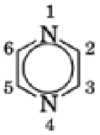
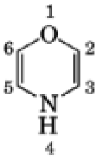
*Kirk-Othmer Encyclopedia of Chemical Technology.*

# AZINE DYES

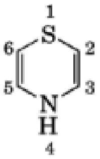
Azine, oxazine, and thiazine dyes were among the earliest of synthetic dyes. The names are derived from the 6-member heterocyclic ring system present in all dyes of these classes: 1,4-diazine [290-37-9] **(1)**, 1,4-oxazine [290-47-1] **(2)**, and 1,4-thiazine [290-57-3] **(3)**.



**(1)**

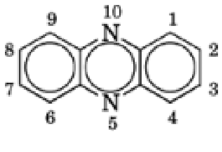


**(2)**

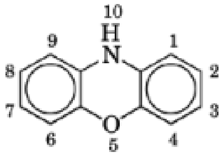


**(3)**

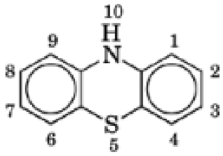
The parent rings are always included in phenazine [92-82-0] **(4)**, phenoxazine [135-67-1] **(5)**, or phenothiazine [92-84-2] **(6)** ring systems.



**(4)**

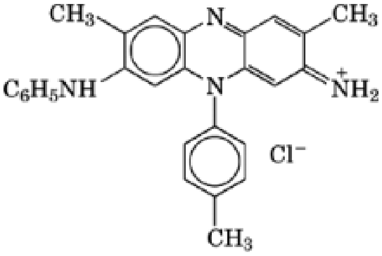


(5)



(6)

The first of these dyes to be made synthetically was Perkin's mauveine [6373-22-4], which is a substituted phenazine of structure **(7)**.



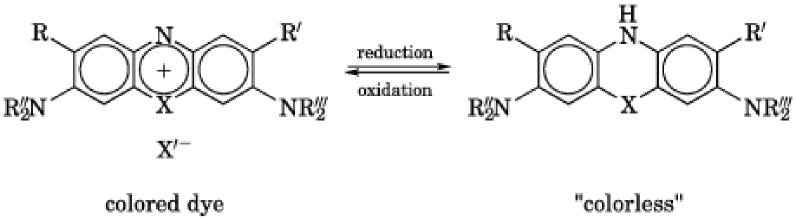
(7)

Mauveine is in a group of azines termed safranine dyes; ie, it is a *N*-phenyl-phenazonium chloride. Although the structures of these dyes are often written to show a positive charge on a particular hetero atom, the charge is in fact distributed through resonance throughout the molecule, thus accounting for their deep color.

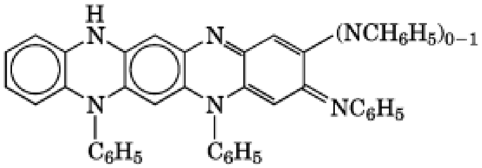
Perkin's discovery of mauveine in 1856 led to a flurry of activity in synthetic organic chemistry in England, which spread to Germany, and flourished through the last half of the nineteenth century, one of the richest periods for synthetic organic chemistry. During this time many synthetic organic methods were developed which are still used today.

Azine, oxazine, and thiazine dyes were historically more important than they are at present. However, at least one example of each, introduced more than 100 years ago, is still offered commercially today (1, 2). Azo and anthraquinone dyes have largely displaced them in commercial application. Azo dyes (qv) offer better fastness and broader shade ranges at more economical prices.

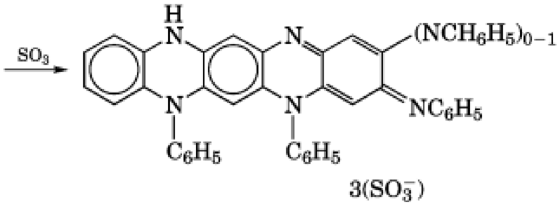
All classes of azine dyes are vattable, ie, they are reduced to "colorless" forms, then oxidized back to the dye (2). They therefore offer good fastness to oxidation (3). Because of this property, many find uses as redox indicators in titrations.



Dyes in these classes are generally basic dyes; ie, the chromophore is cationic. Some structures have been sulfonated to acid dyes, eg, the Nigrosine, (CI Solvent Black 5; CI 50415), **(8)** to CI Acid Black 2 [8005-03-6] (CI 50420) **(9)**.

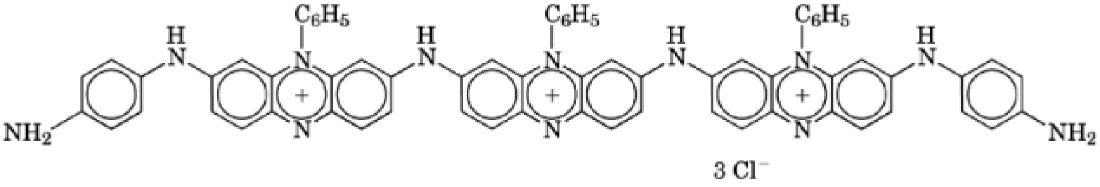


**(8)**



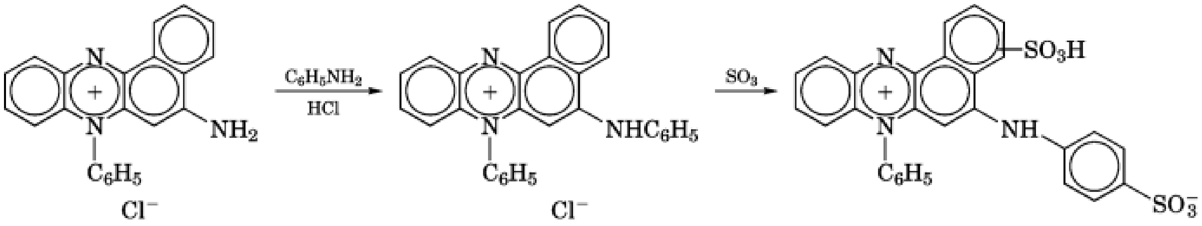
**(9)**

Both Nigrosine and Acid Black 2 are mixtures, and the structures shown are only typical components. The purer azine dyes of this structure are prepared by controlled stepwise synthesis by reaction of an azobenzene with aniline and aniline hydrochloride. Nigrosine, prepared by oxidizing aniline and aniline hydrochloride with nitrobenzene in the presence of ferric chloride, is similar in structure to nongreening Aniline Black [13007-86-8] (CI Pigment Black 1; CI 50440) **(10)**, prepared by oxidizing aniline and aniline hydrochloride with dichromate or sodium chlorate in the presence of an oxygen carrier such as a copper, vanadium, or iron salt. Aniline blacks are prepared in the dyebath with the material to be dyed.



**(10)**

Phenylrosinduline **(11)** has been sulfonated to CI Acid Red 101, CI 50085, **(12)**; such dyes are no longer commercial items.



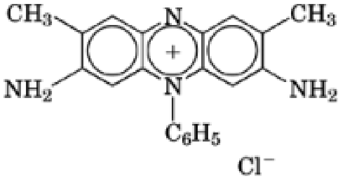
**(11)** **(12)**

There are oxazine disperse dyes reported (4) and several reactive dyes containing the oxazine ring and a few containing thiazine (5) (see Dyes, reactive).

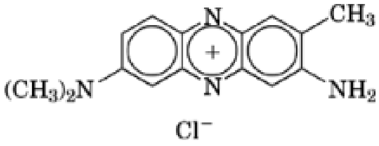
## 1. Azines

Azines were the first of the synthetic dyes. Perkins oxidized a crude mixture of aniline containing toluidines and obtained mauveine **(7)**.

Azine dyes are relatively unimportant as a class of dyes but are used extensively as biological stains. Colors are mostly yellow to red. Durability of some of these dyes is supported by the 1990 *AATCC Buyers Guide*, published by the American Association of Textile Chemists and Colorists, which lists Basic Red 2, Safranine T [477-73-6], **(13)** and Basic Red 5, Neutral Red [553-24-2], **(14)**, discovered in 1859 and 1879, respectively (1). Basic Red 2 is a safranine similar to mauveine **(7)**.

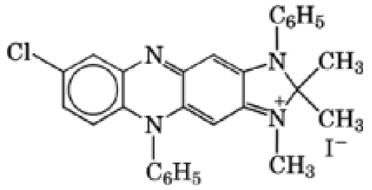


**(13)**



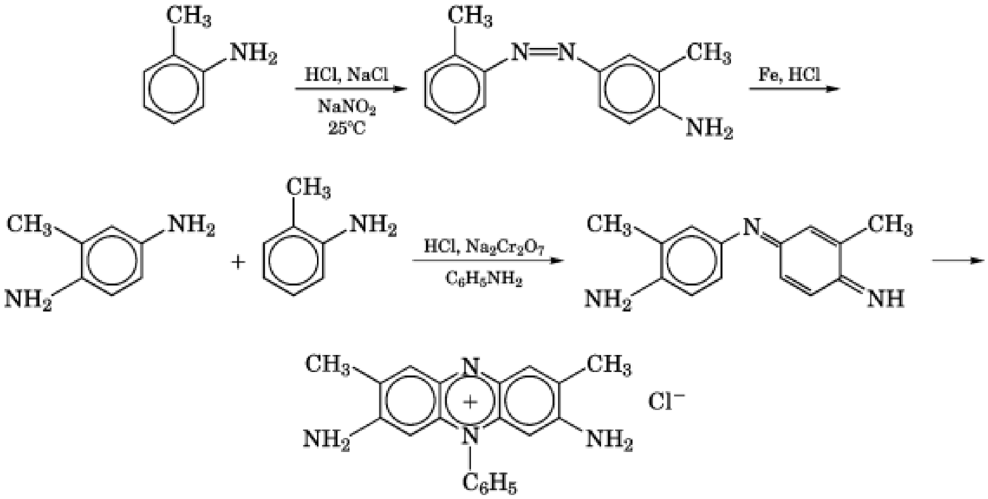
**(14)**

There are approximately one dozen references to azine dyes reported in *Chemical Abstracts* traceable literature since 1976. Of these references, all but one refers to titration indicators. One basic dye is reported, but it is not a commercial product (6):



### 1.1. Synthesis

Methods of synthesis have changed little since the synthesis of Basic Red 2. One method starts with *o*-toluidine [95-53-4], $C_7H_9N$, which is diazotized and coupled to form amino azotoluene [97-56-3], $C_{14}H_{15}N_3$. Amino azotoluene is reduced to one mole each of *o*-toluidine and 2,5-diaminotoluene [95-70-5], $C_7H_{10}N_2$. Condensation and oxidation with aniline [62-53-3], $C_6H_7N$, gives the desired dye **(13)**.



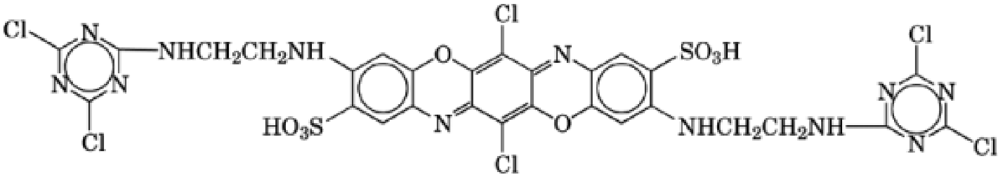
**(13)**

The method described in reference 6 differs only in that quaternization is an additional step.

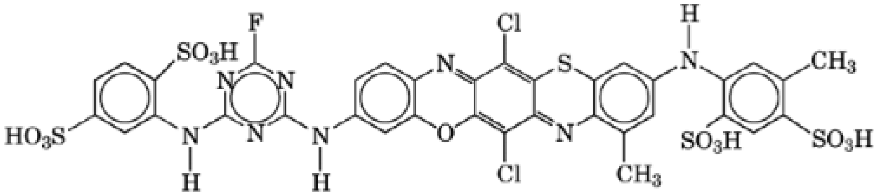
## 2. Oxazine Dyes

There have been approximately 80 references to oxazine dyes in the past 15 years. Several are references to their use as laser dyes and titration indicators. Thirty of these references are to oxazine dyes for either acrylic fibers or leather (qv) (7) (see Fibers, acrylic).

There are also examples of reactive dyes having only oxazine heterocyclic rings in the chromophore such as **(15)** [58104-86-2], as well as those having both oxazine and thiazine rings such as **(16)** [97140-65-3].

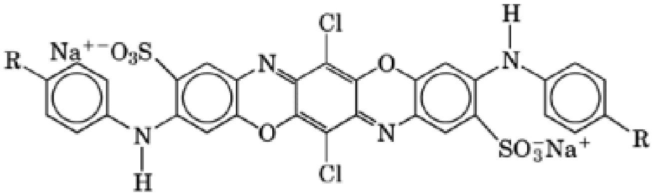


(**15**)



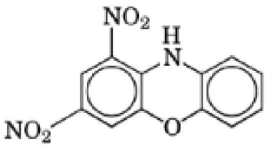
(**16**)

CI Direct Blues 106 (CI 51300) (**17**, R = H) and 190 (CI 51305) (**17**, R = Cl) are oxazine dyes.

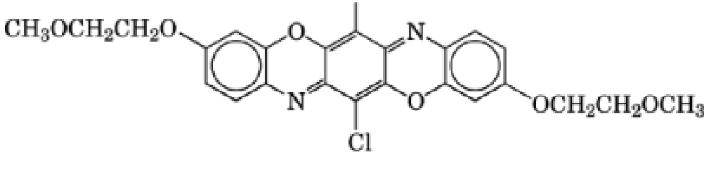


(**17**)

Additional examples have been reported (5). Disperse dyes which contain an oxazine ring include the yellow 1,3-dinitro-10*H*-phenoxazine [26103-32-2] **(18)** and the bright orange red **(19)** [66115-93-3] (4).



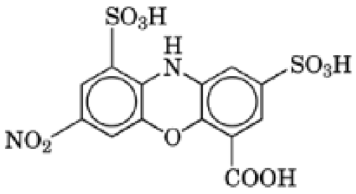
(**18**)



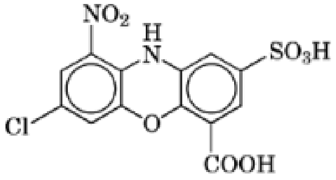
(**19**)

Neither of these dyes has been reported as a commercial item.

Oxazine dyes containing sulfonic acid groups and claimed to be suitable for dyeing leather in brown shades include [89477-76-9] **(20)** and [87617-03-6] **(21)** (8).



**(20)**



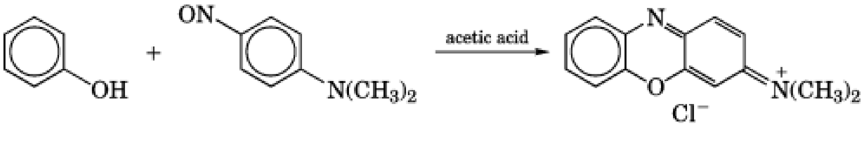
**(21)**

Cationic oxazine dyes suitable for dyeing acrylic fibers have been reported (7).

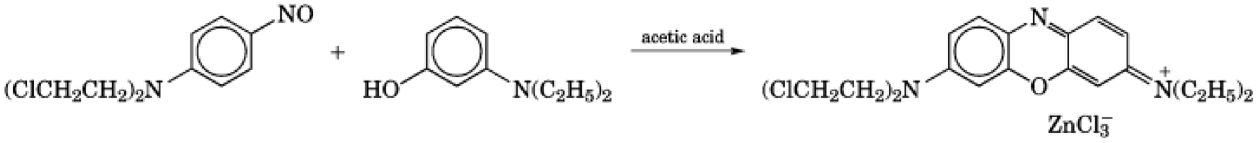
### 2.1. Synthesis

Several synthetic methods have been reported for oxazine dyes. The following are representative:

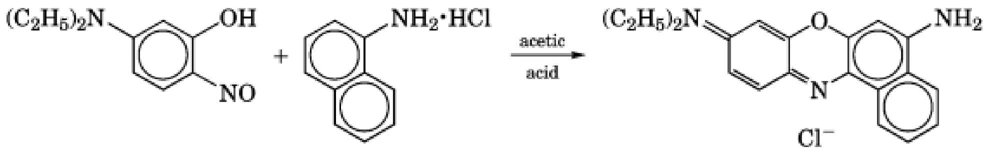
Condensation of phenol [108-95-2], $C_6H_6O$, with *p*-nitroso-*N,N*-dimethyl-aniline [138-89-6], $C_8H_{10}N_2O$, in acetic acid (9).



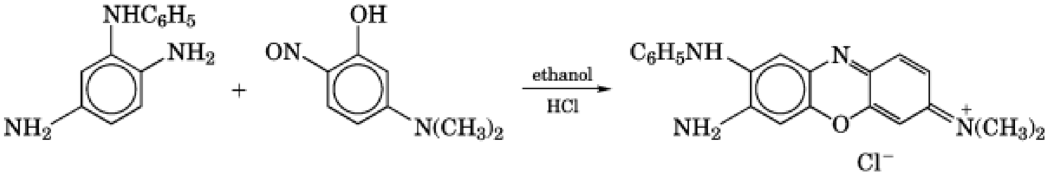
The following condensation produces the dye [58378-00-00], a trichlorozincate.



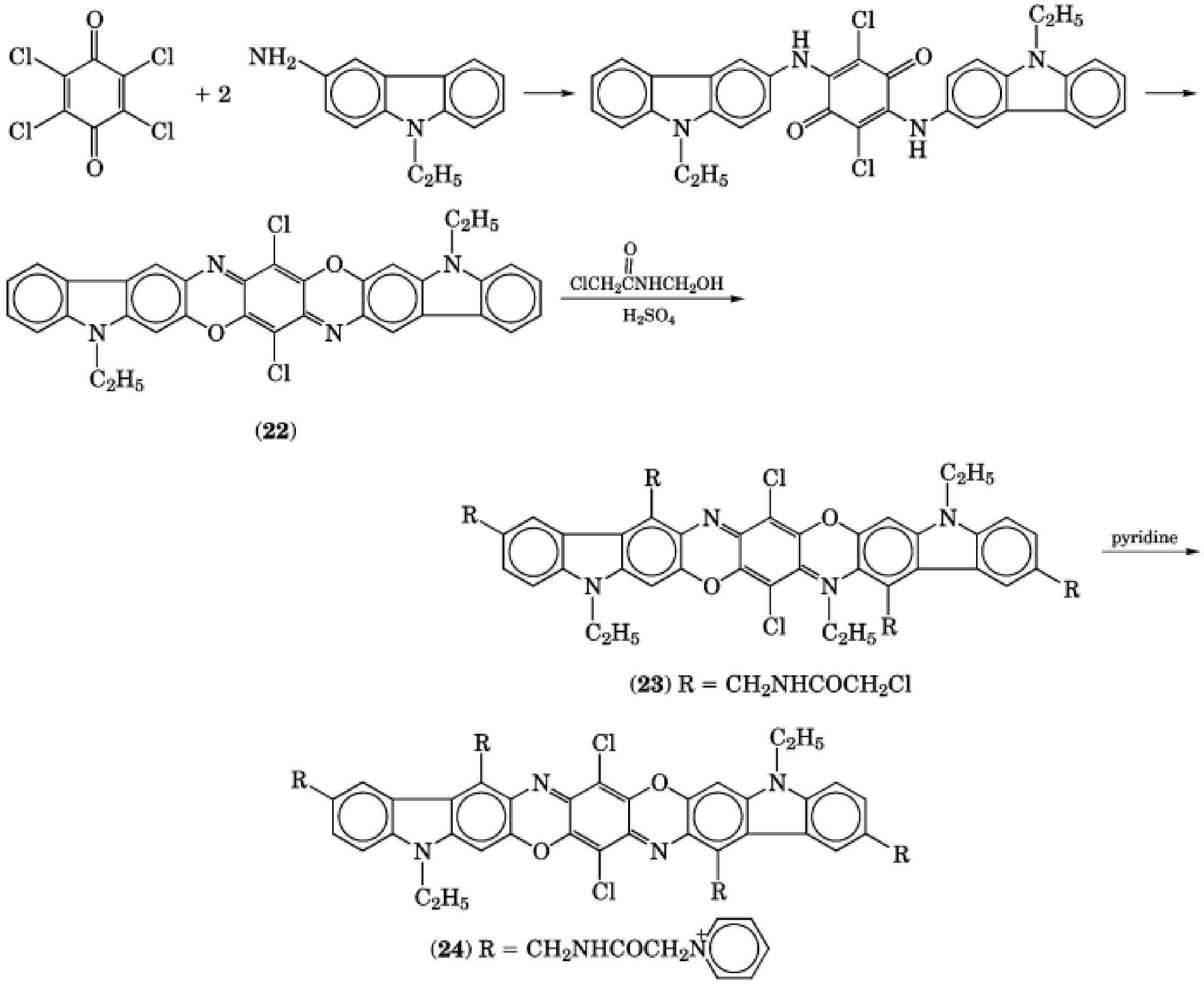
Condensation of an *o*-nitrosophenol with an amine hydrochloride in acetic acid (10): Nile Blue [2381-85-3] is formed from the hydrochloride of 1-naphthylamine.



The dye [57713-93-6] is formed from 2,5-diamino-diphenylamine:



Condensation of 2,3,5,6-tetrachloro-2,5-cyclohexadiene [118-75-2], $C_6Cl_4O_2$, with 9-ethyl-9*H*-carbazol-3-amine [132-32-1], $C_{14}H_{14}N_2$, (11) leads first to **(22)** [6358-30-1]. Treatment with *N*-methylol-$\alpha$-chloroacetamide [2832-19-1] and sulfuric acid produces **(23)** [87564-36-1], which forms the pyridinium salt **(24)** [87564-37-2].



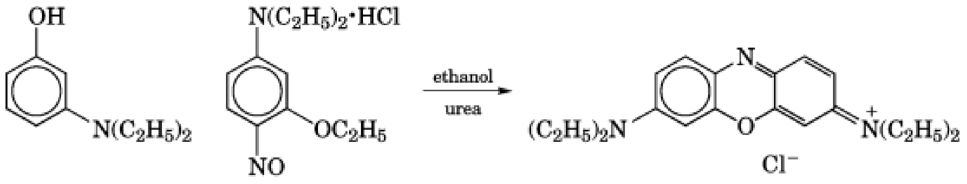
(22)

(23) R = $CH_2NHCOCH_2Cl$

(24) R = $CH_2NHCOCH_2N^+$

Concerns have arisen recently over potential presence of dioxins in dyes produced from 2,3,5,6-tetrachloro-2,5-cyclohexadiene [118-75-2].

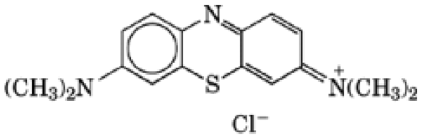
It has often been necessary to isolate oxazine dyes as insoluble zinc salts. Addition of urea [57-13-6], $CH_4N_2O$, or thiourea [62-56-6], $CH_4N_2S$, to the reaction mixture is reported to give good yields without using zinc (12), eg, the salt **(25)** [33203-82-6] is formed.



(25)

## 3. Thiazine Dyes

Methylene Blue [61-73-4] CI Basic Blue 9 (CI 52015), **(26)**, is the classic thiazine dye still in use today. This dye was first reported in 1876 (1).



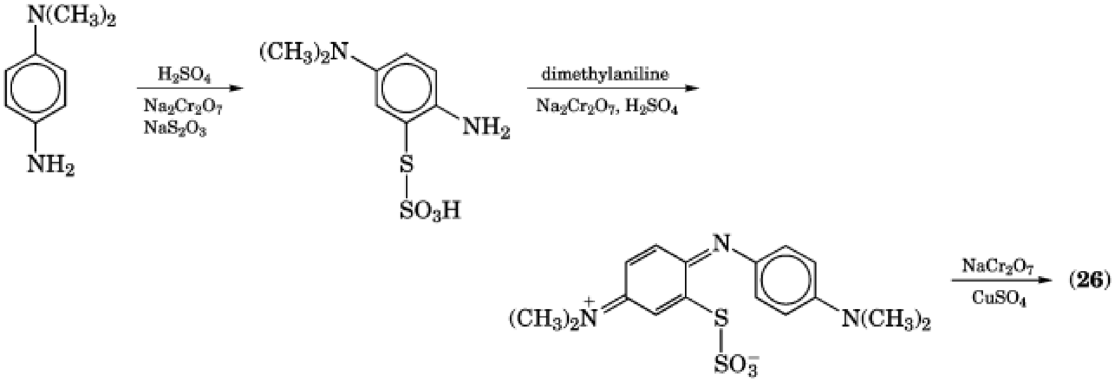
**(26)**

There have been approximately 60 references to thiazine dyes in the past 15 years of *Chemical Abstracts*. Although most of these references are to titration indicators, photophysical evaluation, and spectral properties, a few refer to structures for use as dyes (13).

Thiazine is not important in dyes as such, but it is a part of some reactive dyes (5). Thiazine is important in sulfur dyes (qv).

### 3.1. Synthesis

The method of synthesis for Methylene Blue described in reference 14 is still the stepwise method of choice for thiazine dyes. *N,N*-Dimethyl-*p*-phenylene diamine [99-98-9], $C_8H_{12}N_2$, reacts with sodium thiosulfate [7772-98-7] to form the thiosulfonic acid which condenses with *N,N*-dimethylaniline [121-69-7], $C_8H_{11}N$, in the presence of sodium dichromate [10588-01-9] to the indamine, then with copper sulfate[18939-61-2] and sodium dichromate to Methylene Blue **(26)**.



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