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.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 444 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

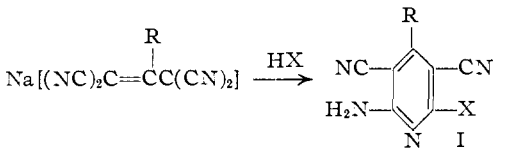
Cyanocarbon Chemistry. X.[1] Pyridines from Tetracyanopropenes

BY E. L. LITTLE, JR., W. J. MIDDLETON, D. D. COFFMAN, V. A. ENGELHARDT AND G. N. SAUSEN

RECEIVED NOVEMBER 14, 1957

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-

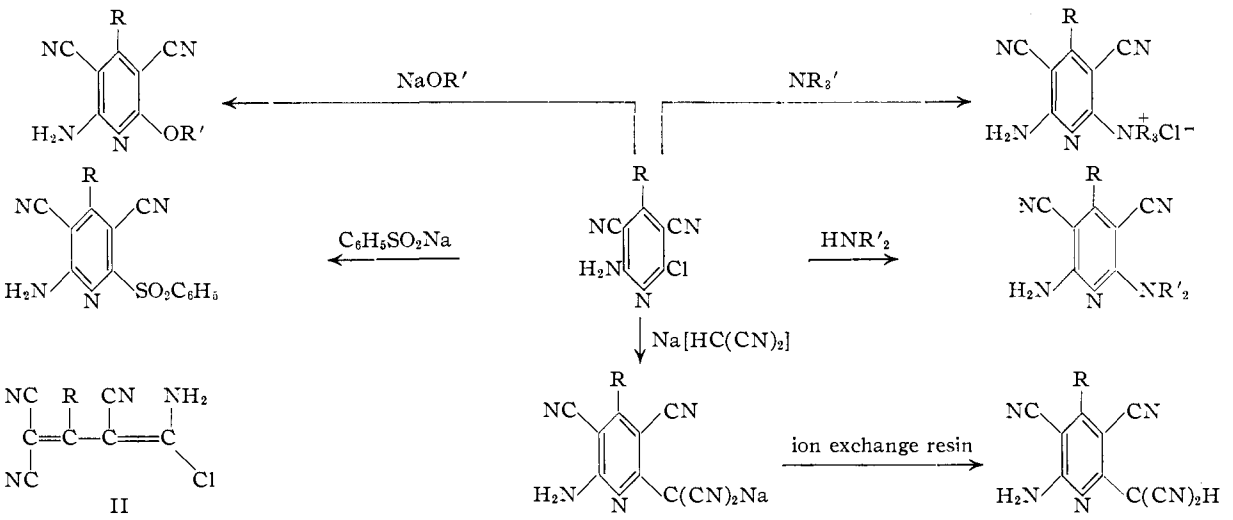
(1) Paper IX, W. J. Middleton and V. A. Engelhardt, THIS JOURNAL, 80, 2829 (1958).

(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).



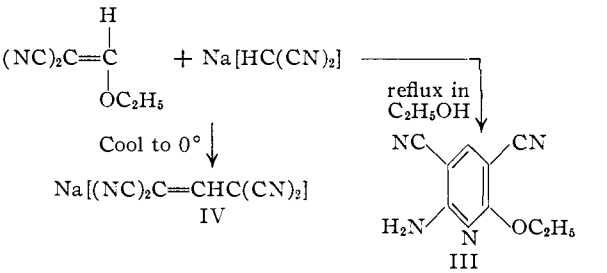
glutaronitrile is in good agreement with the melting point of 89–89.5°, which Hertog and Wibaut[6] reported for 2-amino-6-bromopyridine.

The 2-amino-6-halo-3,5-dicyanopyridines (Table I) have been prepared by passing dry hydrogen halide into a solution of a salt of the substituted 1,1,3,3-tetracyanopropene in an inert solvent such as acetone. These materials are white to yellow high-melting solids which can be purified readily by sublimation.

The pyridine structure is assigned to these products as a result of the following considerations. Interpretation of the infrared spectra indicates the presence of amino groups and thus rules out all other possible structures with the exception of a linear structure II. These products are not acidic, whereas compounds such as 1-amino-1-chloro-2,2-dicyanoethylene, which are very similar in structure to II, have been found to be very acidic.[2] The similarity of this proposed reaction to the known cyclization reactions[3,4] also supports the pyridine structure.

The reactive halogen atom of these pyridines has been utilized in a number of transformations which are outlined in the following diagrammatic scheme. Thus, the halogen atom has been replaced by amino, alkoxy, arylsulfonyl and dicyanomethyl groups. The cyanocarbon acid, 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine, is a strong acid (pK_A 2.3) and is unique among the known cyanocarbon acids[2] because of its thermal stability (m.p. above 300°).

Further study of the synthesis of 2-amino-6-alkoxy-3,5-dicyanopyridines has shown that they can be prepared directly from the salts of 1,1,3,3-tetracyanopropenes by refluxing the salts in alcohols in the presence of concentrated sulfuric acid. Comparison of the properties of 2-amino-6-ethoxy-3,5-dicyanopyridine with those of the by-product obtained in the synthesis of the sodium salt of 1,1,3,3-tetracyanopropene[7] has demonstrated that they are identical. Closer examination of the reactions of the sodium salt of malononitrile with ethoxymethylenemalononitrile has shown that control of temperature is very important. If the reaction is allowed to proceed without cooling, a 95% yield of the pyridine III is obtained. Cooling of the reaction to 0° resulted in a 90% yield of the sodium salt of 1,1,3,3-tetracyanopropene (IV). Similar cyclizations have been noted in the reactions of alcoholic solutions of the sodium salt of malononitrile with α-methoxybenzylidenemalononitrile and tricyanovinylbenzene.



Although 2,3-diamino-6-halo-3,5-dicyanopyridines were prepared by adding hydrogen halides to aqueous solutions of 2-amino-1,1,3,3-tetracyanopropenes, attempts to prepare these pyridines by saturating acetone solutions of the 2-amino-1,1,3,3-tetracyanopropenes with anhydrous halogen halides resulted in the formation of other products. These products resulted from the addition of hydrogen halide and acetone to the aminotetracyanopropenes with the concomitant loss of water. The infrared spectra of these products indicate the presence of a methyl group, a cyano group, amino groups and a high degree of aromaticity. It seems likely that the products are substituted naphthyridines.

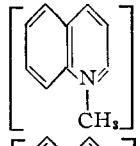
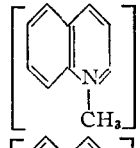
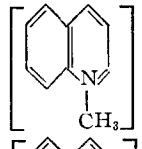
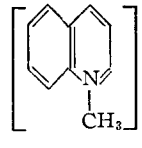
Two different naphthyridines could be formed from this reaction, as indicated in equations 1 and 2. Participation of the amine group of 2-amino-1,1,3,3-tetracyanopropene is doubtful since 2-methylamino-1,1,3,3-tetracyanopropene will also form a naphthyridine under the same conditions. Thus, the product formed is apparently either VII or IX. Structure VII and reaction scheme 1 seem plausible since acid-catalyzed reactions of aromatic amines with ketones to form Schiff bases are known, and the bromopyridine V is known to be formed when 2-amino-1,1,3,3-tetracyanopropene is treated with hydrogen bromide in the absence

(6) H. J. den Hertog, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **51**, 381 (1932); **55**, 122 (1936).

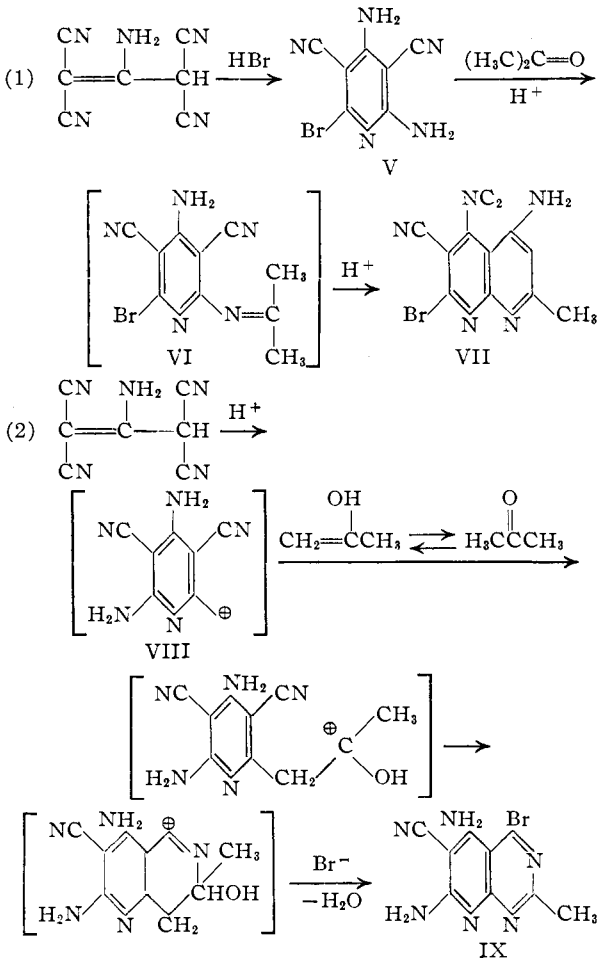
(7) Y. Urushibara, *Bull. Chem. Soc., Japan*, **2**, 278 (1927).

TABLE I

2-AMINO-6-HALO-3,5-BICYANOPYRIDINES

Pyridine Name	Formula	Method of synthesis	Reactants: Salt	Hydrogen halide	Solvent	Yield, %	Recrystn. solvent	Melting point, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
2-Amino-6-chloro-3,5-dicyano-pyridine	$C_7H_3N_4Cl$	A	$Na[(NC)_2C{=}CHC(CN)_2]\cdot H_2O$	HCl	Acetone	90	Acetone	Sublimes	47.10		1.68		31.40		19.9	
								>200		47.20		1.90		31.55		19.84
2-Amino-6-bromo-3,5-dicyano-pyridine	$C_7H_3N_4Br$	A	$Na[(NC)_2C{=}CHC(CN)_2]\cdot H_2O$	HBr	Acetone	93.5	Acetone	Sublimes	37.75		1.34		25.10		35.80	
								>200		37.90		1.56		24.96		35.57
2-Amino-6-chloro-3,5-dicyano-4-ethoxypyridine	$C_9H_7N_4OCl$	A	$Na[(NC)_2C{=}C(OEt)C(CN)_2]$	HCl	Acetone	77.7	Acetone	264–265	48.50		3.14		25 10		15.99	
									48.80		3.14		25.10		16.19	
2-Amino-6-chloro-3,4,5-tricyanopyridine	$C_8H_2N_5Cl$	B	$[(H_3C)_4N][(NC)_2C{=}C(CN)C(CN)_2]$	HCl	Acetone	69.5	EtOH–water	227–228	47.19		0.99		34.40		17.42	
									47.42		1.16		34.45		17.45	
2-Amino-6-bromo-3,4,5-tricyanopyridine	$C_8H_2N_5Br$	B	$[(H_3C)_4N][(NC)_2C{=}C(CN)C(CN)_2]$	HBr	Acetone	90	EtOH–water	229–230	38.73		0.81		28.24		32.32	
									38.72		0.95		28.31		32.01	
2-Amino-6-chloro-3,5-dicyano-4-phenylpyridine	$C_{13}H_7N_4Cl$	A	$[(H_3C)_4N][(NC)_2C{=}C(C_6H_5)C(CN)_2]$	HCl	Dioxane	87.6	Chloroform	303–308	61.3		2.78		22.00		13.99	
									60.88		2.80		22.05		14.24	
2-Amino-6-chloro-3,5-dicyano-4-(*p*-dimethylaminophenyl)-pyridine	$C_{15}H_{12}N_5Cl$	A	$[(H_3C)_4N][(NC)_2C{=}C(p\text{-}C_6H_4N(Me)_2)\text{-}C(CN)_2]$	HCl	Dioxane	86	Dimethyl-formamide	>320	60.50		4.06		23.52		11.91	
									60.68		4.30		23.53		11.98	
2-Amino-6-chloro-3,5-dicyano-4-dimethylaminopyridine	$C_9H_8N_5Cl$	A	$Na[(NC)_2C{=}C(N(Me)_2)C(CN)_2]$	HCl	Acetone	10	Ethanol	244–245	48.77		3.64		31.60		...	
									48.92		3.75		31.82		...	
2,4-Diamino-6-bromo-3,5-dicyanopyridine	$C_7H_4N_5Br$	B	 $[(NC)_2C{=}C(NH_2)C(CN)_2]$	HBr	Water	82	Ethanol	Sublimes	35.31		1.69		29.42		33.57	
								>270		35.24		1.87		29.49		33.61
2-Amino-4,6-dibromo-3,5-dicyanopyridine	$C_7H_2N_4Br_2$	A	 $[(NC)_2C{=}C(Br)C(CN)_2]$	HBr	Acetone	93	H_2O–dimethyl-formamide	>300	27.84		0.67		18.56		52.93	
									28.05		0.76		18.60		52.94	
2,4-Diamino-6-iodo-3,5-dicyanopyridine	$C_7H_4N_5I$	B	 $[(NC)_2C{=}C(NH_2)C(CN)_2]$	HI	Water	72	H_2O–dimethyl-formamide	>300	29.50		1.41		24.57		44.52	
									30.24		1.68		24.33		44.32	
2,4-Diamino-6-chloro-3,5-dicyanopyridine	$C_7H_4N_5Cl$	A	 $[(NC)_2C{=}C(NH_2)C(CN)_2]$	HCl	Acetonitrile	52	H_2O–dimethyl-formamide	>300	43.42		2.08		36.18		...	
									43.68		2.37		36.15		...	

of acetone. However, an attempt to convert V to the bromonaphthyridine VII by saturating a suspension of the bromopyridine V in acetone with hydrogen bromide was unsuccessful, thus indicating that IX may be the product formed in this reaction



and that the intermediate VIII is common to the formation of both the pyridine and the naphthyridine. At present, the structure of the naphthyridine is in doubt.

Experimental

2-Amino-6-halo-3,5-dicyanopyridines.—The 2-amino-6-halo-3,5-dicyanopyridines listed in Table I were prepared by treating a salt of a 1,1,3,3-tetracyanopropene with either an anhydrous hydrogen halide or a concentrated aqueous solution of the hydrogen halide.[8] Syntheses of pyridines using both methods are illustrated by the following typical examples.

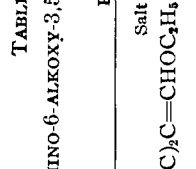
Method A. 2-Amino-6-chloro-3,5-dicyanopyridine.—A solution of 9.1 g. (0.05 mole) of the sodium salt of 1,1,3,3-tetracyanopropene in 500 ml. of acetone was saturated with hydrogen chloride by passing in an excess of the gas during a period of 20 minutes. A precipitate of 2.9 g. of sodium chloride formed and was removed by filtration. The filtrate was allowed to stand at room temperature for two days, during which time 8.5 g. (90%) of 2-amino-6-chloro-3,5-dicyanopyridine slowly crystallized. It was separated by filtration. This white crystalline solid sublimes without melting at 200°.

Method B. 2-Amino-6-chloro-3,4,5-tricyanopyridine.—A solution of 18 g. of tetramethylammonium 1,1,2,3,3-pentacyanopropenide in 100 ml. of acetone and 100 ml. of 36%

(8) E. L. Little, Jr., and W. J. Middleton, U. S. Patent 2,790,805, April 30, 1957.

TABLE II

2-AMINO-6-ALKOXY-3,5-DICYANOPYRIDINES

Pyridine Name	Formula	Method of synthesis	Reactants Salt	Solvent	Yield, %	Recrystn. solvent	Melting point, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2-Amino-6-ethoxy-3,5-dicyanopyridine	$C_9H_8N_4O$	C	$(NC)_2C{=}CHOC_2H_5 + Na[HC(CN)_2]$	Ethanol	96	Ethanol	223–224	57.40	57.22	4.25	4.25	29.70	29.75
2-Amino-6-ethoxy-3,4,5-tricyanopyridine	$C_{10}H_7N_5O$	B	$[(H_3C)_4N][(NC)_2C{=}C(CN)_2] + C_2H_5OH$ (CN)	Ethanol	75	Ethanol	231	56.33	56.42	3.31	3.32	32.85	32.83
2-Amino-6-isopropoxy-3,4,5-tricyanopyridine	$C_{11}H_9N_5O$	B	$[(H_3C)_4N][(NC)_2C{=}C(CN)_2] + H_3CCHCH_3$ (CN, OH)	*i*-PrOH	31	Ethanol	255–257	58.14	58.43	3.99	4.17	30.82	30.85
2-Amino-6-methoxy-3,5-dicyano-4-phenylpyridine	$C_{14}H_{10}N_4O$	A	 + $NaOCH_3$	Methanol	85.7	$CHCl_3$	259–261	67.20	66.87	4.03	4.12	22.40	22.48
2-Amino-6-ethoxy-3,5-dicyano-4-phenylpyridine	$C_{15}H_{12}N_4O$	A	Same + $NaOC_2H_5$	Ethanol	93.4	$CHCl_3$	238–239	68.16	68.12	4.58	4.53	21.20	21.23

hydrochloric acid was heated to boiling for 10 minutes. The solution was cooled and the precipitate which formed was collected on a filter and recrystallized from ethyl alcohol–water. There was obtained 11.0 g. of 2-amino-6-chloro-3,4,5-tricyanopyridine in the form of very light yellow needles, m.p. 227–228°.

2-Amino-6-alkoxy-3,5-dicyanopyridines.—The 2-amino-6-alkoxy-3,5-dicyanopyridines listed in Table II were prepared by treating a halopyridine with sodium alkoxide, by reaction of a salt of 1,1,3,3-tetracyanopropene with an alcohol in the presence of sulfuric acid, or by reaction of the sodium salt of malononitrile with an alkoxydicyanoethylene. Syntheses of pyridines using these methods are illustrated by the following typical examples.

Method A. 2-Amino-6-methoxy-3,5-dicyano-4-phenylpyridine.—A solution of 0.5 g. of 2-amino-6-chloro-3,5-dicyano-4-phenylpyridine and 0.2 g. of sodium methoxide in 30 ml. of methanol was heated under reflux for 75 minutes. The solution was cooled and poured onto ice. The white precipitate was filtered, washed with water and dried to give 0.42 g. (85.7%) of crude 2-amino-6-methoxy-3,5-dicyano-4-phenylpyridine. Recrystallization from chloroform yielded colorless, microcrystalline needles which melted at 259–261°.

Method B. 2-Amino-6-ethoxy-3,4,5-tricyanopyridine.—A mixture of 12.0 g. (0.05 mole) of tetramethylammonium 1,1,2,3,3-pentacyanopropenide, 3.0 ml. (0.052 mole) of concentrated sulfuric acid and 250 ml. of ethyl alcohol was heated under reflux for 3 days. The solution was poured into 600 ml. of hot water, and the light yellow precipitate was collected on a filter, washed with hot water and dried. There was obtained 8 g. (75%) of crude 2-amino-6-ethoxy-3,4,5-tricyanopyridine, m.p. 200–210°. A portion of this product was recrystallized from ethyl alcohol to give a purer sample in the form of long, nearly white needles, m.p. 231°.

Method C. 2-Amino-6-ethoxy-3,5-dicyanopyridine.—A solution of 30 g. (0.25 mole) of ethoxymethylenemalononitrile in 100 ml. of ethyl alcohol was added slowly to a solution of 22.5 g. (0.25 mole) of the sodium salt of malononitrile in 175 ml. of ethyl alcohol. A crystalline precipitate slowly formed. This solid was filtered and recrystallized from ethyl alcohol to yield 45 g. (96%) of 2-amino-6-ethoxy-3,5-dicyanopyridine which melted at 223–224°. When the reaction described above was carried out in an ice-bath, 46 g. (90%) of the sodium salt of 1,1,3,3-tetracyanopropene was obtained.

2,6-Diamino-3,5-dicyanopyridines.—The 2,6-diamino-3,5-dicyanopyridines listed in Table III were prepared by treating 2-amino-6-halo-3,5-dicyanopyridines with amines.[9] Synthesis of these diaminopyridines is illustrated by the following typical example.

2,6-Diamino-3,4,5-tricyanopyridine.—A solution of 5.0 g. of 2-amino-6-chloro-3,4,5-tricyanopyridine in 25 ml. of acetone was saturated with anhydrous ammonia. A yellow precipitate formed; 50 ml. of water was added, the mixture was cooled and the yellow precipitate was collected on a filter. This material was washed with water and recrystallized from dimethylformamide–water to give 30 g. (95%) of 2,6-diamino-3,4,5-tricyanopyridine in the form of yellow needles which sublimed above 250°.

Salts of 2-Amino-6-dicyanomethyl-3,5-dicyanopyridines.—The salts of 2-amino-6-dicyanomethyl-3,5-dicyanopyridines listed in Table IV were prepared by mixing an aqueous solution of the crude sodium salt of the 2-amino-6-dicyanomethyl-3,5-dicyanopyridine with an aqueous solution of an appropriate salt. Synthesis of the crude sodium salt of the pyridine and its conversion to another salt is illustrated by the following typical example.

Tetraethylammonium Salt of 2-Amino-6-dicyanomethyl-3,4,5-tricyanopyridine.—An ethyl alcohol solution of the sodium salt of malononitrile was prepared by dissolving 1.15 g. (0.05 mole) of sodium in 100 ml. of ethyl alcohol, and then adding 3.3 g. (0.05 mole) of malononitrile. To this solution was added 6.2 g. (0.025 mole) of 2-amino-6-bromo-3,4,5-tricyanopyridine, and the mixture was stirred until all the solid went into solution. After standing at room temperature for one hour, a yellow-orange precipitate of the crude sodium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine formed. This solid was collected on a filter, washed with a small amount of ethyl alcohol and dissolved in 50 ml. of water. To this aqueous solution was added a solution of 10.9 g. (0.05 mole) of tetraethylammo-

(9) W. J. Middleton, U. S. Patent 2,794,803, June 4, 1957.

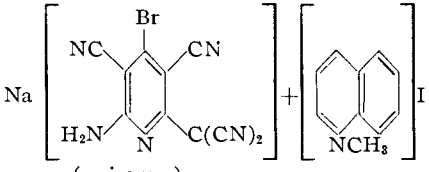
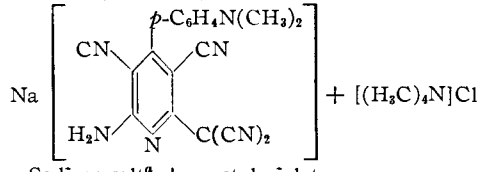
TABLE III

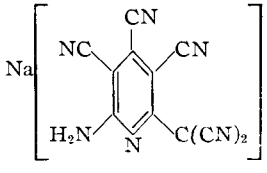
2,6-DIAMINO-3,5-DICYANOPYRIDINES

Name	Formula	Reactants: Pyridine	Reactants: Amine	Solvent	Yield, %	Recrystn. solvent	Melting point, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
2,6-Diamino-3,5-dicyanopyridine	$C_7H_5N_5$	2-Amino-6-chloro-3,5-dicyanopyridine	Aq. ammonia	Acetone	58	.....	Sub. >200	52.85	52.79	3.15	3.16	...	...
2,6-Diamino-3,4,5-tricyanopyridine	$C_8H_4N_6$	2-Amino-6-chloro-3,4,5-tricyanopyridine	Anhyd. ammonia	Acetone	95	H_2O–dimethylformamide	Sub. >250	52.17	52.44	2.19	2.32	45.64	45.69
2-Amino-6-methylamino-3,4,5-tricyanopyridine	$C_9H_6N_6$	2-Amino-6-chloro-3,4,5-tricyanopyridine	Aq. methylamine	Acetone	88	H_2O–dimethylformamide	Sub. >250	54.54	54.33	3.05	3.05	42.41	42.39
2-Amino-6-piperidino-3,4,5-tricyanopyridine	$C_{13}H_{12}N_6$	2-Amino-6-chloro-3,4,5-tricyanopyridine	Piperidine	Acetone	70	Ethanol	218	61.89	61.90	4.91	4.74	33.32	33.34
2-Amino-6-anilino-3,4,5-tricyanopyridine	$C_{14}H_8N_6$	2-Amino-6-bromo-3,4,5-tricyanopyridine	Aniline	Ethanol	71	Ethanol	275	64.62	64.92	3.10	3.30	32.30	32.28
2-Amino-6-*p*-chloroanilino-3,4,5-tricyanopyridine	$C_{14}H_7N_6Cl$	2-Amino-6-bromo-3,4,5-tricyanopyridine	*p*-Chloroaniline	Acetone	88	H_2O–dimethylformamide	315–316	57.05	56.94	2.39	2.34	28.52	28.54
2-(6-Amino-3,4,5-tricyanopyridyl)-dimethyldodecylammonium chloride	$C_{22}H_{33}N_6Cl$	2-Amino-6-chloro-3,4,5-tricyanopyridine	Dimethyldodecylamine	Acetone	92	.....	.....	63.36	63.65	7.98	8.10	20.16	20.32
N-(2-[6-Amino-3,4,5-tricyanopyridyl])-quinolium chloride	$C_{17}H_9N_6Cl$	2-Amino-6-chloro-3,4,5-tricyanopyridine	Quinoline	Acetone	96	EtOH–water	189–192	61.36	61.36	2.73	2.65	25.26	25.30

TABLE IV

SALTS OF 2-AMINO-6-DICYANOMETHYL-3,5-DICYANOPYRIDINES

Name	Formula	Reactants	Recrystn. solvent	Melting point, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Tetraethylammonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine	$C_{19}H_{22}N_8$	Sodium salt[a] + $[(C_2H_5)_4N]Br$	Water	190–191	62.96	62.91	6.12	6.15	30.96	30.92
Tetramethylammonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine	$C_{15}H_{14}N_8$	Sodium salt[a] + $[(H_3C)_4N]Cl$	Water	>300	58.81	59.29	4.61	4.80	36.59	36.61
Trimethylsulfonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine	$C_{14}H_{11}N_7S$	Sodium salt[a] + $[(H_3C)_3S]I$	Water	.....	54.35	54.46	3.58	3.55	31.70	31.77
Cupric salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine	$CuC_{22}N_{14}H_4 \cdot {}^1/_2H_2O$[b]	Sodium salt[a] + $CuSO_4$	Water	.....	49.30	49.39	0.93	1.05	36.50	36.72
Cobaltous salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine	$CoC_{22}H_{14}N_4 \cdot 8H_2O$[c]	Sodium salt[a] + $CoSO_4$	Water	.....	39.60	40.19	3.00	3.01	29.40	29.74
N-Methylquinolinium salt of 2-amino-4-(or 2)-bromo-2-(or 4)-3,5-dicyanopyridine	$C_{20}H_{12}N_7Br$	 (or isomer)	Water	Dec. >260	55.84	56.11	2.81	2.96	22.79	22.63
Tetramethylammonium salt of 2-amino-6-dicyanomethyl-4-(*p*-dimethylaminophenyl)-3,5-dicyanopyridine	$C_{22}H_{24}N_8$	 + $[(H_3C)_4N]Cl$	MeOH	>300	65.98	66.18	6.04	6.04	27.98	28.07
Tris-(*p*-dimethylaminophenyl)-carbonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine	$C_{36}H_{32}N_{10}$	Sodium salt[a] + crystal violet	*n*-BuOH	208–209	71.50	71.70	5.33	5.35	23.17	23.16

[a]  [b] Calcd.: Cu, 11.85. Found: Cu, 12.37. [c] Calcd.: Co, 8.83. Found: Co, 8.58.

nium bromide in 50 ml. of water. The orange precipitate which formed was collected on a filter, washed with water and recrystallized from water. There was obtained 6.5 g. of the tetraethylammonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine in the form of orange, matted needles, m.p. 190–191°.

2-Amino-6-dicyanomethyl-3,4,5-tricyanopyridine.—A solution of 30 g. of the tetraethylammonium salt of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine in 500 ml. of acetone was passed slowly through a column packed with a sulfonic acid ion exchange resin. Evaporation of the effluent yielded 20 g. of 2-amino-6-dicyanomethyl-3,4,5-tricyanopyridine in the form of a light yellow solid which melted above 300°.

Anal. Calcd. for $C_{11}H_3N_7$: C, 56.70; N, 42.00; neut. equiv., 233. Found: C, 56.95; N, 41.80; neut. equiv., 240.

2-Amino-6-benzenesulfonyl-3,4,5-tricyanopyridine.—To a solution of 3.28 g. (0.02 mole) of sodium benzenesulfinate in 20 ml. of 50% ethyl alcohol was added a hot solution of 4.07 g. (0.02 mole) of 2-amino-6-chloro-3,4,5-tricyanopyridine in 100 ml. of ethyl alcohol. The solution was heated under reflux for 5 minutes and then cooled. The precipitated salt was removed by filtration, and the filtrate was mixed with 300 ml. of cold water. The yellow precipitate which formed was collected on a filter, washed with water, and recrystallized from ethyl alcohol. There was obtained 3.5 g. of 2-amino-6-benzenesulfonyl-3,4,5-tricyanopyridine in the form of yellow needles, m.p. 254–256° dec.

Anal. Calcd. for $C_{14}H_7N_5SO_2$: C, 54.36; H, 2.29; N, 22.64; S, 10.36. Found: C, 54.24; H, 2.59; N, 22.59; S, 10.27.

Bromodiaminocyanomethylnaphthyridine.—A solution of 3.0 g. (0.01 mole) of N-methylquinolinium 2-amino-1,1,3,3-tetracyanopropenide in 50 ml. of acetone was saturated with anhydrous hydrogen bromide. The solution was cooled and mixed with 150 ml. of water. The precipitate which formed was collected on a filter, washed with water and then alcohol, and dried. There was obtained 2.0 g. (72%) of a very light yellow crystalline solid which sublimed above 235° and decomposed slowly above 250°.

Anal. Calcd. for $C_{10}H_5N_5Br$: C, 43.19; H, 2.90; N, 25.18; Br, 28.74. Found: C, 43.18; H, 2.97; N, 25.07; Br, 28.19.

Aminobromocyanomethyl-(methylamino)-naphthyridine.—A mixture of 2.0 g. of sodium 2-methylamino-1,1,3,3-tetracyanopropenide in 50 ml. of acetone was saturated with anhydrous hydrogen bromide. The reaction was exothermic. The hot solution was filtered, and the filtrate was cooled to 0°, and mixed with 100 ml. of water. The solid which separated was collected on a filter, washed with alcohol, and dried. There was obtained 0.93 g. (33%) of aminobromocyanomethyl-(methylamino)-naphthyridine in the form of light yellow crystalline solid, m.p. 207–208°.

Anal. Calcd. for $C_{11}H_{10}N_5Br$: C, 45.22; H, 3.45; N, 23.97; Br, 27.36. Found: C, 45.25; H, 3.35; N, 24.08; Br, 27.59.

Chlorocyanodiaminomethylnaphthyridine.—A solution of 5.0 g. of tetraethylammonium 2-amino-1,1,3,3-tetracyanopropenide in 25 ml. of acetone was saturated with anhydrous hydrogen chloride, and then mixed with 100 ml. of ice-water. The crystals which formed upon standing were collected on a filter and washed with water. There was obtained 3.0 g. (70%) of chlorocyanodiaminomethylnaphthyridine in the form of white needles which sublimed above 240° and decomposed slowly above 260°.

Anal. Calcd. for $C_{10}H_5N_5Cl$: C, 51.40; H, 3.45; N, 29.98; Cl, 15.17. Found: C, 51.18; H, 3.62; N, 30.05; Cl, 15.18.

WILMINGTON, DELAWARE

[CONTRIBUTION NO. 445 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Cyanocarbon Chemistry. XI.[1] Malononitrile Dimer

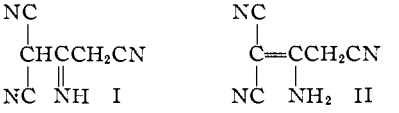
BY R. A. CARBONI, D. D. COFFMAN AND E. G. HOWARD

RECEIVED NOVEMBER 14, 1957

Malononitrile dimer, 2-amino-1,1,3-tricyanopropene, has been prepared by several routes, including dimerization of malononitrile in the presence of bases and acids. Some reactions of the dimer are described.

A variety of nitriles have been converted to dimers and trimers by means of alkaline or acidic reagents. For example, mononitriles such as acetonitrile and propionitrile have been dimerized to 3-iminobutyronitrile and 2-methyl-3-iminovaleronitrile, respectively, by treatment with sodium followed by hydrolysis of the resulting sodium derivatives with water.[2] Cyclic trimers of acetonitrile and propionitrile[3] and of malononitrile[4] have been formed by treatment of the monomers with sodium alkoxides and other bases. This paper describes the preparation and some of the properties of 2-amino-1,1,3-tricyanopropene (hereafter called "malononitrile dimer") under both acidic and alkaline conditions.

The dimer was obtained conveniently by treating a solution of malononitrile in an inert solvent such as ether or tetrahydrofuran with sodium and hydrolyzing the resulting solid with a strong mineral acid at 5°. Elemental analyses and molecular weight determinations are in accord with the formula $C_6H_4N_4$. The product, m.p. 172–173°, which presumably forms through a Thorpe type reaction between two molecules of the dinitrile may be formulated as I or II. The spectral evidence favors



the ene–amine structure II as the predominant form. The infrared spectrum shows three bands at 4.22, 4.51 and 4.55 μ which are associated with the unconjugated and conjugated nitrile groups, respectively. A pair of bands at 2.98 and 3.10 μ are attributed to the amino function.

The dimer also was formed when dry hydrogen chloride was passed through a benzene solution of malononitrile. When hydrogen bromide was employed, the reaction proceeded vigorously to give a nitrile-substituted 2,4-diamino-6-bromopyridine (III).[1] Since the same product resulted when the dimer was used rather than malononitrile, the re-

(1) Paper X, E. L. Little, W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, THIS JOURNAL, 80, 2832 (1958).

(2) R. J. Holtzwart, *J. prakt. Chem.*, [2] 39, 230 (1889); H. Adkins and G. M. Whitman, THIS JOURNAL, 64, 150 (1942).

(3) R. Schwarze, *J. prakt. Chem.*, [2] 42, 1 (1890).

(4) R. Schenck and H. Finken, *Ann.*, 462, 267 (1928).