[CONTRIBUTION FROM THE LABORATORY OF LYMAN CHALKLEY]

Hydrophilic Dye Cyanides. II.[1] Rhodamine B Cyanide

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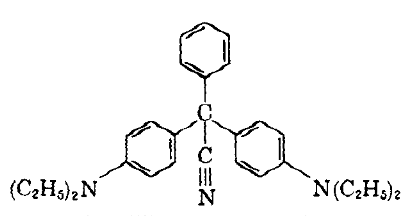
Received May 3, 1960

Rhodamine B cyanide (III) has been prepared and found to have a remarkably reactive nitrile group in strong contrast to the behavior of the familiar triphenylmethane dye cyanides, such as I. In aqueous solution rhodamine B cyanide rapidly reverts at room temperature to the parent dye (II) and sodium cyanide. In dilute mineral acid the nitrile group hydrolyzes at room temperature to the carboxylic acid (V). Photolysis of rhodamine B cyanide (III) may yield not only rhodamine B (II) but also cornflower blue (VII). The carboxylic acid (V) is both photosensitive and a strong reducing agent, being readily oxidized to carbon dioxide and rhodamine B.

Triphenylacetonitrile and many of its derivatives are characterized by great stability of the nitrile group.[2] The *p*-amino derivatives are commonly referred to as dye cyanides and may be typified by brilliant green cyanide (I). They are readily prepared by mixture of aqueous solutions of sodium cyanide and of a basic triphenylmethane dye at room temperature. The nitrile precipitates while the solutions are being mixed, and the reaction proceeds to completion. Once formed, the basic triphenylmethane dye cyanides are stable, and no report has been found of their conversion into the parent dye and inorganic cyanide except by the photochemical reaction discovered by Lifschitz.[3]



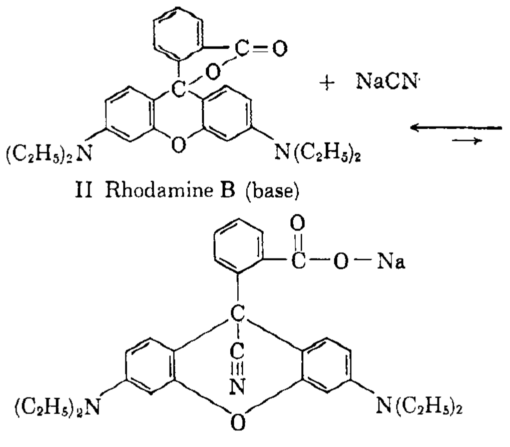
I. Brilliant green cyanide
4,4′-Bisdiethylaminotriphenylacetonitrile

The triphenylmethane dye cyanides also are quite stable against hydrolysis to the corresponding triphenylacetic acid and its amide. No reference has been found to such a reaction, and the dye cyanides may be halogenated,[4] nitrated,[4] and sulfonated[5] without destruction of the nitrile group.

Photolysis of triphenylmethane dye cyanides in a suitable solvent leads to the formation of the original dye,[3] although the formation of new dyes among photolysis products of two sulfonated dye cyanides has been briefly noted.[1]

The present paper deals with a dye cyanide that has properties in striking contrast with those of the previously known triphenylmethane dye cyanides. In rhodamine B cyanide (III) not only is the nitrile group highly reactive but the substance undergoes readily a photolysis to a different type of dye. The structural differences accompanying the contrasting properties may be seen by a comparison of the formula of brilliant green cyanide (I) with that of the new rhodamine B cyanide, 3,6-bisdiethylamino-9-cyano-9-(2-carboxyphenyl)xanthene (III).

Rhodamine B (II) did not react with hydrogen cyanide in neutral or acid solution. In alkaline solution it reacted to form the dye cyanide (III)



II Rhodamine B (base)

III Rhodamine B cyanide

(1)

The formation of rhodamine B cyanide was reversible, and in dilute aqueous solution at least 98% of the dye cyanide decomposed into rhodamine B (II) and sodium cyanide. At 31° the rate constant for this first order reaction was 2×10^{-5}. Therefore, in the preparation of rhodamine B cyanide it was necessary to employ a considerable excess of sodium cyanide to obtain a good yield.

In acid solution the nitrile group of rhodamine B cyanide hydrolyzed readily at room temperature to the carboxylic acid, 3,6-bisdiethylamino-9-carboxy-9-(2-carboxyphenyl)xanthene (V)

The dicarboxylic acid (V) also proved to be highly reactive. In aqueous solution as the hydrochloride (V) it was oxidized at room temperature by ferric chloride to carbon dioxide and rhodamine B chloride (VI)

A solution of the hydrochloride of the dicarboxylic acid (V) was relatively stable in air. Only a few per cent were oxidized to dye by air during storage in the dark at room temperature for over a year. In

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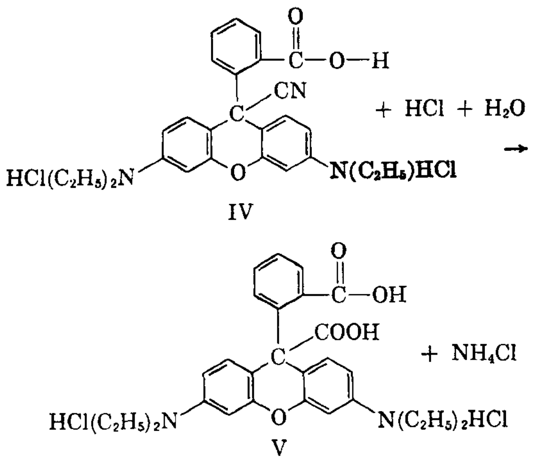
(1) L. Chalkley, *J. Am. Chem. Soc.*, **77**, 1848 (1955).

(2) Emil and Otto Fischer, *Ann.*, **194**, 274 (1878).

(3) J. Lifschitz, *Ber.*, **52B**, 1919 (1919).

(4) L. Chalkley, U. S. Patent **2,366,179**, Jan. 2, 1945.

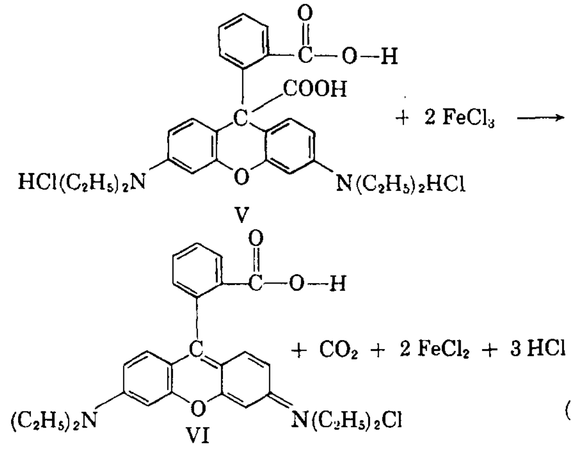
(5) L. Chalkley, U. S. Patent **2,877,167**, March 10, 1959.



(2)

neutral and alkaline solution the dicarboxylic acid became a stronger reducing agent and was rapidly oxidized by air to rhodamine B (II).

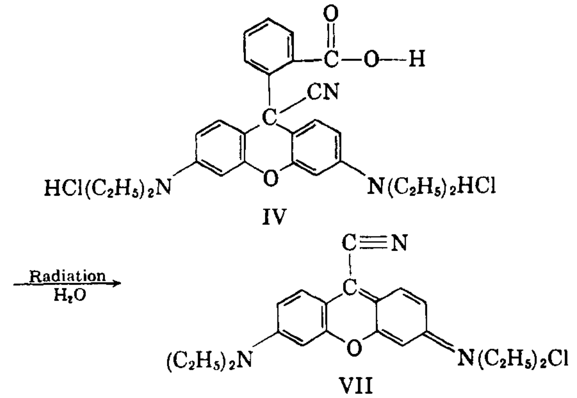
In both acid and neutral media the oxidation of the dicarboxylic acid by air was greatly accelerated by light. In some circumstances, at least, the photo-oxidation was optically sensitized by rhodamine B. Thus, the dry barium salt of the dicarboxylic acid, which was reasonably stable in the dark in contact with air, was quickly oxidized by air in the presence of a little adsorbed rhodamine B on exposure to light of wave lengths as long as those absorbed by rhodamine B. This behavior was similar to that of the leuco bases of xanthene and some other classes of dyes discovered by Gros.[6] In oxygen free atmosphere ultraviolet radiation also converted the dicarboxylic acid (V) into rhodamine B. The course of this reaction has not been investigated.



(3)

Rhodamine B cyanide (III) was found to undergo two different photochemical decompositions. In neutral or alkaline aqueous solution, or in neutral hydrocolloid films, radiation of wave lengths shorter than about 3350 Å split off the nitrile group with reformation of the dye, *i.e.*, reversed Equation 1. This reaction took place more slowly in the dark, as already mentioned. It appeared quite analogous to that of the familiar hydrophobic triphenylmethane dye cyanides,[3] such as brilliant green cyanide (I).

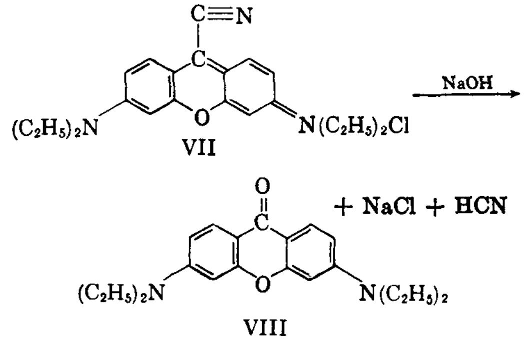
In acid solution rhodamine B cyanide (IV) was found to undergo a novel reaction induced by radiation of wave lengths shorter than about 3100 Å. In this photolysis one of Ehrlich and Benda's[7] cornflower blue dyes (VII) was formed



Cornflower Blue (4)

Except for a brief mention of anomalous dye formation,[1] no reference has been found to a reaction of this type. In fact, there was an early report that dye cyanides dissolved in aqueous solutions of mineral acids, *i.e.*, when converted into their salts, were not photosensitive,[8] but this appears to have been erroneous.[9]

Cornflower blue (VII) is itself unstable, decomposing in alkaline aqueous solution into the xanthone (VIII) and inorganic cyanide[7]



(5)

This reaction proved useful in identification of the dye formed from rhodamine B cyanide.

EXPERIMENTAL

Materials and methods. Rhodamine B was the drug and cosmetic dye, D & C Red No. 19.[10] Pyronine B was the commission certified biological stain.[10]

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(6) O. Gros, *Z. physik. Chem.*, **37**, 157 (1901).

(7) Paul Ehrlich and L. Benda, *Ber.*, **46**, 1931 (1913); Leopold Cassella & Co., German Patent **274,358** issued May 19, 1914.

(8) J. Lifschitz and L.-C. Joffe, *Z. physik. Chem.*, **97**, 431 (1921).

(9) L. Chalkley, U. S. Patent **2,936,276**, May 10, 1960.

(10) Manufactured by the National Aniline Division of Allied Chemical & Dye Corp., 40 Rector St., New York, N. Y.

Colorimetric determination of dyes was carried out with a selenium barrier layer cell photometer equipped with the color filters specified later under the different dyes. The instrument was calibrated by solutions of pure dyes. The colorimetric assays were accurate to 2 to 3%.

Some reaction products, such as ammonia, carbon dioxide and hydrogen cyanide, were not isolated but were determined by analysis. While standard quantitative methods were used in the analyses, it should be kept in mind that the samples to be analyzed were taken from ordinary organic preparations that were not carried out by rigorous quantitative manipulation. Therefore, small differences derived from the quantitative analytical data should not be made the basis for generalization.

Preparation of rhodamine B cyanide. A solution of 25 g. of 93% rhodamine B chloride (D & C Red No. 19[10]) in 125 ml. of boiling water was cooled to room temperature and mixed with a solution of 25 g. of 97% sodium cyanide in 130 ml. of water and 65 ml. of *n*-propyl alcohol. The mixture was stirred and heated in a flask at 80–85° for 2.5 hr. The flask was cooled, allowed to stand at 25° for 15 hr., and the precipitate was collected on a filter. The precipitate was washed with an ice-cold solution of 5 g. of sodium cyanide in 100 ml. of water followed by 25 ml. of pure ice water. It was then dried *in vacuo* over sulfuric acid. It weighed 12.7 g.

To the mother liquor from the initial precipitate were added the wash waters. The mixture was stirred and heated to 60° in a three necked flask through which air was blown until the *n*-propyl alcohol had evaporated. The flask was cooled, allowed to stand for 24 hr., and the solution was filtered. The precipitate was washed on the filter with 50 ml. of ice water. Too much washing at this stage caused the precipitate to become gelatinous. The precipitate was dried *in vacuo* over sulfuric acid. It weighed 9.5 g.

Thus, the total yield of crude rhodamine B cyanide sodium salt (III) was 22.2 g. The products contained about 0.2 of 1% of rhodamine B and a little tarry material. They were pure enough for preparative and other experimental use.

For analysis the product was further purified by recrystallization from acetonitrile, using 25 ml. of boiling solvent for each gram of substance. The product was dried at 100° *in vacuo* over phosphorus pentoxide.

Anal. Calcd. for $C_{29}H_{30}O_3N_3Na$: C, 70.85; H, 6.15; N, 8.55; Na, 4.67. Found: C, 67.55, 69.88; H, 6.57, 6.42; N, 8.41; Na, 4.70.

The low and erratic carbon analyses are to be noted. The sample was mixed with potassium dichromate and burned in the usual way, but in the second analysis the combustion was carried out at a higher temperature. Initial decomposition of the substance to form dry sodium cyanide (see below) before the sample burned may have had something to do with the difficult combustion for carbon. Because the substance was well characterized by its method of formation and reactions, and the other analyses were satisfactory, it was considered unnecessary to undertake an analytical research to try to determine the cause of the erratic results for carbon.[11]

The dry rhodamine B cyanide sodium salt (III) was a white powder which kept well in closed containers. In an atmosphere having 50% relative humidity the product absorbed water to a composition corresponding to a hexahydrate.

Anal. Calcd. for $C_{29}H_{30}O_3N_3Na.6H_2O$: H_2O, 18.59. Found: H_2O, 17.93.

Dry rhodamine B cyanide sodium salt when heated partly melted at 210–220° with development of a deep red color. A sample quickly heated to 250° and immediately removed from the melting point apparatus was assayed to determine the rhodamine B formed in heating. This corresponded to the decomposition of 17% of the dye cyanide. The cooled melt of rhodamine B cyanide sodium salt was a hard, impervious glassy lump that dissolved only slowly in dilute aqueous acid and therefore was not in a form suitable for test for the presence of ionizable cyanide, *i.e.*, sodium cyanide. To make this test 12.5 mg. of pure rhodamine B cyanide sodium salt was mixed with 200 mg. of infusorial earth, heated in a crucible to 250° and cooled. The mixture remained a powder. It was wet with 5 drops of 2*N* sulfuric acid and the crucible covered by a paper moistened with copper acetate–benzidine reagent.[12] A positive test was obtained for hydrogen cyanide. A control test performed on unheated rhodamine B cyanide sodium salt gave a negative result. Thus, on heating to as low as 250°, dry rhodamine B cyanide sodium salt decomposed into the dye and sodium cyanide.

Decomposition of rhodamine B cyanide in aqueous solution. A solution of 0.2403 g. of rhodamine B cyanide sodium salt in 0.5 ml. of dimethylformamide and 400 ml. of water was held in a thermostat at 31° while samples were periodically withdrawn, acidified, and colorimetrically assayed for rhodamine B, using a Wratten No. 99 filter.[13] Rhodamine B was formed in a first order reaction with a rate constant of 2×10^{-5}.

After 72 hr. the reaction mixture was titrated for cyanide ion with 0.05*M* silver nitrate, using the Treadwell and Hall apparatus[14] equipped with a No. 29 Wratten filter[13] to eliminate fluorescence. Cyanide ion was found to the extent of 0.86 mole per mole of rhodamine B cyanide started with.

Reaction of rhodamine B cyanide with aqueous acid. Crude rhodamine B cyanide sodium salt (1 g.) was dissolved in 11 ml. of 2*N* sulfuric acid and allowed to stand for 57 hr. at 25°. No carbon dioxide was formed as was shown by bubbling argon through the solution followed by a barium hydroxide absorption bulb. The acid reaction mixture in a Kjeldahl flask was made alkaline with sodium hydroxide, distilled into measured 0.1*N* hydrochloric acid and the excess acid titrated. Volatile base was found corresponding to 0.88 equivalent per mole of rhodamine B cyanide.

The dicarboxylic acid (V) formed by the acid hydrolysis of rhodamine B cyanide was relatively stable in acid solution but was rapidly oxidized to rhodamine B by air in neutral and alkaline solutions. It was precipitated as the barium salt by addition of a mixture of 7 ml. of 0.5*M* barium chloride solution and 3.5 ml. of concd. ammonium hydroxide to a solution of 1 g. of crude rhodamine B cyanide sodium salt in 4 ml. of 4*N* hydrochloric acid with water to 25 ml. that had stood at 25° for 3 days and then been diluted with water to 100 ml. These operations were carried out in an atmosphere of propane. The precipitate was digested in the mother liquor for 1 hr. at 100°, collected on a filter, washed rapidly with cold water, placed immediately in an Abderhalden type of drying apparatus[15] and dried *in vacuo* at 100° over a large quantity of phosphorus pentoxide.

The dry salt obtained in this way assayed 0.6% of rhodamine B base. The barium analysis showed it to be the normal salt but not pure.

Anal. Calcd. for $C_{29}H_{30}O_5N_2Ba$: Ba, 22.05. Found: Ba, 21.09.

Oxidation of 3,6-bisdiethylamino-9-carboxy-9-(2-carboxyphenyl)xanthene to rhodamine B and carbon dioxide. To a

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[11] I am grateful to Dr. Carl Tiedcke, who carried out the combustions, for advice on this problem.

[12] C. Pertusi and E. Gastaldi, *Chem. Ztg.*, 37, 609 (1913); A. Sieverts and A. Hermsdorf, *Z. angew. Chem.*, 34, 3 (1921); Fritz Feigl, *Spot Tests*, 4th ed., Elsevier Publishing Co., New York, N. Y., 1954, Vol. 1, p. 259.

[13] Manufactured by the Eastman Kodak Co., Rochester, N. Y.

[14] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 7th ed., John Wiley & Sons, New York, N. Y., 1930, Vol. 2, p. 607, Fig. 122.

[15] Catalog No. 3690, Corning Glass Works, Corning, N. Y.

solution of 25 mg. of crude rhodamine B cyanide sodium salt in 0.11 ml. of 4*N* hydrochloric acid and 0.02 ml. of water that had stood for 2 days at 25° was added 0.2 g. of ferric chloride dissolved in 1.5 ml. of water. The mixture was held at 25° for 24 hr. while the carbon dioxide formed was slowly swept by a stream of argon into measured barium hydroxide solution. Titration of the remaining barium hydroxide showed the formation of 0.94 mole of carbon dioxide from each mole of rhodamine B cyanide.

In a second experiment the rhodamine B formed by oxidation of the dicarboxylic acid (V) by ferric chloride was determined colorimetrically as 0.95 mole from each original mole of rhodamine B cyanide.

The atmospheric oxidation of the dicarboxylic acid (V) was accelerated by light, running through the ultraviolet to about 5800 Å. There also appeared to be a nonoxidative photochemical conversion of the diacid (V) to rhodamine B exhibited when an aqueous solution of V in a quartz flask filled with argon was exposed to the radiation from a 250-watt "Uviarc" lamp.[16]

Normal photolysis of rhodamine B cyanide. In neutral and alkaline aqueous and alcoholic solution rhodamine B cyanide (III) formed rhodamine B on irradiation with wave lengths shorter than 3350 Å. The dye was identified by spectroscopic comparison with authentic rhodamine B. This behavior was entirely analogous to that of the triphenylmethane dye cyanides. Rhodamine B cyanide also behaved as a hydrophilic dye cyanide and was photoactivated by cellulose in paper which had been impregnated with an aqueous solution and dried.[17] However, paper impregnated with rhodamine B cyanide colored in a few days in the dark and thus had a poor shelf life.

Photolysis of rhodamine B cyanide in acid solution. When a solution of rhodamine B cyanide (IV) in aqueous hydrochloric or sulfuric acid was irradiated by wave lengths shorter than about 3100 Å. a new blue dye was formed. Carboxylic acid V did not form this dye on photolysis. Therefore in order to prepare the blue dye it was necessary to photolyze the rhodamine B cyanide solution as promptly after its preparation as possible in order to minimize loss of the dye cyanide through hydrolysis by the reaction of Equation 2.

The photolysis apparatus consisted of a 15-watt germicidal lamp[16] mounted by rubber stoppers within a glass tube having an inside diameter of 37 mm. Since the outside of the germicidal lamp had a diameter of 25 mm., the space between it and the enclosing tube formed a cylindrical vessel to contain a layer of solution 6 mm. thick. The lamp discharge was formed between electrodes 36 cm. apart. Thus, the irradiated solution was in the form of a cylinder with 6 mm. wall thickness and about 36 cm. in length. More than 95% of the ultraviolet energy radiated by the lamp fell in the 2537 Å line.

A solution of 0.6 g. of crude rhodamine B cyanide sodium salt in 3 l. of 0.1*N* aqueous sulfuric acid that had been cooled to 0° was filtered through infusorial earth to yield a clear pale pink filtrate. The solution was kept at a low temperature to retard the hydrolysis of the nitrile group by the acid. The filtrate was held in a 3-l. flask packed in a bucket of snow and used as a reservoir to feed the photolysis apparatus. From this reservoir the solution was run into the top of the vertical photolysis apparatus through a rubber tube in which the solution was warmed by the air of the room. The heat of the lamp effected additional warming and maintained the solution near the top of the lamp at about 23°, and at somewhat higher temperature as it ran through to the bottom, where the solution was drawn off by a tube through the lower rubber stopper. The rate of flow of the photolysis solution was about 800 ml. an hour.

During irradiation the rhodamine B cyanide solution developed a rich blue color and a new absorption band extending to the red end of the visible spectrum, showing the presence of a blue dye. Because the absorption of rhodamine B ends for practical purposes at about 6200 Å[18] relative amounts of the blue dye could be determined by wave lengths longer than 6200 Å in presence of rhodamine B. Such light was obtained by the use of Wratten filters Nos. 15 and 34A[13] combined with a 1 cm. thickness of heat absorbing plate glass to reduce the near infrared. Colorimetric assays made in this way were unaffected by the presence of rhodamine B.

The blue dye was relatively stable in acid solution. Thus, the irradiated solution could be boiled down to half of its volume with the loss of not over 10% of the blue color. On the other hand, the blue was very sensitive to alkali. In a weakly alkaline solution the blue color faded in a few minutes to a few hours. When the blue solution was mixed with an excess of strong sodium hydroxide solution, the blue color faded as rapidly as the two solutions could be mixed. Alkaline solutions from which the blue color had faded had a pink or red color due to the presence of rhodamine B and were cloudy. When such solutions were acidified again by hydrochloric acid, the cloud dissolved but the blue color did not return.

The blue color interfered with the colorimetric determination of rhodamine B by light through a green filter. However, rhodamine B could be readily determined if the blue color were first destroyed by alkali and the solution then acidified to about 0.01*N* hydrochloric acid.

The dyes formed by photolysis, both the rhodamine B and the new blue dye, were precipitated by the addition of 9 g. of potassium thiocyanate in a little water to the photolyzed solution. Precipitation was incomplete, but 0.1 g. of desiccator dried dye mixture was obtained.

Identification of the blue dye. The new blue dye was identified by comparison of some of its properties with those of the cornflower blue (VII) prepared from pyronine B[10] by the method of Ehrlich and Benda.[7] The cornflower blue was prepared as the thiocyanate, which was less soluble than the nitrate used by Ehrlich and Benda.[7]

Spectroscopic comparison showed that the red end of the absorption band, caused by the new blue dye, in a solution of the dyes from the photolysis of rhodamine B cyanide coincided with that of a solution of authentic cornflower blue (VII).

Descending paper chromatograms of the dyes from photolysis and of authentic cornflower blue were developed by water alone. The blue bands on both chromatograms had the same R_f value, 0.06, and showed visually identical colors. Rhodamine B, with an R_f value of 0.6, was easily and completely separated from the blue dye. Pyronine B, which might be present as a contaminant in cornflower blue, moved more slowly than the blue dye and could be separated from it but not so rapidly as rhodamine B. The cornflower blue used in these comparisons had very little pyronine B in it. From the chromatographic evidence the blue dye produced by photolysis was identical with authentic cornflower blue.

Rates of decomposition in alkaline solution. As a further check on the identity of the blue dye produced by photolysis, its rate of bleaching in aqueous sodium bicarbonate solution was compared with that of authentic cornflower blue. A solution was prepared of 7.7 mg. of the mixed dyes from photolysis in 100 ml. of 0.006*N* hydrochloric acid, and of 5.6 mg. of authentic cornflower blue thiocyanate in 100 ml. of 0.006*N* hydrochloric acid. These two solutions showed approximately the same optical density for the blue dye.

While the dye thiocyanates would dissolve at room tem-

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[16] (16) Manufactured by the General Electric Co., Cleveland 12, Ohio.

[17] (17) L. Chalkley, U. S. Patent 2,855,303, October 7, 1958.

[18] (18) W. E. Forsythe, *Smithsonian Physical Tables*, 9th ed., Smithsonian Institution, Washington, D. C., 1954, p. 541.

perature in $0.001N$ hydrochloric acid, solution was slow and required many days for completion. A more rapid method for the preparation of solutions of known dye concentration was to moisten the weighed sample of dye with concentrated hydrochloric acid and then dilute with water.

To start the decomposition reaction 25 ml. of dye solution was mixed with an equal volume of $0.5M$ sodium bicarbonate solution in a 30° thermostat. Experiments on the two dyes were carried out side by side in the same thermostat at the same time except that one was commenced 5 min. after the other to permit time for manipulation while maintaining identical periods for reaction. At measured times 5-ml. samples of the dye reaction solutions were pipeted into 10 ml. volumetric flasks containing 2 ml. of $1N$ hydrochloric acid. Acidification arrested the decomposition while leaving the color of the blue dye unaffected for colorimetric determination after the solution had been diluted to 10 ml. with water.

The rate of decomposition of the blue dye produced by photolysis of rhodamine B cyanide was the same as that of authentic cornflower blue. The reaction was of first order over most of its course. The rate constant was 6×10^{-5} at 30°.

On the basis of these comparative tests, the blue dye formed by photolysis of rhodamine B cyanide was identified as cornflower blue with the structure (VII).

The yield of dyes obtained in the photolysis carried out as described above from 0.6 g. of perhaps 90% rhodamine B cyanide sodium salt (III) was determined colorimetrically as 50 mg. of rhodamine B as base and 160 mg. of cornflower blue as thiocyanate. A little less than half of this amount of dye was precipitated from the photolysis solution by potassium thiocyanate. Other products of photolysis were not identified.

Acknowledgment. It is a pleasure to express gratitude to Dr. Eugene Lorand for some of the apparatus used in this work.

WASHINGTON 22, D. C.

[CONTRIBUTION FROM STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Base-Catalyzed Reaction of Nitriles with Alcohols. A Convenient Route to Imidates and Amidine Salts

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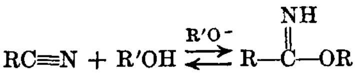
The base-catalyzed reaction of nitriles with alcohols to form imidates has been established as an attractive synthetic method which is useful for a wide variety of electronegatively substituted aliphatic and aromatic nitriles. This reaction is used as the basis for a convenient procedure for the preparation of amidine salts.

Recent developments in the chemistry of alkyl imidates in our Laboratory have led us to evaluate the alternative methods for their preparation. This paper deals with the base-catalyzed addition of alcohols to nitriles,



$$\mathrm{RC{\equiv}N + R'OH \xrightleftharpoons{R'O^-} R{-}\overset{\overset{NH}{\|}}{C}{-}OR'}$$

The reaction was discovered by Nef in 1895 in his work with cyanogen.[1] Shortly thereafter in papers by his students, easy base-catalyzed formation of imidates from substituted malonitriles was reported.[2] The general reaction was studied in considerable detail by Stieglitz[3] and Acree[4] and their collaborators in the course of work on the nature of homogeneous catalysis. Marshall and Acree[4a] in particular determined the position of equilibrium in the reaction of several nitriles with ethanol in the presence of sodium ethoxide at 25°. Their studies established that the reaction was alkoxide-catalyzed and that imidate formation was promoted by the presence of electron-attracting groups in the nitrile. Moreover, this work demonstrated that the equilibrium constants for the reactions of several common nitriles were sufficiently large to be useful.[5] Despite these promising early results, virtually no further use had been made of this reaction until the present work was undertaken.[6-8] We have now extended somewhat the

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(1) J. U. Nef, *Ann.*, **287**, 265 (1895), reported the reaction of cyanogen with an aqueous ethanol solution of potassium cyanide to give ethyl 1-cyanoformimidate and diethyl oxalimidate. H. M. Woodburn, A. B. Whitehouse, and B. G. Pautler, *J. Org. Chem.*, **24**, 210 (1959), have recently extended this reaction to other alcohols.

(2) (a) B. C. Hesse, *Am. Chem. J.*, **18**, 723 (1896). (b) J. C. Hessler, *Am. Chem. J.*, **22**, 169 (1899).

(3) (a) J. Stieglitz and H. I. Schlesinger, *Am. Chem. J.*, **39**, 738 (1908). (b) R. H. McKee, *Am. Chem. J.*, **26**, 209 (1901); **36**, 208 (1906); **42**, 1 (1909).

(4) (a) E. K. Marshall, Jr., and S. F. Acree, *Am. Chem. J.*, **49**, 127 (1913). (b) E. K. Marshall, Jr., J. P. Harrison, and S. F. Acree, *Am. Chem. J.*, **49**, 369 (1913).

(5) It has been pointed out by N. S. Bayliss, R. L. Heppolette, L. H. Little, and J. Miller, *J. Am. Chem. Soc.*, **78**, 1978 (1956), that the data of Marshall and Acree are inaccurate because of the analytical method employed although the general conclusions remain valid. Bayliss, *et al.* proposed improvements in technique which are essentially those used in the present work.

(6) Several instances have been reported of the unexpected occurrence of base-catalyzed addition of an alcohol to a nitrile group in the course of other work. (a) K. W. Breukink, *et al.*, *Rec. trav. chim.*, **76**, 401 (1957); (b) H. Bretschneider and G. Sporidi, *Monatsh.*, **85**, 1119 (1954); (c) R. L. Heppolette, J. Miller, and V. A. Williams, *J. Am. Chem. Soc.*, **78**, 1975 (1956); (d) K. Gundermann and H. Rose, *Chem. Ber.*, **92**, 1081 (1959); (e) T. Cuvigny, *Bull. soc. chim.*, **24**, 655 (1957); (f) J. Miller, *J. Am. Chem. Soc.*, **76**, 448 (1954); (g) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67**, 1012 (1945).