc. London **82A,** 256 (1909); Chem. Zentr. **1909,** II, 74; Brit. Chem. Abstracts **1909,** II, 531; J. Soc. Chem. Ind. **28,** 697 (1909).

(83) Mills, W. H., and Braunholtz, W. T. K.: J. Chem. Soc. **121,** 1489 (1922); Chem. Zentr. **1923,** I, 934; J. Soc. Chem. Ind. **41,** 804A (1922).

(84) Fischer, O., Scheibe, G., Merkel, P., and Müller, R.: J. prakt. Chem. **100,** 91 (1919); Chem. Zentr. **1920,** III, 513; Brit. Chem. Abstracts **1921,** I, 54.

(85) Compare König, W.; Z. angew. Chem. **38,** 743 (1925); Chem. Zentr. **1926,** I, 92; Brit. Chem. Abstracts **1925,** I, 1184.

(86) König, W., Schramek, W., and Rösch, G.: Ber. **61,** 2074 (1928); Chem. Zentr. **1928,** II, 2239; Brit. Chem. Abstracts **1928,** A, 1375.

(87) Browning, C. H., Cohen, J. B., and Gulbransen, R.: Brit. Med. J. **1922,** I, 514; Chem. Zentr. **1922,** III, 1381; Brit. Chem. Abstracts **1922,** I, 1097. See also references 87a-b.

(87a) Browning, C. H., Cohen, J. B., Ellingworth, S., and Gulbransen, R.: Proc. Roy. Soc. London **96B,** 317 (1924); Chem. Zentr. **1924,** II, 1229; Brit. Chem. Abstracts **1924,** I, 911.

(87b) Karwacki, Léon, and Biernacki, Stanislas: Ann. inst. Pasteur **39,** (1925); Chem. Zentr. **1925,** II, 832; Brit. Chem. Abstracts **1925,** I, 1015.

(88) Heilbron, I. M., Holt, S. L., and Kitchen, F. N.: J. Chem. Soc. **1928,** 936; Chem. Zentr. **1928,** II, 53; Brit. Chem. Abstracts **1928,** A, 650.

(89) In regard to the bleaching and photoxidation of cyanine dyes, see references 89a-e.

(89a) Lazarew, P.: Ann. Physik **24,** 661 (1907); Chem. Zentr. **1908,** I, 200.

(89b) LAZAREFF, P. P.: J. Russ. Phys. Chem. Soc. **39**, 236 (1907); Brit. Chem. Abstracts **1908**, II, 4.
(89c) WAWILOW, S.: Z. physik. Chem. **88**, 35 (1914); Chem. Zentr. **1914**, II, 602; Brit. Chem. Abstracts **1914**, II, 640.
(89d) PLOTNIKOW, J.: Z. Elektrochem. **32**, 13 (1926); Chem. Zentr. **1926**, I, 2881.
(89e) ZCHODRO, N.: J. chim. phys. **26**, 59 (1929); Chem. Zentr. **1929**, I, 3072; Brit. Chem. Abstracts **1929**, A, 523; and subsequent papers.
(90) German patent 459,616; Chem. Zentr. **1928**, I, 3119.
(91) KUHN, R., WINTERSTEIN A., AND BALSER, G.: Ber. **63**, 3176 (1930).
(92) MEES, C. E. K., AND WRATTEN, H. S.: Phot. J. **48**, 25 (1908).
(93) VOGEL, H. W.: Ber. **8**, 95 (1875); Chem. Zentr. **1875**, 178; Brit. Chem. Abstracts **28**, 604 (1875). See also references 93a-d.
(93a) VOGEL, H. W.: Ber. **8**, 1635 (1875); Chem. Zentr. **1876**, 129; Brit. Chem. Abstracts **1876**, I, 510.
(93b) VOGEL, H. W.: Ber. **6**, 1302 (1873); Chem. Zentr. **1874**, 49; Brit. Chem. Abstracts **27**, 217 (1874).
(93c) BECQUEREL, E.: Compt. rend. **79**, 185 (1874); Brit. Chem. Abstracts **28**, 30 (1875).
(93d) WATERHOUSE: Phot. J. **44**, 165 (1904): **55**, 123 (1915).