into water, and the yellow solid was separated by filtration, washed with water and dried to give 1.2 g. (36%) of **2-phenyl-3-cyanomaleimide**, m.p. 216–217.5°. Recrystallization from methanol–water gave yellow needles, m.p. 218–219°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 360 mμ (ε 8840), 278 mμ (ε 5710).

Anal. Calcd. for $C_{11}H_6N_2O_2$: C, 66.66; H, 3.05; N, 14.14; mol. wt., 198. Found: C, 66.62; H, 3.16; N, 14.27, 14.25; mol. wt., 204, 195.

The infrared spectrum showed bands at 5.6 and 5.85 μ (cyclic –CONHCO–), 3.0 μ (–NH), 4.50 μ (conjugated –CN) and 6.22, 6.27, 6.39 μ (aromatic and olefinic carbon–carbon double bonds). The proton magnetic resonance spectrum showed a peak, probably assignable to the imide hydrogen, which was displaced from the normal frequency for the hydrogen atom of a carboxyl group. These results suggest the imide formulation rather than the isomeric (1-carboxy-2,2-dicyanovinyl)-benzene. The compound showed good thermal stability; unchanged imide was recovered after pyrolysis in the presence of "basic" lead carbonate at 300°.

Concentration of the filtrate gave 0.9 g. (25%) of crude **2-phenyl-3-cyanomaleic acid**, m.p. 137–150°. The crude maleic acid was purified by recrystallization from dilute hydrochloric acid and obtained as an off-white solid, m.p. 144–148° (with previous softening), $\lambda_{\max}^{\mathrm{EtOH}}$ 292 mμ (ε 10,730), λ_{hump} 220–225 mμ (reported[10] m.p. 145–146°).

Anal. Calcd. for $C_{11}H_7NO_4$: C, 60.83; H, 3.25; N, 6.45. Found: C, 60.24; H, 3.56; N, 6.60, 6.73.

Mild heating of 2-phenyl-3-cyanomaleic acid readily converted it to the anhydride, obtained as a deep yellow solid, m.p. 144.5–146°. Anhydride formation occurred even below the melting point of the diacid and the melting point observed for the acid is actually that of the anhydride.[10]

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 442 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. VIII.[1] Heterocyclic Compounds from Tetracyanoethylene

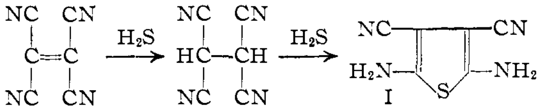
BY W. J. MIDDLETON, V. A. ENGELHARDT AND B. S. FISHER

RECEIVED NOVEMBER 14, 1957

2,5-Diamino-3,4-dicyanothiophene has been prepared by the reaction of tetracyanoethylene with hydrogen sulfide. Sodium hydroxide catalyzes the rearrangement of this thiophene to 2-amino-3,4-dicyano-5-mercaptopyrrole. Thiols react with tetracyanoethylene to give 1,4-bis-(alkylthio)-1,4-diamino-2,3-dicyanobutadienes. These butadienes cyclize under acidic conditions to give either 2-amino-3,4-dicyano-5-alkylthiopyrroles or 2,5-bis-(alkylthio)-3,4-dicyanopyrroles. Reaction of tetracyanoethane with hydrogen bromide produces 2-amino-5-bromo-3,4-dicyanopyrrole, and reaction of sodium bisulfite with tetracyanoethane yields 5-amino-3,4-dicyanopyrrole-5-sulfonic acid. A number of acyl, alkyl and benzylidene derivatives of these heterocyclic compounds have been prepared and characterized.

Thiophenes and pyrroles that contain electron-donating substituents such as amino and thio groups are generally difficult to prepare and quite unstable, and consequently not much is known of their chemistry. If electron-withdrawing substituents, such as cyano groups, were also present, the resulting heterocyclic compounds would be expected to be much more stable. The discovery of a facile synthesis for tetracyanoethylene[2] has made readily available an intermediate which can be converted easily to 3,4-dicyanothiophenes and pyrroles that also contain amino and/or thio substituents. This paper deals with the syntheses and properties of a number of these substituted thiophenes and pyrroles.

2,5-Diamino-3,4-dicyanothiophene.—2,5-Diamino-3,4-dicyanothiophene was prepared by the reaction of tetracyanoethylene with sodium sulfide or hydrogen sulfide in the presence of a basic catalyst. The reaction proceeds in two steps. First, tetracyanoethylene is reduced to tetracyanoethane by the sulfide ion, and then the elements of hydrogen sulfide add to the tetracyanoethane under the influence of a basic catalyst. The stepwise nature of this reaction was demonstrated by first preparing and isolating tetracyanoethane[3] and then converting it to the thiophene I by treating it with sodium sulfide. When sodium sulfide was used to convert tetracyanoethylene to I, no added catalyst was needed; but if hydrogen sulfide was used instead of sodium sulfide, the reaction stopped with the formation of tetracyanoethane and sulfur, and it was necessary to add a basic catalyst, such as pyridine, triethylamine or sodium hydroxide to complete the reaction.


I

2,5-Diamino-3,4-dicyanothiophene is almost completely insoluble in most common organic solvents with the exception of dimethylformamide. The thiophene is also high melting, and is stable up to its melting point of 240°. Molecular weight determinations in dimethylformamide indicate that the thiophene is monomeric. The basicity of the amino groups is reduced to a considerable extent, for 2,5-diamino-3,4-dicyanothiophene is insoluble in dilute mineral acids. However, the amino groups still retain some basic character. The aminothiophene was acylated easily by acetic anhydride and by benzoyl chloride in pyridine.

Stable anils were prepared from 2,5-diamino-3,4-dicyanothiophene and aromatic aldehydes. Dianils (II) were prepared from benzaldehyde, *p*-nitrobenzaldehyde, *p*-dimethylaminobenzaldehyde and *p*-bis-(2-cyanoethyl)-aminobenzaldehyde by heating the thiophene and aldehyde together at a temperature sufficient to distil the water formed in the condensation.

Under the same conditions, the monoanil was formed by reaction of the thiophene with 2,4-di-

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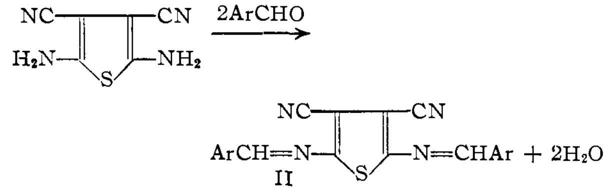
(1) Paper VII, G. N. Sausen, V. A. Engelhardt and W. J. Middleton, THIS JOURNAL, 80, 2815 (1958).

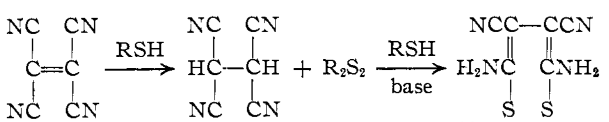
(2) Paper I, T. L. Cairns, *et al.*, *ibid.*, 80, 2775 (1958).

(3) Paper III, W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *ibid.*, 80, 2783 (1958).



hydroxybenzaldehyde, but no reaction at all occurred with salicylaldehyde. However, the dianil with salicylaldehyde was formed when a catalytic amount of *p*-toluenesulfonic acid was added to the reaction mixture. The dianils of 2,5-diamino-3,4-dicyanothiophene are all highly colored. The maximum light absorption is in the visible region, from 426 mμ for the dianil from benzaldehyde to 525 mμ for the dianil from *p*-dimethylaminobenzaldehyde. These anils also possess extremely high molecular extinction coefficients, ranging from 30,600 for the benzaldehyde derivative to 58,300 for the *p*-bis-(2-cyanoethyl)-aminobenzaldehyde derivative.

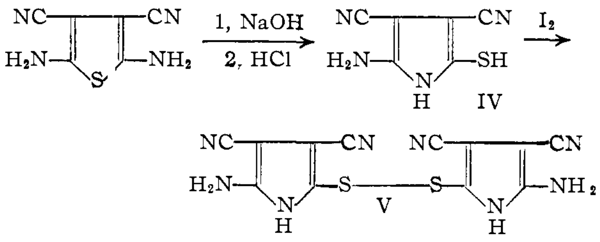
Thiols react like hydrogen sulfide to give the expected straight chain analog of 2,5-diamino-3,4-dicyanothiophene. Thus, butadienes (III, R = C_2H_5, CH_3 and CH_2CH_2OH) were prepared by the base-catalyzed reaction of tetracyanoethylene with



ethanethiol, methanethiol and 2-hydroxyethanethiol. Again it was demonstrated that tetracyanoethane was an intermediate, for reaction of ethanethiol with tetracyanoethane produced the same butadiene (III, R = C_2H_5) that was prepared from tetracyanoethylene. In the first step of the reaction of tetracyanoethylene with thiols, tetracyanoethane and a disulfide are formed. In some cases, the by-product disulfide was found to be difficult to separate from the butadiene. Thus, it was sometimes advantageous to start with tetracyanoethane and avoid the formation of the disulfide. For example, 1,4-bis-(phenylthio)-1,4-diamino-3,4-dicyanobutadiene (III, R = C_6H_5) was formed by the reaction of tetracyanoethane with benzenethiol, and the problem of separating diphenyl disulfide from the butadiene was avoided.

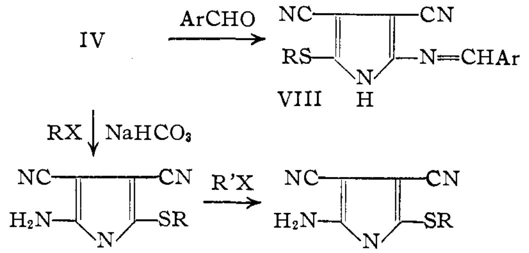
The 1,4-bis-(alkylthio)-1,4-diamino-2,3-dicyanobutadienes (III) were obtained as stable, white crystalline compounds with definite melting points. In common with the diaminothiophene I, they are not soluble in dilute mineral acids. The infrared spectra of the butadienes III indicate the presence of amino groups and conjugated cyano groups. These butadienes were found to be useful intermediates in the preparation of a number of substituted pyrroles, and additional proof of their structure is based upon these reactions.

3,4-Dicyanothiopyrroles.—A number of 3,4-dicyanothiopyrroles were prepared from 2,5-diamino-3,4-dicyanothiophene and 1,4-bis-(alkylthio)-1,4-diamino-2,3-dicyanobutadienes. 2-Amino-3,4-dicyano-5-mercaptopyrrole (IV) was formed by a base-catalyzed rearrangement of 2,5-diamino-3,4-dicyanothiophene. This interesting rearrangement was accomplished by heating the diamino-

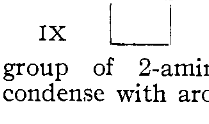


thiophene in aqueous sodium hydroxide until solution was complete, and then acidifying the resulting solution to precipitate the mercaptopyrrole IV. 2-Amino-3,4-dicyano-5-mercaptopyrrole (IV) is quite acidic. Since no satisfactory recrystallization solvent was found for IV, it was purified by dissolving in sodium bicarbonate solution, and then reprecipitating with acid. Oxidation of a bicarbonate solution of the mercaptopyrrole with iodine resulted in the formation of its disulfide V, a bright orange compound that formed an intensely purple colored complex with cupric ion.

The mercapto group of IV is easily alkylated. Thus, when a bicarbonate solution of IV was mixed with methyl iodide, benzyl chloride, 2-chloroethanol or chloroacetic acid, the corresponding S-alkylated derivative (VI, R = CH_3, $C_6H_5CH_2$, CH_2CH_2OH and CH_2COOH) precipitated from the aqueous solution in good yield. These 2-amino-3,4-dicyano-5-alkylthiopyrroles, although no longer soluble in bicarbonate solution, are still quite acidic because of the NH group of the pyrrole nucleus, and all will dissolve in dilute sodium hydroxide. The pK_a of 2-amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole was determined to be 9.4.



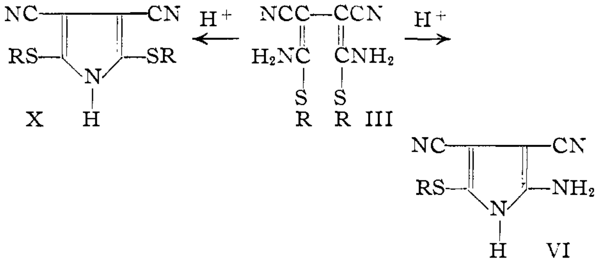
In addition to the mercapto group of IV, the pyrrole nitrogen can also be alkylated by employing slightly more vigorous conditions. Thus, 2-amino-5-benzylthio-3,4-dicyano-1-methylpyrrole (VII, R = $C_6H_5CH_2$, R′ = CH_3) was formed when an alcoholic solution of the sodium salt of VI (R = CH_2-C_6H_5) was treated with methyl iodide. An unusual bicyclic compound, IX, was prepared in a similar manner from the reaction of an alcoholic solution of the disodium salt of IV with ethylene bromide.


IX

The amino group of 2-amino-3,4-dicyano-5-thiopyrrole will condense with aromatic aldehydes to form anils, much in the same fashion as did the diaminothiophene I. Two colored anils were formed from 2-amino-5-benzylthio-3,4-dicyanopyrrole; a light yellow anil, λ_{max} 362 mμ, from benzaldehyde, and a bright yellow anil, λ_{max} 411 mμ, from *p*-methylaminobenzaldehyde.

As is typical of pyrroles in general, the 2-amino-3,4-dicyano-5-alkylthiopyrroles are more sensitive to acids than to bases. 2-Amino-3,4-dicyano-5-methylthiopyrrole was converted to succinic acid by refluxing aqueous sulfuric acid, but refluxing aqueous sodium hydroxide only hydrolyzed one of the cyano groups to an amide group, and left the pyrrole ring intact.

Pyrroles from 1,4-Bis-(alkylthio)-1,4-diamino-2,3-dicyanobutadienes.—As previously mentioned, 2-amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole (VI, R = CH_2CH_2OH) was prepared by the alkylation of the sodium salt of 2-amino-3,4-dicyano-5-mercaptopyrrole with 2-chloroethanol. This same pyrrole also was formed by the acid-catalyzed elimination of 2-mercaptoethanol from 1,4-bis-(2-hydroxyethylthio)-1-4-diamino-2,3-dicyanobutadiene (III, R = CH_2CH_2OH).

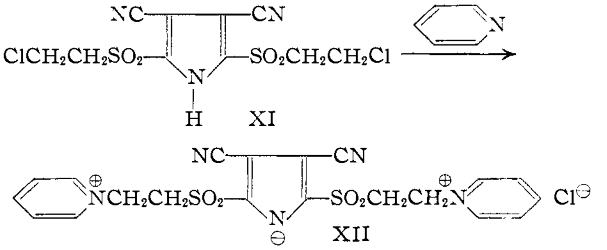


X III VI

Boiling dilute hydrochloric acid was found to be an effective agent for this transformation. A diacetylated derivative of this same pyrrole was formed by heating the butadiene in acetic anhydride. 2-Amino-3,4-dicyano-5-phenylthiopyrrole (VI, R = C_6H_5) also was formed by heating 1,4-bis-(phenylthio)-1,4-diamino-2,3-cyanobutadiene (III, R = C_6H_5) with dilute hydrochloric acid. In this instance, the acid catalyst was not necessary, for when III (R = C_6H_5) was heated above its melting point, benzenethiol was eliminated and VI (R = C_6H_5) was formed.

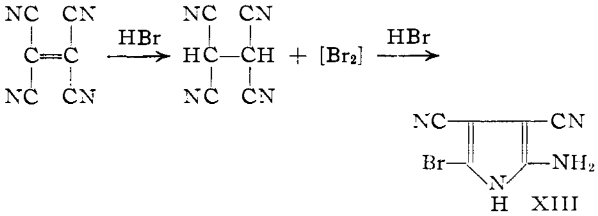
Attempts to extend this reaction to the preparation of additional 2-amino-3,4-dicyano-5-alkylthiopyrroles were not successful. Instead, a new class of pyrroles, the 2,5-bis-(alkylthio)-3,4-dicyanopyrroles (X) were formed. Thus, when 1,4-bis-(ethylthio)-1,4-diamino-2,3-dicyanobutadiene was heated with dilute hydrochloric acid, 2,5-bis-(ethylthio)-3,4-dicyanopyrrole was formed instead of the expected VI (R = C_2H_5). Similarly, 2,5-bis-(methylthio)-3,4-dicyanopyrrole was formed from III (R = CH_3). In these two cases, it is apparent that the elements of ammonia, instead of a thiol, are being removed. In the belief that the concentration of the acid might determine the course of the reaction and the products formed, each of the butadienes III was treated with both dilute and concentrated acids. In all instances, only the amino-(phenylthio)-pyrrole (X, R = C_6H_5) was formed from 1,4-bis-(phenylthio)-1,4-diamino-3,4-dicyanobutadiene, and only the bis-(alkylthio)-pyrroles (X, R = CH_3 and C_2H_5) were formed from 1,4-bis-(methylthio)- and 1,4-bis-(ethylthio)-1,4-diamino-2,3-dicyanobutadienes, regardless of the concentration of the acid. However, 2-amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole was formed when 1,4-bis-(2-hydroxyethylthio)-1,4-diamino-2,3-dicyanobutadiene was heated with dilute hydrochloric acid, and 2,5-bis-(2-hydroxyethylthio)-3,4-dicyanopyrrole was formed when the same butadiene was treated with cold, concentrated hydrochloric acid; III (R = CH_2CH_2OH) was the only butadiene that could be converted to either the aminothiopyrrole VI or the bis-thiopyrrole X, depending upon the conditions of the reaction. The factors controlling the course of the reaction have not as yet been fully determined.

The 2,5-bis-(alkylthio)-3,4-dicyanopyrroles (X) are acidic compounds. 2,5-Bis-(2-hydroxyethylthio)-3,4-dicyanopyrrole possesses a pK_a of about 7.6, as compared to a pK_a of 9.4 for 2-amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole. Both of these compounds are strongly acidic as compared to pyrrole itself. As the number of electron-withdrawing substituents on the pyrrole nucleus is increased, the acidity of the pyrrole should also increase. Therefore, the corresponding sulfones of X should be strong acids. In order to prepare an acid of this type, 2,5-bis-(2-hydroxyethylthio)-3,4-dicyanopyrrole was oxidized in concentrated hydrochloric acid with hydrogen peroxide. This treatment not only oxidized the thio group, but replaced the hydroxyl groups of X (R = CH_2CH_2OH) with chloro groups, and the disulfone XI was obtained. As was expected, this disulfone was quite acidic; it possessed a pK_a of 2.6. A stable crystalline tetramethylammonium salt of XI was precipitated when aqueous solutions of the disulfone and tetramethylammonium chloride were mixed. Another interesting derivative, the inner-salt XII, was prepared by the reaction of XI with pyridine.



XI XII

2-Amino-5-bromo-3,4-dicyanopyrrole was formed by the reaction of tetracyanoethylene with hydrogen bromide in acetone. This reaction proceeds in at least two steps. Tetracyanoethylene is first reduced to tetracyanoethane by the hydrogen bromide, and then more hydrogen bromide adds to the tetracyanoethane to form the pyrrole. The bro-



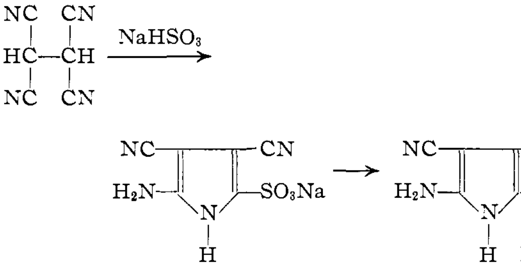
XIII

mine formed in the reduction step is consumed by the acetone solvent, as was evidenced by the loss of bromine color and the formation of a severe lachrymator upon completion of the reaction. When methyl formate or tetrahydrofuran was used in place of the acetone solvent, no pyrrole was isolated. Therefore, it appears that bromine must be removed from the reaction medium to prevent the oxidation of tetracyanoethane back to tetracyanoethylene. Hydrogen bromide also converted preformed tetracyanoethane to the bromopyrrole XIII.

2-Amino-5-bromo-3,4-dicyanopyrrole, in common with the other dicyanopyrroles, possesses definite acidic properties. It is quite soluble in dilute aqueous sodium hydroxide, and can be reprecipitated unchanged upon acidification. However, the 2-amino group still maintains some of its basic character, for it was acetylated easily with acetic anhydride.

Two alkylated derivatives of 2-amino-5-bromo-3,4-dicyanopyrrole also were prepared. 2-Amino-5-bromo-3,4-dicyano-1-methylpyrrole was formed by treating an alcoholic solution of the sodium salt of XIII with methyl iodide, and a dibenzyl derivative, 1-benzyl-2-benzylamino-5-bromo-3,4-dicyanopyrrole, was formed from XIII and benzyl bromide. The N-alkyl derivatives, of course, do not have acidic properties.

5-Amino-3,4-dicyano-2-pyrrolesulfonic Acid.—Attempts to prepare this acid by the reaction of sodium bisulfite with tetracyanoethylene resulted instead in the formation of 1,1,2,2-tetracyanoethanesulfonic acid.[3] However, when tetracyanoethane was treated with a boiling aqueous solution of sodium bisulfite, a moderate yield of 5-amino-3,4-dicyanopyrrole-2-sulfonic acid, as a solution of its sodium salt, was formed. The free acid XIV was isolated from this solution by first precipitating it as a N-methylquinolinium salt, and then treating this salt with an acidic ion exchange resin. The free acid XIV was obtained as a very hygroscopic solid that seemed to be unstable in contact with the atmosphere. Titration of XIV with sodium hydroxide, using a potentiometric procedure with a glass–calomel electrode pair, gave two breaks in the curve corresponding to neutralization of the hydrogen atoms on the sulfonic group and on the nitrogen of the pyrrole nucleus. The N-methylquinolinium salt of XIV in contrast to the free acid is quite stable hydrolytically. This salt still exhibits acidic properties. It is soluble in dilute sodium bicarbonate solution and can be recovered unchanged upon acidification.



XIV

Experimental

2,5-Diamino-3,4-dicyanothiophene.[4] A. **From Tetracyanoethylene and Hydrogen Sulfide.**—A solution of 12.8 (0.1 mole) g. of tetracyanoethylene in 150 ml. of acetone and 150 ml. of carbon disulfide was saturated with hydrogen sulfide gas. The cloudy solution was cooled in an ice-bath, and 50 ml. of pyridine was added slowly. The solution became clear, and was again saturated with hydrogen sulfide. The precipitate was collected on a filter, washed with acetone and dried. There was obtained 15.1 g. (92% yield) of crude 2,5-diamino-3,4-dicyanothiophene in the form of a yellow crystalline powder. This material was recrystallized from dimethylformamide–water (75:25) to give 9.0 g. of near-colorless needles which sublimed at 240–244° with some decomposition.

Anal. Calcd. for $C_6H_4N_4S$: C, 43.90; H, 2.48; N, 34.13; S, 19.53; mol. wt., 164. Found: C, 44.11; H, 2.54; N, 34.09; S, 19.48; mol. wt., 159.

B. **From Tetracyanoethane and Sodium Sulfide.**—A cooled solution of 12.0 g. (0.05 mole) of sodium sulfide decahydrate in 100 ml. of water was mixed rapidly with a solution of 6.5 g. (0.05 mole) of tetracyanoethane in 30 ml. of acetone. The precipitate that formed was collected on a filter, washed with water, and recrystallized from aqueous dimethylformamide. There was obtained 2.0 g. of 2,5-diamino-3,4-dicyanothiophene as needles that sublimed at 240–244° with some decomposition.

2,5-Bis-(acetamido)-3,4-dicyanothiophene.—A mixture of 1.64 g. (0.01 mole) of 2,5-diamino-3,4-dicyanothiophene and 10.2 g. (0.10 mole) of acetic anhydride was heated to reflux for 30 minutes. The thiophene slowly dissolved and a bulky mass of crystals separated from solution. The mixture was cooled in ice, the crystals collected on a filter, washed thoroughly with benzene and dried in a vacuum desiccator. There was obtained 2.12 g. (85.5%) of nearly white needles, which did not melt, decompose or sublime up to 300°. Recrystallization from dimethylformamide–water (5:1) and treatment with decolorizing charcoal gave 0.91 g. of white needles insoluble in most organic solvents.

Anal. Calcd. for $C_{10}H_8O_2N_4S$: N, 22.58; S, 12.90. Found: N, 22.70; S, 13.21.

2,5-Bis-(benzamido)-3,4-dicyanothiophene.—2,5-Diamino-3,4-dicyanothiophene (1.64 g., 0.01 mole) was treated with a mixture of 5.62 g. (0.04 mole) of benzoyl chloride and 1.58 g. (0.02 mole) of pyridine. Reaction proceeded exothermically with solution of the thiophene and formation of a yellow color. Light colored crystals separated from solution. The mixture was cooled in ice and the excess acid chloride was destroyed by careful addition of 20 ml. of methanol. The light yellow precipitate was collected on a filter, washed with methanol and dried in a vacuum desiccator. There was obtained 3.05 g. (82%) of light yellow powder. Two recrystallizations from dimethylformamide–water and treatment with decolorizing charcoal gave 1.05 g. of white powder which did not melt, decompose or sublime up to 300°. The product was soluble in dilute aqueous potassium hydroxide to form a yellow solution. Acidification of the alkaline solution with hydrochloric acid produced a white precipitate. The product was insoluble in most organic solvents.

Anal. Calcd. for $C_{20}H_{12}O_2N_4S$: C, 64.51; H, 3.25; N, 15.05; S, 8.60. Found: C, 64.42; H, 3.33; N, 15.07; S, 8.44.

Dianils of 2,5-Diamino-3,4-dicyanothiophene.—Dianils of 2,5-diamino-3,4-dicyanothiophene were prepared from the thiophene and aromatic aldehydes by the following general procedure: 2,5-Diamino-3,4-dicyanothiophene was heated with excess aldehyde at 130–180° for 15–20 minutes. Approximately an equal volume of nitrobenzene was added, and the mixture was heated for an additional 15–20 minutes and then cooled. The solid was collected and recrystallized. In this manner, **2,5-bis-(benzylidenamino)-3,4-dicyanothiophene** was prepared in 94% yield from the thiophene and benzaldehyde. After recrystallization from chlorobenzene, the dianil was obtained as long, bright yellow needles, m.p. 297–298°, $\lambda_{max}^{acetone}$ 426 mμ (ϵ 30,600).

Anal. Calcd. for $C_{20}H_{12}N_4S$: C, 70.58; H, 3.55; N, 16.48; S, 9.40. Found: C, 70.76; H, 3.70; N, 16.43; S, 9.46.

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[4] W. J. Middleton, U. S. Patent 2,801,908 (1957).

2,5-Bis-(*p*-nitrobenzylidenamino)-3,4-dicyanothiophene was prepared in 92% yield from the thiophene and *p*-nitrobenzaldehyde. After recrystallization from 5:1 chlorobenzene–nitrobenzene the dianil was obtained as golden orange prisms, m.p. <300°, $\lambda_{\max}^{\text{acetone}}$ 436 mμ (ϵ 36,100).

Anal. Calcd. for $C_{20}H_{10}N_6O_4S$: C, 55.82; H, 2.34; N, 19.53; S, 7.44. Found: C, 55.99; H, 2.43; N, 19.26; S, 7.29.

2,5-Bis-(*o*-hydroxybenzylidenamino)-3,4-dicyanothiophene[5] was prepared in 91% yield from 2,5-diamino-3,4-dicyanothiophene and salicylaldehyde.[6] After recrystallization from dimethylformamide the dianil was obtained as an orange solid, m.p. >300°, $\lambda_{\max}^{\text{acetone}}$ 445 mμ (ϵ 37,600).

Anal. Calcd. for $C_{20}H_{12}N_4OS$: C, 64.5; H, 3.3; N, 15.1. Found: C, 64.8; H, 3.3; N, 15.0.

2,5-Bis-(*p*-dimethylaminobenzylidenamino)-3,4-dicyanothiophene was prepared in 75% yield from 2,5-diamino-3,4-dicyanothiophene and *p*-dimethylaminobenzaldehyde. After recrystallization from 4:1 chlorobenzene–nitrobenzene the dianil was obtained as violet-green needles which sublimed at 270° and decomposed at 300°, $\lambda_{\max}^{\text{acetone}}$ 525 mμ (ϵ 50,400).

Anal. Calcd. for $C_{24}H_{22}N_6S$: N, 19.71. Found: N, 19.66.

2,5-Bis-[*p*-di-(2-cyanoethyl)-aminobenzylidenamino]-3,4-dicyanothiophene was prepared in 97% yield from 2,5-diamino-3,4-dicyanothiophene and *p*-di-(2-cyanoethyl)-aminobenzaldehyde. After recrystallization from dimethylformamide–water the dianil was obtained as bright vermilion needles, m.p. >300°, $\lambda_{\max}^{\text{acetone}}$ 515 mμ (ϵ 58,300).

Anal. Calcd. for $C_{32}H_{26}N_{10}S$: C, 65.97; H, 4.50; N, 24.04; S, 5.49. Found: C, 66.08; H, 4.59; N, 24.40; S, 5.82.

The monoanil **2-amino-3,4-dicyano-5-(2,4-dihydroxybenzylidenamino)-thiophene** was prepared in quantitative yield from 2,5-diamino-3,4-dicyanothiophene and 2,4-dihydroxybenzaldehyde when these reactants were heated together under the same conditions that resulted in dianil formation with the other aldehydes. After recrystallization from dimethylformamide-water, this monoanil was obtained as a bright orange crystalline powder, m.p. >300°, $\lambda_{\max}^{\text{acetone}}$ 425 mμ (ϵ 31,200).

Anal. Calcd. for $C_{13}H_8N_4O_2S$: C, 55.00; H, 2.82; N, 19.71; S, 11.27. Found: C, 55.39; H, 2.97; N, 19.38; S, 10.96.

1,4-Diamino-2,3-dicyano-1,4-bis-(2-hydroxyethylthio)-butadiene.[7]—A solution of 12.8 g. (0.1 mole) of tetracyanoethylene in 70 ml. of acetone was mixed with a solution of 2 ml. of triethylamine in 30 ml. of 2-mercaptoethanol. The resultant solution was cooled in an ice-bath for ten minutes, and then poured into 1 liter of water. After standing at room temperature for about one hour, the crystalline precipitate that formed was collected on a filter, washed with water and dried. There was obtained 22.5 g. (81% yield) of 1,4-diamino-2,3-dicyano-1,4-bis-(2-hydroxyethylthio)-butadiene in the form of long, white, highly refractive needles, m.p. 176–177°. The same product was obtained in a similar manner when pyridine was used as a catalyst in place of the triethylamine.

Anal. Calcd. for $C_{10}H_{14}N_4O_2S_2$: C, 41.94; H, 4.95; N, 19.57; S, 22.39. Found: C, 42.02; H, 5.02; N, 19.57; S, 22.28.

1,4-Diamino-2,3-dicyano-1,4-bis-(ethylthio)-butadiene. A. From Tetracyanoethylene and Ethanethiol.—A solution of 1.28 g. (0.01 mole) of tetracyanoethylene in 5 ml. of acetone was mixed with 3.0 ml. (0.04 mole) of ethanethiol. The reaction mixture was cooled in an ice-bath for five minutes, and 10 ml. of 10% sodium hydroxide solution was added. The solution was diluted with water, and the white precipitate that formed was collected on a filter, washed with water and recrystallized from ethyl alcohol. There was obtained 0.5 g. of 1,4-diamino-2,3-dicyano-1,4-bis-(ethylthio)-butadiene in the form of white needles, m.p. 162–163°.

Anal. Calcd. for $C_{10}H_{14}N_4S$: C, 47.22; H, 5.55; N, 22.07; S, 25.21. Found: C, 47.31; H, 5.67; N, 22.06; S, 25.26.

B. From Tetracyanoethane and Ethanethiol.—A solution of 6.5 g. (0.05 mole) of tetracyanoethane in 200 ml. of acetone was mixed with a solution of 15 ml. of ethanethiol (0.2 mole) in 50 ml. of 10% sodium hydroxide solution. The solution was allowed to stand at room temperature overnight. The long crystals that formed were collected on a filter, washed with water and recrystallized from alcohol. There was obtained 5.1 g. of 1,4-diamino-2,3-dicyano-1,4-bis-(ethylthio)-butadiene in the form of white needles, m.p. 162–163°. A mixed melting point of this material and the material prepared from tetracyanoethylene and ethanethiol was not depressed.

1,4-Diamino-2,3-dicyano-1,4-bis-(methylthio)-butadiene.—Methanethiol was bubbled into a cooled solution of 12.8 g. (0.5 mole) of tetracyanoethylene in 100 ml. of acetone until the volume of the solution had increased about 25%; 200 ml. of aqueous 10% sodium hydroxide was added to the solution. The white precipitate that formed upon standing was collected on a filter, washed with water and then dried. There was obtained 19.5 g. (86% yield) of 1,4-diamino-2,3-dicyano-1,4-bis-(methylthio)-butadiene as a white crystalline powder, m.p. 190–192°.

Anal. Calcd. for $C_8H_{10}N_4S_2$: C, 42.46; H, 4.45; N, 24.76. Found: C, 42.57; H, 4.61; N, 24.60.

1,4-Diamino-2,3-dicyano-1,4-bis-(phenylthio)-butadiene.—A solution of 6.5 g. (0.05 mole) of tetracyanoethane in 20 ml. of acetone was added to a mixture of 22.0 g. (0.2 mole) of benzenethiol and 50 ml. of 10% sodium hydroxide solution. The reaction mixture became warm. After the reaction mixture had cooled to room temperature it was poured into 200 ml. of water. The light yellow oil that separated solidified upon standing. The solid was collected on a filter, washed with water and recrystallized from ethyl alcohol to give 12.3 g. (70% yield) of 1,4-diamino-2,3-dicyano-1,4-bis-(phenylthio)-butadiene in the form of white prisms, m.p. 157–158°.

Anal. Calcd. for $C_{18}H_{14}N_4S_2$: C, 61.60; H, 4.03; N, 15.99; S, 18.30. Found: C, 61.49; H, 4.30; N, 16.01; S, 18.18.

2-Amino-3,4-dicyano-5-mercaptopyrrole.[8]—A mixture of 3.28 g. (0.02 mole) of 2,5-diamino-3,4-dicyanothiophene, 25 ml. of water and 50 ml. of 10% sodium hydroxide solution was heated under reflux until all of the solid had gone into solution. The solution, which had become very dark, was cooled immediately, treated with decolorizing charcoal and then filtered. The filtrate was acidified with hydrochloric acid, and the precipitate that formed was collected on a filter, washed with water and redissolved in 5% sodium bicarbonate solution. The resultant solution was treated with decolorizing charcoal again and filtered, and the filtrate was acidified with 5% hydrochloric acid. The precipitate that formed was collected on a filter, washed with water and dried. There was obtained 2.0 g. of 2-amino-3,4-dicyano-5-mercaptopyrrole in the form of a white powder which began to decompose without melting at 220°.

Anal. Calcd. for $C_6H_4N_4S$: C, 43.90; H, 2.46; N, 34.13; S, 19.48. Found: C, 43.96; H, 2.66; N, 34.10; S, 19.43.

Bis-(5-amino-3,4-dicyano-2-pyrryl) Disulfide.—To a solution of 12.0 g. (0.073 mole) of 2-amino-3,4-dicyano-5-mercaptopyrrole in 250 ml. of 5% sodium bicarbonate solution was added dropwise a solution of 7.5 g. of iodine and 15 g. of potassium iodide in 75 ml. of water. The orange-brown precipitate that formed was collected on a filter, washed with water, and recrystallized from alcohol–water with decolorizing charcoal. There was obtained 9.0 g. of bis-(5-amino-3,4-dicyano-2-pyrryl) disulfide in the form of bright orange needles which decomposed when heated above 280°.

Anal. Calcd. for $C_{12}H_6N_5S_2$: N, 34.34; S, 19.65. Found: N, 34.40; S, 19.81.

2-Amino-3,4-dicyano-5-methylthiopyrrole.—A solution of 5 g. (0.03 mole) of 2-amino-3,4-dicyano-5-mercaptopyrrole in 50 ml. of 5% sodium bicarbonate solution was shaken vigorously for 5 minutes in a stoppered bottle with 25 ml. of methyl iodide. The bottle was cooled and the precipitate that formed was collected on a filter, washed with

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(5) We wish to thank Dr. B. C. McKusick for the preparation of this compound.

(6) A catalytic amount of *p*-toluenesulfonic acid was necessary to effect this condensation.

(7) W. J. Middleton, U. S. Patent 2,779,780 (1957).

(8) W. J. Middleton, U. S. Patent 2,779,766 (1957).

water and recrystallized from alcohol–water with decolorizing charcoal. There was obtained 3.5 g. (65% yield) of 2-amino-3,4-dicyano-5-methylthiopyrrole in the form of white needles, m.p. 224–226°.

Anal. Calcd. for $C_7H_6N_4S$: C, 47.18; H, 3.39; N, 31.54; S, 17.99. Found: C, 47.34; H. 3.43; N, 31.51; S, 18.28.

Hydrolysis of 2-Amino-3,4-dicyano-5-methylthiopyrrole. A. With Aqueous Acid.—A mixture of 1.78 g. (0.01 mole) of 2-amino-3,4-dicyano-5-methylthiopyrrole in 25 ml. of 25% sulfuric acid was heated to reflux until solution was complete (3 hours). The reaction mixture was neutralized with ammonium hydroxide, brought to a *p*H of 3 by acidification with hydrochloric acid and evaporated to dryness. The solid residue was extracted with ether. Succinic acid, 0.15 g., was recovered from the ether extracts.

B. With Aqueous Alkali.—2-Amino-3,4-dicyano-5-methylthiopyrrole (1.78 g., 0.01 mole) was dissolved in a solution of 2.40 g. (0.06 mole) of sodium hydroxide in 25 ml. of water. The solution was heated under reflux for 4 hours, cooled, and acidified with hydrochloric acid. The precipitate that formed was collected on a filter, washed with water and recrystallized from water with decolorizing charcoal. There was obtained 0.68 g. (35% yield) of **2-amino-3(or 4)-carbamyl-4(or 3)-cyano-5-methylthiopyrrole** as light pink needles, m.p. 230–231° dec.

Anal. Calcd. for $C_7H_8N_4OS$: C, 42.86; H. 4.11; N, 28.56; S, 16.32. Found: C, 42.95; H, 4.09; N, 28.52; S, 16.23.

2-Amino-5-benzylthio-3,4-dicyanopyrrole.—Crude 2-amino-3,4-dicyano-5-mercaptopyrrole prepared from 24.6 g. (0.15 mole) of 2,5-diamino-3,4-dicyanothiophene was dissolved in 450 ml. of 10% sodium bicarbonate solution and then filtered, and the clear yellow filtrate was diluted with water to a volume of 700 ml. To this solution was added, dropwise with stirring, a solution of 19.0 g. (0.15 mole) of benzyl chloride in 200 ml. of methanol. The bulky yellow-white precipitate that formed was collected on a filter, washed with water and recrystallized from 1:1 methanol–water. There was obtained 29.7 g. (78% yield) of 2-amino-5-benzylthio-3,4-dicyanopyrrole as white prisms, m.p. 213–214° dec.

Anal. Calcd. for $C_{13}H_{10}N_4S$: C, 61.41; H, 3.96; N, 22.04; S, 12.59. Found: C, 61.63; H, 3.90; N, 21.92; S, 12.74.

2-Amino-5-benzylthio-3,4-dicyano-1-methylpyrrole.—Methyl iodide (5.68 g., 0.04 mole) was added to a solution of 5.08 g. (0.02 mole) of 2-amino-5-benzylthio-3,4-dicyanopyrrole and 1.08 g. (0.02 mole) of sodium methoxide in 25 ml. of absolute methanol, and the resulting solution was heated to reflux for ten minutes. The reaction mixture was cooled and poured into 100 ml. of ice-water. The oil that separated solidified when subjected to reduced pressure in a vacuum desiccator. The solid was collected on a filter, washed successively with water and benzene, and dried. There was obtained 4.55 g. (85% yield) of 2-amino-5-benzylthio-3,4-dicyano-1-methylpyrrole as a light tan powder. A sample was further purified by chromatography in methanol over activated alumina to give long colorless needles, m.p. 183–184°, insoluble in sodium hydroxide solution.

Anal. Calcd. for $C_{14}H_{12}N_4S$: C, 62.68; H, 4.51; N, 20.89. Found: C, 62.47; H, 4.64; N, 20.88.

2-Benzylidenamino-5-benzylthio-3,4-dicyanopyrrole.—A mixture of 2.54 g. (0.01 mole) of 2-amino-5-benzylthio-3,4-dicyanopyrrole and 3.18 g. (0.03 mole) of benzaldehyde was heated on an oil-bath at 140–150° for 15 minutes. The pyrrole dissolved completely to form a yellow solution which was cooled and diluted with benzene. The light yellow crystals that separated were collected on a filter and washed with benzene. There was obtained 3.14 g. (92% yield) of 2-benzylidenamino-5-benzylthio-3,4-dicyanopyrrole. Recrystallizations from chlorobenzene and then benzene gave light yellow needles, m.p. 173–173.5°, $\lambda_{\max}^{\text{acetone}}$ 362 mμ (ϵ 14,700). This product was soluble in dilute aqueous potassium hydroxide.

Anal. Calcd. for $C_{20}H_{14}N_4S$: C, 70.16; H, 4.12. Found: C, 70.31; H, 4.26.

5-Benzylthio-2-*p*-dimethylaminobenzylidenamino-3,4-dicyanopyrrole.[5]—A mixture of 1.27 g. of 2-amino-5-benzylthio-3,4-dicyanopyrrole and 0.75 g. of *p*-dimethylaminobenzaldehyde was heated at 140–150° for 15 minutes, and the product was crystallized from ethyl alcohol to give 0.80 g. (42% yield) of 5-benzylthio-2-*p*-dimethylaminobenzylidenamino-3,4-dicyanopyrrole, m.p. 164–164°, $\lambda_{\max}^{\text{acetone}}$ 411 mμ (ϵ 40,400).

Anal. Calcd. for $C_{22}H_{19}N_5S$: C, 68.6; H, 5.0; N, 18.2. Found: C, 68.7; H, 5.0; N, 17.9.

2-Amino-5-carboxymethylthio-3,4-dicyanopyrrole Monohydrate.—The crude 2-amino-3,4-dicyano-5-mercaptopyrrole prepared from 3.28 g. (0.02 mole) of 2,5-diamino-3,4-dicyanothiophene was dissolved in 60 ml. of 5% sodium bicarbonate solution and then filtered. To the filtrate was added a solution of 3.78 g. (0.04 mole) of chloroacetic acid in excess aqueous sodium bicarbonate solution. The mixture was heated on a steam-bath for several minutes, cooled, and acidified with hydrochloric acid. The crystals that formed were collected and recrystallized twice from water. There was obtained 2.35 g. of 2-amino-5-carboxymethylthio-3,4-dicyanopyrrole monohydrate in the form of white needles that lost water when heated above 100° and melted with decomposition at 201°.

Anal. Calcd. for $C_8H_6O_2N_4S \cdot H_2O$: neut. equiv. (COOH), 240; neut. equiv. (COOH + NH), 120. Found: neut. equiv. (COOH), 243; neut. equiv. (COOH + NH), 120; pK_a (COOH), 3.60; pK_a (NH), 9.12.

5-Amino-3,4-dicyanopyrro[2.1-b]thiazolidine.—2-Amino-3,4-dicyano-5-mercaptopyrrole (15.3 g., 0.093 mole) was converted to the disodium salt by dissolving in a solution of 10.2 g. (0.186 mole) of sodium methoxide in 10 ml. of absolute methanol. Ethylene dibromide (17.7 g., 0.1 mole) was added in one portion and the mixture was heated to reflux over a steam-bath for five minutes. The crystals that separated were collected on a filter, washed with methanol and dried. There was obtained 11.5 g. (65% yield) of 5-amino-3,4-dicyanopyrro[2,1-b]thiazolidine as a light tan crystalline powder. The material was further purified by chromatography in dimethylformamide over activated alumina and recrystallized from dimethylformamide–water to give long, very light pink needles, m.p. >300°, insoluble in most organic solvents.

Anal. Calcd. for $C_8H_6N_4S$: N, 29.47; S, 16.83. Found: N, 29.48; S, 17.06.

2-Amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole. A. Preparation from 1,4-Diamino-1,4-bis-(2-hydroxyethylthio)-2,3-dicyanobutadiene.—A mixture of 21.5 g. (0.075 mole) of 1,4-bis-(2-hydroxyethylthio)-1,4-diamino-2,3-dicyanobutadiene and 200 ml. of water containing 5 ml. of concentrated hydrochloric acid was heated under reflux until solution was complete. The solution was filtered, and the filtrate was cooled. The crystals which separated were collected on a filter, washed with water and recrystallized from water. There was obtained 12.0 g. (78% yield) of 2-amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole as white plates, m.p. 186–187°, pK_a 9.4.

Anal. Calcd. for $C_8H_8N_4OS$: C, 46.18; H, 3.87; N, 26.91; S, 15.40. Found: C, 46.17; H, 3.91; N, 26.59; S, 15.47.

B. Preparation from 2-Amino-3,4-dicyano-5-mercaptopyrrole.—A solution of 1.64 g. (0.01 mole) of 2-amino-3,4-dicyano-5-mercaptopyrrole and 1.61 g. (0.02 mole) of 2-chloroethanol in 20 ml. of 5% sodium bicarbonate solution was heated under reflux for ten minutes and then cooled. The crystals that separated were collected on a filter, washed with water and recrystallized from water. There was obtained 1.5 g. of 2-amino-3,4-dicyano-5-(2-hydroxyethylthio)-pyrrole as white plates, m.p. 186–187°.

2-Acetamido-5-(2-acetoxyethylthio)-3,4-dicyanopyrrole.—A mixture of 30 g. of 1,4-diamino-1,4-bis-(2-hydroxyethylthio)-2,3-dicyanobutadiene in 185 ml. of acetic anhydride was heated under reflux for one hour. About 85 ml. of solvent was removed by distillation and the residue was allowed to stand at room temperature for 24 hours. The solid that precipitated was collected on a filter, washed with ether and recrystallized from 1 liter of water. There was obtained 6.0 g. of 2-acetamido-5-(2-acetoxyethylthio)-3,4-dicyanopyrrole in the form of long, white needles, m.p. 188–189°.

Anal. Calcd. for $C_{12}H_{12}N_4O_3S$: N, 19.17; S, 10.97. Found: N, 19.20; S, 10.90.

2-Amino-3,4-dicyano-5-phenylthiopyrrole. A. By Acid Catalysis.—Water, 100 ml., containing 10 ml. of concentrated hydrochloric acid was added to a solution of 7.0 g.

(0.02 mole) of 1,4-diamino-1,4-bis-(phenylthio)-2,3-dicyanobutadiene in 100 ml. of hot ethyl alcohol, and the resultant solution was heated under reflux for 10 minutes and then filtered. The filtrate was diluted with 150 ml. of water and allowed to cool. The white, flaky precipitate that formed was collected on a filter, washed with water and recrystallized from alcohol. There was obtained 4.55 g. (95% yield) of 2-amino-3,4-dicyano-5-phenylthiopyrrole as white needles, m.p. 233–234°.

Anal. Calcd. for $C_{12}H_8N_4S$: C, 59.98; H, 3.38; N, 23.34; S, 13.34. Found: C, 60.02; H, 3.51; N, 23.17; S, 13.47.

B. **By Pyrolysis.**—1,4-Diamino-1,4-bis-(phenylthio)-2,3-dicyanobutadiene, 2.2 g., was heated in a vapor bath of ethylene glycol (197°) for 10 minutes. The material at first melted and then turned dark and solidified. The dark residue (1.5 g.) was recrystallized from water–alcohol with decolorizing charcoal. There was obtained 1.0 g. of 2-amino-3,4-dicyano-5-phenylthiopyrrole as white needles, m.p. 233–234°.

2,5-Bis-(2-hydroxyethylthio)-3,4-dicyanopyrrole.[9]—A solution of 25 g. of 1,4-bis-(2-hydroxyethylthio)-1,4-diamino-2,3-dicyanobutadiene in 100 ml. of 36% hydrochloric acid was allowed to evaporate at room temperature in a draft of air. The solid residue was collected on a filter, washed with water and recrystallized from water with decolorizing charcoal. There was obtained 13.0 g. (55% yield) of 2,5-bis-(2-hydroxyethylthio)-3,4-dicyanopyrrole in the form of white plates, m.p. 108–110°, pK_a 7.6.

Anal. Calcd. for $C_{10}H_{11}N_3O_2S_2$: C, 44.59; H, 4.12; N, 15.61; S, 23.81; mol. wt., 269. Found: C, 44.79; H, 3.84; N, 15.75; S, 23.85; neut. equiv., 266.

2,5-Bis-(2-chloroethylsulfonyl)-3,4-dicyanopyrrole.—A solution of 4.25 g. of 2,5-bis-(2-hydroxyethylthio)-3,4-dicyanopyrrole in 50 ml. of 36% hydrochloric acid was cooled to 0°, and 25 ml. of 30% hydrogen peroxide was added dropwise to the stirred solution at such a rate that the temperature was kept below 10° at all times. After the addition, the solution was stirred for 2 hours longer at ice-bath temperature and then allowed to slowly warm to room temperature. The white solid (4.0 g., 69% yield) that formed was collected on a filter, washed with water, and recrystallized from water. 2,5-Bis-(2-chloroethylsulfonyl)-3,4-dicyanopyrrole was obtained in the form of white needles, m.p. 210–212°, pK_a 2.6.

Anal. Calcd. for $C_{10}H_9Cl_2N_3O_4S_2$: C, 32.44; H, 2.45; Cl, 19.15; N, 11.35; S, 17.32. Found: C, 32.55; H, 2.64; Cl, 19.26; N, 11.37; S, 17.40.

The filtrate from the recrystallization was mixed with an aqueous solution of tetramethylammonium chloride, and the white precipitate that formed was collected on a filter, washed with water and recrystallized from water. There was obtained the **tetramethylammonium** salt of 2,5-bis-(2-chloroethylsulfonyl)-3,4-dicyanopyrrole as long white needles, m.p. 185–186°.

Anal. Calcd. for $C_{14}H_{20}Cl_2N_4O_4S_2$: C, 37.92; H, 4.55; N, 12.64; S, 14.46. Found: C, 37.94; H, 4.55; N, 12.71; S, 14.66.

2,5-Bis-(2-pyridinioethylsulfonyl)-3,4-dicyanopyrrolide Chloride Dihydrate.—A solution of 5.0 g. of 2,5-bis-(2-chloroethylsulfonyl)-3,4-dicyanopyrrole in 25 ml. of pyridine was allowed to stand at room temperature for two hours and then heated under reflux for 5 minutes. The white precipitate that formed (4.5 g.) was collected on a filter, washed with ether and recrystallized from water. There was obtained 3.7 g. of 2,5-bis-(2-pyridinioethylsulfonyl)-3,4-dicyanopyrrolide chloride dihydrate, in the form of white needles that melted first at 158–160°, resolidified, and then remelted at 245–248°.

Anal. Calcd. for $C_{20}H_{22}ClN_5O_6S_2$: Cl, 6.72; N, 13.27; S, 12.14. Found: Cl, 6.70; N, 13.16; S, 12.00.

2,5-Bis-(methylthio)-3,4-dicyanopyrrole.—A mixture of 100 ml. of water, 50 ml. of 36% hydrochloric acid, 150 ml. of ethyl alcohol and 17 g. (0.075 mole) of 1,4-bis-(methylthio)-1,4-diamino-3,4-dicyanobutadiene was heated under reflux with stirring until all solid material had gone into solution. This required about 30 minutes. The solution was cooled, and a white crystalline precipitate formed. The precipitate was collected on a filter and washed with water. Water was added to the filtrate and an additional amount of precipitate formed. This precipitate was also collected, combined with the first precipitate, and recrystallized from ethyl alcohol. There was obtained 13 g. (83% yield) of 2,5-bis-(methylthio)-3,4-dicyanopyrrole in the form of long white needles, m.p. 224–225°.

Anal. Calcd. for $C_8H_7N_3S_2$: C, 45.91; H, 3.37; N, 20.08; S, 30.64. Found: C, 46.04; H, 3.44; N, 20.06; S, 30.36.

2,5-Bis-(ethylthio)-3,4-dicyanopyrrole was prepared in a similar manner from 1,4-bis-(ethylthio)-1,4-diamino-1,4-dicyanobutadiene and was obtained as white needles, m.p. 140–141°.

Anal. Calcd. for $C_{10}H_{11}N_3S_2$: C, 50.60; H, 4.67; N, 17.71; S, 27.02. Found: C, 50.97; H, 4.33; N, 17.62; S, 27.38.

2-Amino-5-bromo-3,4-dicyanopyrrole. A. From Tetracyanoethylene and Hydrogen Bromide.—A solution of 25.6 g. (0.2 mole) of tetracyanoethylene in 100 ml. of acetone was cooled to −40° and saturated with anhydrous hydrogen bromide gas. The solid that precipitated was collected on a filter, washed with cold (−40°) acetone and then thoroughly washed with cold water. There was obtained 13.8 g. (33% yield) of crude 2-amino-5-bromo-3,4-dicyanopyrrole. After two recrystallizations from ethyl alcohol, the pyrrole was obtained as long white needles (purple cast) which slowly decomposed when heated above 250°.

Anal. Calcd. for $C_6H_3BrN_4$: C, 34.15; H, 1.43; Br, 37.87; N, 26.55; neut. equiv., 211. Found: C, 34.42; H, 1.50; Br, 37.69; N, 26.68; neut. equiv., 214.

This pyrrole is acidic and will dissolve in aqueous sodium hydroxide solution but not in aqueous sodium bicarbonate solution. A dilute alcoholic solution of this pyrrole mixed with a dilute aqueous solution of copper acetate resulted in an intensely colored purple solution.

B. **From Tetracyanoethane and Hydrogen Bromide.**—A solution of 13.0 g. (0.1 mole) of tetracyanoethane in 50 ml. of acetone was cooled to 10° and anhydrous hydrogen bromide was passed in until the solution was filled with solid. The mixture was quickly filtered and the collected solid was washed with cold acetone. The solid was triturated with water, collected on a filter and recrystallized twice from ethyl alcohol. There was obtained 2.1 g. (10% yield) of 2-amino-5-bromo-3,4-dicyanopyrrole in the form of white needles (purple cast) which decomposed slowly when heated above 250°.

2-Acetamido-5-bromo-3,4-dicyanopyrrole.—Ten grams of crude 2-amino-5-bromo-3,4-dicyanopyrrole was heated to boiling with 100 ml. of acetic anhydride and then cooled. The solid was collected on a filter, washed with water and recrystallized from dimethylformamide–water. There was obtained 6.0 g. of 2-acetamido-5-bromo-3,4-dicyanopyrrole as an off-white, crystalline powder which decomposed on heating above 170°.

Anal. Calcd. for $C_8H_5BrN_4O$: C, 37.97; H, 1.99; Br, 31.58; N, 22.14. Found: C, 38.09; H, 2.25; Br, 31.55; N, 22.09.

2-Amino-5-bromo-3,4-dicyano-1-methylpyrrole.—Crude 2-amino-5-bromo-3,4-dicyanopyrrole (5.27 g., 0.025 mole) was dissolved in a solution prepared from 0.575 g. (0.025 gram atom) of sodium and 25 ml. of ethyl alcohol; 10 ml. of methyl iodide was added and the solution was allowed to stand at room temperature for 3 hours, and then mixed with 100 ml. of water. The solid that precipitated was collected on a filter, washed with 1% sodium hydroxide solution and then recrystallized from alcohol with decolorizing charcoal to give 2.9 g. (52% yield) of 2-amino-5-bromo-3,4-dicyano-1-methylpyrrole in the form of white needles, m.p. 212–214° dec.

Anal. Calcd. for $C_7H_5B_2N_4$: C, 37.35; H, 2.24; Br, 35.51; N, 24.09. Found: C, 37.52; H, 2.53; Br, 35.54; N, 24.43.

1-Benzyl-2-benzylamino-5-bromo-3,4-dicyanopyrrole.—Crude 2-amino-5-bromo-3,4-dicyanopyrrole (5.27 g., 0.025 mole) was dissolved in an alcoholic solution of sodium ethoxide (prepared from 0.575 g. of sodium and 25 ml. of ethyl alcohol). Five ml. (7.2 g., 0.042 mole) of benzyl bromide was added, the mixture was allowed to stand at room temperature for 4 hours, and then mixed with 200 ml. of water. The solid that precipitated was collected on a filter and recrystallized twice from ethyl alcohol with decolorizing char-

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(9) W. J. Middleton, U. S. Patent 2,793,215 (1957).

coal to give 3.5 g. (43% yield based on benzyl bromide) of 1-benzyl-2-benzylamino-5-bromo-3,4-dicyanopyrrole in the form of white plates which became green when heated to 168° and melted with decomposition at 176–178° when heated rapidly.

Anal. Calcd. for $C_{20}H_{15}BrN_4$: C, 61.39; H, 3.86; Br, 20.43; N, 14.32. Found: C, 61.71; H, 3.85; Br, 20.16; N, 14.26.

N-Methylquinolinium 5-Amino-3,4-dicyano-2-pyrrolesulfonate.—A mixture of 4.8 g. (0.037 mole) of tetracyanoethane, 7.7 g. (0.074 mole) of sodium bisulfite and 50 ml. of water was heated until solution was complete. The solution was cooled and mixed with a solution of 10 g. (0.037 mole) of N-methylquinolinium iodide in 30 ml. of water. The flaky precipitate that formed was collected on a filter, washed with water and recrystallized from water. There was obtained 3.5 g. (27% yield) of N-methylquinolinium 5-amino-3,4-dicyano-2-pyrrolesulfonate in the form of glistening yellow plates, m.p. 255–257°.

Anal. Calcd. for $C_{16}H_{13}N_5O_3S$: C, 54.07; H, 3.69; N, 19.71; S, 9.02. Found: C, 54.28; H, 3.82; N, 19.75; S, 8.80.

This salt was insoluble in cold water, but was quite soluble in 5% sodium bicarbonate solution.

5-Amino-3,4-dicyano-2-pyrrolesulfonic Acid.[10]—A solution of 3.0 g. of N-methylquinolinium 5-amino-3,4-dicyano-2-pyrrolesulfonate in 50 ml. of hot water was passed slowly through a column heated with steam and containing 14 g. of an acidic ion exchange resin, Amberlite IR-120. The solution was evaporated at room temperature under nitrogen and finally dried under reduced pressure over phosphorus pentoxide. There was obtained 1.5 g. of 5-amino-3,4-dicyano-2-pyrrolesulfonic acid which decomposed on melting, was very hygroscopic, and became dark on exposure to air.

Anal. Calcd. for $C_6H_4N_4O_3S$: neut. equiv. (1) 212, (2) 106. Found: neut. equiv. (1) 212, (2) 106.

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[10] We wish to thank Dr. C. L. Dickinson for this preparation.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 443 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. IX.[1] Heterocyclic Compounds from Dicyanoketene Acetals

BY W. J. MIDDLETON AND V. A. ENGELHARDT

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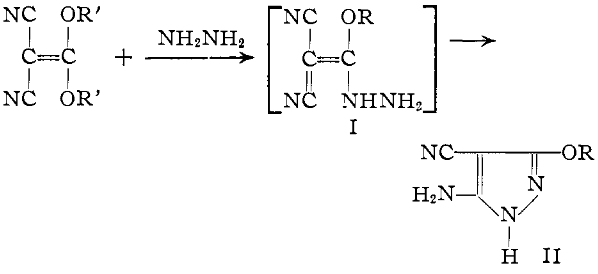
A variety of heterocyclic compounds have been prepared by the reaction of dicyanoketene acetals with certain nitrogen bases. 5-Amino-4-cyano-3-substituted pyrazoles, 5-amino-4-cyano-3-substituted isoxazoles and 4-amino-5-cyano-2,6-disubstituted pyrimidines were formed by the action of hydrazine, hydroxylamine and amidines, respectively, on dicyanoketene acetals and other closely related compounds.

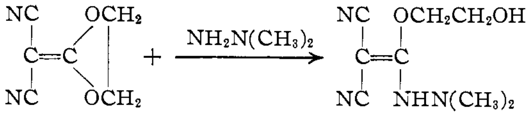
Previous work in this Laboratory has demonstrated that dicyanoketene acetals react with ammonia and primary and secondary amines to yield 1-amino-1-alkoxy-2,2-dicyanoethylenes and 1,1-diamino-2,2-dicyanoethylenes.[2] The apparent ease of replacing the alkoxyl groups in dicyanoketene acetals with amino groups led us to examine the reaction of these ketene acetals with other functional compounds containing basic amino groups, such as hydrazine, hydroxylamine and amidines.

Pyrazoles.—The reaction of dicyanoketene acetals with hydrazine has led to a new pyrazole synthesis. 5-Amino-4-cyano-3-ethoxypyrazole (II, R = C_2H_5) was prepared by the reaction of dicyanoketene diethyl acetal and hydrazine, and 5-amino-4-cyano-3-(2-hydroxyethoxy)-pyrazole (II, R = CH_2CH_2OH) was prepared from dicyanoketene ethylene acetal and hydrazine. Presumably a 2,2-dicyano-1-alkoxyvinylhydrazine (I) was an intermediate in these reactions.

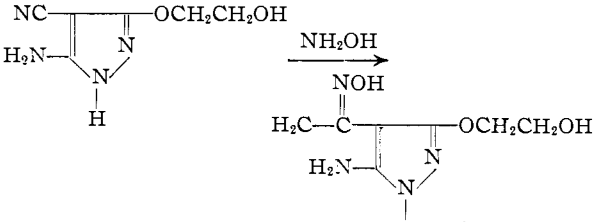

I

II

Attempts to isolate such an intermediate from the reaction of dicyanoketene ethylene acetal with hydrazine were unsuccessful. However, when 1,1-dimethylhydrazine was used in place of the unsubstituted hydrazine, so that no cyclization was possible, a new substituted hydrazine III was isolated.


III

In order to demonstrate conclusively that reaction of the dicyanoketene acetals with hydrazine had given a pyrazole, the cyano groups of a suspected pyrazole were "counted" by reaction with excess hydroxylamine. Thus when II (R = CH_2CH_2OH) was allowed to react with excess hydroxylamine, only one equivalent of hydroxylamine was consumed and the product IV contained no cyano groups as determined by its infrared spectrum; therefore II (R = CH_2CH_2OH) contains only one cyano group and must then contain a pyrazole ring.


IV

Both the infrared and ultraviolet spectra of the hydrazine–dicyanoketene acetal products are quite different from those of III, and also support the pyrazole structure II.

The basicities of the pyrazoles II and the substituted hydrazine III are also quite different.

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[1] Paper VIII, W. J. Middleton, V. A. Engelhardt and B. S. Fisher, THIS JOURNAL, 80, 2822 (1958).

[2] Paper IV, W. J. Middleton and V. A. Engelhardt, *ibid.*, 80, 2788 (1958).