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.

(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

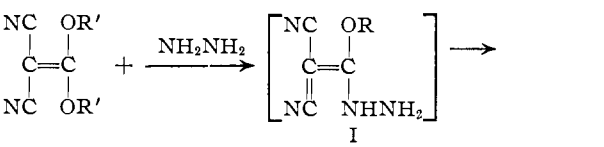
BY W. J. MIDDLETON AND V. A. ENGELHARDT

RECEIVED NOVEMBER 14, 1957

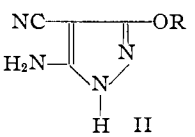
A variety of heterocyclic compounds have been prepared by the reaction of dicyanoketene acetals with certain nitrogen bases. 5-Amino-4-cyano-3-substituted pyrazoles, 5-amino-4-cyano-3-substituted isoxazoles and 4-amino-5-cyano-2,6-disubstituted pyrimidines were formed by the action of hydrazine, hydroxylamine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

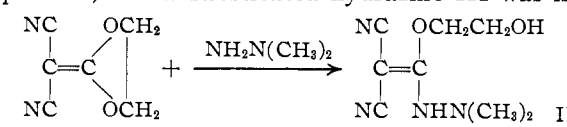


I

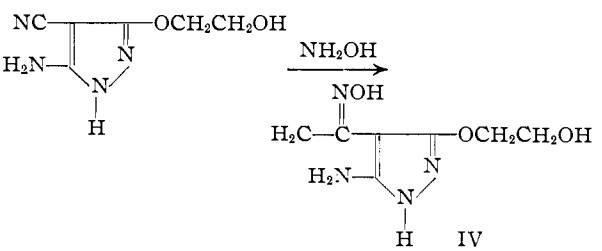


II

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. 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



III



IV

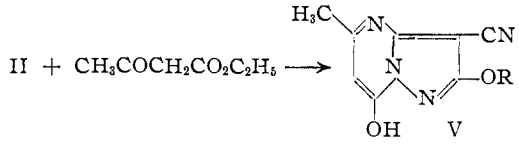
hydroxylamine, only one equivalent of hydroxylamine was consumed and the product IV contained no cyano groups as determined by its infrared spectrum; therefore II (R = CH_2CH_2OH) contains only one cyano group and must then contain a pyrazole ring. Both the infrared and ultraviolet spectra of the hydrazine–dicyanoketene 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.

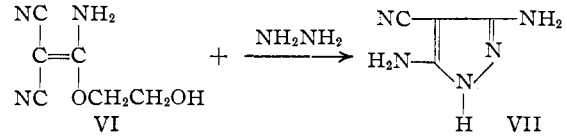
(1) Paper VIII, W. J. Middleton, V. A. Engelhardt and B. S. Fisher, THIS JOURNAL, **80**, 2822 (1958).

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

While an aqueous solution of III exhibits a basic *p*H, aqueous solutions of the pyrazoles II are slightly acidic. However, the 5-amino group in the pyrazoles is sufficiently basic to be acetylated easily with acetic anhydride. The aminopyrazoles II also will react with ethyl acetoacetate to form pyrazolopyrimidines V.

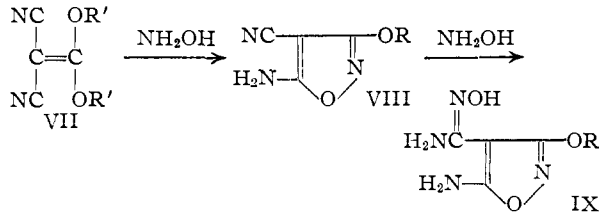


This new synthesis of pyrazoles was extended to the preparation of 3,5-diamino-4-cyanopyrazole (VII). This pyrazole was prepared by the reaction of hydrazine with 1-amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene.

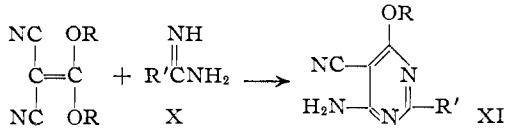


In contrast to the 5-amino-3-alkoxy-4-cyanopyrazoles, 3,5-diamino-4-cyanopyrazole shows a basic reaction in water and forms a picrate easily.

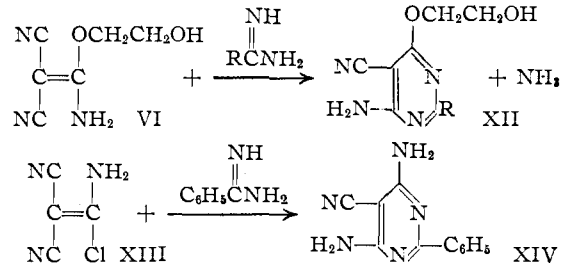
Isoxazoles.—Substituted isoxazoles were formed by the reaction of dicyanoketene acetals with equivalent amounts of hydroxylamine. This reaction is directly analogous to the reaction of hydrazine with the acetals to form pyrazoles. Two isoxazoles were prepared in this manner: 5-amino-3-ethoxy-4-cyanoisoxazole (VIII, R = C_2H_5) from dicyanoketene diethyl acetal and 5-amino-3-(2-hydroxyethoxy)-4-cyanoisoxazole (VIII, R = CH_2CH_2OH) from dicyanoketene ethylene acetal. When dicyanoketene ethylene acetal was allowed to react with excess hydroxylamine, two equivalents of hydroxylamine were consumed and a product was formed that no longer contained a cyano group. Thus it appears that the cyanoisoxazole VIII which first forms reacts further with hydroxylamine to yield 5-amino-3-(2-hydroxyethoxy)-4-isoxazolecarboxamide oxime (IX). If cyclization to the isoxazole had not taken place, the ketene acetal would have reacted with an additional equivalent of hydroxylamine.



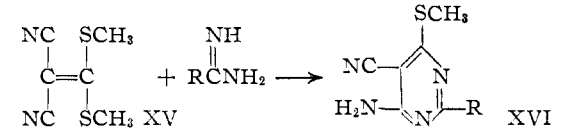
Pyrimidines.—4-Amino-5-cyano-6-alkoxypyrimidines (XI) were prepared by the reaction of a dicyanoketene acetal with amidines in aqueous or methanolic solution. 4-Amino-5-cyanopyrimidines which contain ethoxy and 2-hydroxyethoxy substituents in the 6-position were prepared from dicyanoketene diethyl acetal and dicyanoketene ethylene acetal, respectively. The substituents in the 2-position were also varied, depending upon the amidine used. Acetamidine (X, R′ = CH_3), benzamidine (X, R′ = C_6H_5), guanidine (X, R′ = NH_2) and methylisothiourea (X, R′ = SCH_3) reacted with dicyanoketene acetals to give correspondingly substituted pyrimidines.



Attempts to prepare pyrimidines with a 6-amino substituent by the reaction of amidines with 1-amino - 1 - (2 - hydroxyethoxy) - 2,2 - dicyanoethylene (VI) were not successful. Instead, 5-cyano - 2,4 - diamino - 6 - (2 - hydroxyethoxy)-pyrimidine (XII, R = NH_2) resulted from reaction of VI and guanidine, and 4-amino-5-cyano-6-(2-hydroxyethoxy)-2-phenylpyrimidine (XII, R = C_6H_5) from VI and benzamidine. These reactions were rather surprising in view of the fact that 3,5-diamino-5-cyanopyrazole was prepared from VI and hydrazine. However, a pyrimidine with a 6-amino group (XIV) was prepared from the reaction of 1-amino-1-chloro-2,2-dicyanoethylene (XIII)[3] and benzamidine.



Two pyrimidines were also formed by the reaction of amidines with dicyanoketene dimethyl mercaptal[4] (XV), the sulfur analog of the dicyanoketene acetals. 4-Amino-5-cyano-6-methylmercapto-2-phenylpyrimidine (XVI, R = C_6H_5) was formed from XV and benzamidine, and 4-amino-2,6-bis-(methylmercapto)-5-cyanopyrimidine (XVI, R = SCH_3) was formed from XV and methylisothiourea. The physical properties of the pyrimidines prepared in this study are listed in Table I. Most of the pyrimidines are high-melting, stable, slightly basic, white crystalline solids. 5-Cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine forms non-hygroscopic sulfate and nitrate salts.



Experimental

5-Amino-4-cyano-3-(2-hydroxyethoxy)-pyrazole.—Five grams (0.1 mole) of hydrazine hydrate was added to a slurry of 13.6 g. (0.1 mole) of dicyanoketene ethylene acetal in 50 ml. of water. The reaction was quite exothermic, and all solids went into solution upon stirring. When the solution was cooled, the white crystals that separated (14.4 g.) were collected on a filter and recrystallized from water. There

(3) Paper V, W. J. Middleton, E. L. Little, D. D. Coffman and V. A. Engelhardt, THIS JOURNAL, **80**, 2795 (1958).

(4) H. D. Edwards and J. D. Kendall, U. S. Patent 2,533,233 (1950).

TABLE I: 4-AMINO-5-CYANOPYRIMIDINES

Pyrimidine Name	Formula	Synthesis method	Reactants: Dicyanoethylene	Reactants: Amidine salt	Yield, %	Recrystn. solvent	Melting point, °C.	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
5-Cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine	$C_7H_9N_5O_2$	A	Dicyanoketene ethylene acetal	Guanidine thiocyanate	70	Water	236–237	43.07		4.65		35.88	
		B	Dicyanoketene ethylene acetal	Guanidine sulfate	55	Water	236–237	42.95		4.83		35.84	
		B	1-Amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene	Guanidine sulfate	45	Water	236–237						
5-Cyano-2,4-diamino-6-ethoxypyrimidine	$C_7H_9N_5O$	A	Dicyanoketene diethyl acetal	Guanidine thiocyanate	61	Ethanol	220–221	46.92		5.06		39.09	
								46.72		4.92		39.39	
4-Amino-5-cyano-6-(2-hydroxyethoxy)-2-methylpyrimidine	$C_8H_{10}N_4O_2$	B	Dicyanoketene ethylene acetal	Acetamidine hydrochloride	53	Water	225–227[a]	49.48		5.19		28.85	
								49.34		5.09		28.89	
4-Amino-5-cyano-6-(2-hydroxyethoxy)-2-phenylpyrimidine	$C_{13}H_{12}N_4O_2$	B	Dicyanoketene ethylene acetal	Benzamidine hydrochloride	63	Ethanol–H_2O	174–176	60.93		4.72		21.86	
		B	1-Amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene	Benzamidine hydrochloride	70	Ethanol–H_2O	174–176	60.99		4.60		21.76	
4-Amino-5-cyano-6-(2-hydroxyethoxy)-2-methylthiopyrimidine	$C_8H_{10}N_4O_2S$[b]	B	Dicyanoketene ethylene acetal	S-Methylisothiouronium sulfate	58	Water	163–164	42.47		4.46		24.77	
								42.54		4.28		24.76	
4-Amino-5-cyano-6-methylthio-2-phenylpyrimidine	$C_{11}H_{10}N_4S$	B[c]	Dicyanoketene dimethyl mercaptal	Benzamidine hydrochloride	87	Ethanol–H_2O	163–165	57.37		4.38		24.22	
								57.13		4.30		24.06	
4-Amino-5-cyano-2,6-bis-(methylthio)-pyrimidine	$C_7H_8N_4S_2$[d]	B[c]	Dicyanoketene dimethyl mercaptal	S-Methylisothiouronium sulfate	60	Ethanol–H_2O	231–232	39.60		3.80		26.39	
								39.69		3.73		26.32	
5-Cyano-4,6-diamino-2-phenylpyrimidine	$C_{11}H_9N_5$	B[c]	1-Amino-1-chloro-2,2-dicyanoethylene	Benzimidine hydrochloride	40	Water	148–149	62.55		4.30		33.16	
								62.53		4.29		33.10	

[a] Melting point was determined in sealed capillary tube because compound sublimed at atmospheric pressure. [b] Calcd.: S, 14.17. Found: S, 14.35. [c] Sodium methoxide was used in place of sodium hydroxide. [d] Calcd.: S, 30.20. Found: S, 30.41.

was obtained 12.0 g. (72% yield) of 2-amino-4-cyano-3-(2-hydroxyethoxy)-pyrazole in the form of long, white needles, m.p. 169–170°.

Anal. Calcd. for $C_6H_8N_4O_2$: C, 42.85; H, 4.79; N, 33.32. Found: C, 43.00; H, 4.61; N, 33.32.

5-Amino-4-cyano-3-ethoxypyrazole, prepared in a similar manner from hydrazine hydrate and dicyanoketene diethyl acetal, was obtained as white needles, m.p. 180–181° (72% yield).

Anal. Calcd. for $C_6H_8N_4O$: C, 47.36; H, 5.30; N, 36.82. Found: C, 47.61; H, 5.23; N, 36.85.

5-Acetamido-4-cyano-3-ethoxypyrazole.—One gram of 5-amino-4-cyano-3-ethoxypyrazole was dissolved in 5 ml. of acetic anhydride and the solution was heated to boiling for 2 minutes; 5 ml. of ethyl alcohol was added and the solution was boiled for an additional minute and then cooled. The precipitate that formed was collected on a filter, washed with water and then recrystallized from ethyl alcohol to give 0.89 g. of 5-acetamido-4-cyano-3-ethoxypyrazole in the form of white needles, m.p. 210°.

Anal. Calcd. for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.26; H, 5.04; N, 28.83.

Reaction of 5-Amino-4-cyano-3-(2-hydroxyethoxy)-pyrazole with Hydroxylamine.—5-Amino-4-cyano-3-(2-hydroxyethoxy)-pyrazole (5.6 g., 0.033 mole) was dissolved in a solution of 7.0 g. (0.1 mole) of hydroxylamine hydrochloride and 3.6 g. (0.09 mole) of sodium hydroxide in 50 ml. of water. This solution was heated to boiling, filtered and the filtrate was cooled overnight. The precipitate that formed was collected on a filter, washed with water and recrystallized from water. There was obtained 3.3 g. of 5-amino-3-(2-hydroxyethoxy)-4-pyrazole carboxamide oxime in the form of white needles, m.p. 185–190°. The nitrile absorption band in the infrared spectrum of this compound was absent.

Anal. Calcd. for $C_6H_{11}N_5O_3$: C, 35.85; H, 5.51; N, 34.81. Found: C, 36.15; H, 5.62; N, 34.81.

4-Cyano-3,5-diaminopyrazole.—To a solution of 4.59 g. (0.03 mole) of 1-amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene in 10 ml. of water was added 1.5 g. (0.03 mole) of hydrazine hydrate in 5 ml. of water. A dense white precipitate formed. The mixture was heated until all solids had gone into solution. White needles formed when the solution was cooled for two hours in an ice–salt-bath. These needles were collected on a filter, washed with a little cold water and dried. There was obtained 2.1 g. of 4-cyano-3,5-diaminopyrazole in the form of long, white needles, m.p. 169–170°. This material was very soluble in water and in alcohol.

Anal. Calcd. for $C_4H_5N_5$: C, 39.02; H, 4.09; N, 56.89. Found: C, 39.07; H, 4.09; N, 56.63.

The picrate of 4-cyano-3,5-diaminopyrazole was prepared in and recrystallized from water and was obtained as yellow needles, m.p. 262–263° dec., with sublimation above 130°.

Anal. Calcd. for $C_{10}H_8N_8O_6$: N, 33.33. Found: N, 33.16.

Reaction of Dicyanoketene Ethylene Acetal with 1,1-Dimethylhydrazine.—To a solution of 14.0 g. of dicyanoketene ethylene acetal in 75 ml. of tetrahydrofuran was added dropwise with cooling 25 ml. of 1,1-dimethylhydrazine. The white precipitate that formed was collected on a filter, washed with ether, and recrystallized twice from water. There was obtained 15 g. of **1,1-dimethyl-2-(2,2-dicyano-1-[2-hydroxyethoxy]-vinyl)-hydrazine** in the form of white needles, m.p. 185–187°.

Anal. Calcd. for $C_7H_{12}N_4O_2$: C, 48.97; H, 6.17; N, 28.56. Found: C, 48.63; H, 6.10; N, 28.50.

5-Amino-4-cyano-3-ethoxyisoxazole.—A suspension of 9.8 g. (0.063 mole) of dicyanoketene diethyl acetal in a solution of 2.52 g. (0.063 mole) of sodium hydroxide and 5.0 g. (0.072 mole) of hydroxylamine hydrochloride in 50 ml. of water was stirred until the initial exothermic reaction had subsided. The mixture was cooled, and the solid was collected on a filter, washed with water and recrystallized from water. There was obtained 7.9 g. (73%) of 5-amino-4-cyano-3-ethoxyisoxazole in the form of long, white needles, m.p. 170–171°.

Anal. Calcd. for $C_6H_7N_3O_2$: C, 47.05; H, 4.61; N, 27.44. Found: C, 47.21; H, 4.75; N, 27.67.

5-Amino-4-cyano-3-(2-hydroxyethoxy)-isoxazole, prepared in a similar manner from hydroxylamine hydrochloride, sodium hydroxide and dicyanoketene ethylene acetal, was obtained as long, white needles, m.p. 182–183°.

Anal. Calcd. for $C_6H_7N_3O_3$: C, 42.60; H, 4.17; N, 24.84. Found: C, 42.26; H, 4.18; N, 24.88.

Reaction of Dicyanoketene Ethylene Acetal with Two Equivalents of Hydroxylamine.—A solution of 10.0 g. (0.143 mole) of hydroxylamine hydrochloride, 4.0 g. (0.1 mole) of sodium hydroxide and 6.8 g. (0.05 mole) of dicyanoketene ethylene acetal in 50 ml. of water was heated to boiling and then allowed to cool overnight. The white, flaky precipitate that formed was collected on a filter, washed with water and recrystallized from water to give 1.9 g. of 5-amino-3-(2-hydroxyethoxy)-4-isoxazolecarboxamide oxime in the form of white needles which fell apart when dried. The dried material had a melting point of 181–182° dec. The infrared spectrum showed that no nitrile group was present.

Anal. Calcd. for $C_6H_{12}N_4O_4$: C, 35.64; H, 4.99; N, 27.71. Found: C, 35.60; H, 4.96; N, 27.69.

4-Amino-5-cyanopyrimidines.—The 4-amino-5-cyanopyrimidines listed in Table I were synthesized by treating an appropriately substituted dicyanoethylene with a free amidine. The free amidines were generated in either methanol or water. Syntheses of pyrimidines using both methods are illustrated by the following typical examples.

Method A. 5-Cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine.—Crystalline dicyanoketene ethylene acetal (13.6 g., 0.1 mole) was added with rapid stirring to a solution of 13.0 g. (0.11 mole) of guanidine thiocyanate and 5.6 g. (0.1 mole) of sodium methoxide in 50 ml. of methanol. The reaction mixture began to boil and the flask was immersed in an ice-bath until the reaction had subsided. The white solid that precipitated was collected on a filter, washed with methanol and recrystallized from water. There was obtained 13.25 g. (70%) of 5-cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine in the form of long, white needles, m.p. 236–237°.

Method B. 4-Amino-5-cyano-6-(2-hydroxyethoxy)-2-phenylpyrimidine.—1-Amino-1-(2-hydroxyethoxy)-2,2-dicyanoethylene (7.65 g., 0.05 mole) was added to a solution of 9.40 g. (0.06 mole) of benzamidine hydrochloride and 2.0 g. (0.05 mole) of sodium hydroxide in 25 ml. of water. After the mixture was warmed slightly, an exothermic reaction ensued and the entire mixture solidified to a white mass; 25 ml. of water was added, the mixture was cooled and the solid was collected on a filter, washed with water and recrystallized from ethyl alcohol–water. There was obtained 18.9 g. of 4-amino-5-cyano-6-(2-hydroxyethoxy)-2-phenylpyrimidine in the form of long, white matted needles, m.p. 174–176°.

5-Cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine Sulfate.—One gram of 5-cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine was dissolved in 10 ml. of hot 10% sulfuric acid. The solution was cooled and the white crystalline precipitate that formed was collected on a filter and washed with alcohol. There was obtained 0.91 g. of the sulfate salt, m.p. 202–204°.

Anal. Calcd. for $(C_7H_9N_5O_2)_2 \cdot H_2SO_4$: S, 6.56. Found: S, 6.53.

5-Cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine Nitrate.—One gram of 5-cyano-2,4-diamino-6-(2-hydroxyethoxy)-pyrimidine was dissolved in 5 ml. of hot 5% nitric acid. The solution was cooled, the white solid that precipitated was collected on a filter, washed with water and recrystallized from water. There was obtained 0.37 g. of the nitrate salt, m.p. 214–217°.

Anal. Calcd. for $C_7H_9N_5O_2 \cdot HNO_3$: C, 32.56; H, 3.90; N, 32.55. Found: C, 32.71; H, 3.91; N, 32.38.

3-Cyano-7-hydroxy-2-(2-hydroxyethoxy)-5-methylpyrazolo[2,3-α]pyrimidine.[5]—A solution of 7.10 g. (0.042 mole) of 3-amino-4-cyano-5-(2-hydroxyethoxy)-pyrazole in 25 ml. of ethyl acetoacetate was heated at 140–150° for 5 hours. The mixture was cooled and diluted with 25 ml. of ethyl alcohol, and the white crystalline precipitate was collected and washed with ethyl alcohol; yield 7.30 g. (73%), m.p. >300°. An analytical sample was prepared by recrystallization from a mixture of dimethylformamide and water.

Anal. Calcd. for $C_{10}H_{10}N_4O_3$: C, 51.28; H, 4.30; N, 23.92. Found: C, 51.47; H, 4.43; N, 22.74.

(5) The authors are indebted to Dr. C. L. Dickinson for the preparation of this derivative.

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Cyanocarbon Chemistry. X.[1] Pyridines from Tetracyanopropenes

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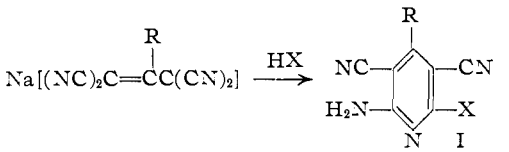
The reaction of a variety of 1,1,3,3-tetracyanopropenes and their salts with hydrogen halides has yielded 2-amino-6-halo-3,5-dicyanopyridines. The halogen atom of these highly substituted pyridines has been replaced by alkoxy, amino, arylsulfonyl and dicyanomethyl groups. The 2-amino-6-alkoxy-3,5-dicyanopyridines also have been prepared by refluxing the salts with alcohols in the presence of sulfuric acid.

Investigation of the chemistry of tetracyanoethylene has resulted in the availability of a large variety of highly acidic 1,1,3,3-tetracyanopropenes.[2] Salts of these organic acids have been found to react with hydrogen halides to yield 2-amino-6-halo-3,5-dicyanopyridines (I).



Although 1,3-dinitriles and their derivatives have been converted to 2,6-dihydroxypyridines by the action of aqueous acids,[3,4] very little attention appears to have been given to the reactions of anhydrous hydrogen halides with dinitriles. It has been reported by Lespieau[5] that β-bromoglutaronitrile was formed when β-hydroxyglutaronitrile was treated with anhydrous hydrogen bromide. As a result of this present study, it is suggested that Lespieau actually obtained 2-amino-6-bromopyridine instead of β-bromoglutaronitrile. The melting point of 87–88° that was reported for β-bromo-

(1) Paper IX, W. J. Middleton and V. A. Engelhardt, THIS JOURNAL, 80, 2829 (1958).

(2) Paper V, W. J. Middleton, E. L. Little, Jr., D. D. Coffman and V. A. Engelhardt, *ibid.*, 80, 2795 (1958).

(3) Thorpe, *J. Chem. Soc.*, 87, 1675 (1905).

(4) Ruhemann and Browning, *ibid.*, 73, 284 (1898).

(5) R. Lespieau, *Bull. soc. chim.*, 33, 725 (1923); *Compt. rend.*, 176, 754 (1923).