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Thirty-Five Years of Studies on the Chemistry of Polymethine Cyanine Dyes

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ABSTRACT

Studies on the chemistry of polymethine cyanine dyes carried out since 1958 at the East China University of Science and Technology (formerly the East China University of Chemical Technology) are reviewed. The dyes studied include polymethine cyanine dyes used in photography and dye lasers. Kinetic studies of the formation of polymethine dyes, and the theory of sensitization are also described.

1 INTRODUCTION

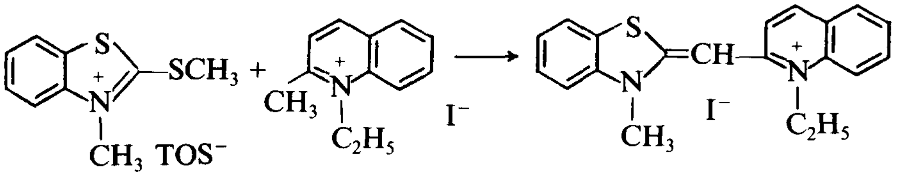
Polymethine cyanine dyes are a type of synthetic dye used both in photography and dye lasers. At the beginning of the development of the photographic industry in China in 1958, we were engaged in the syntheses of polymethine cyanine dyes which were very important in the production of photofilms. Later, the theory of sensitization was studied in order to improve the qualities of the films. Since polymethine cyanine dyes had well established difficulties in their preparation, mechanistic studies were also carried out. More recently, some polymethine cyanine dyes have been found to be of value as infrared laser dyes. Studies of polymethine cyanine dyes in our Cyanine Dye Laboratory have continued for over 35 years; details of our research are briefly reviewed in the following paper.

2 SYNTHESES OF POLYMETHINE CYANINE DYES USED IN PANCHROMATIC AND AERIAL BLACK AND WHITE FILMS

(1) Syntheses of monomethine cyanine dyes

Thia-2'-cyanine and seleno-2'-cyanine

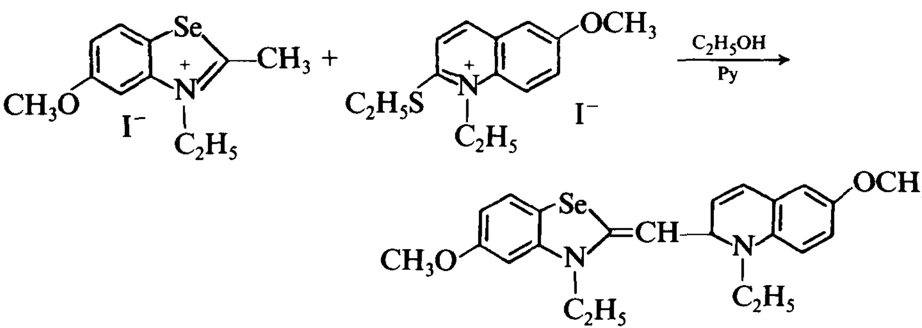
Monomethine cyanine dyes are one of the simplest type of dyes used in aerial black and white films. 3-Methyl-1'-ethyl-thia-2'-cyanine iodide is prepared by reacting quinaldine-3-methyl iodide with 2-thiomethyl-3-methyl benzothiazole p-toluenesulfonate in boiling pyridine for 6 h,[1,2] as outlined in Scheme 1.



Scheme 1

This dye is useful as a supersensitizer for 2,2'-cyanines and also acts as a sensitizer with simple merocyanines made from rhodamine and 4-methylthiopyridinum salts as supersensitizer.

Thia-2-cyanine is widely used in both aerial and lithographic films. One of the most important spectral sensitizers used in ortho and panchromatic films is N 1555, a seleno-2-cyanine. Its preparation is shown in Scheme 2:[3]



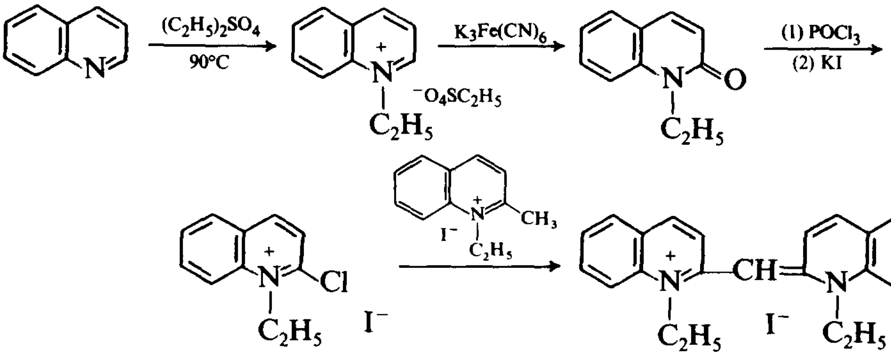
N 1555

Scheme 2

Compound N 1555 has $\lambda_{max} = 505$ nm, $S_{max} = 555$ nm and is used in conjunction with N 798 in panchromatic black and white films.

(2) 2,2'-cyanines

1,1'-Diethyl-2,2'-cyanine is one of the oldest dyes, but is still used today. Its preparation may be represented as shown in Scheme 3:



Scheme 3

The resulting compound has λ_{max} = 525 nm, S_{max} = 570 nm. Diethyl 2,2'-cyanine iodide is used together with 2,2'-thiacyanine as a supersensitizer in aerial film.

(3) Thiacarbocyanine dyes

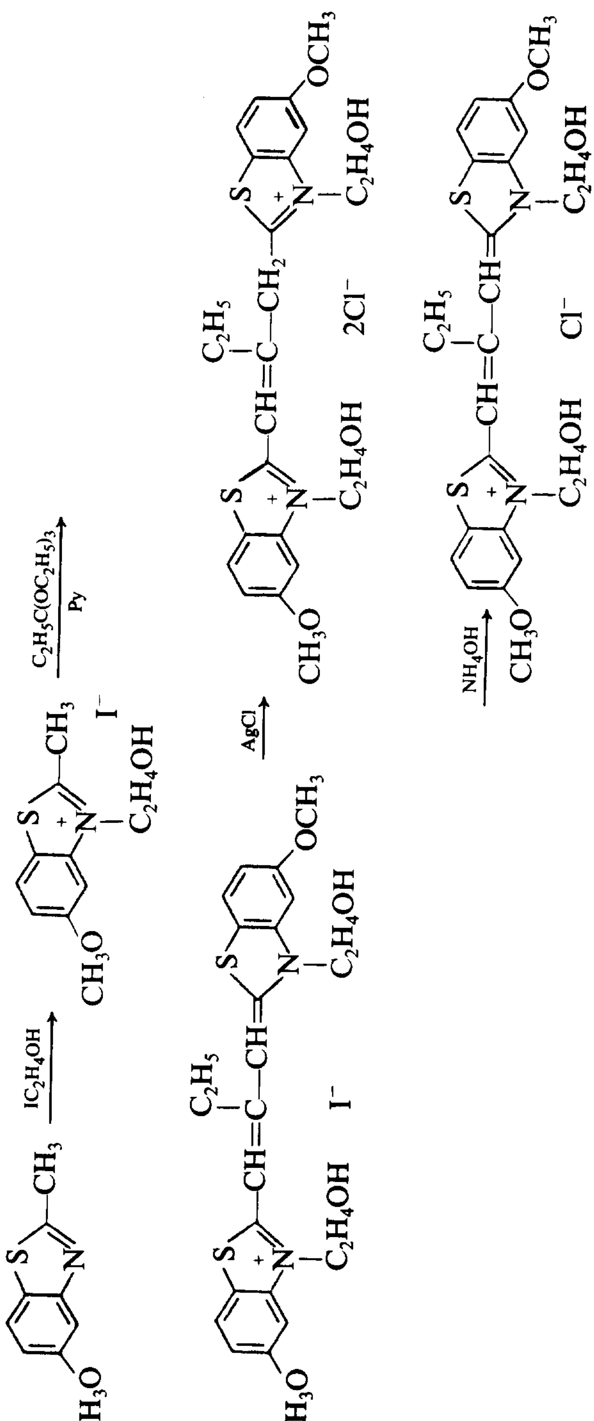
The most important thiacarbocyanine is N 798, which is now used in black and white panchromatic film. The structure and method of preparation is shown in Scheme 4. N 798 has λ_{max} = 560 nm, S_{max} = 650 nm, and is used in conjunction with N 1555 for panchromatic film.[4]

(4) Selenocarbocyanines

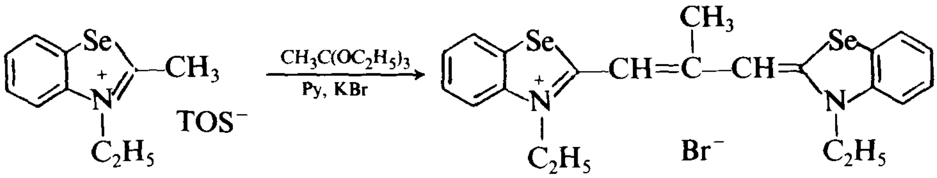
The most important selenocarbocyanine is 3,3-diethyl-9-methyl selenocarbocyanine bromide; its preparation is shown in Scheme 5. This meso-methyl selenocarbocyanine dye has λ_{max} = 552·5 nm, and is used together with the supersensitizer thia-2-cyanine to form a supersensitizing combination with S_{max} = 600 nm.[1]

(5) Naphthothiacarbocyanines

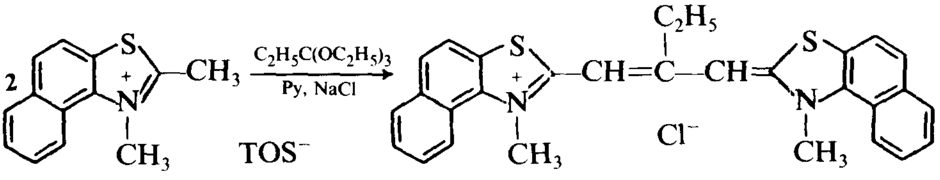
The most important naphthothiacarbocyanine dye, widely used today, is mesoethylnaphthothiacarbocyanine chloride. Its method of preparation is shown in Scheme 6.


IC2H4OH
C2H5C(OC2H5)3
Py
AgCl
NH4OH
CH3O
OCH3
CH3
C2H4OH
C2H5
CH=C—CH=
CH=C—CH2
I⁻
2Cl⁻
Cl⁻
N 789

Scheme 4



Scheme 5

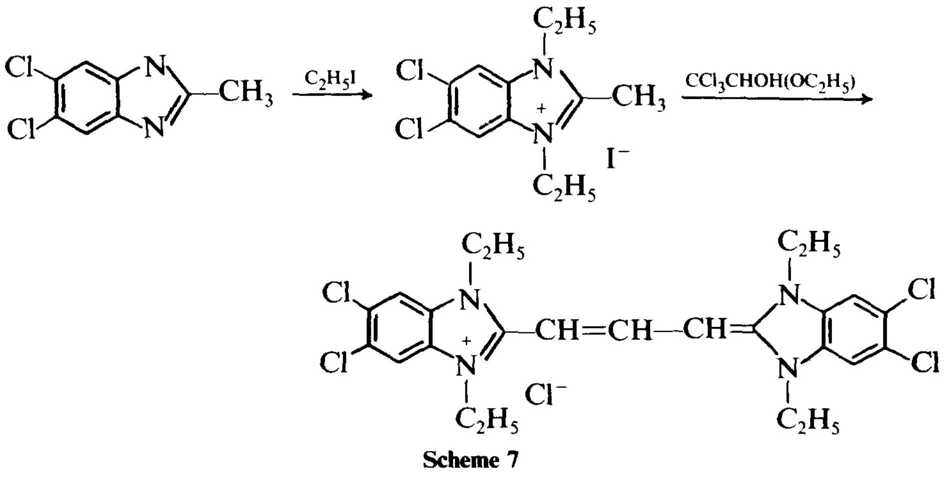


Scheme 6

The dye has λ_{max} = 571 nm, and is used, with a holopolar trinuclear cyanine dye, to form a supersensitizing combination with S_{max} = 680 nm, and a relative speed from 8·05 to 97. Therefore, this supersensitizing combination is much better than N 798, which has S_{max} = 650 nm and a lower sensitivity and which is used in aerial film.[1]

(6) Tetrachloro imidazolocarbocyanines

The most important imidazolocarbocyanine dye is the tetrachloro derivative. Its structure and method of preparation is shown below:

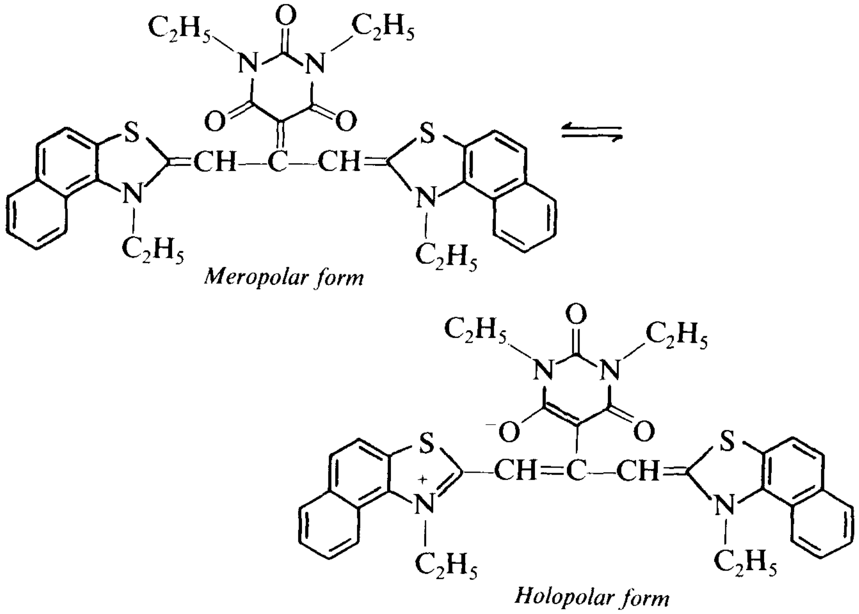


Scheme 7

The dye has λ_{max} = 518 nm and is used with thia-2-cyanine to form a supersensitizing combination with S_{max} = 570 nm. It is also used as a green sensitizing dye in colour film.[1]

(7) Holopolar trinuclear cyanine dyes

The holopolar trinuclear cyanine dyes and the holopolar isomerism may be represented by the following scheme:[6]



Meropolar form

Holopolar form

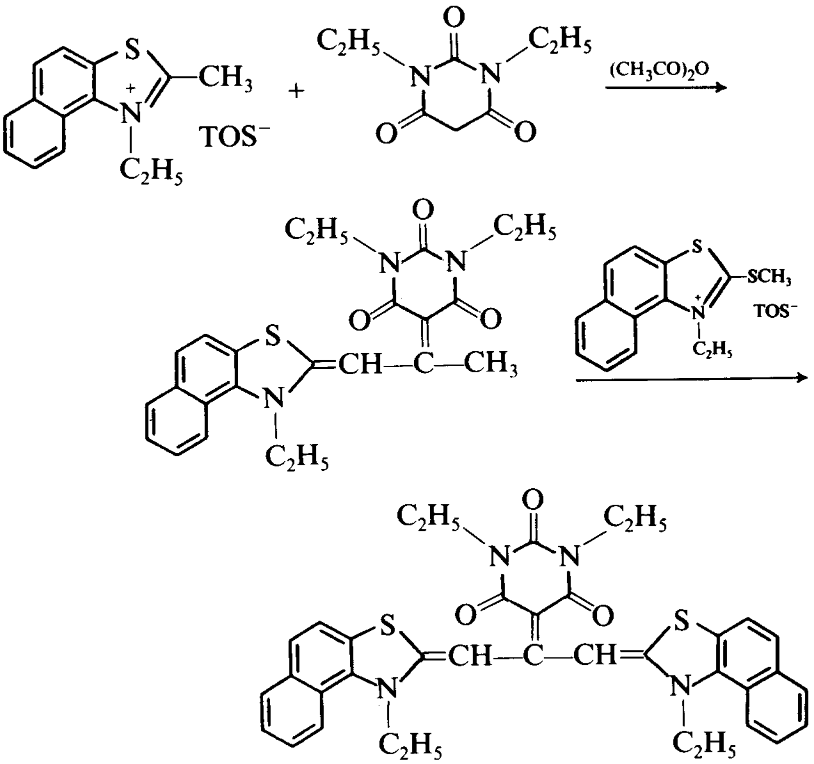
The method of preparation of trinuclear holopolar cyanine dyes derived from barbituric acid may be illustrated as shown in Scheme 8. Similar trinuclear holopolar cyanine dyes derived from acidic nuclei other than barbituric acid are shown in Scheme 9. TNC I is used, together with a naphthothiacyanine, for aerial film to form a supersensitizing combination with $S_{\max} = 680$ nm, the relative speed S increasing from 24 to 48.[5,6]

When TNC II is used in place of TNC I, $S_{\max} = 690$ nm is obtained. This is a better supersensitizing combination for red light in aerial film because it has an extended red sensitization range compared to TNC I and D 4.

(8) Supersensitizing combination of sensitizing dyes

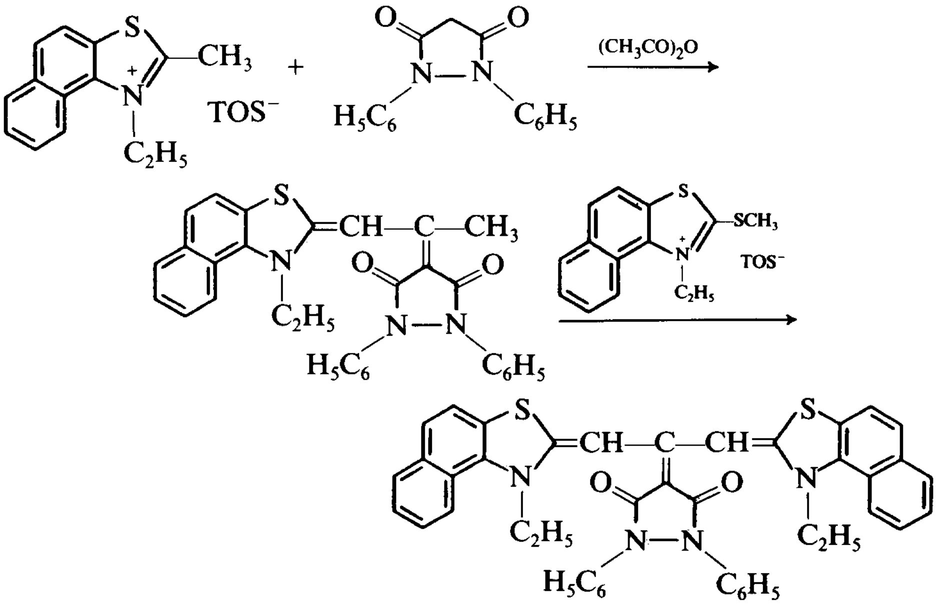
Supersensitization is the observable or measurable enhancement of the effect of a combination of sensitizers compared with that of the same amount of individual components.

Since supersensitization is of great importance from the viewpoints of photographic science and technology, many studies have been made on supersensitizing combinations with different end applications (see, for example, refs 1, 6 and 7).



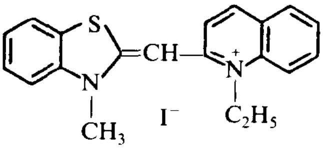
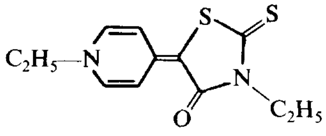
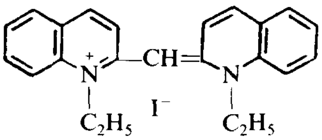
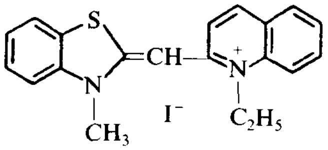
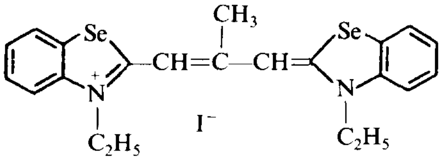
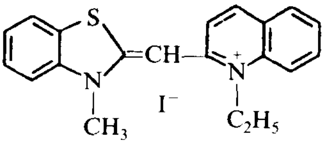
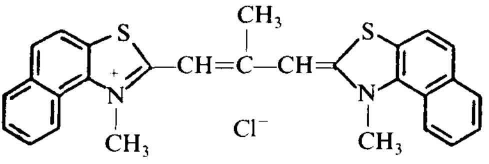
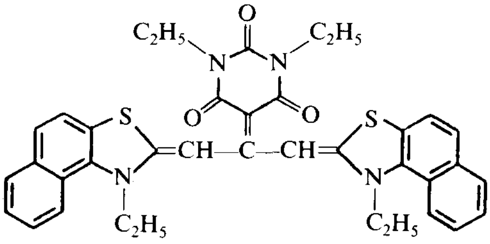
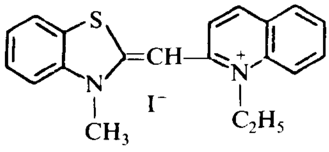
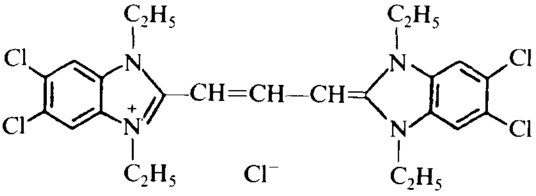
TNC I

Scheme 8



Scheme 9

TABLE 1
Useful Supersensitizing Combinations

No.	*Sensitizer*	*Supersensitizer*
1		
2		
3		
4		
5		

3 SYNTHESES OF POLYMETHINE CYANINE DYES USED IN COLOUR FILMS

Polymethine cyanine dyes used in multiple layer colour films must exhibit certain unique properties, viz.:

(i) they must not diffuse from one layer to another;
(ii) they must be of relatively high sensitivity;

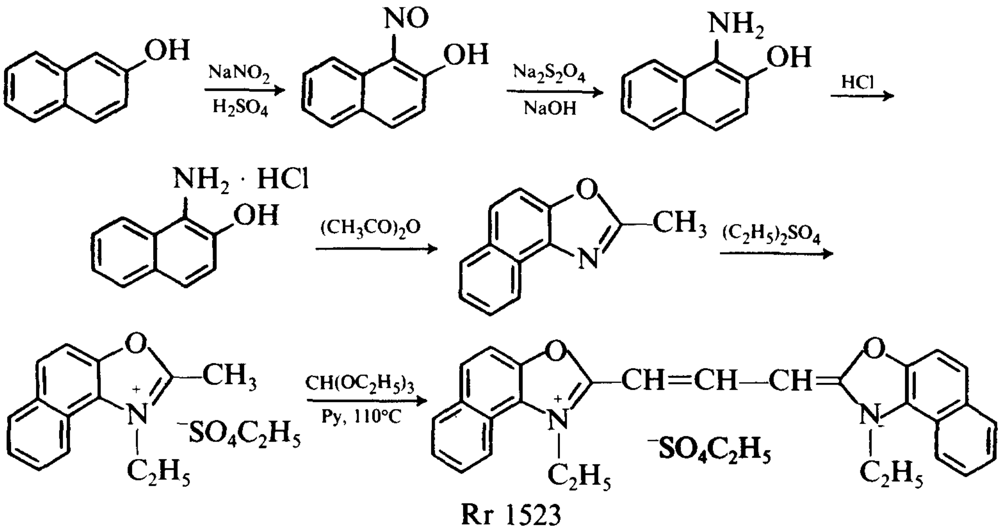
(iii) they must be strongly adsorbed on AgBr grains, even in the presence of colour couplers which are liable to desorb the cyanine dyes from the AgBr grains; and

(iv) for cyanine dyes used in positive colour film, the maximum wavelength of absorption of the cyanine dyes should be equal to the maximum absorption wavelength of the colour image formed in colour development from colour couplers added in respective layers of negative colour film.

(1) Oxacarbocyanine dyes

Rr 1523

The structure and preparation of Rr 1523 is shown in Scheme 10:

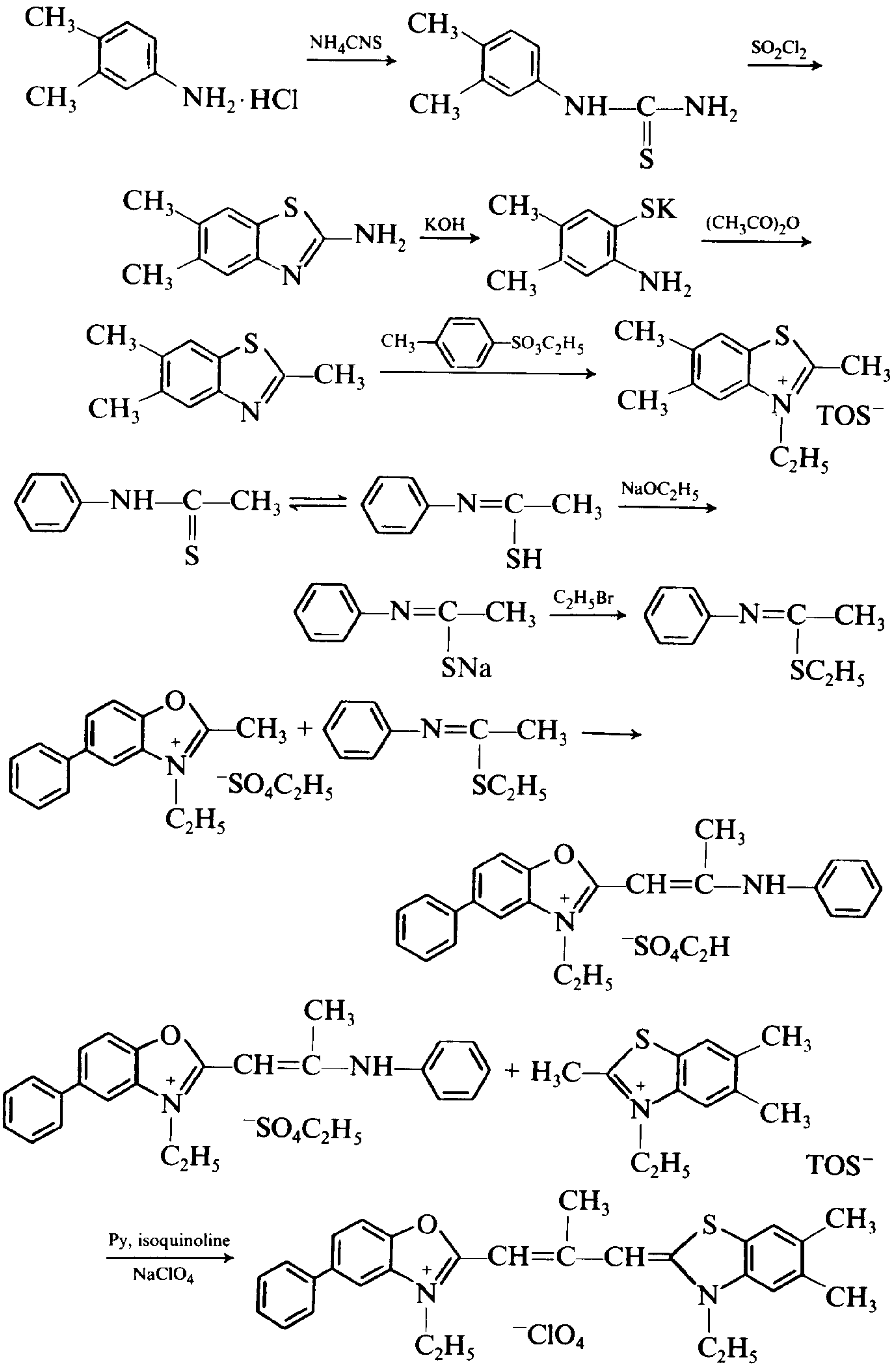


Scheme 10

Rr 1523 has S_{max} = 525 nm. It is used together with Rr 340 with S_{max} = 545–550 nm and Rr 1650 with S_{max} = 555–560 nm, in the green-sensitizing layer of negative colour film.[8]

Rr 1650

The structure and preparation of Rr 1650 is shown in Scheme 11. Rr 1650 has S_{max} = 555–560 nm and is used together with Rr 1523 and Rr 340 in the green-sensitizing layer.[9]

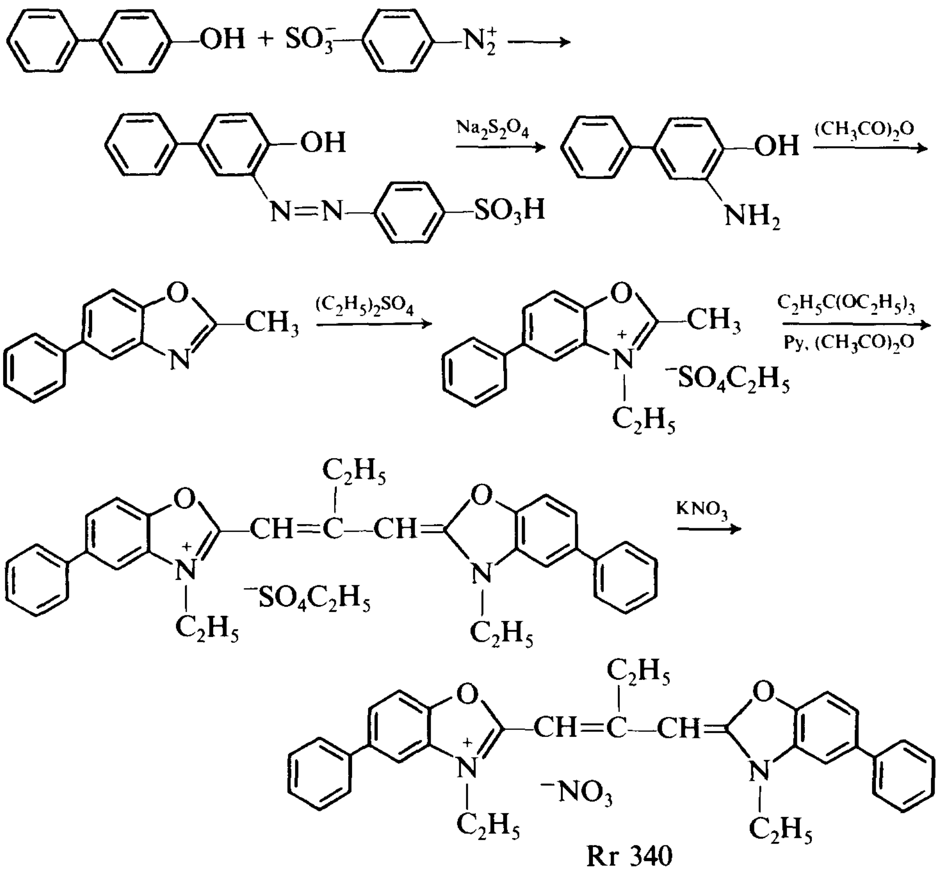


Scheme 11

Rr 1653

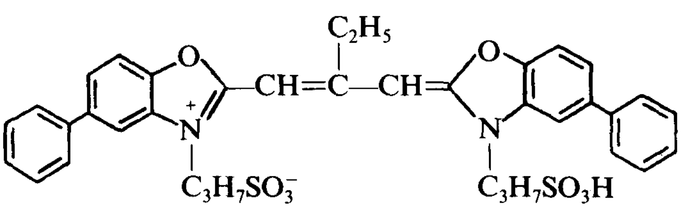
Rr 340

The structure and preparation of Rr 340 is shown below:



Scheme 12

An acceptable substitute for Rr 340 is D 1143:

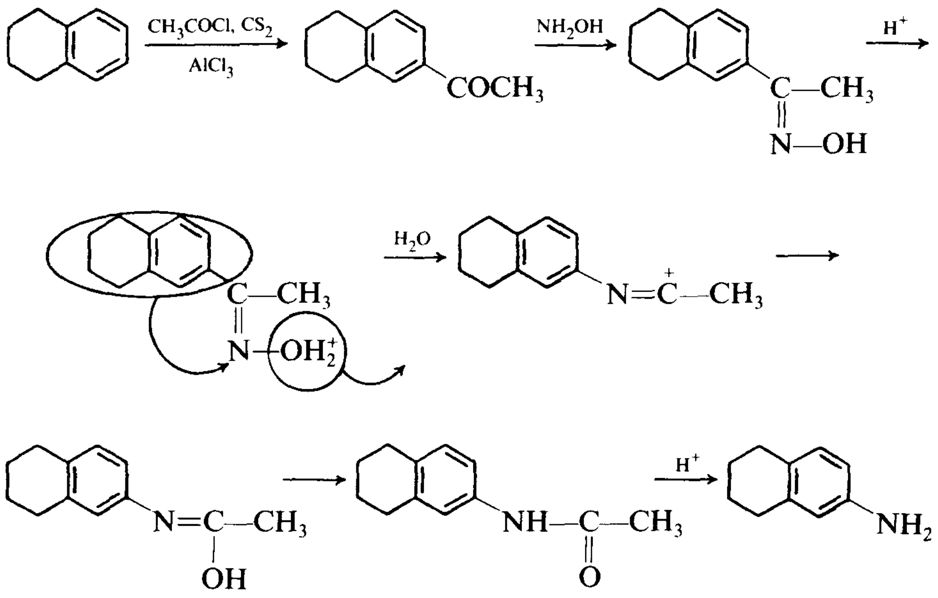


Rr 340 or D 1143 are used in green-sensitizing layers, both in negative colour or positive colour films.[10]

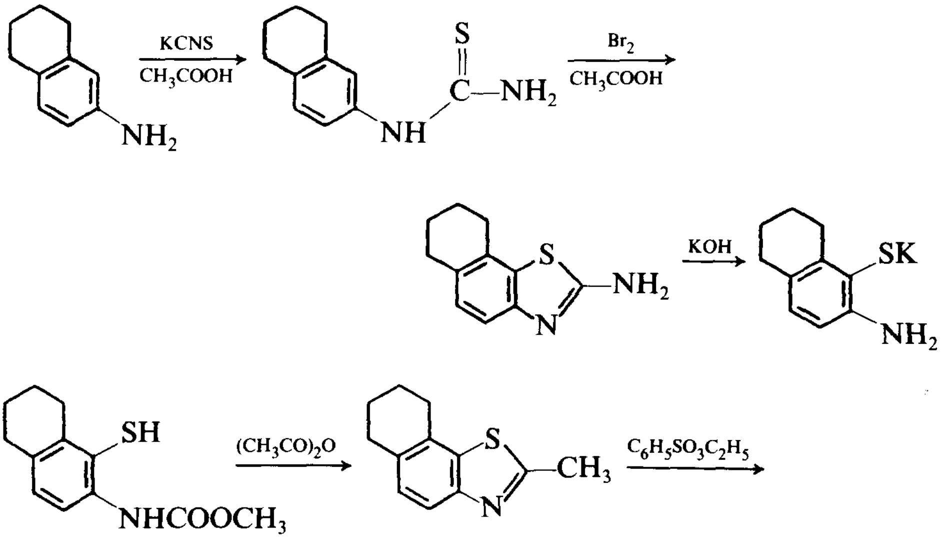
(2) Rhodacyanine dyes derived from alkyl-rhodamines

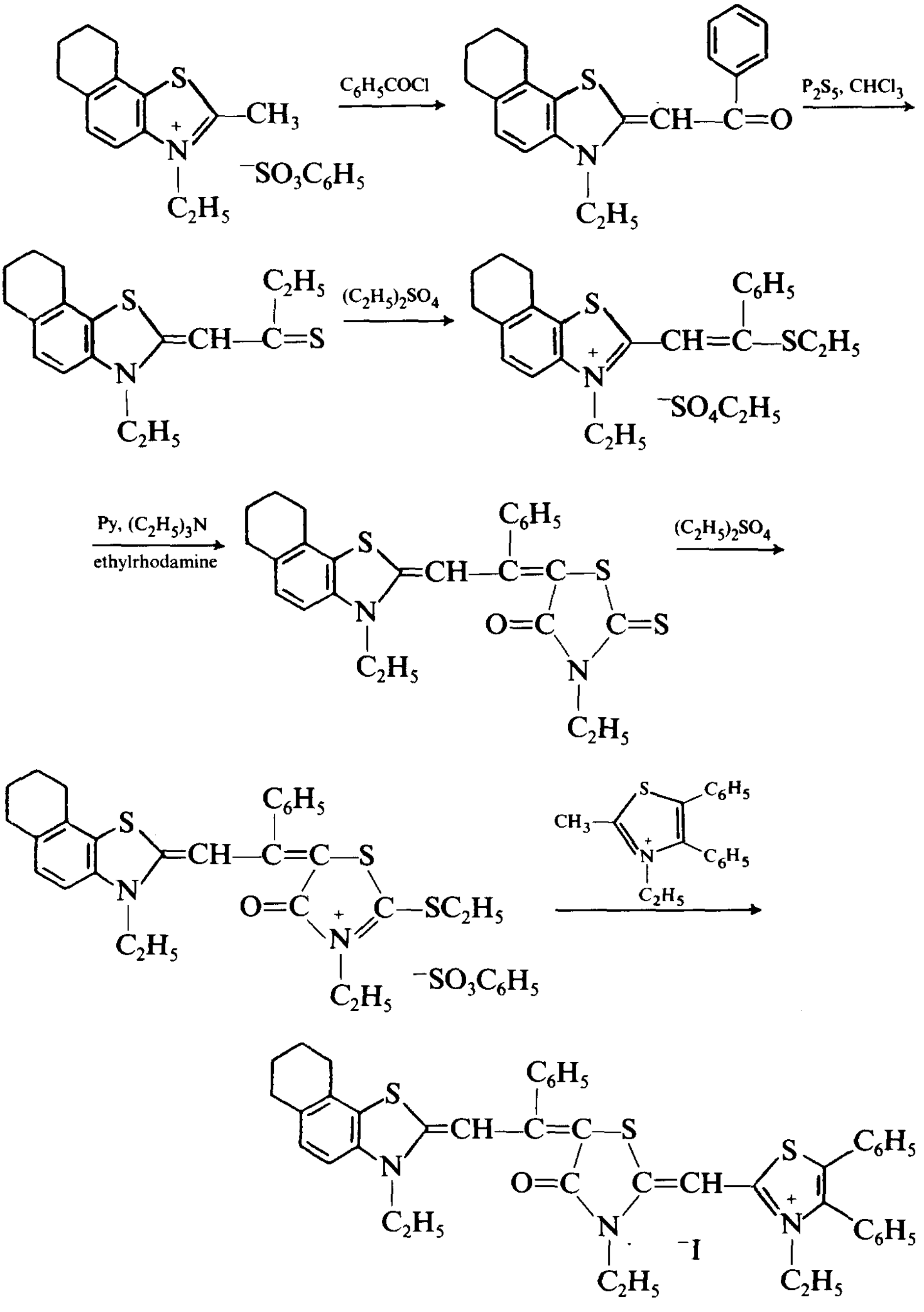
Ma 1088

The starting material for the preparation of Ma 1088 is 2-amino-tetrahydronaphthalene, which is prepared from tetralin by acetylation, oxime formation and Beckmann rearrangement:



Scheme 13



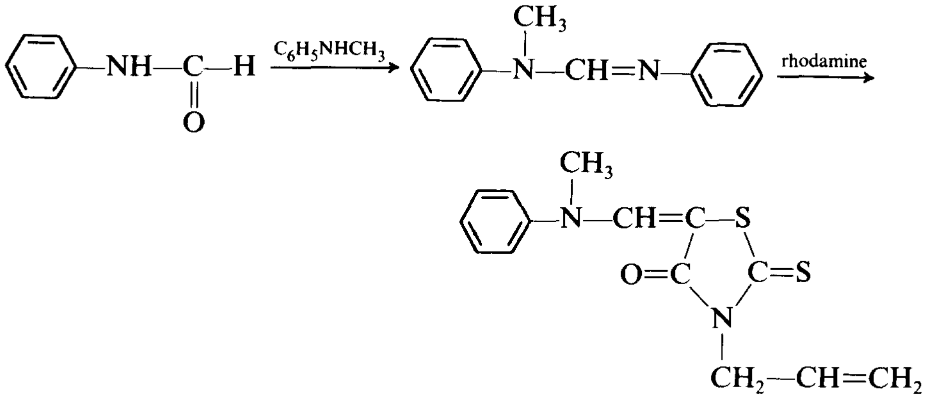


Scheme 14 Ma 1088

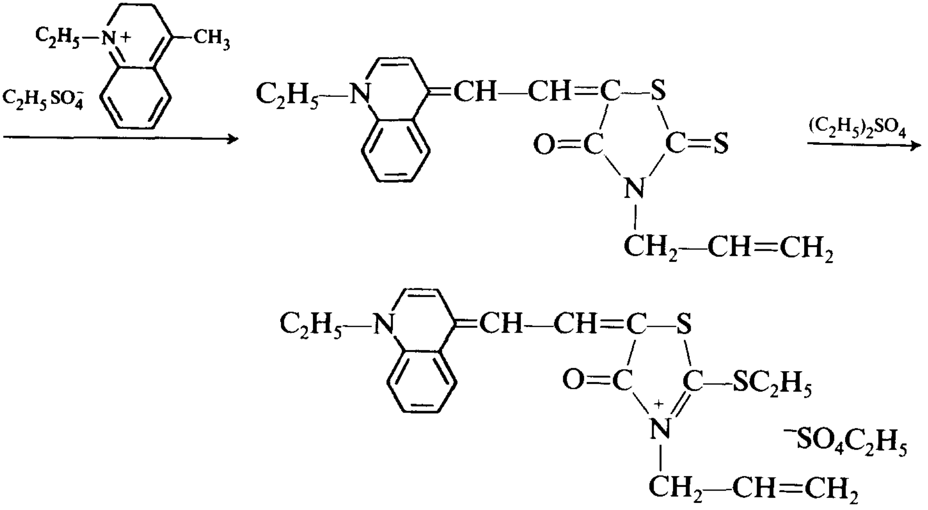
Ma 1088 has $\lambda_{max} = 613$ nm, $S_{max} = 645$ nm (670–680), and may be used in the red-sensitizing layer.[11]

Rr 1953

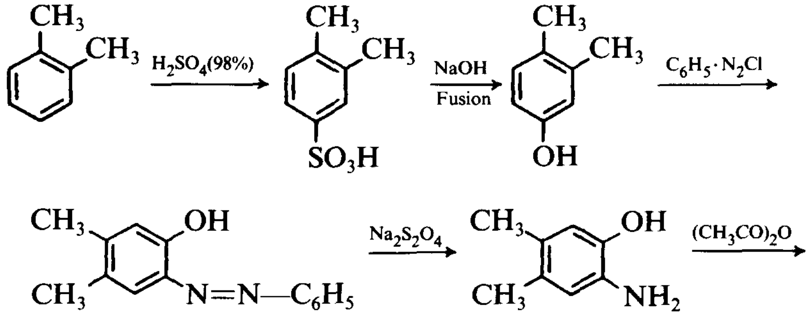
The structure and method of preparation of Rr 1953 is shown in the following schemes:

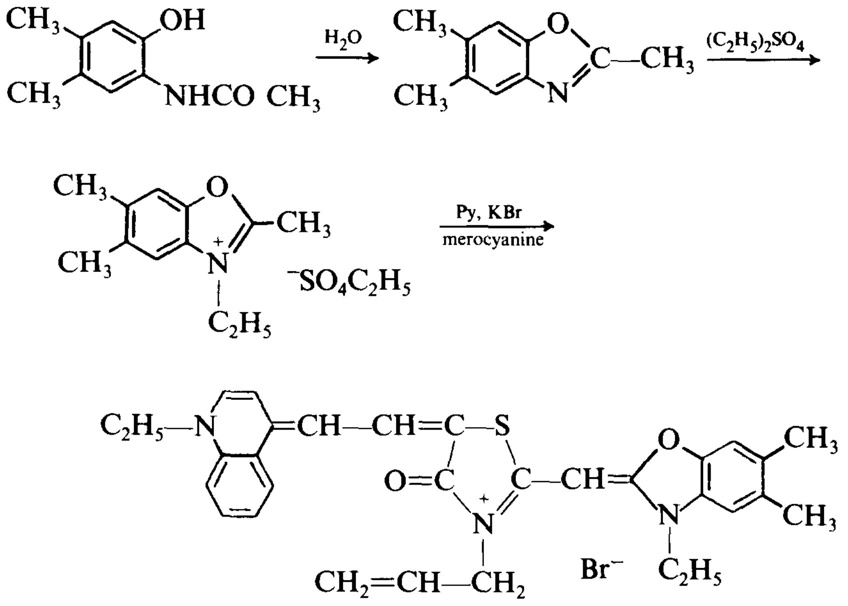


Scheme 15(a)



Scheme 15(b): preparation of merocyanine



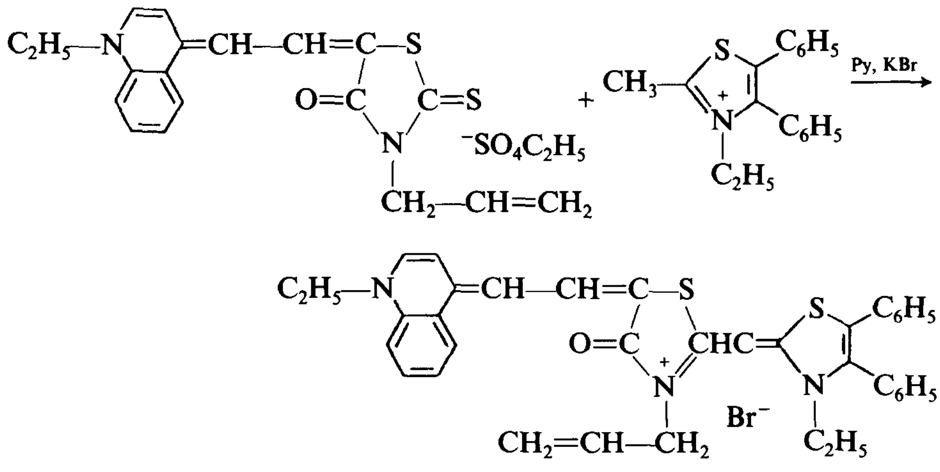


Scheme 15(c): preparation of Rr 1953

Rr 1953 has λ_{max} = 650 nm, S_{max} = 700–705 nm, a sensitizing range from 610 to 725 nm, and may be used in the red-sensitizing layer of positive colour film.[12]

Rr 1833

Rr 1833 can be used as a replacement for Rr 1953; the structure and method of preparation is shown in Scheme 16:[13]



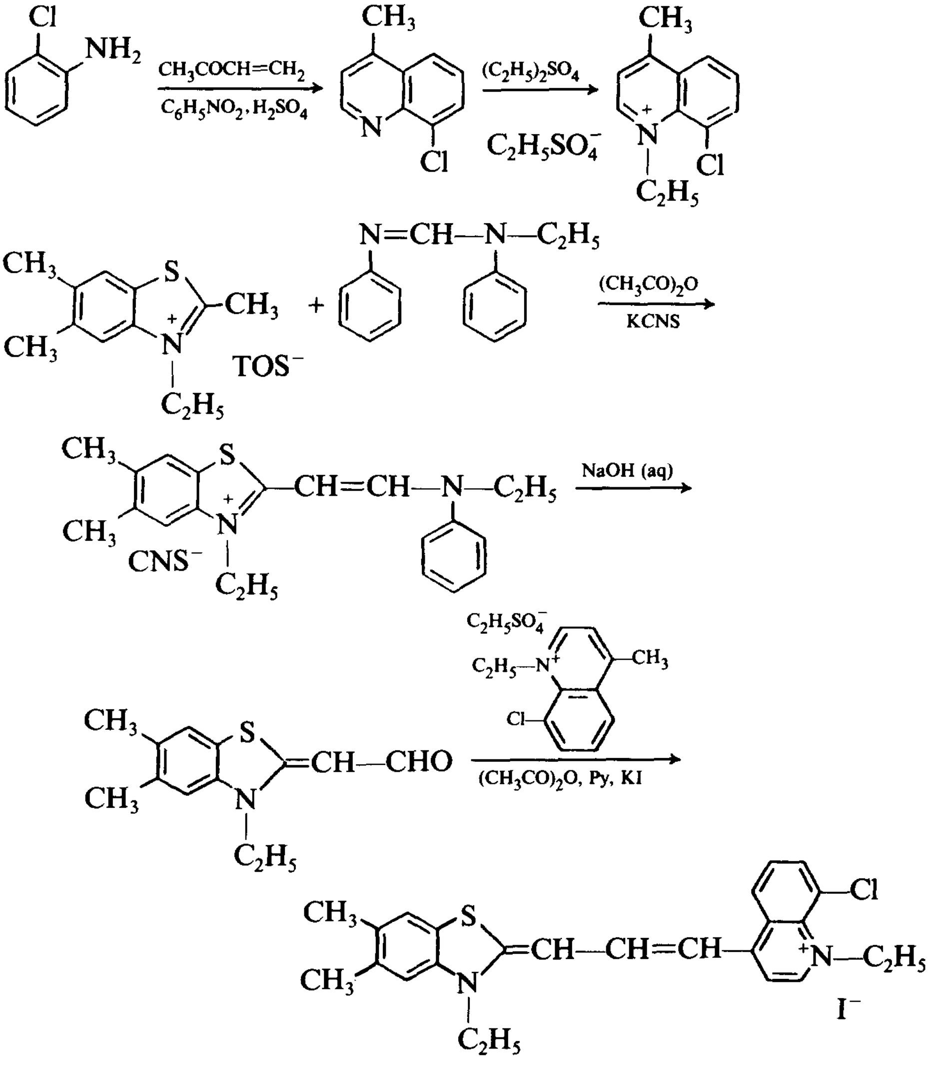
Scheme 16 Rr 1833

Rr 1853 has λ_{max} = 660 nm, S_{max} = 700–705 nm, and is used in the red-sensitizing layer of positive colour film as a substitute for Rr 1953.[13]

(3) Unsymmetrical thia-4-carbocyanines

Ma 2116

The structure and method of preparation is shown in the following scheme:[14]

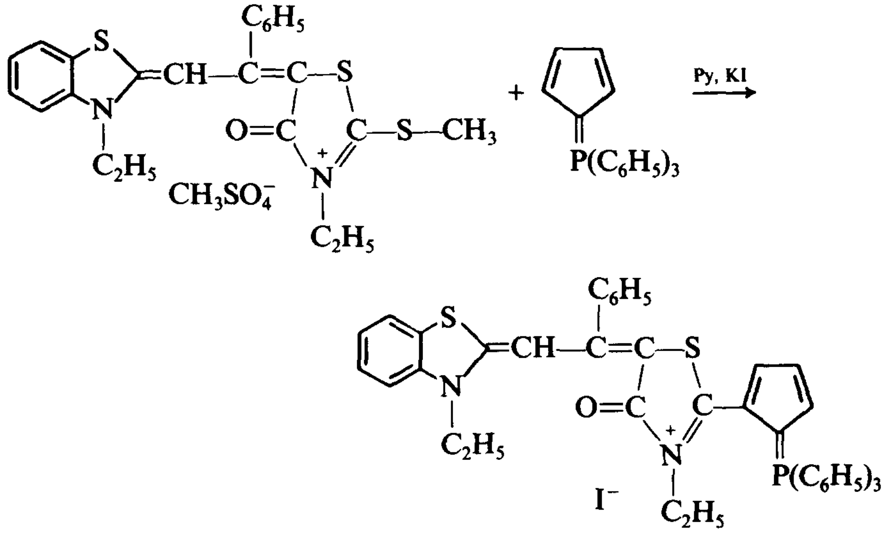


Scheme 17

Ma 2116 has λ_{max} = 650 nm, S_{max} = 640–690 nm, a sensitizing range of 600–720 nm and may be used in colour paper.[14]

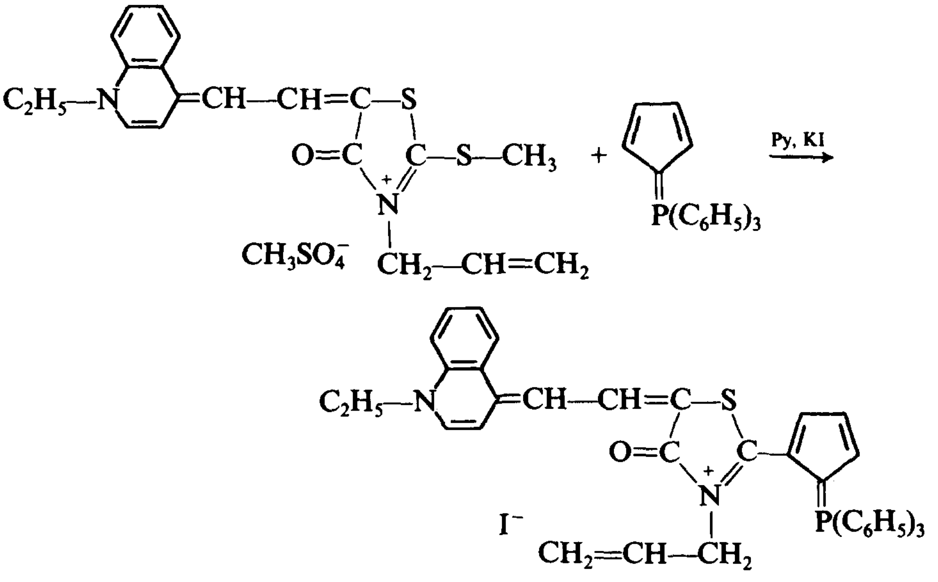
(4) Phosphorous containing trinuclear rhodamine dyes

Many phosphorous containing trinuclear rhodamine dyes having λ_{max} between 610 and 680 nm have been prepared, and they can be used in the red-sensitizing layer, both in positive and negative films.[15]



λ_{max} = 610 nm

Scheme 18



λ_{max} = 670 nm

Scheme 19

4 SYNTHESES OF INFRARED POLYMETHINE CYANINE DYES IN INFRARED FILMS

Polymethine cyanine dyes used in infrared photographic films must meet the following requirements:

(i) They must have a sufficient wavelength of adsorption (greater than 650–700 nm) and a sufficient wavelength of maximum sensitization (>700 nm).

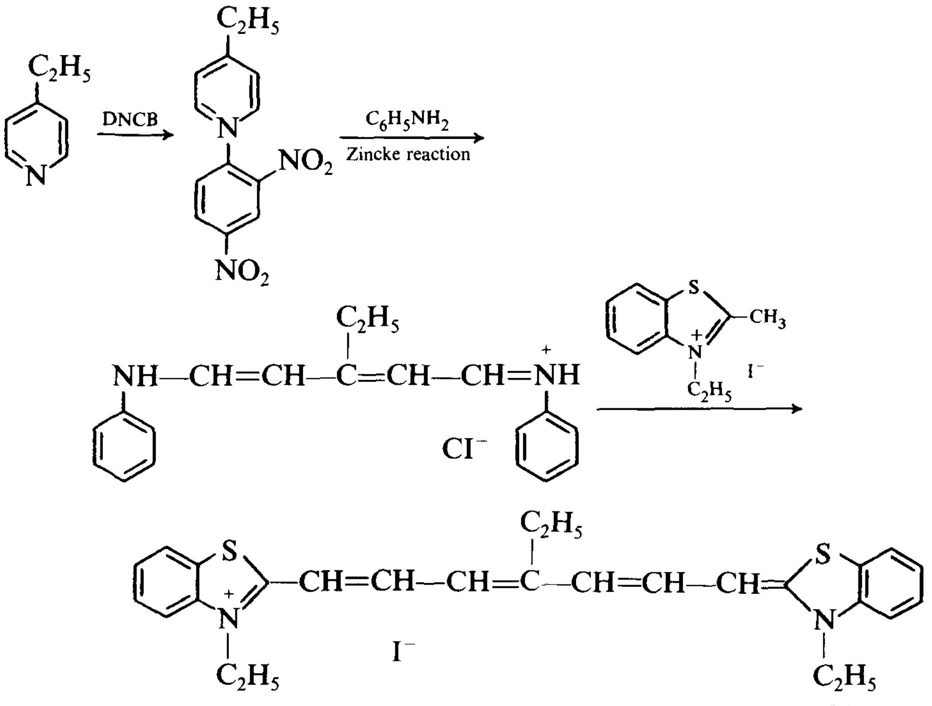
(ii) They must have sufficient sensitivity in the sensitization range to be used in the infrared film. Usually, a supersensitizer is used together with an infrared sensitizer, e.g. a triazine stilbenedisulfonic acid.

(iii) They must have sufficient photostability, otherwise the infrared film thus produced is not commercially viable.

(1) Thiatricarbocyanine dyes

Simple thiatricarbocyanine dyes are well known in cyanine dye chemistry. In order to improve the practically useful properties, various methods involving the introduction of one or two substituents into the heptamethine chain have been devised.

One method, involving the introduction of alkyl, halogeno or other

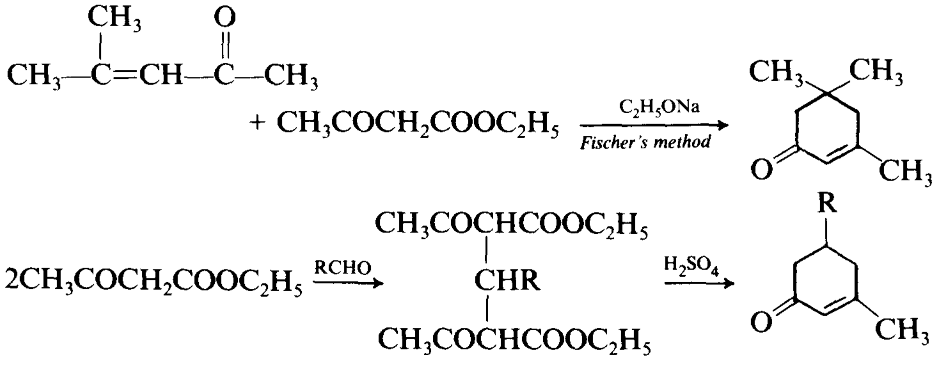


Scheme 20

λ_{max} = 785 nm

substituents at the meso position of the heptamethine chain is shown in Scheme 20. The various meso-substituted R, e.g. CH_3, C_3H_7, n-C_4H_9, Cl and CN, may be introduced via the corresponding 4-substituted pyridines, followed by the Zincke reaction; the properties of the resultant tricarbocyanines are very much improved.[16]

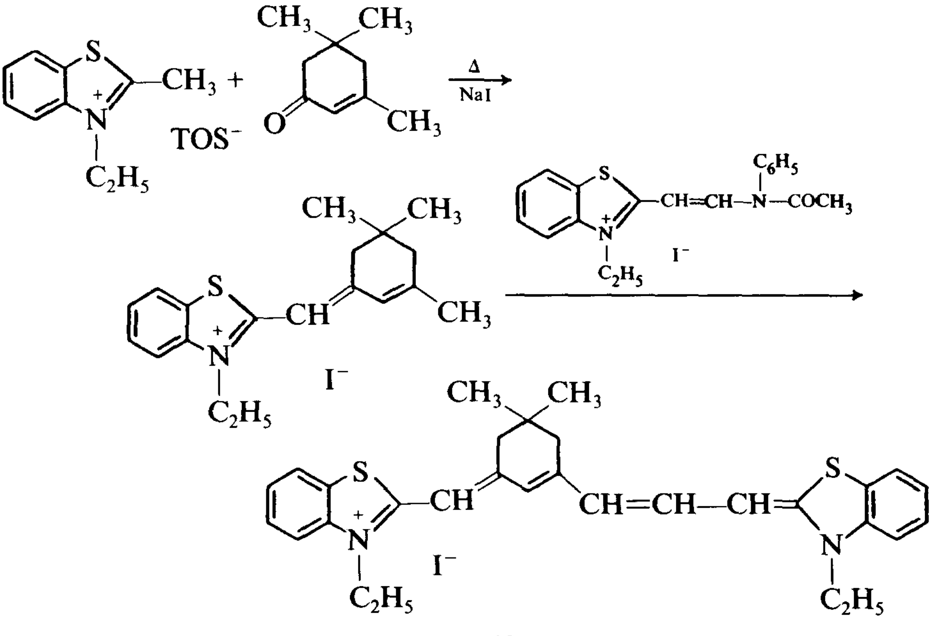
A second method to improve the photostability and to increase the sensitivity is by using partial rigidization of the heptamethine chain. In this way, isophorone and similar compounds have been prepared:



[R=H, CH_3 or C_2H_5]

Scheme 21

Isophorone or related compounds are then reacted to form the tricarbocyanine dyes according to the following scheme:

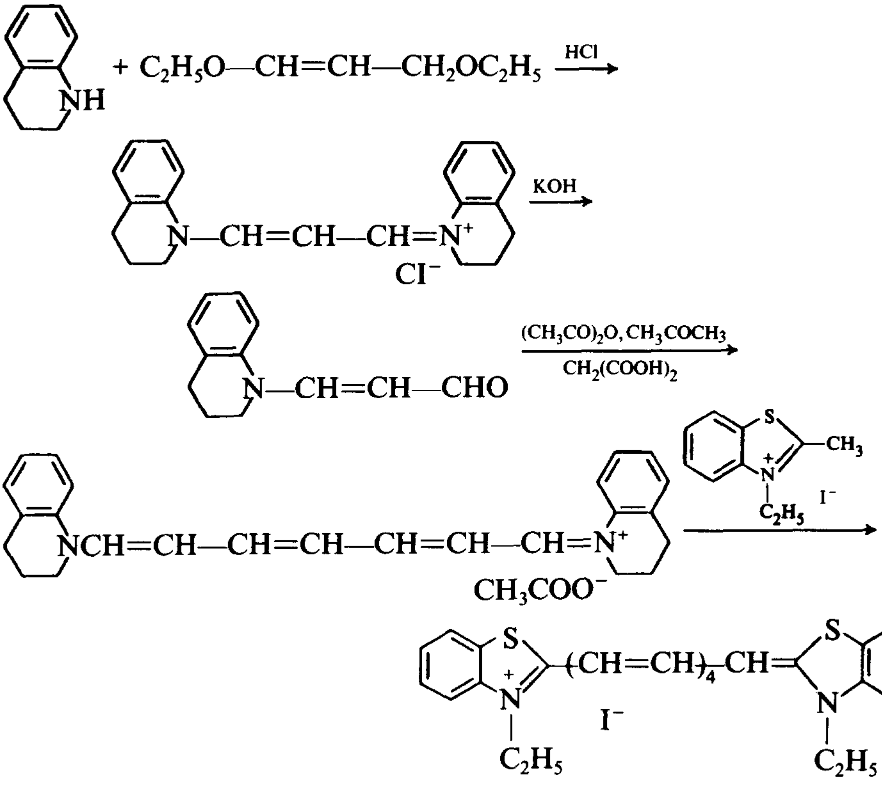


Scheme 22

The resulting dyes have much higher photostability than the straight chain heptamethine dyes.[17]

(2) Tetracarbocyanine dyes

To prepare tetracarbocyanine dyes, the first step is to prepare the condensing agent:[17]



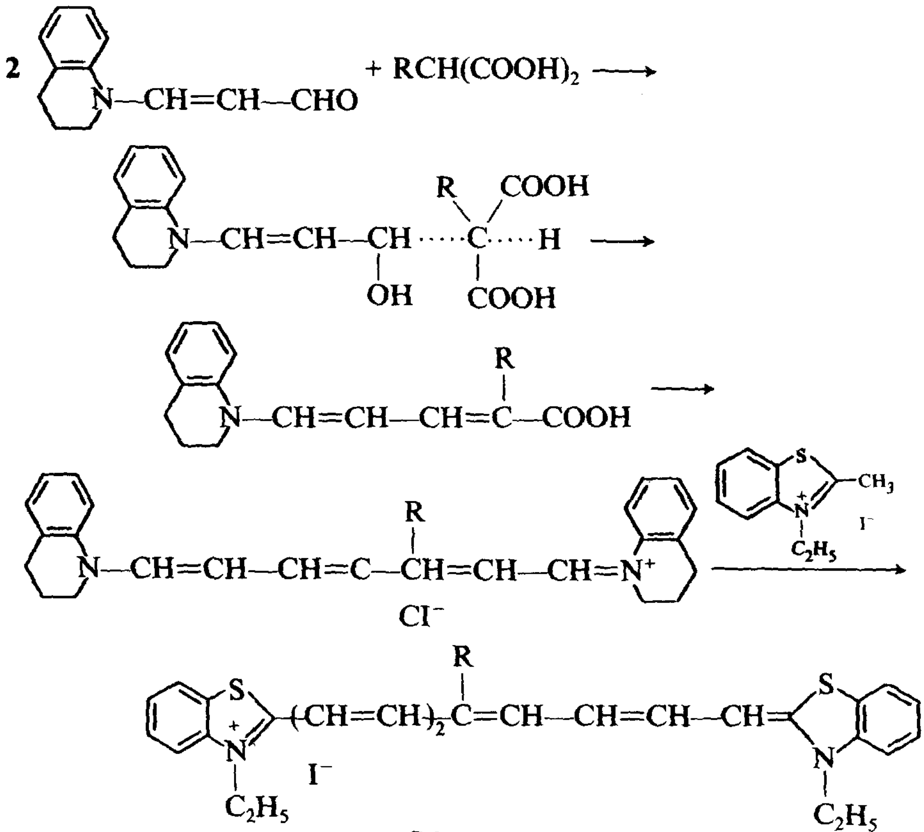
Scheme 23

In an analogous manner, meso-substituted tetrocarbocyanine dyes may be produced (Scheme 24).

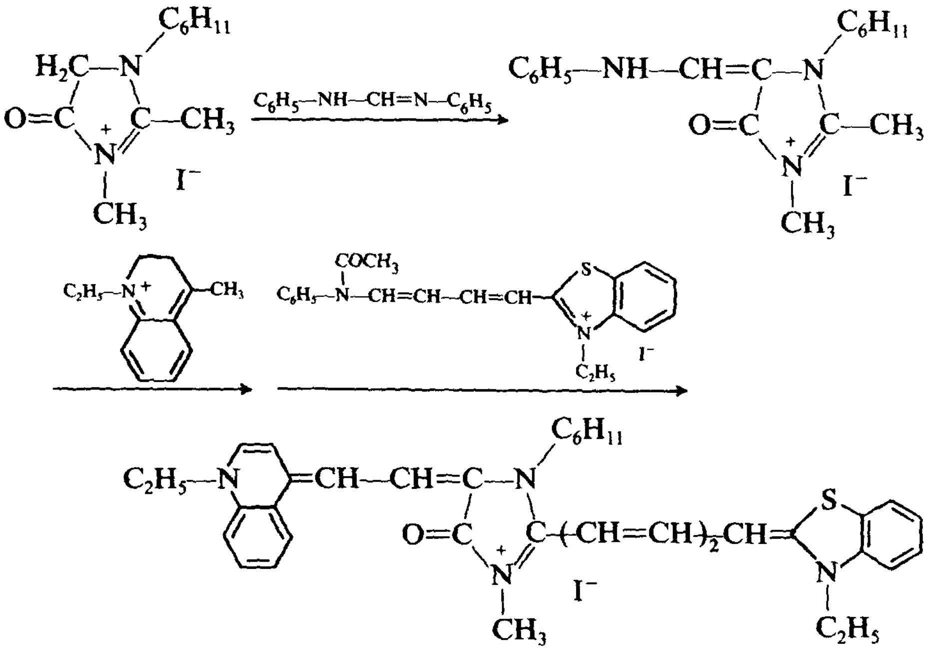
A similar tetracarbocyanine dye with a polymethine chain condensed with an isophorone residue has been prepared.[18]

(3) Infrared hydancyanine dyes

The merocyanine derived from a hydantion acidic nucleus may be used to prepare infrared hydancyanine dyes. The method of preparation is shown in Scheme 25.[19]



Scheme 24

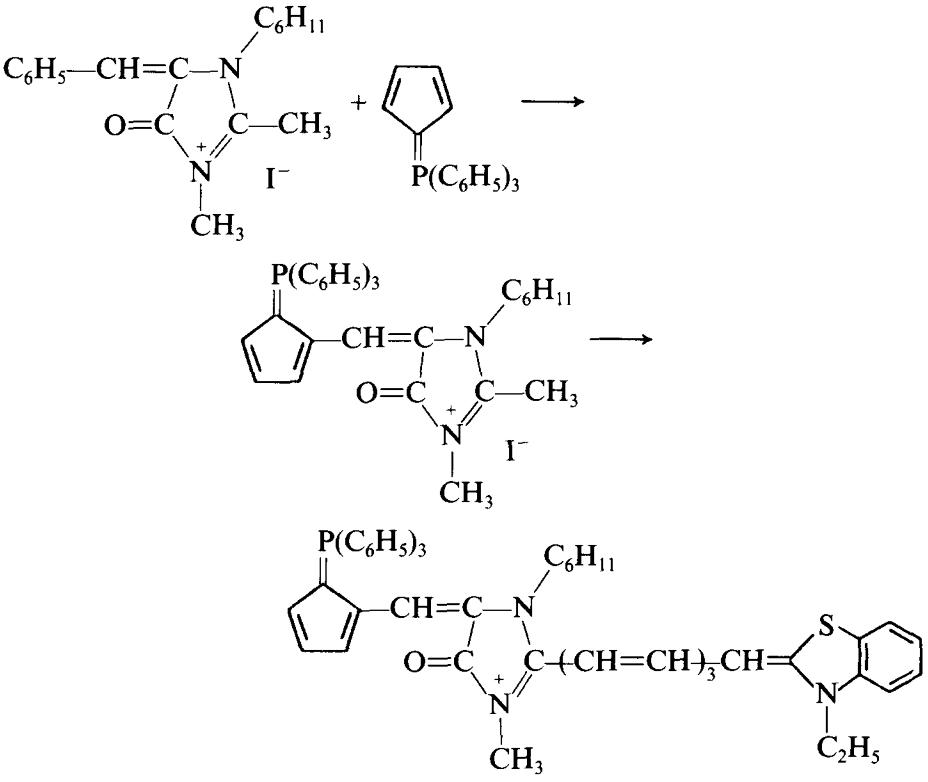


Scheme 25

The resulting compound has λ_{max} = 750 nm, S_{max} = 825 nm. Similar dyes can also be prepared. All these dyes have higher sensitivity when added to AgBr emulsion.[20]

(4) Phosphorus-containing infrared hydancyanine dye

The title compound can be prepared according to following scheme:[21]



Scheme 26

The resulting compound has λ_{max} = 655 nm, S_{max} = 800 nm and a sensitizing range of 680–900 nm.

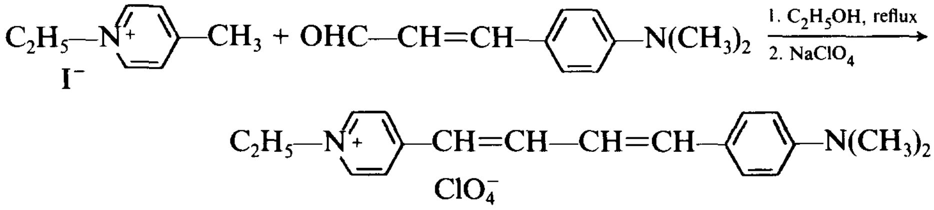
5 SYNTHESES OF POLYMETHINE CYANINE DYES USED IN LASERS

The polymethine cyanine dyes used in lasers are usually infrared-lasing dyes. These dyes should have properties quite distinctive from those of dyes used in photography, viz.:

(i) they must have higher photostability; and
(ii) they must have a higher lasing energy conversion efficiency.

(1) Tetramethine styryl dyes

The styryl dyes may be prepared by the following route:



Scheme 27

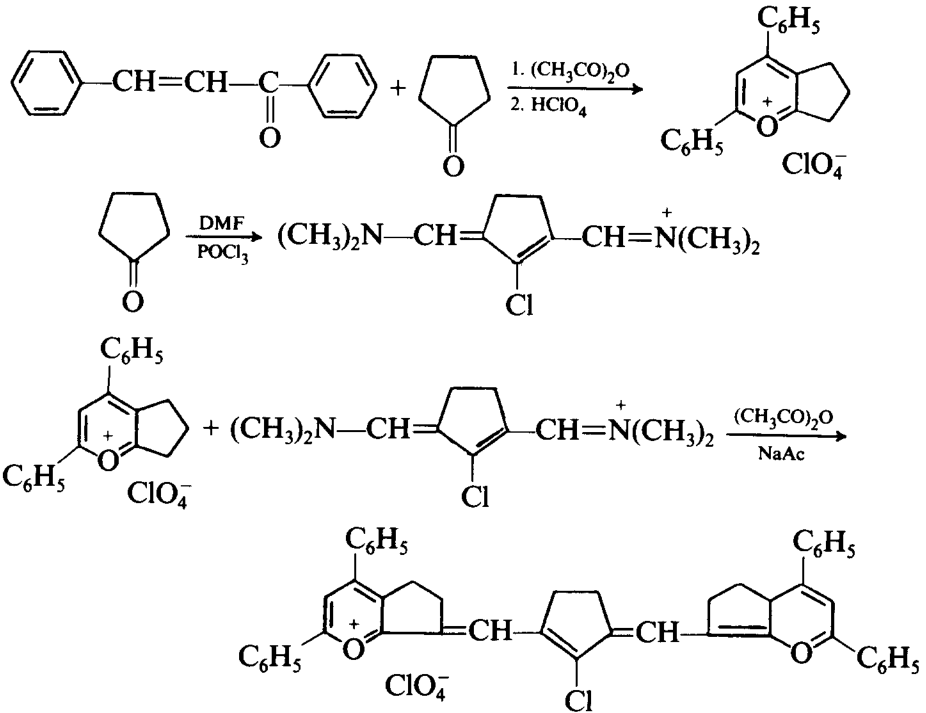
The laser output characteristics of this dye may be examined with the pump source of the frequency doubled pulsed Nd:YAG laser (532 nm, pulse with 10 ms). The maximum dye laser wavelength of the dyes is 716 nm, and the conversion efficiencies obtained are 9% after second-order amplifications.[22]

(2) Heptamethine pyrylium and thiopyrylium dyes

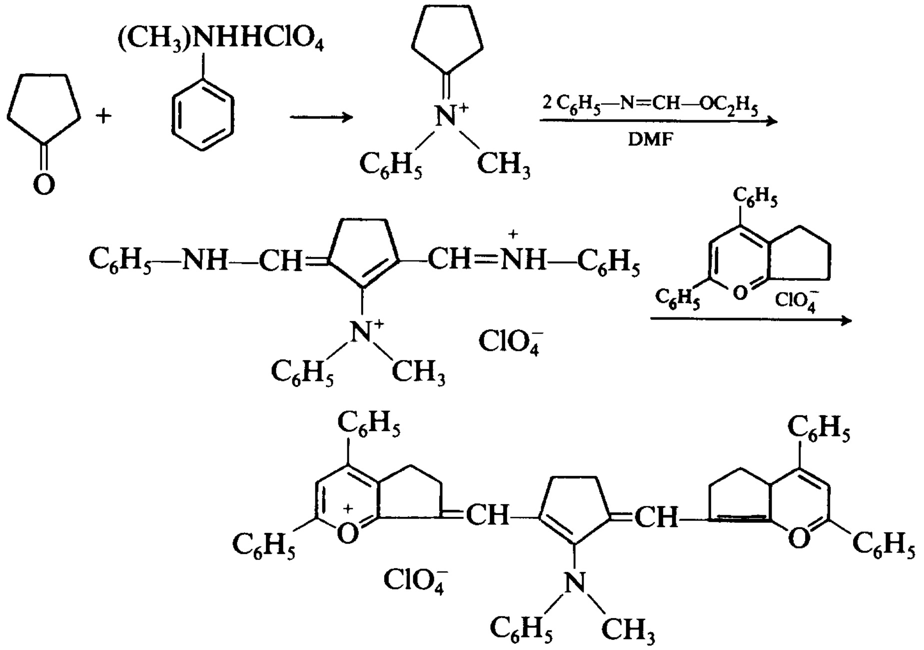
The importance of photostability is much greater for an infrared lasing dye. In our study, the rigidization of the polymethine chain was first emphasized.

The first rigidized pyrylium dye was prepared according to Scheme 28.[23] Surprisingly this dye is photostable, but is a dye with a lower energy conversion efficiency. To improve its energy conversion efficiency, other dye structures were systematically studied. A better dye, having both higher photostability and higher lasing energy conversion efficiency, was derived as shown in Scheme 29.

Similarly, a very good thiopyrylium dye was obtained[24] (Scheme 30). These new heptamethine pyrylium or thiopyrylium dyes contained a disubstituted amino group on the meso position on their bridged chain. Solutions of the dyes in 1,2-dichloroethane at concentrations ca. 10^{-3} M act as laser dyes, transversely pumped by a Q-switched Nd:YAG laser as a pumping source; 5·6–9·6% of the pump energy was converted to an intense infrared pulse with frequencies between 1·30 and 1·65 μm. These dyes showed a remarkable photostability upon 1·06 μm laser excitation and excellent storage stability without degassing.[25]

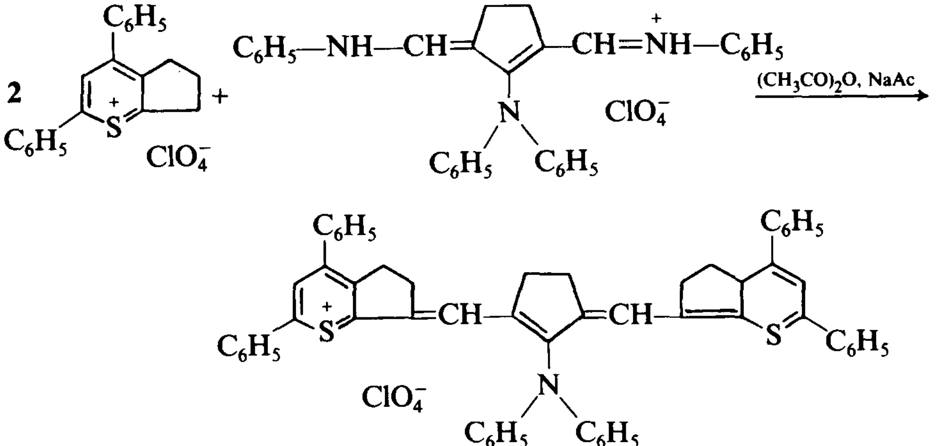


Scheme 28



Scheme 29

λ_{max} = 1218 nm

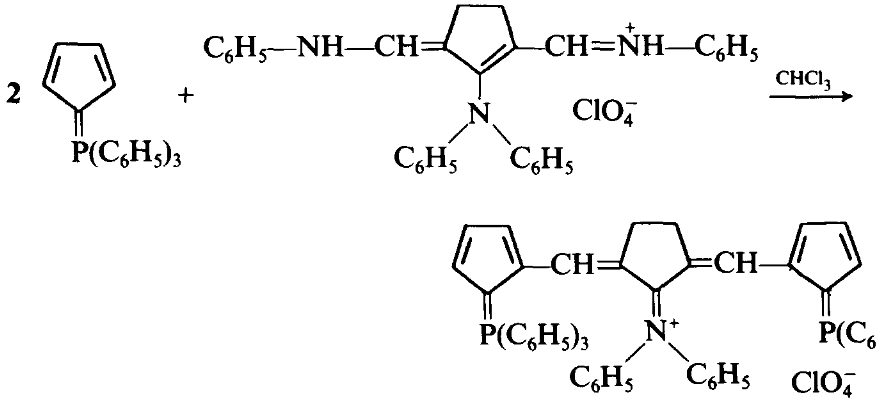


$\lambda_{max} = 1218$ nm

Scheme 30

(3) Bridged pentamethine phosphinines

Some bridged pentamethine phosphinines used as infrared lasing dyes were prepared as shown in Scheme 31:

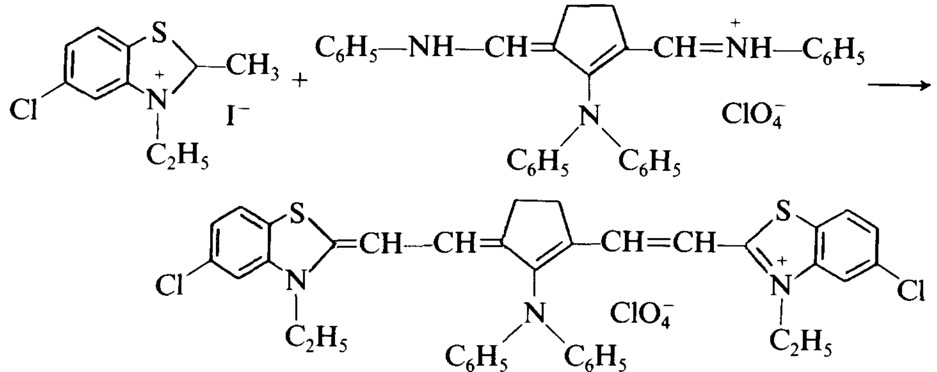


Scheme 31

Using a nitrogen laser as pumping source, the dyes have a tunable range of 760–830 nm and an energy conversion efficiency of 2·4–5·3% at the maximum emission wavelength.[26]

(4) Bridged heptamethine cyanines

Some bridged heptamethine thia-, seleno- and oxocyanine dyes were similarly prepared:



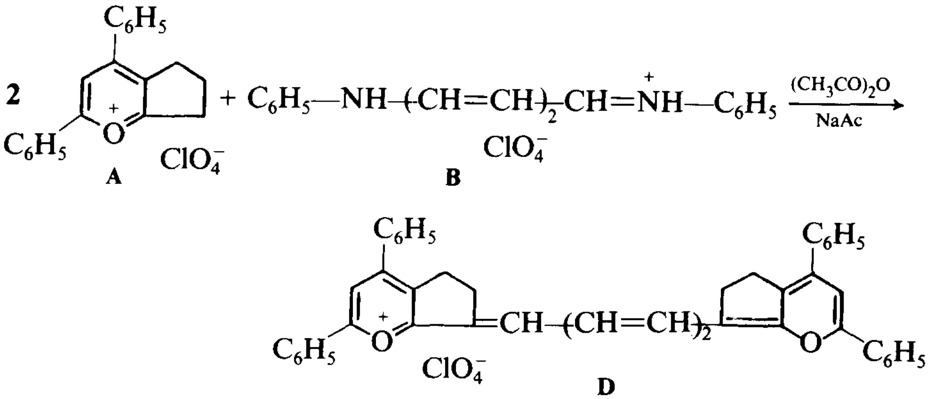
$\lambda_{max} = 809{\cdot}4$ nm

Scheme 32

The first dye has fluorescence at $\lambda_{max} = 860$ nm and is an efficient laser dye for the pulsed Nd:YAG laser, tunable range 700–900 nm, with a conversion efficiency between 6·6 and 9·0%. These dyes may also be used as infrared dyes in photography.[27,28]

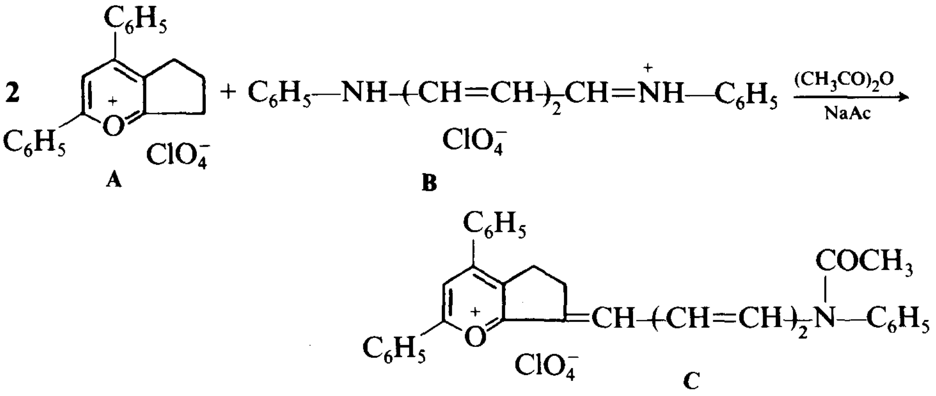
6 KINETIC STUDIES OF THE FORMATION OF POLYMETHINE CYANINE DYES

The formation of polymethine cyanine dyes was studied kinetically using the thin-layer chromatograph double scanning method. During the reaction, the concentration changes of the reactants and of the products were determined as outlined below:[29,30]



Scheme 33

In a preliminary study, it was found that an intermediate hemicyanine **C** was formed:



Scheme 34

The reactants, intermediate and product were repeatedly purified and known weights of purified **A**, **B**, **C** and **D** were applied to TLC plates. The peak areas of **A**, **B**, **C** and **D** were zig-zag scanned; on plotting the weights *versus* peak areas, standard curves of **A**, **B**, **C** and **D** were obtained. Equal mols of **A** (0·1862 g) and **B** (0·1423 g) were reacted in 10 cm^3 acetic anhydride at 125°C; aliquot portions were taken every 2 min and added to cooled acetic anhydride to stop the reaction. Using a micro-injector, the reaction solution was applied to a TLC plate, the spots developed and the peak areas of the various spots were zig-zag scanned.

The changes of peak areas of intermediate **C** are shown in Table 2. Since $C_{MB} = C_{MBO} - M_C$, the concentration change of C_B can be calculated. On plotting $1/C_{MB} - 1/C_{MBO}$ against reaction time t, a straight line is obtained; the slope of the plot is k, i.e. the rate constant of the above second order reaction. Here we have $1/C_{MB} = 5{\cdot}5t + 19{\cdot}88$, $r = 0{\cdot}993$, $k = 5{\cdot}50\ \mathrm{M}^{-1}\ \mathrm{min}^{-1}$.

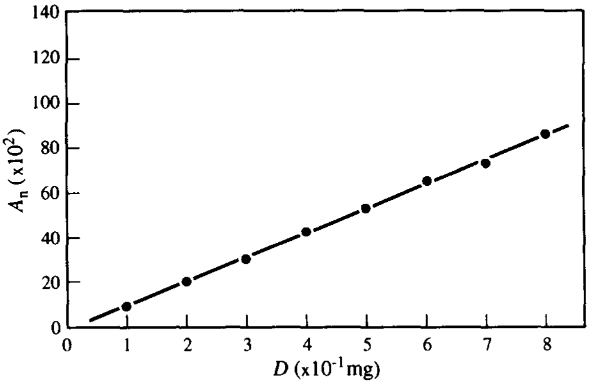
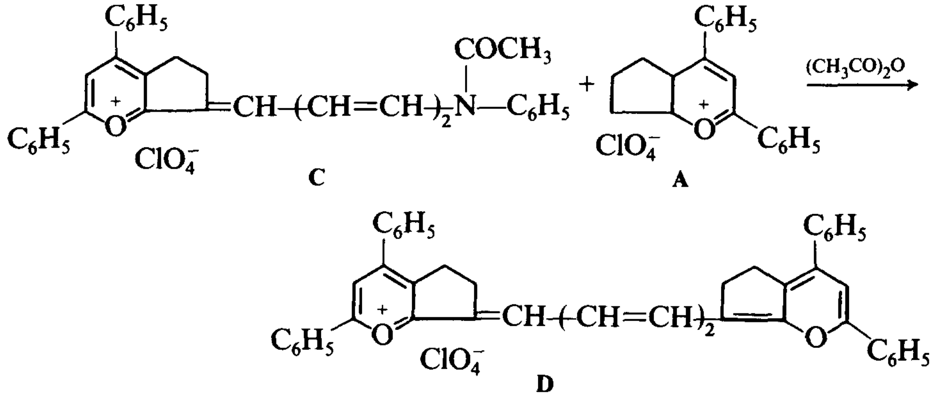


Fig. 1. Standard curve of intermediate **C**.

TABLE 2

Time (min)	*0*	*2*	*4*	*6*	*8*	*10*	*12*	*14*
AM_C	0	2099·9	3111·02	3632·97	4133·08	4502·73	4627·55	4892·4
WM_C (μg)	0	0·203	0·296	0·344	0·390	0·424	0·441	0·450
CM_C ($\times 10^{-2}$)	0	1·78	2·60	3·02	3·42	3·72	3·87	3·95

Similarly, the kinetics of the reaction shown in Scheme 35 were investigated, and the rate constant of the reaction thus obtained.



Scheme 35

Here $k' = 14{\cdot}97\ M^{-1}\ min^{-1}$ at 120°C (in the presence of NaAc).

The kinetic results of the above reaction showed that the reaction was a consecutive second-order one. The first reaction proceeds much quicker

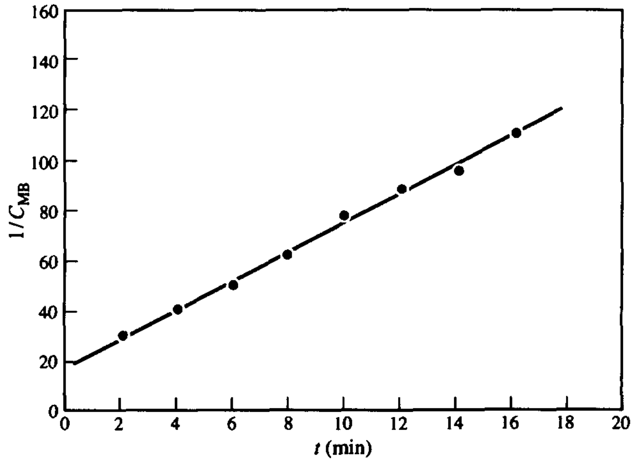


Fig. 2. Change of $1/C_{MB}$ with reaction time t (in min).

than the second reaction. On the basis of the kinetic results, a mechanism for the formation of polymethine cyanine dyes could be formulated (Scheme 36). This mechanism can also be deduced from general electronic theory.

7 STUDIES OF SENSITIZATION AND SUPERSENSITIZATION OF POLYMETHINE CYANINE DYES

Sensitization and supersensitization are of great importance from the viewpoint of both photographic science and technology. In 1972, Gilman proposed the 'hole trapping theory'. When sensitizers are adsorbed on AgBr grains and exposed to light, photoelectrons and dye-positive holes are produced by two different routes, viz:

(a) $AgBr \rightarrow Br^{\cdot} + Ag^{+} + e^{-}$
$Dye + Br^{\cdot} \rightarrow Dye^{+} + Br^{-}$
(b) $Dye \rightarrow Dye^{*}$
$Dye^{*} \rightarrow Dye^{+} + e^{-}(AgBr)$

where: Dye = dye-positive hole (dye-positive free radical); Dye* = excited dye (or Freekel dye exiton); and e = photoelectron. The behaviour of the photoelectrons and dye-positive holes in the photographic process was studied experimentally, as outlined below.

(1) Studies of sensitization and supersensitization by the Dember effect[31,32]

The diffusion and recombination behaviour of photoelectrons and dye-positive holes were studied using the Dember effect; a block diagram of the Dember measuring circuit is shown in Fig. 3.

A single AgBr crystal ($\approx 0{\cdot}2\ \mu m$) was prepared and the sensitizing dye or supersensitization combination of dyes evaporated on the surface of this single AgBr crystal. Under non-homogeneous exposure, the product

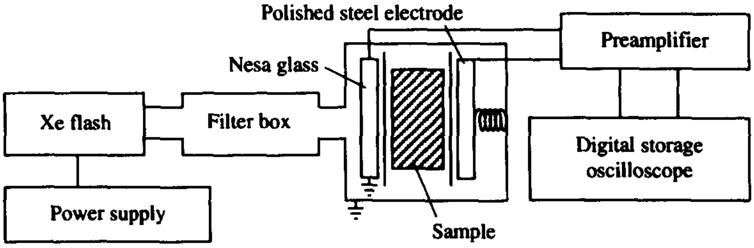
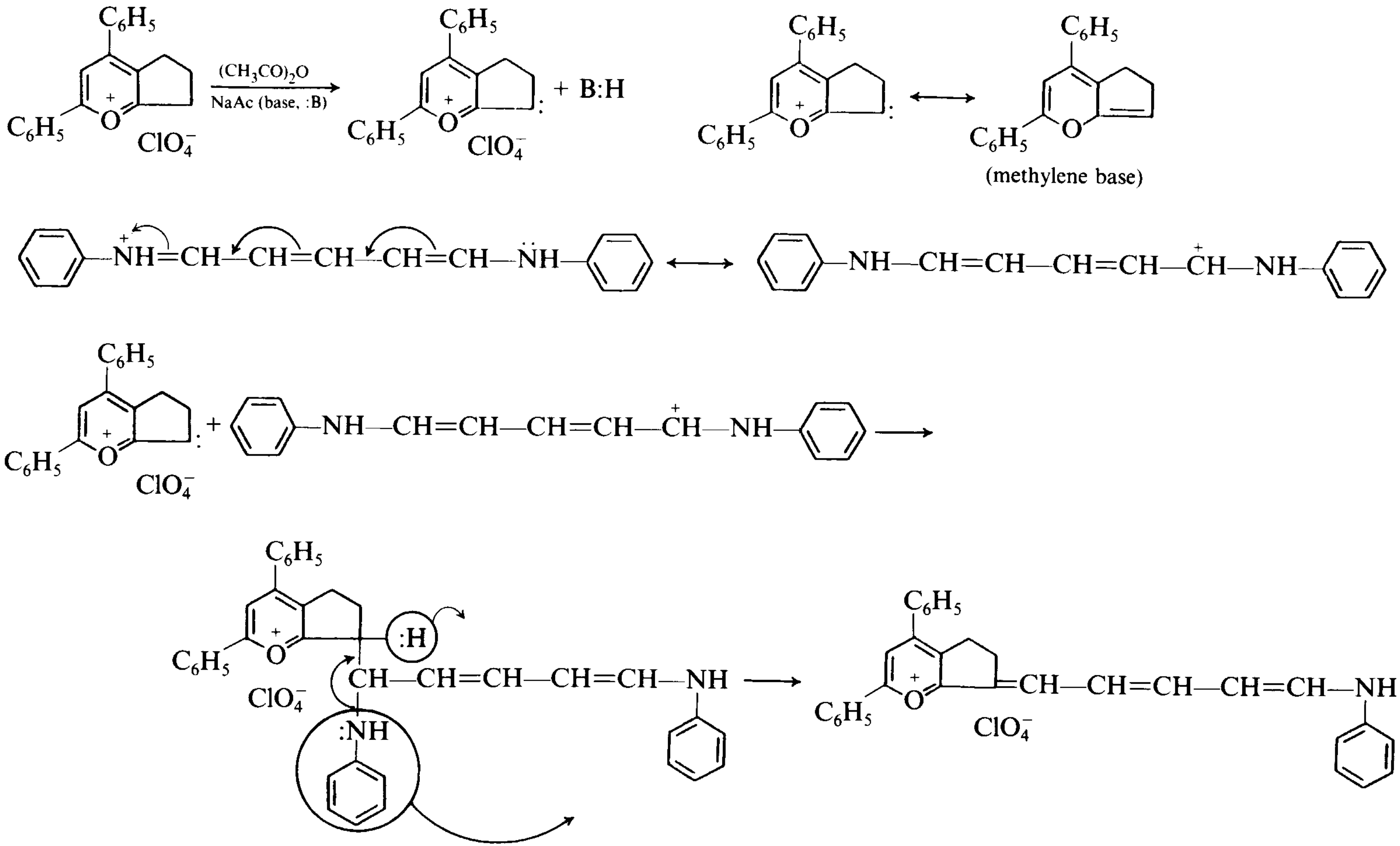
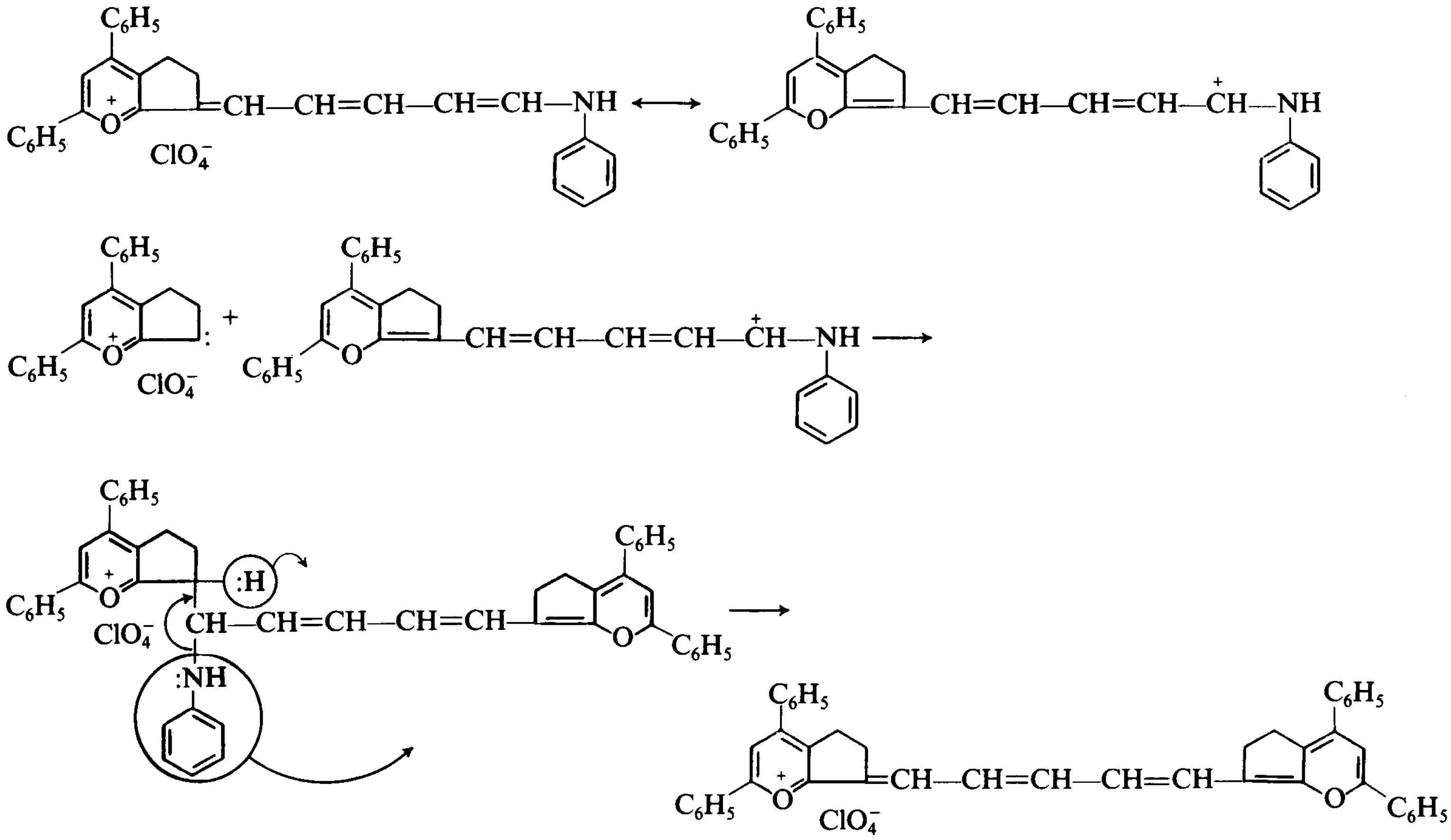


Fig. 3. Block diagram of measuring circuit for the Dember effect.



C6H5
ClO4−
(CH3CO)2O
NaAc (base, :B)
+ B:H
(methylene base)
NH=CH—CH=CH—CH=CH—NH
NH—CH=CH—CH=CH—CH—NH
:H
:NH
CH—CH=CH—CH=CH—NH
=CH—CH=CH—CH=CH—NH


C6H5
ClO4−
CH—CH=CH—CH=CH—NH
CH=CH—CH=CH—CH—NH
:H
:NH
CH—CH=CH—CH=CH
CH—CH=CH—CH=CH

Scheme 36

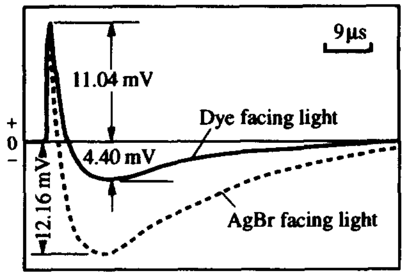


Fig. 4. Photovoltage measurement on dye 2/single crystal AgBr system (white light exposure, incident on different faces).

of the number and diffusion paths of free electrons is unequal to that of the number and diffusion paths of free holes. Therefore, the net charge-path difference results in a Dember photovoltage.

The photovoltage measurement for 2,2'-diethylmethylselenocarbocyanine bromide is shown in Fig. 4. The positive signal reveals the behaviour of photoelectrons, decaying rapidly. An electron is injected and a free hole is produced, which then migrates in the direction of the trapped electrons. Therefore, under the experimental conditions used, the negative Dember signal was attributed mainly to the slow diffusion of photo-holes.

When dye 2 and dye 8 are 'added' on the surface of a single AgBr crystal system and exposed to light (λ = 504 nm), the photovoltage measurement is as shown in Fig. 5. These Dember photovoltage measurements are evidence for Gilmans 'hole trapping theory'. When a cyanine dye is adsorbed on the AgBr crystal and exposed, a photoelectron is injected into the conductance band of AgBr and silver clusters gradually grow due to the reaction of photoelectrons. The role of the supersensitizer is clearly shown, in that both positive signals (due to photoelectrons) and negative signals (due to dye-positive holes) are larger than when the

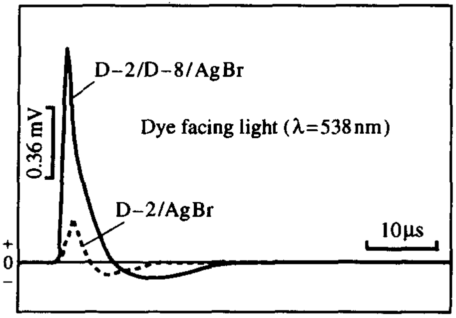


Fig. 5. Photovoltage measurement on dye 2/single crystal AgBr system.

supersensitizer is absent. The supersensitizing process might be expressed as follows:

$$\text{Dye} + h\nu \longrightarrow {}'\text{Dye}^*$$
$$'\text{Dye}^* + \text{ss} \longrightarrow \text{Dye} + \text{ss}^{\oplus} + \text{e}^-(\text{AgBr})$$

or:

$$'\text{Dye}^* \longrightarrow \text{Dye}^{\oplus} + \text{e}^-(\text{AgBr})$$
$$\text{Dye}^{\oplus} + \text{ss} \longrightarrow \text{Dye} + \text{ss}^{\oplus}$$

(2) Studies of the sensitization and supersensitization of some green-sensitizing dyes by ESR[33]

The experimental observation of a dye-positive hole is direct evidence confirming Gilman's positive hole trap theory, but there are conflicting results from ESR measurements. Some workers reported that the ESR signals of 2,2'-quinocyanine, oxacarbocyanines and benzimidazolocyanine were either absent or very weak. We carried out an ESR study of some green sensitizing dyes adsorbed on the surface of silver iodobromide grains at 110 or 130 K and at room temperature (297 K). Some green-sensitizing dyes, thought to trap photo-holes, gave no ESR signals at 297 K, but gave signals at 110 or 130 K. The ESR signals originate from the presence of dye-positive holes. At low temperature, e.g. 110 or 130 K, the measurement is more sensitive. The dye-positive holes have different temperature-dependent stabilities. At a given temperature, only those dye-positive holes with lifetimes longer than the response time of the ESR spectrophotometer will be detected.

(3) Studies of the supersensitization by some allopolar trinuclear cyanine dyes[34]

ESR studies have been carried out on the supersensitization of naphthothiacarbocyanine (NTCC) by some holopolar trinuclear cyanine dyes (TNC). It was found that some allopolar trinuclear cyanine dyes containing an acidic nucleus can supersensitize NTCC very well. There was a correlation between I_{ESR} ($I_{\text{ESR}} = H_{\text{pp}}{}^2 \times Y_{\text{max}}$) and the increased value of photographic sensitivity ΔS. Since the ESR signal results from the paramagnetic centre of a light induced dye, I_{ESR} represents an increase in the number of positive holes when the supersensitizer is added. The total positive hole count is increased at the expense of the positive holes produced from sensitizing dye. Thus, the recombination of photoelectrons in the conductance band and the dye-positive holes from the exposed adsorbed sensitizing dye is retarded. This result also supports both

Gilman and Tani's mechanism of supersensitization, i.e. that the supersensitizer acts as a positive hole trap of the sensitizing dye A.

(4) Studies of the supersensitization of some bridged dicarbocyanines by triazino stibenedisulfonic acids[35]

The positively charged bridged dicarbocyanine A is supersensitized by the negatively charged triazinostilbenedisulfonic acids B; IR spectra show that there is an interaction between A and B.

To evaluate the function of the supersensitizer, the rise in intensity of ESR when the supersensitizer is added to the dyed emulsion was measured. At the same time, the films coated with sensitizer A, and with sensitizer A plus supersensitizer B, were separately exposed. The increase in the photographic speed of sensitization of emulsions with A (E1) and A + B (E2) were measured. The results showed that the speed of sensitization of emulsion with dye and supersensitizer increased with the rise of the ESR signal intensity, in comparison with the dye alone.

Thus, an interaction exists between the positively charged sensitizing dye and supersensitizer, and this interaction will cause these types of molecules to be adsorbed alternatively. The internal transfer of excitation energy within a dye aggregate on the surface of the AgBr is reduced. As a result, spectral sensitization is reinforced and the concentration of dye free radicals is increased.

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