California Institute of Technology

Pasadena, California

CLASS OF 1922

Department of Chemistry

Undergraduate Theses of

Gordon A.Alles

Paul R.Ames

Willard J.Beman

Frank R.Bridgeford

Jesse C.Burks

Robert W.Gillies

Alfred W.Knight

Maynard S.Reynolds

Charles Fisher Ritchie

Howard G.Vesper

Lester O. Warner

THESES 1922

Alles, Gordon A	A new acridine dye.
Ames, Paul R	The specific heat capacity of heavy petroleum products.
Beman, Willard J	The Löwig process for caustic soda using trona as a raw material.
Bridgeford, Frank R.	A process for the utilization of pyrite ash.
Burks, Jesse C	Semi-works development of a germanium extraction process.
Gillies, Robert W	An attempt to dehydrogenate cottonseed oil.
Knight, Alfred W	Perchloric acid from ammonium perchlorate and oxides of nitrogen.
Reynolds, Maynard S	The utilization of a deposit of magnesite located near Porterville, California as a source of raw material for the manufacture of C.P. Epsom salts.
Ritchie, Charles Fisher	An investigation on the production of sodium thiosulfate from trona.
Vesper, Howard G	The preparation of carbon monosulphide and hydrocyanic acid by the use of activated carbon.
Warner, Lester O	The reaction between nitrogen and methane in the silent electric discharge.

A New Acridine Dye.

Thesis

by

Gordon A. Alles

In partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

California Institute of Technology

Pasadena, California.

1922.

A New Acridine Dye.

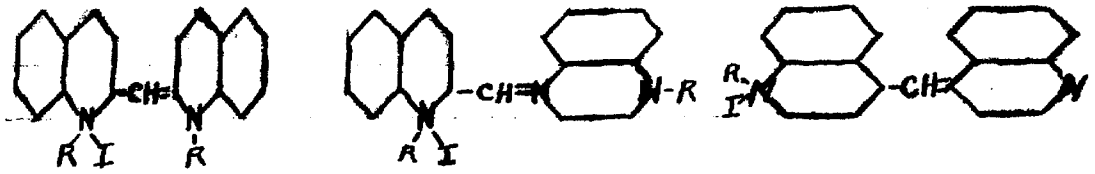
Silver halide emulsions, such as are used in photography are sensitive only to the shorter wave lengths of light. The sensibility of the emulsion is a maximum in the violet and decreases to nearly zero in the green. However if the emulsion be stained with a suitable dye, it may be made sensitive to the longer wave lengths, the sensitization being dependent upon the dye used. Thus the dye erythrosin sensitizes to green, pinaverdol to green and yellow, pinacyanol to orange and dicyanin to red.

The dyes mentioned above, with the exception of the erythrosin, belong to a general class known as cyanines. The characteristic of this class is that they are all derived from alkyl salts of quinoline derivatives. The various dyes of this class are divided into groups, division being chiefly made upon a correlation of spectrographic properties and empirical methods of preparation. Considerable work has been done in an effort to definitely determine the structure of the different dyes in order to find the relation between color and structure of the different dyes. During the last few years there have been published several articles on this subject, the most complete being those published by Otto Fischer [1] and assistants and those by W.H. Mills [2] and co-workers at Cambridge.

The cyanine dyes are divided into two main groups, the cyanines and the carbocyanines. The cyanines are the dyes

formed by condensation whenhalf of the total alkyl salt of a αor γ methyl substituted quinoline is converted into the base. Formation of the cyanines takes place in the absence of oxidizing or condensing agents. Carbocyanines are formed in a similar manner except the presence of some oxidizing agents, formaldehyde, chloroform or some similar compound is required in the condensation. Carbocyanines absorb light of longer wave length and correspondingly sensitizes to longer wave lengths than the cyanines.

The structure of the cyanines has been worked and speculated upon a great deal [3] and at present it is well agreed that they are composed of two quinoline nuclei, joined thru a -CH2 group, either α,α'or α,γ'or $\gamma,\gamma'$to the nitrogen of the two nuclei. Thus the probable forms are,



where R represents an alkyl group.

The determination of the structure of the carbocyanines offers a more difficult problem because of the additional side reactions caused by the presence of other materials in the condensation process. It is generally agreed that they are similar to the cyanines except the nuclei are joined by a longer chain of carbon atoms. The introdddction of the longer chain causes a deepening of color, which means that light of longer wave length is absorbed.

Fischer [1] suggests and offers fairly good evidence that the nuclei are joined by the chain -CH=C= while Mills [2] has apparently proven that the joining is thru the chain -CH=CH-CH=, at least in the case of the carbocyanine dye pinacyanol, formed from quinaldine ethiodide in presence of formaldehyde. This structure indicates that the formaldehyde is necessary for the formation of the dye, whereas the same carbocyanine can be obtained by merely oxidizing the quinaldine ethiodide. However, in view of the fact that alcohol is present in the preparation of the dye that the alcohol takes part in the condensation reaction causing a grouping -CH=CR-CH= where R might be H or CH_3 depending upon conditions. The presence of the group CH_3 in one dye and not another might not have had enough effect to have been noticed by rough comparison of absorption data. For this reason taken with the fact that -CH=CH is not a conjugate chain grouping it seems that the structures, indicated by Mills formula for the pinacyanol, for the carbocyanines are probably correct.

In view of the fact that the carbocyanine dyes formed from γ methyl and α,γ dimethyl quinolines absorb and sensitize to longer wave lengths than other dyes of this group , it should be expected that a derivative in which both α and β positions of the quinoline ring are substituted might produce a dye absorbing even longer wave lengths. The shift of absorption would be greater the heavier the

substitutents in these positions. Another fact entering into consideration as to susbstituents would be to use non-reactive ones to prevent side reactions along with the condensation reaction. With these facts in mind the writer decided to find out if it were possible to derive a dye from the alkyl salts of meso-methyl acridine that would be analogous to the carbocyanines. In this compound both the and positions are bonded into a benzene ring, thus tending to fulfill the desirable properties outlined above.

The formation of the dyes is in general ascribed to two characteristics of or methyl substituted quinolines. The first is that the hydroxyl group of the quaternary ammonium base shift to the or position. The other characteristic is that the methyl groups are very reactive, condensing with aldehydic and nitroso compounds with ease. Meso-methyl acridine exhibits these characteristics to nearly the same degree as the methyl quinolines do. Hantsch[4] has measured the rate of the shifting of the hydroxyl group of the base and finds it comparable to that of the quinolines. Friedländer [5] and Borsche [6] have studied the condensation of the methyl group with aldehydes and nitroso compounds, finding close analogy to the reactivity of the methyl group in either lepidine or quinaldine.

Meso-methyl acridine for the experimental work was made by the dehydration of acetyl diphenylamine with anhydrous zinc chloride in an open flask rather than using the method of Bernsthen [7] in order to avoid the use of glass bombs.

The yield was not quite as high but the reaction was more convenient to carry out. The alkyl iodides of the methyl acridine were formed by heating the constituents in a closed iron bomb, giving a good product. It was found impossible to properly crystallize the iodides from either alcohol or water and the final procedure adopted was to wash the finely ground product from the bomb with ether several times. This gave a suuficiently pure compound to carry out the experiments on dye preparation.

Considerable experimenting was done in an effort to determine the best conditions for dye preparation and to find what influence the different constituents in the reaction have upon the dye formation. The experimental work is difficult to interpret and the preparation of the dye is chiefly a matter of following an experimentally determined method if a yield is to be obtained at all. The best dye formation apparently takes place with methyl acridine methiodide in ethyl alcohol of about 99% in the presence of formaldehyde, although this latter does not appear to be essential to the reaction other than a suitable oxidizing agent or caltalyst whichever it may be. Dye formation seems to vary with the concentration of alcohol, methiodide and the time of heating.

The solutions of the dye are green, alcohol being used as solvent as the dye is not very soluble in water. The solutions reflect purple-blue light and have a yellow color along with the green. The dye as obtained is probably a mixture of

mixture of several different color substances along with the dye substance desired. Attempts to obtain pure crystals of the dye were not very succesful although some purification can be obtained by crystallizing from alcohol by evaporation in vacuo.

The absorption of the dye solutions was roughly determined by photographing the absorption spectra upon an Ilford panchromatic plate on a Hilger spectrophotometer. This work was performed by Sinclair Smith and Arthur Klein of the Physics department of the college and the writer wishes to express his thanks for their help. The absorption data shows that the dyes prepared from the methiodide in either methyl or ethyl alcohol are probably identical. Also that the dyes prepared with formaldehyde can be made with benzaldehyde as the absorption data is nearly the same. The absorption of the green dyes prepared in the different manners begins about 6 00 Angstrom units and extends out further, the upper limit not being determinable with the apparatus and plates that were used.

An experiment was tried to find if the dye sensitizes photograghic emulsions. The experiment indicates that there is sensitization at about 6600 A and another sensitization band at 7000 A although the latter band is rather weak. Due to lack of time it was not possible to more carefully determine the sensitization. This work was also performed by the men mentioned above, to whom the writer owes his thanks. Prints of the plates obtained are shown in the experimental part of this paper.

Experimental.

Preparation of acetyl-diphenylamine. - Diphenyl amine is refluxed with a 15% excess of acetic anhydride for several hours then product is poured, with stirring into ice-water Filter off the acetyl-diphenylamine wash and dry. M.P. 100°C.

Preparation of meso-methyl acridine. - Equal weights of the acetyl-diphenylamine and zinc chloride are heated together for about 12 hours at 220°C. The product is extracted with fairly strong H_2SO_4 , solution poured into water, filtered and then the methyl acridine is precipitated out with NH_4OH. Yields obtained with various times and temperatures varied from 30%- 45% of theory.

Purification of methyl acridine. - 10 g. of methyl acridine in 50 cc alcohol, to which is added, with stirring, a solution of 10 g. of tartaric acid in 100 cc of alcohol. Filter, wash then mix with water to form a sludge which is stirred into Na_2CO_3 solution. Filter off and wash the pure methyl acridine. It may be recrystallized from alcohol or alcohol-water solutions.

Preparation of methyl acridine methiodide. - 10 g. of methyl acridine and 11 g. of methyl iodide are sealed in a bomb and kept at 90°C. for several hours. The product is ground, washed with ether several times and dried. Yield is about 13 g.

The ethiodide is prepared in identical manner.

Reactions concerning dye preparation.

Formation of pseudo-base. - 1 g. of Me-A-MeI dissolved in water, addition of NaOH causes white precipitate that coagulates to yellow chunks. This is the pseudo-base as the quaternary ammonium hydroxide would be soluble.

Reaction in water solution.

1. 0.001 mol Me-A-MeI in 60 cc water, 0.0005 mols NaOH added. Boiled in CO_2 for 30 min. giving red ppt. from yellow solution.
2. Same as 1. with addition of 0.5cc 40% formaldehyde. Result was identical with 1 as far as observable.
3. Same as 1 with air bubbling thru solution. Less red precipitate and darker colored solution than 1.
4. Same as 1. with .228g (0.001 mol) ammonium persulphate. Black precipitate from light yellow solution.

Reaction in 50% ethyl alcohol-water solution.

The procedure was same as above with 50% alcohol as solvent. The general results are the same except that yellow-brown solutions with green reflection are formed. This indicates greater dye formation.

Reaction in 95% alcohol solutions.

Procedure was repeated in the stronger alcohol solutions.

1. Intensely yellow brown solution with some green coloration.
2. Same as 1. of this set.
3. Yellow solution with strong green coloration indicating great dye formation in this case.
4. Oxidation with persulphate with this concentration of alcohol was not tried.

The reactions outlined on the preceding page were performed in only a general qualitative way as no attempt was made to determine dye formation other than by a comparison of colors formed. The following are more quantitative.

1. 0.0005 mols Me-A-MeI in 30 cc methyl alcohol, to which is added, in boiling solution 5cc 0.5 N Namethylate solution containing 1cc 40% formaldehyde solution. The solution is cooled whereupon .24g of black tarry solid came down. Black solid gives yellow solution changing to green after long standing.

2. Experiment was repeated using Na ethylate solution. Results were the same, yielding .27 g solid.

2. 30cc ethyl alcohol were used as solvent, with Na ethylate. Gave a brown precipitate weighing .53 g and on addition of a little water gave a further red precipitate of .10g. Both of these precipitates give yellow solutions changing to dark green and standing two days. Ethyl alcohol was the solvent.

3. The ethiodide is used in methyl alcohol with Na ethylate. Gave .11g brown precipitate with 0.06g of a black solid on the addition of some water. The precipitates give yellow-brown solutions, the alcohol precipitate solution changing to green in about three days.

4. The ethiodide is used in ethyl alcohol.

0.22 g of red-brown precipitate came down and .18 g more precipitated on addition of water. The solution of the precipitates in alcohol was yellow changing to green on standing a few days.

The precipitates in the case of 2 and4 were the greatest. Time seems to be the necessary factor to form the green dye.

Preparation of the dye.(Best methods)

Methyl acridine methiddide in methyl alcohol solution.
0.01 mol in 60cc methyl alcohol, and to boiling solution is slowly added 10 cc 0.5N sodium methylate solution containng 1.5 cc 40% formaldehyde. After long boiling the solution is cooled. A few tarry yellow black crystals separate out from the yellow solution. Yield about .5 g which dissolve in alcohol to yellow solution which changes to the green dye solution.

Methyl acridine methiodide in ehtly alcohol solution.
0.01 mol in 60cc ethyl alcohol to which is added the same as above under same conditions. After long boiling the solution is cooled whereby considerable red-brown-black precipitate is formed from darkagreen solution. 0.5 to 1.25g

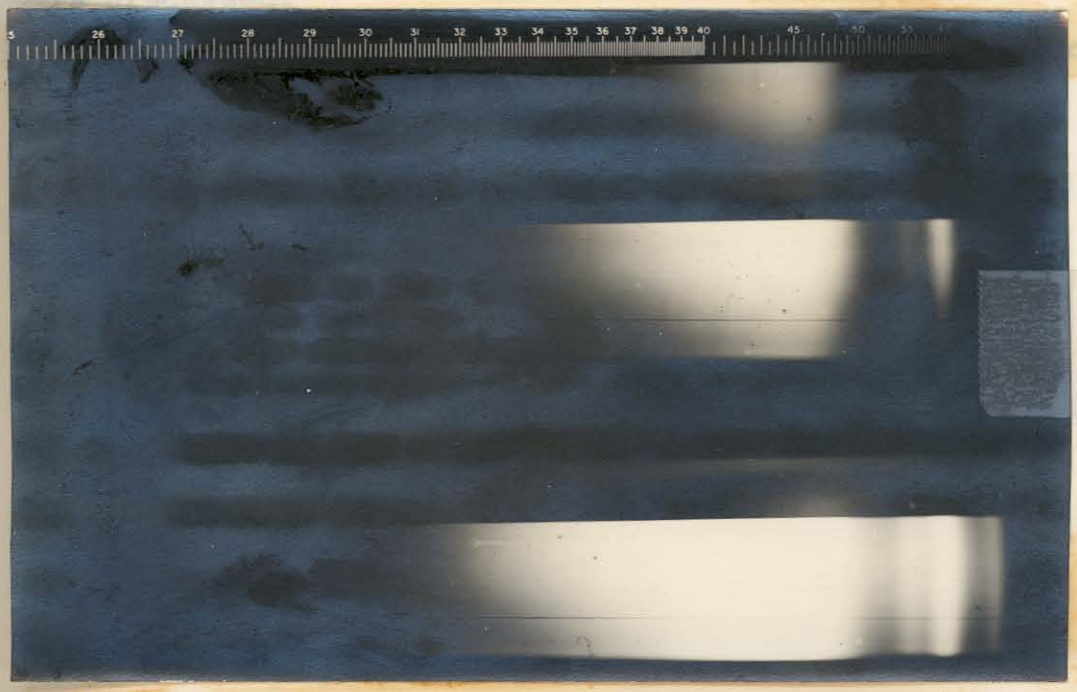
Methyl acridine methiodide in ethyl alcohol with benzaldehyde
0.01 mol in 60cc ethyl alcohol to which is added in boiling solution 10 cc 0.5N sddium methylate solution with 0.6g benzaldehyde. After long boiling solution is cooled, giving green-yellow solution with black tarry sediment. This will dissolve in ethyl alcohol giving a clear green solution.

The dyes uded in the spectrographic work were prepared according to the above procedure.

The prints of the plates made on the spectrometer are shown on the next page.

Absorption spectra of the different dye preparations.

1. is blamk 2. is dye from Me-A-MeI in ethyl alcohol with formaldehyde. 3. is dye from Me-A-MeI in methyl alcohol with formaldehyde. 4. is dye from Me-A-MeI in ethyl alcohol with benzaldehyde. (40 second exposures)



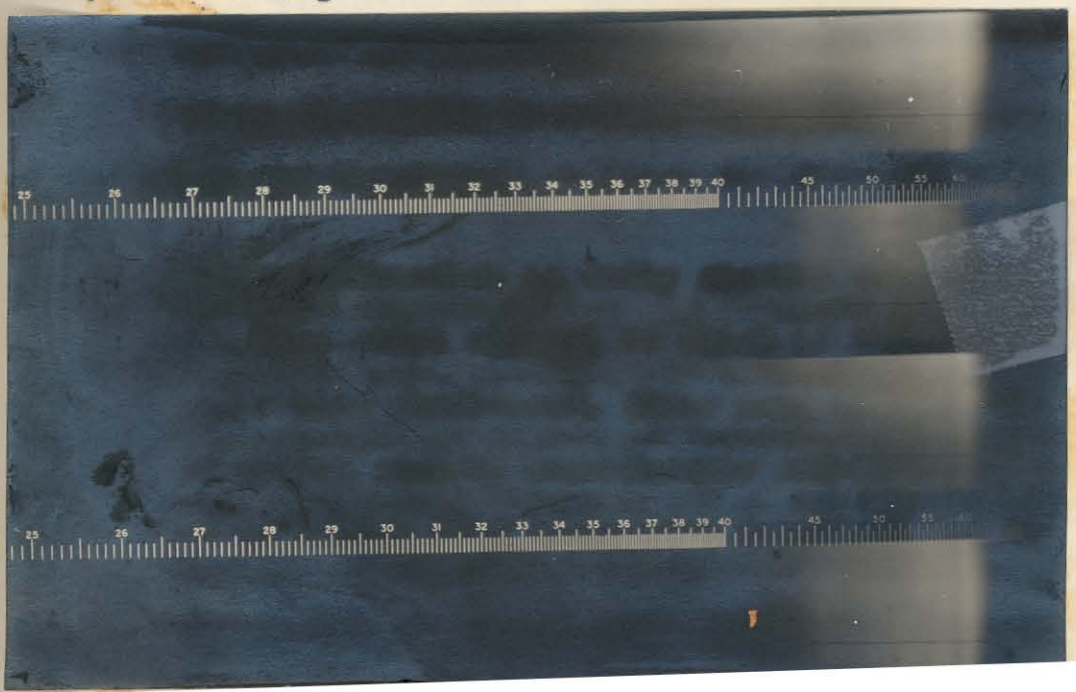
1.

2.

3.

4.

Plate showing sensitivity with 5,15 and 300 sec. exposures.



5 sec.

15 sec.

5 min.

Summary.

1. A general discussion of the cyanine dyes is given.

2# The relation of the properties of methyl acridine and those considered essential to formation of cyanine dyes is discussed.

3. The preparation of the dye from the alkyl iodides of methyl acridine is described and discussed.

4. Some spectrographic measurements are shown, showing the absorption and sensitization property of the dye.

Bibliography.

1. Quinocyanines(Pinacyanol,Dicyanines) I. Otto Fischer

C.A. 13: 1448 Original J.Prakt.Ch 98: 204-32
J.C.S.(1919) Ai 172

Quinocyanines II. Otto Fischer & Gunter Schiebe

C.A. 14: 3636 Original J.Prakt.Ch 100:86-105
J.C.S.(1919)

2. Cyanine dyes I. Constitution of the isocyanines
Mills & Wishart.
J.C.S. (1920) 117 T 579

Cyanine dyes II. Synthesis of o-amino cinnamylidene methiodide
Mills & Evans.
J.C.S. (1920) 117 T 1035

Cyanine dyes III. Constitution of pinacyanol.
Mills & Hamer.
J.C.S. (1920) 117 T 1550

3. Constitution of the cyanine dyes. I. Miethe & Book
B. 37: 2008-2022 (1904)

Constitution of the cyanine dyes. II. Miehte & Book
B. 37: 2821-2824 (1904)

Constitution of the cyanine dyes. III. Book
B. 38: 3804-6 (1905)

Constitution of the cyanine dyes. W.König
J.C.S.(1906) Ai 207 Original J.Prakt.Ch 73: 100-8

Constitution of the cyanine dyes. Vongerichten & Höfchen
B. 41: 3054-62 (1908)

Quinoline dyes. I. apoCyanines. Kaufmann & Strubin
B. 44: 690-701 (1911)

Quinoline dyes. II. Constitution, Synthesis, etc.
B. 45: 1404-19 (1911) Kaufmann & Vanderwahl

4. Hantsch, Kalb B. 32: 3124

5. Friedländer B. 38: 2840

6. Borsche C(1911) II. 289

7. Bernsthen A. 224: 35