Foundation, Yellow Springs, Ohio, for determining the infrared spectra with a double-beam Perkin–Elmer instrument. We also are grateful to Professor T. S. Ma of the New York University Microchemical Laboratory for performing some of the combustion analyses. Mr. Gilbert Farfel assisted with some of the preparative work on benzylhydrazine.

YELLOW SPRINGS, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF LYMAN CHALKLEY]

Hydrophilic Dye Cyanides. I. Ethyl Green and Xylene Blue Cyanides

BY LYMAN CHALKLEY

RECEIVED OCTOBER 8, 1954

The addition of a hydrophilic group (quaternary ammonium or sulfonic acid) to an aminotriphenylmethane dye cyanide produces substances that are photosensitive in aqueous solution. The preparation is described of ethyl green cyanide (I), xylene blue VS cyanide (II) and xylene blue AS cyanide (III).

The photosensitive system composed of the cyanide of a basic triphenylmethane dye and alcohol[1] is of theoretical interest and has found practical applications in actinometry.[2] When alcoholic solutions of certain triphenylmethane dye cyanides, which are initially colorless, are exposed to ultraviolet light they take on the color of the dye, the end effect being the ionization of the dye cyanide

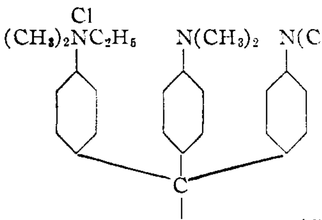
$$\underset{\text{(colorless)}}{Ar_3C—CN} \xrightarrow{\text{Light}} \underset{\text{(colored)}}{Ar_3C^+ + CN^-} \qquad (1)$$

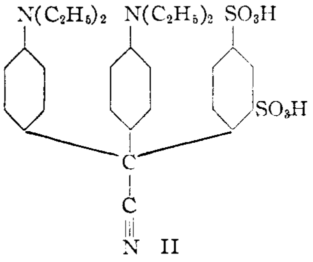
The alcohol plays an essential role in the photochemical reaction. Without it, or some substance that can perform an equivalent photoactivating function, the dye cyanide does not undergo the characteristic reaction. Water can act as a photoactivator if the dye cyanide contains a hydrophilic group.[3] The two dye cyanides of this type examined by Lifschitz yield dyes, phenolphthalein and benzaurine, of somewhat limited utility for actinometry and other practical applications.

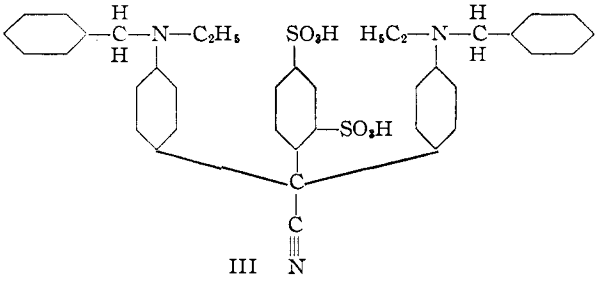
An objective of the present work is to provide new dye cyanides through which to extend the study of the fundamental photochemical reaction, and which may have practical advantages in actinometry over the dye cyanides used in the past. The first goal, and that toward which this paper is entirely directed, is the preparation of hydrophilic cyanides of the aminotriphenylmethane dyes, none of which have been found in the literature. The author hopes later to present studies of photochemical properties, which will be mentioned in the present paper only very briefly and qualitatively.

Salt forming groups, quaternary ammonium and sulfonic acid, were used to confer hydrophilic properties on aminotriphenylmethane dye cyanides. The compounds whose preparation is described are ethyl green cyanide (I), xylene blue VS cyanide (II), and xylene blue AS cyanide (III).

Ethyl green cyanide was prepared by the conventional reaction of the dye with sodium cyanide at room temperature.


I


II


III

The xylene blue dyes, on the other hand, did not react readily with sodium cyanide at room temperature. Solutions of these dyes containing excess sodium cyanide were examined colorimetrically. After 48 hours at 25° they had not lost 2% of their optical density, indicating that the reaction at room temperature is very slow if it proceeds at all. When solutions of the dyes and sodium cyanide were boiled, hydrogen cyanide was lost by hydrolysis and evaporation, and the dyes underwent an alkaline hydrolysis of an amino group like that described by the Erdmanns[4] for Patent Blue V. However, it was found that if the dye were heated with sodium cyanide solution in a pressure bottle a good yield of dye cyanide could be obtained.

Photosensitivity.—Aqueous solutions of the new dye cyanides were all colored by exposure to ultraviolet light. The ethyl green cyanide solution behaved photochemically much like an alcoholic

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(1) J. Lifschitz, *Ber.*, **52B**, 1919 (1919); J. Lifschitz and L. C. Joffe, *Z. physik. Chem.*, **97**, 426 (1921).

(2) (a) W. Frankenburger, R. Robl and W. Zimmermann, U. S. Patent 1,845,835 (Feb. 16, 1932); (b) L. Harris, J. Kaminsky and R. G. Simard, THIS JOURNAL, **57**, 1151 (1935); (c) L. Harris and J. Kaminsky, *ibid.*, **57**, 1154 (1935); (d) J. G. Calvert and H. J. L. Rechen, *ibid.*, **74**, 2101 (1952); (e) L. Chalkley, *J. Opt. Soc. Am.*, **42**, 387 (1952).

(3) J. Lifschitz, *Ber.*, **58B**, 2434 (1925).

(4) E. and H. Erdmann, *Ann.*, **294**, 376 (1897).

solution of malachite green cyanide, which has been extensively investigated.[2b,2c,2d]

Aqueous solutions of the xylene blue cyanides on exposure to ultraviolet light underwent more complex reactions than those exhibited by alcoholic solutions of the cyanides of the basic dyes. Color formation was slower, and, under suitable conditions, at least two dyes were formed from a single dye cyanide—the original xylene blue and in addition, a substance with a different absorption band.

Experimental

Ethyl Green Cyanide (I).—Ethyl green (Colour Index No. 685) appears to be commercially available in America only in the form of the certified biological stain,[5] "Methyl Green." The National Aniline[6] stain was used. This was the zinc chloride double salt. One analyzed sample contained 8.1% of zinc.

The procedure followed was to precipitate the zinc as carbonate, reconstitute the dye from the base formed during the zinc precipitatation, and to convert a portion of it into the dye cyanide by treatment with sodium cyanide at room temperature.

To 12 g. of methyl green (labeled 77% total dye content) in 300 ml. of water was added 100 ml. of 0.8 molar sodium carbonate. After 24 hours at room temperature the violet colored filtrate from the precipitated zinc carbonate was treated with 10 ml. of concd. hydrochloric acid and then with 2 *N* hydrochloric acid to a *p*H of 3.5. The solution was heated to boiling, cooled immediately to room temperature and treated with 2.5 g. of 95% sodium cyanide in 25 ml. of water. After 1 day in the dark at room temperature the solution was treated with 50 ml. of saturated sodium chloride solution, and allowed to stand in the dark for 12 days. The following operations were carried out in yellow light.

The solution was filtered. The brown precipitate, both that collected on the filter and adhering to the walls of the flask, was washed once with 5% sodium chloride solution, taken up in 55 ml. of *N*/2 hydrochloric acid and heated to boiling in the hood until all hydrogen cyanide was driven off. After cooling, the *p*H of the solution was adjusted to between 6 and 7 with sodium hydroxide and hydrochloric acid. Proper acidity of the solution was necessary not only for complete precipitation but in order to obtain the precipitate in a crystalline rather than tarry form.

The solution was mixed with 50 ml. of saturated sodium chloride solution. After 1 day at room temperature the precipitate was collected, washed with 25 ml. of 2% sodium chloride solution and dried in a 35° oven. The yield of crude ethyl green cyanide (I) was 4.5 g. The principal impurities in it were crystal violet cyanide and ethyl green base.

Purification was effected by dissolution of the crude product in 10 times its weight of water at 85°, filtration from the insoluble crystal violet cyanide, and crystallization for 1 month at room temperature. The colorless microcrystals were collected, washed on the filter with 10 ml. of ice-water and dried over sulfuric acid *in vacuo*. The filtrate was treated with $^1/_5$th of its volume of saturated sodium chloride solution and a second crop of crystals collected after 5 days. The total recovery was 3.8 g.

Anal. Calcd. for $C_{28}H_{35}N_4Cl$: N, 12.10. Found: N, 11.91.[7]

A sample in equilibrium with air at 18° and 56% relative humidity contained 4.48% of water.

Ethyl green cyanide (I) sintered at 258° and, when heated very slowly, melted at 260–262° (uncor.). It was soluble in water, isopropyl alcohol, *n*-butyl alcohol, *t*-amyl alcohol, dioxane, acetonitrile, acetic acid and nitroethane; slightly soluble in benzene; and insoluble in diisopropyl ether, carbon tetrachloride and ethyl acetate. It formed a zinc chloride double salt, less soluble in water than the original substance. The double salt could also be prepared directly from the commercial dye by treating it with 4 moles of sodium cyanide per mole of dye. This salt tended to lose zinc on recrystallization from water, a sample giving analyses of, N, 10.28[7]; Zn, 3.87, corresponding roughly to 1 atom of zinc in 3 molecules of dye cyanide. Ethyl green cyanide also formed a slightly soluble double salt with stannic chloride and a quite insoluble double salt with zinc thiocyanate, which also gave an insoluble double salt with the parent dye. Among the simple salts of ethyl green cyanide, the iodide and thiocyanate were slightly soluble and the phosphotungstate and phosphomolybdate insoluble.

The dry dye cyanide (I) and its zinc chloride double salt were not colored by exposure to ultraviolet light. Their aqueous solutions were strongly colored blue-green by ultraviolet irradiation, having a sensitivity of the order of that of alcoholic solutions of malachite green cyanide. The aqueous solutions were sensitive to the mercury 3342 Å. line, but not to 3650 Å.

When ethyl green cyanide was heated above its melting point and cooled, colorless needles were obtained. A solution of these in acetic acid developed a strong violet color on exposure to ultraviolet light. No green dye was formed. These results indicated the loss of one molecule of alkyl iodide.

Xylene Blue VS Cyanide (II).—Xylene blue VS (Colour Index No. 672) was commercially available under a number of trade names. The products used in this work were "National Biological Stain Patent Blue V,"[8] and commercial Alphazurine 2G, both manufactured by the same firm.[9]

To a solution of 25 g. of commercial Alphazurine 2G in 150 ml. of water was added 4.5 g. of 95% sodium cyanide and the mixture heated in a pressure bottle in a boiling water-bath for 1 hour. Suitable precautions were taken to avoid cuts by glass wet with cyanide solution in the event of the explosion of the bottle. The solution was cooled to room temperature, allowed to stand for 1 day and filtered from 11 g. of precipitated crude, colorless disodium salt of the dye cyanide. This salt formed soapy, anisotropic solutions in water, from which it could not be easily purified by recrystallization. It was recrystallized from a mixture of methyl alcohol and diisopropyl ether.

Anal. Calcd. for $C_{28}H_{31}O_6N_3S_2Na_2$: Na, 7.47. Found: Na, 7.23.

Eleven grams of crude disodium salt was dissolved in 100 ml. of boiling water, treated with 11.2 ml. of concentrated hydrochloric acid and allowed to stand at room temperature for 48 hours to yield a precipitate of 6.5 g. of the colorless free acid of the dye cyanide (II).

A solution of 0.51 g. of the free acid in 90 ml. of boiling water was cooled, immediately neutralized with 0.1 *N* barium hydroxide solution and allowed to stand for 3 days to yield 0.67 g. of beautiful needle crystals of the barium salt. This was recrystallized from 500 times its weight of water.

Anal. Calcd. for $C_{28}H_{31}O_6N_3S_2Ba$: N, 5.94; Ba, 19.43. Found: N,[7] 5.98; Ba, 19.17.

In equilibrium with air at 20° and 55% relative humidity the barium salt was hydrated.

Anal. Calcd. for $C_{28}H_{31}O_6N_3S_2Ba \cdot 7H_2O$: H_2O, 15.14. Found: H_2O, 14.73.

The free acid form of the dye cyanide (II) recrystallized from 120 times its weight of water as a pentahydrate, which was dried in air at 20° and 55% relative humidity.

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(5) A "Methyl Green, technical" bought from a laboratory chemical supply house turned out to be methylene green (Colour Index No. 924).

(6) Manufactured by the National Aniline Division, Allied Chemical & Dye Corp., 40 Rector Street, New York.

(7) Nitrogen and sulfur analyses by Oakwold Laboratories, Alexandria, Va.

(8) There is some confusion in the industry over the names and identities of these dyes. The original patent blue dyes, Colour Index Nos. 712 and 714, are no longer commercially available. Dyes still sold under the name "patent blue" are the xylene blues, Colour Index Nos. 672 and 673. I am grateful to Dr. Otto Stallman, Jackson Laboratory, E. I. du Pont de Nemours & Co., for very helpful information and advice on the commercial situation in regard to these dyes, and also to Farbwerke Hoechst AG, Frankfurt (M)-Hoechst. *Cf.* "Beilstein Handbuch der organischen Chemie," 4th ed. Vol. XIV, 2nd supplement, Springer-Verlag, Berlin, 1951, p. 511, footnotes 1 and 2.

(9) National Aniline Division, Allied Chemical & Dye Corporation, 40 Rector Street, New York, N. Y. In a private communication this firm kindly identified Alphazurine 2G as Colour Index No. 672. Their identification has been accepted without attempting experimentally to place the sulfonic acid groups, although W. C. Holmes, *Ind. Eng. Chem.*, **15**, 833 (1923), stated that Alphazurine 2G was made from benzaldehyde-2,5-disulfonic acid.

Anal. Calcd. for $C_{29}H_{33}O_6N_3S_2\cdot5H_2O$: H_2O, 14.13. Found: H_2O, 14.33.

All of the water was lost below 160°. The free acid II did not have a sharp melting point but decomposed with evolution of much gas when heated above 350°. Electrometric titration (glass electrode) with barium hydroxide showed the equivalence point for neutralization of both sulfonic acid groups to be *p*H 8.4. Solutions of the acid II could be titrated with phenol red as indicator.

On exposure to light with wave length of 2537 Å. an aqueous solution of the dye cyanide (II) developed a blue color, but much more slowly than do alcoholic solutions of the basic dye cyanides. Spectroscopic examination of the irradiated solution showed the absorption band of xylene blue VS and also a new absorption band at longer wave lengths.

Xylene Blue AS Cyanide (III).—Xylene blue AS (Colour Index No. 673) was commercially available under several trade names. The starting product used in this work was Calcocid Blue AX Double. This was identified by its manufacturer[10] as Colour Index No. 714 but proved on examination to be No. 673.

To 25 g. of the dye in 150 ml. of hot water was added 9 g. of 95% sodium cyanide, and the solution in a pressure bottle was heated in a boiling water-bath for 1 hour. After cooling and standing overnight the precipitated sodium salt of the dye cyanide was collected on a filter. The yield of crude salt was 16.8 g.

The free acid III was precipitated from a solution of 15 g. of the crude sodium salt in 400 ml. of water by addition of 22.5 ml. of 2 *N* hydrochloric acid. After standing for several days 13 g. of acid was collected. This was recrystallized from 1000 times its weight of water.

Anal.[7] Calcd. for $C_{38}H_{37}O_6N_3S_2$: N, 6.04; S, 9.22. Found: N, 6.16; S, 9.96, 9.18, 9.40.

The product did not have a sharp melting point, but when heated above 270° gradually decomposed with evolution of gas.

Electrometric titration with a glass electrode gave the equivalence point as *p*H 8.0 for the neutralization of both sulfonic acid groups.

On neutralization with barium hydroxide the free acid formed a slightly-soluble barium salt.

On exposure to light of wave length 2537 Å. aqueous solutions of xylene blue AS cyanide (III) slowly developed a green color. Spectroscopic examination showed the absorption band of xylene blue AS and also a new band in the violet.

Washington, D. C.

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[10] American Cyanamid Company, Calco Chemical Division, Bound Brook, New Jersey.

[Contribution from Los Alamos Scientific Laboratory, University of California]

2,5-Diaryloxazoles and 2,5-Diaryl-1,3,4-oxadiazoles

By F. Newton Hayes, Betty S. Rogers and Donald G. Ott

Received October 29, 1954

A number of previously unreported 2,5-diaryloxazoles and 2,5-diaryl-1,3,4-oxadiazoles have been prepared by cyclization of 1,4-diaryl-2-aza-1,4-diketones and 1,2-diaroylhydrazines.

The discovery that 2-phenyl-5-(4-biphenylyl)-oxazole[1] functioned as an efficient scintillation solute prompted the synthesis of a large number of 2,5-diaryloxazoles and related compounds which might possess certain desired characteristics for organic solution scintillators.[2] Until this discovery was made *p*-terphenyl was the only efficient organic scintillation solute known.

A convenient abbreviation system was originated in the course of this investigation and has since become commonly used by research workers, as well as commercial organizations, in the organic scintillator field. This system uses the letter P for phenyl, B for 4-biphenylyl, N for naphthyl, O for oxazole, D for oxadiazole, and so forth, with M signifying a methyl *p*-toluenesulfonate quaternary salt. Thus, for example, 2-(1-naphthyl)-5-(4-biphenylyl)-oxazole becomes αNBO, and 2-(4-biphenylyl)-5-phenyloxazole is BPO. The convention of giving first the 2-substituent, secondly the 5-substituent, and then the ring system is not utilized with the more complicated structures, *e.g.*, 5,5′-diphenyl-2,2′-bioxazolyl (POOP) or 1,4-di[2-(5-phenyl-1,3,4-oxadiazolyl)]-benzene (PDPDP). For such compounds the abbreviations are derived from the order in which the rings appear in the structure.

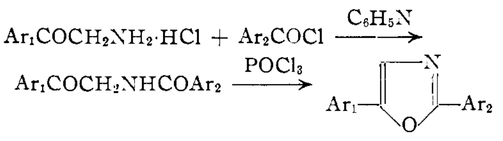

Fig. 1.—Synthesis of 2,5-diaryloxazoles.

For the most part, the new compounds listed in the tables were prepared by known methods. The oxazoles (Table I) resulted from cyclization of 2-aza-1,4-diketones (Fig. 1). POPOP, BOPOB and POOP were prepared by an extension of the method to difunctional acid chlorides. The general procedure for dissolving a 2-aza-1,4-diketone in sulfuric acid and precipitating with water to give the oxazole[3] is a simple reaction to execute but fails to yield the desired product in certain cases. This failure occurred in the attempted preparations of 2-(3,4-methylenedioxy)-5-phenyloxazole, POPOP, POOP, and in all cases involving the 4-biphenylyl group. Each of these compounds was successfully prepared by refluxing its amide with phosphorus oxychloride, a method which is now used exclusively.

Phosphorus oxychloride was also employed in the preparation of the 2,5-diaryl-1,3,4-oxadiazoles (Table II) from 1,2-diaroylhydrazines (Fig. 2).

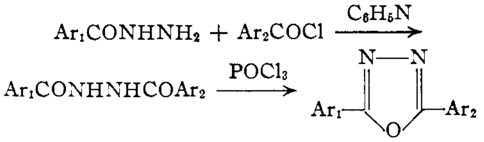

Fig. 2.—Synthesis of 2,5-diaryl-1,3,4-oxadiazoles.

The intermediate 2-aza-1,4-diketones and 1,2-diaroylhydrazines usually could be satisfactorily

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[1] F. N. Hayes, L. C. King and D. E. Peterson, This Journal, **74**, 1106 (1952).

[2] The application of these compounds as organic scintillators is being reported elsewhere.

[3] J. Lister and R. Robinson, *J. Chem. Soc.*, 1297 (1912).