thiophene[12a,b] in 10 ml. of glacial acetic acid was cooled in an ice bath, and 3.2 g. (0.02 mole) of 2,5-diethoxytetrahydrofuran was added in one portion. The cooling bath was removed, and the mixture was stirred at room temperature overnight. The dark solution was then heated at reflux for one hour and allowed to cool. The crude 2,5-di(*N*-pyrrolyl)-3,4-dicyanothiophene was filtered, washed with cold acetic acid, and dried. There was obtained 0.58 g. (22%). Recrystallization from acetic acid gave material with m.p. 164–165°.

Anal. Calcd. for $C_{14}H_8N_4S$: C, 63.6; H, 3.05; N, 21.2, S, 12.1. Found: C, 63.5, H, 3.35; N, 20.4; S, 12.1.

Cyanocarbon Chemistry. XXII.[1] 3,4-Dicyano-1,2,5-triaminopyrrole and Its Derivatives

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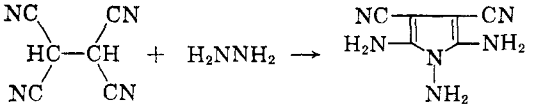
Tetracyanoethane and hydrazine hydrate react to form 3,4-dicyano-1,2,5-triaminopyrrole. All three amino groups in this compound condense with aldehydes to form anils. With 1,2- and 1,3-dicarbonyl compounds cyclization occurs to form pyrrolotriazines and pyrrolotriazepines, two new ring systems.

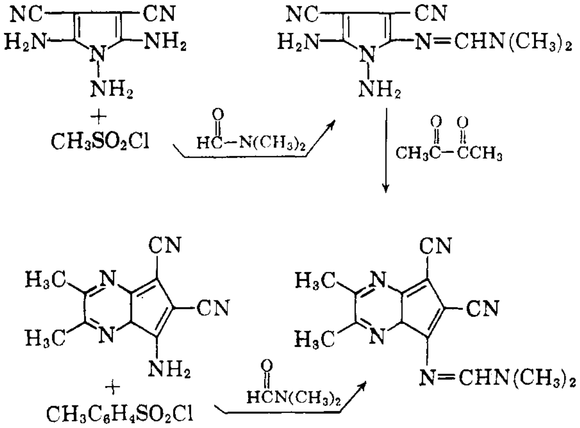
The addition of hydrazine to nitriles is a well known reaction that leads to triazoles and triazines.[2] We have found that 1,1,2,2-tetracyanoethane reacts rapidly with hydrazine hydrate in aqueous solution under mild conditions to give 3,4-dicyano-1,2,5-triaminopyrrole. This reaction is analogous to the reaction of hydrogen sulfide with tetracyanoethane to give 2,5-diamino-3,4-dicyanothiophene.[3]



I

This pyrrole is insoluble in 5% hydrochloric acid in spite of the three amino groups, and it is only slightly soluble in most organic solvents but dissolves readily in dimethylformamide.

The three amino groups can be condensed with dimethylformamide under the influence of three moles of *p*-toluenesulfonyl chloride to give a trisamidine. This reaction serves to emphasize the character of the amino groups, since only weakly basic amines undergo this reaction. For example, we observed this same reaction with 2,5-diamino-3,4-dicyanothiophene and with *p*-nitroaniline, while aniline and *p*-chloroaniline give the sulfonanilides under these conditions. The condensation of tertiary amides with the amino group of sulfonamides has been reported.[4] When only one mole of *p*-toluenesulfonyl chloride is used, a monoamidine results. This was shown to be in the 2-position for it condensed readily with biacetyl to give a product identical with that obtained running the condensations in reverse order.



Condensation with aromatic aldehydes gives either dianil (II) or trianil (III) derivatives, depending upon the aldehyde and the conditions. Formation of a trianil establishes that compound I has the pyrrole structure and not the alternative 3,6-diamino-1,2-dihydropyridazine structure.

There are two possible structures for the dianil. We favor the 1,2-dianil over the 2,5-dianil structure. The initial condensation would be expected to occur in the 2-position from the result with dimethylformamide and *p*-toluenesulfonyl chloride. However, when we attempted to prepare a monobenzal derivative, the only product that we isolated was the dibenzal derivative in greater than 50% yield. This was true even when the reaction was run at room temperature in dimethylformamide with acid catalysis. While it is difficult to explain why the formation of the benzal derivative should activate either the 1 or 5 amino groups, one would expect that the 5-amino would be deactivated under these circumstances and the 1-amino group

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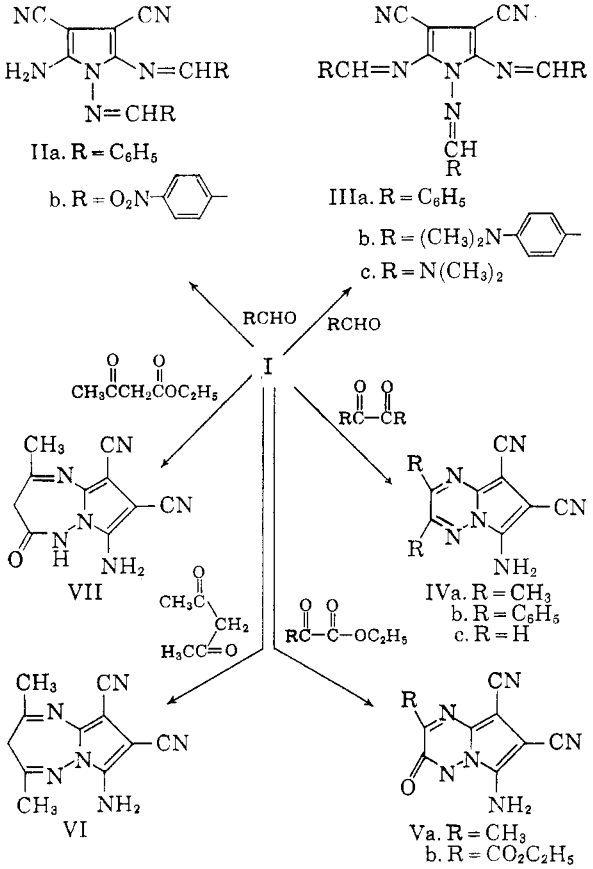
(1) Paper XXI, R. H. Boyd, *J. Chem. Phys.*, **65**, 1834 (1961).

(2) V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, 1947, pp. 73–76.

(3) W. J. Middleton, V. A. Engelhardt, and B. S. Fisher, *J. Am. Chem. Soc.*, **80**, 2822 (1958).

(4) E. Enders, German Patent 949,285 (1956).



is therefore more probable. From this, one would expect 2,5-diamino-3,4-dicyanothiophene to give a monobenzal derivative under similar conditions, and this was the result that we obtained. The difference between the dimethylformamide condensation and the benzaldehyde condensation can be explained by the fact that the product of the former is the hydrochloride of the amidine.

The condensation with 1,2- and 1,3-dicarbonyl compounds has led to two new ring systems. With biacetyl and benzil, 6-amino-7,8-dicyanopyrrolo[*b*]-*as*-triazines (IV) are obtained. The 2,3-dimethyl compound is orange with λ_{max} 461 mμ, while the 2,3-diphenyl compound is red with λ_{max} 511 mμ. The amino group in each of these compounds was condensed with benzaldehyde. The λ_{max} for the anil from IVa shifted from 461 mμ to 546 mμ, the direction that is expected. The anil from IVb, however, had the λ_{max} shift from 511 mμ to 460 mμ. This is the reverse of the direction that one would expect. We have no explanation for this anomalous behavior.

Ethyl pyruvate and ethyl oxomalonate react with I to give the same ring system as above, and only one compound can be isolated although there are two possible isomers. Since the keto group of the starting material is more reactive than the ester group, this should react with the more reactive amino group. The 2-amino group has been shown to react initially, and we believe that the correct isomer is the one shown.

Condensations with acetylacetone or ethyl acetoacetate have led to 7-amino-8,9-dicyanopyrrolo[*b*][1,2,4]triazepines (VI and VII). These are colorless compounds. In the case of VII, we again have the possibility of isomers, but we isolated only one compound. The above arguments favor the structure that is shown.

Experimental

3,4-Dicyano-1,2,5-triaminopyrrole (I).[5a]—Hydrazine hydrate (100 g., 2.0 moles) was added to an ice-cooled suspension of 60 g. (0.46 mole) of tetracyanoethane[5b] in 500 ml. of water. The flask was swirled until a solution was obtained and allowed to stand in an ice bath for 12 to 15 min. The precipitate of off-white crystalline 3,4-dicyano-1,2,5-triaminopyrrole was collected; yield 35 g. (47%). An additional 5 g. was obtained from the filtrate after an additional 10 min., but this was less pure than the first fraction. An analytical sample prepared by recrystallization from dimethylformamide–water melted above 300°.

Anal. Calcd. for $C_6H_6N_6$: C, 44.4; H, 3.7; N, 51.8. Found: C, 44.6; H, 4.0; N, 51.5.

2,5-Diamino-3,4-dicyano-1-methylaminopyrrole.—A solution of 1.75 g. (0.04 mole) of methylhydrazine was added to an ice-cooled mixture of 2.60 g. (0.02 mole) of tetracyanoethane in 10 ml. of water. A solution was obtained immediately and after several minutes crystals began to precipitate. After 20 min. the precipitate was collected; yield 0.50 g. (14%). The compound decomposed above 200°, but did not melt. Attempted recrystallization from acetic acid and from dimethylformamide–water led to further decomposition so that an analytical sample could not be obtained. The compound was converted to a bisbenzylidene derivative which could be purified and characterized.

2,5-Bis(benzylideneamino)-3,4-dicyano-1-methylaminopyrrole (VIII).—A mixture of 1.00 g. (0.0057 mole) of 2,5-diamino-3,4-dicyano-1-methylaminopyrrole, 3 ml. of benzaldehyde, and a trace of *p*-toluenesulfonic acid was heated at 140° for 2 hr. The mixture was cooled and diluted with 50 ml. of ethyl acetate, and 1.60 g. (80%) of the dianil was collected as a yellow precipitate. An analytical sample was prepared by recrystallization from dioxane, m.p. 225–226° dec., $\lambda_{max}^{dioxane}$ 421 mμ, ϵ_{max} 14,000.

Anal. Calcd. for $C_{21}H_{16}N_6$: C, 71.6; H, 4.5; N, 23.9. Found: C, 71.3; H, 4.7; N, 23.4.

1(5)-Amino-2,5(1)-bis(benzylideneamino)-3,4-dicyanopyrrole (IIa).—A mixture of 2.50 g. (0.015 mole) of 3,4-dicyano-1,2,5-triaminopyrrole and 15 ml. of benzaldehyde was heated at 130° for 2 hr. The bright orange needles obtained were filtered and washed with benzene in order to remove the benzaldehyde; yield 5.00 g. (98%); m.p. 224.5–229°. The sample of dianil was recrystallized from acetic acid for analysis; m.p. 239–241°, $\lambda_{max}^{C_2H_5OH}$ 434 mμ (ϵ 12,800).

Anal. Calcd. for $C_{20}H_{14}N_6$: C, 71.0; H, 4.1; N, 24.8. Found: C, 71.0; H, 4.2; N, 24.5.

Infrared bands at 2.95 μ and 3.05 μ indicate that an —NH_2 group is present; and therefore rule out a pyridazine structure.

1(5)-Amino-2,5(1)-bis(*p*-nitrobenzylideneamino)-3,4-dicyanopyrrole (IIb).—A mixture of 3.24 g. (0.02 mole) of 3,4-dicyano-1,2,5-triaminopyrrole and 10.57 g. (0.07 mole) of *p*-nitrobenzaldehyde was heated at 160° for 5 min. The mass became solid and 10 ml. of nitrobenzene was added to

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(5a) W. J. Middleton, U. S. Patent 2,961,447.

(5b) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

increase the mobility of the mass. After about 1 hr. the flask was allowed to cool and a deep red precipitate of the dianil was collected and washed thoroughly with benzene; yield 7.90 g.; m.p. > 300°. The sample was recrystallized several times from dimethylformamide.

Anal. Calcd. for $C_{20}H_{12}N_8O_4$: C, 56.1; H, 2.8. Found: C, 56.3; H, 2.9.

3,4-Dicyano-1,2,5-tris(benzylideneamino)pyrrole (IIIa).—A mixture of 3.24 g. (0.02 mole) of 3,4-dicyano-1,2,5-triaminopyrrole, 10 ml. of benzaldehyde, and 0.5 g. of *p*-toluenesulfonic acid was heated at 140°. After a few minutes an orange solid formed, and after 40 min. there was a mixture of orange and yellow solids. At this point, 10 ml. more of benzaldehyde was added, and the heating was continued for 20 min. The flask was cooled, ethyl acetate was added, and the bright yellow crystals were collected and washed with ethyl acetate; yield 7.35 g. (69%), m.p. 247–252°. Several recrystallizations from dioxane gave a product that melted at 263–264°; $\lambda_{\max}^{C_2H_5OH}$ 408 mμ, $\epsilon_{\max}$ 23,400.

Anal. Calcd. for $C_{27}H_{18}N_6$: C, 76.1; H, 4.2; N, 19.7. Found: C, 76.4; H, 4.2; N, 19.6.

When an attempt was made to recrystallize the yellow tribenzal derivative from acetic acid, the orange dibenzal derivative was obtained as shown by a mixed melting point determination.

3,4-Dicyano-1,2,5-tris(*p*-dimethylaminobenzylideneamino)pyrrole (IIIb).—A mixture of 3.24 g. (0.02 mole) of 3,4-dicyano-1,2,5-triaminopyrrole, 9.00 g. (0.06 mole) of *p*-dimethylaminobenzaldehyde, 0.3 g. of *p*-toluenesulfonic acid, and 11 ml. of nitrobenzene was heated at 160–165° for 15 hr. The mixture was cooled and diluted with 100 ml. of 95% alcohol. The orange precipitate was collected and washed with 95% alcohol; yield 8.50 g. (76%). A sample was recrystallized from dioxane for analysis; $\lambda_{\max}^{C_2H_5OH}$ 451 mμ $\epsilon_{\max}$ 40,500.

Anal. Calcd. for $C_{33}H_{33}N_9$: C, 71.4; H, 5.9; N, 22.70. Found: C, 71.0; H, 6.0; N, 23.0.

3,4-Dicyano-1,2,5-tris(dimethylaminomethyleneamino)-pyrrole (IIIc).—*p*-Toluenesulfonyl chloride (5.70 g., 0.03 mole) and 1.62 g. (0.01 mole) of 3,4-dicyano-1,2,5-triaminopyrrole were dissolved in 15 ml. of dimethylformamide. After a short time an exothermic reaction took place and the temperature rose to 70°. The reaction mixture was allowed to cool, diluted with 75 ml. of water, and was made basic with aqueous ammonia. The off-white solid that separated was collected; yield 2.60 g. (80%), m.p. 188–189.5°. Recrystallization from ethanol gave the tris(dimethylaminomethyleneamino)pyrrole as colorless crystals that started to melt at 193° but then stopped melting completely and finally melted at 204–205°.

Anal. Calcd. for $C_{15}H_{21}N_9$: C, 55.0; H, 6.4; N, 38.5. Found: C, 55.0; H, 6.5; N, 38.3.

1,2-Diamino-3,4-dicyano-5-dimethylaminomethyleneaminopyrrole.—A solution of 1.62 g. (0.01 mole) of 3,4-dicyano-1,2,5-triaminopyrrole and 1.90 g. (0.01 mole) of *p*-toluenesulfonyl chloride in 10 ml. of dimethylformamide was warmed on a steam bath for 5 min. and allowed to cool. The crystals that separated upon standing dissolved when 25 ml. of water was added. The solid that separated when the solution was made basic with ammonium hydroxide was collected and recrystallized from ethanol; yield 0.80 g. (35%), m.p. 229–231°.

Anal. Calcd. for $C_9H_{11}N_7$: C, 49.8; H, 5.1. Found: C, 49.8; H, 5.3.

7,8-Dicyano-2,3-dimethyl-6-dimethylaminomethyleneaminopyrrolo-[b]-*as*-triazine. a. From 1,2-Diamino-3,4-dicyano-5-dimethylaminomethyleneaminopyrrole.—A solution of 0.80 g. (0.035 mole) of 1,2-diamino-3,4-dicyano-5-dimethylaminomethyleneaminopyrrole and 0.50 g. (0.06 mole) of biacetyl in 10 ml. of glacial acetic acid was heated on a steam bath for 30 min. The orange crystalline product that separated upon cooling was collected; yield 0.58 g. (62%), m.p. 242–243°. A sample was recrystallized from acetic acid for analysis.

Anal. Calcd. for $C_{13}H_{13}N_7$: C, 58.4; H, 4.9. Found: C, 58.6; H, 4.9.

b. From 6-Amino-7,8-dicyano-2,3-dimethylpyrrolo-[b]-*as*-triazine.—A solution of 2.12 g. (0.01 mole) of 6-amino-7,8-dicyano-2,3-dimethylpyrrolo-[*b*]-*as*-triazine and 1.90 g. (0.01 mole) of *p*-toluenesulfonyl chloride in 20 ml. of dimethylformamide was warmed on a steam bath for 5 min. The solution was allowed to cool and diluted with 50 ml. of water. The precipitate was collected and recrystallized from glacial acetic acid, yield 1.8 g., m.p. 239–241°. A mixed melting point with the sample from part a showed no depression, and their infrared spectra were identical.

2-Amino-3,4-dicyano-5-benzalaminothiophene.—A solution of 0.81 g. (0.005 mole) of 2,5-diamino-3,4-dicyanothiophene, 0.53 g. (0.005 mole) of benzaldehyde, and 0.1 g. of *p*-toluenesulfonic acid in 10 ml. of dimethylformamide was warmed on a steam bath for 5 min., cooled and diluted with 15 ml. of water. The yellow solid that was collected was recrystallized from acetic acid–dimethylformamide and melted at 255–257°.

Anal. Calcd. for $C_{13}H_8N_4S$: C, 61.9; H, 3.2; S, 12.7. Found: C, 62.3; H, 3.5; S, 12.5.

Under identical conditions, 3,4-dicyano-1,2,5-triaminopyrrole gave the dibenzal derivative.

2-Amino-3,4-dicyano-5-dimethylaminomethyleneaminothiophene.—To a solution of 1.62 g. (0.01 mole) of 2,5-diamino-3,4-dicyanothiophene[6] in 15 ml. of dimethylformamide was added 1.90 g. (0.01 mole) of *p*-toluenesulfonyl chloride. The resulting solution was heated on a steam bath for 30 min. and then poured into 100 ml. of water. The yellow precipitate that formed when this solution was neutralized with ammonium hydroxide was collected, yield 1.71 g. (75%), m.p. 197–199°. After recrystallization from ethanol, the melting point was 210–213°.

Anal. Calcd. for $C_9H_9N_5S$: C, 49.3; H, 4.1; N, 32.0; S, 14.6. Found: C, 49.3; H, 4.40; N, 31.6; S, 14.6.

3,4-Dicyano-2,5-bis(dimethylaminomethyleneamino)-thiophene.—A solution of 16.2 g. (0.1 mole) of 2,5-diamino-3,4-dicyanothiophene and 38.0 g. (0.02 mole) of *p*-toluenesulfonyl chloride in 125 ml. of dimethylformamide was warmed on a steam bath for 1–2 min. and then removed. An exothermic reaction took place, and after several minutes the flask was filled with solid. After 30 min. the contents of the flask were poured into 500 ml. of water and the solid was collected on a filter; yield 19.2 g., m.p. 215–222°. The filtrate was made basic with ammonium hydroxide, and the yellow solid was collected, yield 5.2 g., m.p. 205–225°. The two fractions were each recrystallized from dimethylformamide–water mixture, and the melting points of the recrystallized materials were identical. The total yield was 20.7 g. (76%), m.p. 229–230.5°.

Anal. Calcd. for $C_{12}H_{14}N_6S$: C, 52.5; H, 5.1; N, 30.6; S, 11.7. Found: C, 52.8; H, 5.2; N, 30.9; S, 12.0.

6-Amino-7,8-dicyanopyrrolo-[*b*]-*as*-triazine (IVc).—To a solution of 8.00 g. (0.05 mole) of 3,4-dicyano-1,2,5-triaminopyrrole in 25 ml. of dimethylformamide was added 10.0 g. of 30% glyoxal solution in water and 0.5 g. of *p*-toluenesulfonic acid. The resulting mixture was heated on a steam bath for 4 hr., cooled, and diluted with 125 ml. of ethanol. The precipitate was collected to give 7.5 g. (81%) of red crystalline pyrrolotriazine, m.p. 281–285°. An analytical sample was prepared by recrystallization from acetic acid, m.p. 288–290°.

Anal. Calcd. for $C_8H_4N_6$: C, 52.2; H, 2.2; N, 45.6. Found: C, 52.5; H, 2.2; N, 45.1.

6-Amino-7,8-dicyano-2,3-dimethylpyrrolo-[*b*]-*as*-triazine (IVa).—A solution of 3.24 g. (0.02 mole) of 3,4-dicyano-1,2,5-triaminopyrrole, 1.72 g. (0.02 mole) of biacetyl, and 0.2 g. of *p*-toluenesulfonic acid in a mixture of 20 ml. of dimethylformamide and 15 ml. of ethanol was heated on a

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[6] W. J. Middleton, *Org. Synthesis*, **39**, 8 (1959).

steam bath for 4 hr. and allowed to cool. The orange precipitate was collected and washed with ethanol; yield 1.10 g. The filtrate was diluted with 100 ml. of 95% alcohol, and the resulting precipitate was collected, yield 1.75 g. The combined yield was 2.85 g. (66%). Recrystallization from acetic acid gave orange crystals, m.p. 276–278° dec., $\lambda_{max}^{C_2H_5OH}$ 461 mμ, ϵ_{max} 3700.

Anal. Calcd. for $C_{10}H_8N_6$: C, 56.6; H, 3.8. Found: C, 56.9; H, 4.00.

6-Amino-7,8-dicyano-2,3-diphenylpyrrolo-[*b*]-*as*-triazine (IVb).—A solution of 4.86 g. (0.03 mole) of 3,4-dicyano-1,2,5-triaminopyrrole, 6.10 g. (0.03 mole) of benzil and 1.0 g. of *p*-toluenesulfonic acid was heated on a steam bath for 5 hr. During this time, deep red crystals formed. The mixture was cooled, diluted with 100 ml. of water, filtered, and the crystals were washed thoroughly with ethanol; yield 9.00 g. (90%), m.p. > 300°. A sample was recrystallized from acetic acid for analysis; $\lambda_{max}^{C_2H_5OH}$ 511 mμ, ϵ_{max} 6000.

Anal. Calcd. for $C_{20}H_{12}N_6$: C, 71.4; H, 3.6; N, 25.00. Found: C, 71.2; H, 3.7; N, 25.0.

6-Amino-7,8-dicyano-3-hydroxy-2-methylpyrrolo-[*b*]-*as*-triazine (Va).—A solution of 3.22 g. (0.02 mole) of 3,4-dicyano-1,2,5-triaminopyrrole and 2.32 g. (0.02 mole) of ethyl pyruvate in a mixture of 10 ml. of dimethylformamide and 10 ml. of ethanol was heated under reflux. A solid began to separate after 1 hr., and after 2 hr. the mixture was cooled. The orange triazine was collected and washed thoroughly with ethanol; yield 2.50 g. (55%), m.p. > 300°. A sample was recrystallized from dimethylformamide–ethanol for analysis.

Anal. Calcd. for $C_9H_6ON_6$: C, 50.5; H, 2.80; N, 39.2. Found: C, 50.5; H, 3.2; N, 39.4.

Ethyl 6-Amino-7,8-dicyano-3-hydroxypyrrolo-[*b*]-*as*-triazine-2-carboxylate (Vb).—A solution of 1.62 g. of 1,2,5-triamino-3,4-dicyanopyrrole, 1.74 g. of diethyl oxomalonate, and 0.5 g. of *p*-toluenesulfonic acid in 10 ml. of dimethylformamide was heated on a steam bath for 3 hr. The deep red solution was diluted with 20 ml. of 95% alcohol and 50 ml. of water, and the precipitate was collected; yield 1.82 g., m.p. > 300°. An analytical sample of the triazine was prepared by recrystallization from acetic acid.

Anal. Calcd. for $C_{11}H_8N_6O_3$: C, 48.6; H, 3.0. Found: C, 48.4; H, 3.4.

6-Benzylideneamino-7,8-dicyano-2,3-dimethylpyrrolo-[*b*]-*as*-triazine.—A mixture of 2.12 g. (0.01 mole) of 6-amino-7,8-dicyano-2,3-dimethylpyrrolo-[*b*]-*as*-triazine, 10 ml. of benzaldehyde, and 0.3 g. of *p*-toluenesulfonic acid was heated at 160° for 1.5 hr. and allowed to cool. Fifteen milliliters of ethanol was added and the magenta solid was collected. This solid was heated with 50 ml. of benzene to remove the benzaldehyde and again collected; yield 2.75 g. (91%), m.p. 260–265°. Recrystallization from acetic acid gave the red crystalline anil, m.p. 263–265°; $\lambda_{max}^{C_2H_5OH}$ 546 mμ, ϵ_{max} 9600.

Anal. Calcd. for $C_{17}H_{12}N_6$: C, 68.0; H, 4.0; N, 28.0. Found: C, 67.6; H, 4.3; N, 27.8.

6-Benzylideneamino-7,8-dicyano-2,3-diphenylpyrrolo-[*b*]-*as*-triazine.—A mixture of 2.00 g. (0.0061 mole) of 6-amino-7,8-dicyano-2,3-diphenylpyrrolo-[*b*]-*as*-triazine, 5 ml. of benzaldehyde, and 0.3 g. of *p*-toluenesulfonic acid was heated at 150–160° for 2 hr. and then allowed to cool. Ethanol (15.0 ml.) was added and the orange crystalline anil was collected; yield 1.70 g. (67%), m.p. 276–277°. It was recrystallized from dimethylformamide–ethanol for analysis, $\lambda_{max}^{C_2H_5OH}$ 460 mμ, ϵ_{max} 5900.

Anal. Calcd. for $C_{27}H_{16}N_6$: C, 76.4; H, 3.8. Found: C, 76.2; H, 4.0.

7-Amino-8,9-dicyano-2,4-dimethylpyrrolo-[*b*]-[1,2,4]-triazepine (VI).—A solution of 6.50 g. (0.04 mole) of 3,4-dicyano-1,2,5-triaminopyrrole, 4.0 g. (0.04 mole) of acetylacetone, and 0.5 g. of *p*-toluenesulfonic acid in 10 ml. of dimethylformamide was heated on a steam bath for 2 hr. During this time a crystalline solid separated. The mixture was cooled and the tan solid was collected, washed with a small amount of dimethylformamide and then thoroughly washed with ethanol; yield 6.10 g. (60%), m.p. 273–279° dec. Recrystallization from acetic acid gave a product that melted at 278–280° dec.

Anal. Calcd. for $C_{11}H_{10}N_6$: C, 58.4; H, 4.4; N, 37.2. Found: C, 58.2; H, 4.5; N, 36.9.

7-Amino-8,9-dicyano-4-hydroxy-2-methylpyrrolo-[*b*]-[1,2,4]-triazepine (VII).—A solution of 6.50 g. (0.04 mole) of 3,4-dicyano-1,2,5-triaminopyrrole, 5.20 g. (0.04 mole) of ethyl acetoacetate, and 0.5 g. of *p*-toluenesulfonic acid in 10 ml. of dimethylformamide was heated on a steam bath for 4 hr. and allowed to cool. The off-white solid was collected and washed thoroughly with ethanol; yield 3.20 g. (35%), m.p. > 300°. The compound was recrystallized from dimethylformamide–ethanol.

Anal. Calcd. for $C_{10}H_8N_6O$: C, 52.6; H, 3.5. Found: C, 52.7; H, 3.7.

Polyfunctional Aliphatic Compounds. II.[1] The Cyclization of Dinitriles by Anhydrous Halogen Acids. Pyridines

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Received January 2, 1962

The action of anhydrous hydrogen bromide or iodide on 3-hydroxyglutaronitriles or glutacononitriles leads to 2-amino-6-halopyridines in excellent yield. In conjunction with the facile method for the synthesis of the starting materials, this represents a mode of easy access to previously unavailable simple pyridine derivatives.

Recently, the reactions of polynitriles with anhydrous halogen acids have received considerable attention.[2-4] Tetracyanoethylene with hydrogen bromide was found to give 2-amino-5-bromo-3,4-dicyanopyrrole, while tetranitriles of structure I led to the corresponding pyridines (II) when treated

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[1] Part I, Francis Johnson, J. P. Panella, and A. A. Carlson, *J. Org. Chem.*, **27**, 2241 (1962).

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