graphed, the most polar fluorescent band cut out, the paper triturated with methanol, and the methanol extract concentrated to near dryness. Water and chloroform were added; the chloroform extract was washed with water, dried over magnesium sulfate, and concentrated to dryness. The crystalline residue (52 mg.) on crystallization from acetone–ether gave pure (+)-7-fluoro-7-dechlorogriseofulvin (VI), m.p. 210–212°; $[\alpha]^{\mathrm{cbf}}_{\mathrm{D}}$ +316° (*c* 0.610); ultraviolet, infrared, n.m.r. spectra, and mobility on paper and alumina (thin layer chromatography) were identical with (±)-VI.

Anal. Calcd. for $C_{17}H_{17}O_6F$: C, 60.71; H, 5.09; F, 5.65. Found: C, 60.74; H, 5.30; F, 5.60.

Dicyanoketenimine (Cyanoform) and Its Reduction Products

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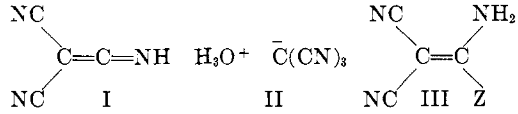
Contribution No. 856 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

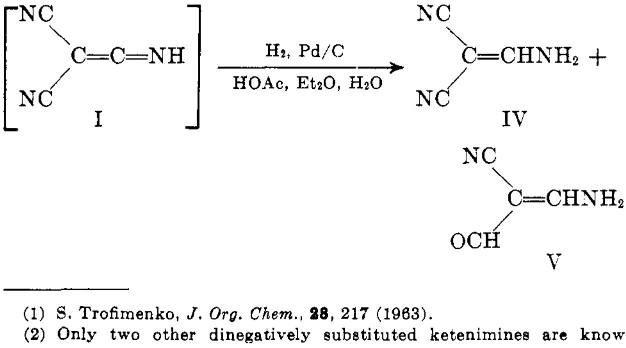
Received April 25, 1963

Aquoethereal cyanoform has been catalytically reduced to yield 3-amino-2-cyanoacrolein and 3-amino-2-cyanoacrylonitrile. Their properties and reactions are discussed, as is the mechanism of cyanoform reduction. High pressure reduction of 3-amino-2-cyanoacrylonitrile gives 2-amino-3,5-dicyanopyridine.

Cyanoform exists as dicyanoketenimine (I) in the free state and as hydronium tricyanomethanide (II) in aqueous or aquoethereal solutions.[1] Nevertheless, the addition of various active hydrogen compounds, HZ, to solutions of cyanoform, with the formation of compounds III, indicates the existence of an equilibrium between the ionized form and dicyanoketenimine. The catalytic hydrogenation of aquoethereal cyanoform was undertaken in order to gain insight into the nature of this unusual ketenimine,[2] especially since catalytic reduction of such systems as $R_2C{=}C{=}NH$ or $R_2C{=}C{=}CH_2$, has, to our knowledge, not been studied.[3] It was expected that the ease of hydrogen uptake and the structure of the products would be of diagnostic value.



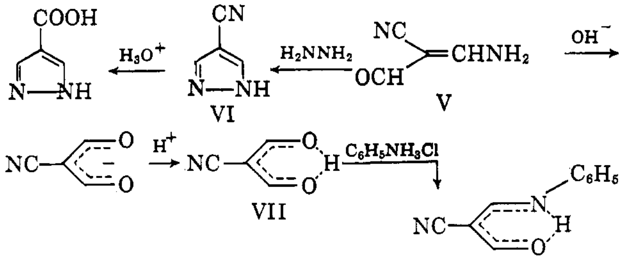
The reduction of aquoethereal cyanoform in the presence of acetic acid and 10% palladium-on-carbon catalyst proceeded very readily at room temperature and low hydrogen pressure. Two products were isolated. The major one was the expected 3-amino-2-cyanoacrylonitrile (IV) easily identified by comparison with authentic material.[4a,b] The other product, obtained in yields up to 50%, was assigned the structure 3-amino-2-cyanoacrolein (V) from spectral and chemical data as outlined.

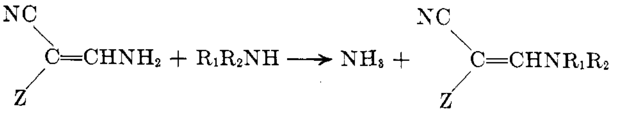


Analysis and molecular weight determination established the formula as $C_4H_4N_2O$. The infrared spectrum showed the presence of an NH_2 group and a conjugated nitrile. The n.m.r. spectrum had three peaks at 1.01, 1.35, and 2.15 τ with relative areas 1:2:1, assigned to the formyl, amino, and vinyl protons, respectively. This evidence was compatible only with structure V and was confirmed further by the following chemical studies.

The presence of the formyl group in V and its N-substituted derivatives was attested by positive, although sluggish, tests with 2,4-dinitrophenylhydrazine.[5]

Compound V reacted readily with hydrazine to form the new 4-cyanopyrazole (VI) identified by its hydrolysis to the known 4-pyrazolecarboxylic acid.[6] Mild alkaline hydrolysis of V yielded the sodium salt of cyanomalonaldehyde as a monohydrate which was converted to the free acid VII and to its reported monoanil.[7] Finally, both IV and V reacted with aliphatic amines to give N-substituted products, VIII and IX, the ultraviolet and n.m.r. spectra of which indicated considerable structural similarity.





IV, Z = CN
V, Z = CHO

VIII, Z = CN
IX, Z = CHO

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[1] S. Trofimenko, *J. Org. Chem.*, **28**, 217 (1963).

[2] Only two other dinegatively substituted ketenimines are known: dialkylsulfonylketenimine [R. Dijkstra and H. J. Backer, *Rec. trav. chim.*, **73**, 569 (1954)] and dinitroketenimine [C. O. Parker, W. D. Emmons, H. A. Rolewicz, and K. C. McCallum, *Tetrahedron*, **15**, 79 (1962)]. Both are strong acids and resemble cyanoform in many respects.

[3] Catalytic hydrogenation of nonterminal allenes has been reported [W. R. Moore, *J. Am. Chem. Soc.*, **84**, 3788 (1962)]; so has the metal–ammonia reduction of, among others, terminal allenes [D. Devaprabhakhara and P. D. Gardner, *ibid.*, **87**, 648 (1963)].

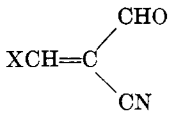
[4] (a) O. Diels, H. Gärtner, and R. Kaack, *Ber.*, **77**, 3429 (1922); (b) M. J. Kamlet, *J. Org. Chem.*, **24**, 714 (1959).

[5] However, 3-dialkylaminoacroleins are reported not to condense with 2,4-dinitrophenylhydrazine [Z. Arnold and F. Sorm, *Collection Czech. Chem. Commun.*, **23**, 452 (1958)].

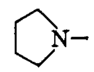
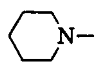
[6] R. G. Jones, *J. Am. Chem. Soc.*, **51**, 3994 (1948).

[7] F. C. Uhle and W. L. Jacobs, *J. Org. Chem.*, **10**, 81 (1945).

TABLE I

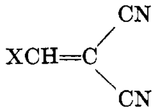
COMPOUNDS OF THE TYPE 

$XCH{=}C(CHO)(CN)$

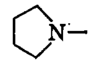
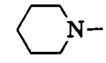
N.m.r.,[a] τ	X	Yield, %	M.p.,[b] °C.	Calcd.			Found			λ_{max}, mμ	log ε
				C	H	N	C	H	N		
1.01 2.15	H_2N–	40–48	215–216[c]	50.0	4.20	29.2	50.2	4.06	29.0	269	4.31
0.70 2.23	*t*-BuNH–	95	122–123[d]	63.1	7.95	18.4	63.6	8.00	18.9	281	4.38
0.91 2.32		87	114–115	64.0	6.71		63.9	6.72		282	4.62
0.81 2.73	CH_3NH–	61	118–119	57.5	5.49		54.4	6.31		277	4.46
0.78 2.57	$(CH_3)_2N$–	85	144–145	58.1	6.50		58.2	6.47		281	4.65
0.86 2.57		68	105–106	65.8	7.34		65.5	7.50		282	4.48

[a] Position of the formyl and vinyl protons, respectively. For X = *t*-BuNH and CH_3NH, the vinyl protons were poorly resolved and the values given are approximate. [b] The compounds were recrystallized from aqueous ethanol. [c] Recrystallized from water. [d] Sublimed.

TABLE II

COMPOUNDS OF THE TYPE 

$XCH{=}C(CN)(CN)$

N.m.r.,[a] τ	X	Yield, %	M.p.,[b] °C.	Calcd.		Found		λ_{max} mμ	log ε
				C	H	C	H		
	H_2N–		147–148[c]					267	4.11[d]
2.58	*t*-BuNH–	71	180–182	64.4	7.43	64.5	7.42	278	4.14
2.66		47	90–92	65.4	6.16	65.4	6.32	282	4.48
2.20	CH_3NH–	92	191–192	56.0	4.71	55.6	4.75	277	4.29
2.91	$(CH_3)_2N$	30[d]	83–84	59.5	5.82	59.9	5.84	282	4.50
2.92		51	93–94	67.1	6.88	67.1	6.78	282	4.36

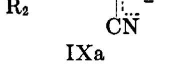
[a] Values for vinyl protons. For X = *t*-BuNH it is given for the strongest peak in the vinyl region; in the case of X = CH_3NH for the center of the strongest doublet. [b] All materials were recrystallized from aqueous ethanol. [c] Material purified by fractional sublimation. [d] This low yield was due largely to solubility losses. No attempt was made to obtain maximum yields.

This reaction is influenced by steric factors. While primary amines and relatively unhindered secondary amines, such as piperidine or dimethylamine, reacted rapidly at room temperature, diethylamine required heating, and diisopropylamine did not react at all. The ultraviolet spectra of compounds VIII and IX are generally similar and exhibit analogous bathochromic shifts and increases in extinction coefficients with increasing substitution on the amino group (Tables I and II).

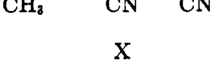
The n.m.r. spectra of compounds VIII and IX were consistent with the proposed structures; they also provided an indication that these compounds ($R_1 \neq H$, $R_2 \neq H$)[8] exist largely in zwitterionic forms.

VIIIa

and



IXa



X

Thus, it was found that VIII ($R_1 = R_2 = CH_3$) has at room temperature two methyl peaks at 6.65 and 6.77 τ coalescing into a singlet at 80°; similarly IX ($R_1 = R_2 = CH_3$) has at room temperature two methyl peaks at 6.55 and 6.68 τ coalescing at 100°. The case is quite analogous to that of N,N-disubstituted amides.[9] It is noteworthy, however, that dimethylaminotricyanoethylene (X) has only a single peak at 6.38 τ. It seems that formation of the zwitterion, responsible for the nonidentity of methyl groups, is prevented in X by steric interference of the methyl hydrogens and the nitrile group, as can be seen from Stuart–Briegleb models, which also show VIIIa to be unhindered.

All these findings unequivocally determine the structure of V if not its genesis. To test for possible intermediacy of IV in the formation of V, the former was subjected to the conditions under which aquoethereal cyanoform was readily hydrogenated. No reaction took place until the conditions were made much more drastic (1000–1500 p.s.i., 70–80°). A product $C_7H_4N_4$

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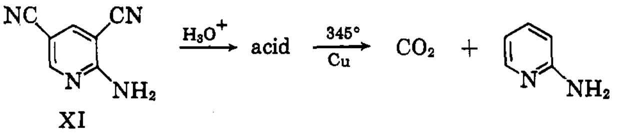
(8) The same holds true for compounds where $R_1 \neq H$, $R_2 = H$, but the n.m.r spectra are more complicated due to coupling of the NH proton with the vinyl and alkyl (where applicable) protons. The spectra of these compounds indicated the preponderance of one stereoisomer. They were not analyzed in detail.

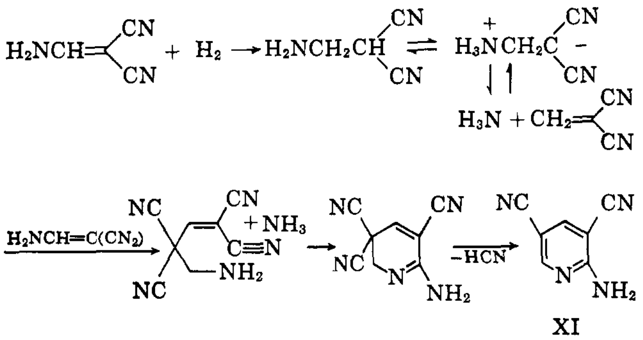
(9) For a general discussion of nonequivalence of identical groups due to hindered rotation see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 366 ff.

was obtained which was assigned the 2-amino-3,5-dicyanopyridine (XI) structure from the following considerations.

The infrared spectrum of the compound contained conjugated nitrile and amino bands. The material was a weak base and could be sublimed, properties more expected of a pyridine structure than of an isomeric straight chain compound.[10] From *a priori* mechanistic considerations one would expect the formation of either 2-amino-3,5-dicyanopyridine or 4-amino-3,5-dicyanopyridine, depending on whether the condensation took place "head to head" or "head to tail." Acid hydrolysis of XI yielded a carboxylic acid that was decarboxylated to 2-aminopyridine, thus locating unequivocally the position of the amino group.

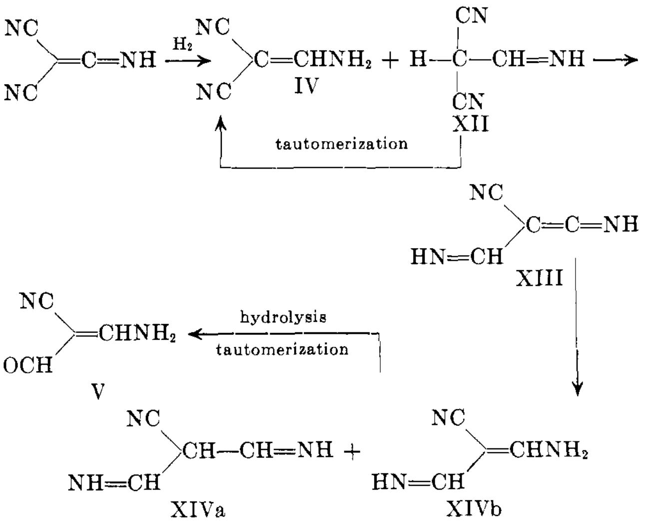


The following is a likely path for the formation of X.



Discussion

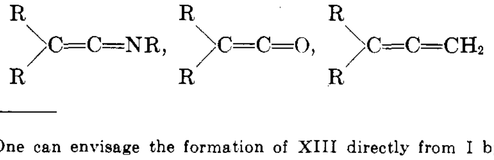
Several facts must be considered to establish the path by which V is formed. The species that is reduced has to be uncharged, since tricyanomethanide ion (aqueous solution of the potassium salt) remained inert under conditions where aquoethereal cyanoform absorbed hydrogen rapidly. Of the two possible tautomers dicyanoketenimine and tricyanomethane, one would expect the latter to be a poor hydrogenation substrate due to "catalyst hindrance"[11] as the sp³ geometry at the central carbon would effectively impede activating adsorption on the catalyst surface. Moreover, the nitrile group is normally not reduced under mild conditions with palladium catalyst.[12] On the other hand, one would expect dicyanoketenimine (I) to be devoid of "catalyst hindrance." In view of the rapid hydrogenation of aquoethereal cyanoform, the conclusions are that (1) dicyanoketenimine exists as a real species in equilibrium with the solvated ion pair and (2) the formation of V proceeds *via* hydrogenation of dicyanoketenimine and may be represented as shown in the above scheme.



The first reduction step could yield either IV or XII. Since IV is known to be unreactive under the conditions employed, the formation of V must proceed through iminomethylmalononitrile (XII). This material can tautomerize in two ways: to the inert IV or to the new ketenimine XIII.[13] Reduction of the latter to either XIVa or XIVb would yield a product that only need be hydrolyzed (with tautomerization in the former case) to produce V.

Although a number of studies on ketenimines and their addition reactions has been made,[14] no addition of hydrogen has been reported. Similarly no reports of selective reduction of 1,1-disubstituted allenes or ketenes could be found. While experimental data on catalytic hydrogenation of these cumulative systems are lacking, certain predictions can be made on theoretical grounds.

If it is assumed that the key step in the reduction is the adsorption of the substrate on the catalyst surface, dicyanoketenimine would be adsorbed with all atoms coplanar.[15] Such an arrangement would only allow effective surface interaction with the π-orbitals of the ketenimine C=C bond and, hence, should favor the formation of XII over IV. The same reasoning is applicable to XIII and to other systems such as the following.



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[10] A similar problem had been previously encountered. E. L. Little, Jr., W. J. Middleton, D. D. Coffman, V. A. Engelhardt, and G. N. Sausen, *J. Am. Chem. Soc.*, **80**, 2832 (1958).

[11] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *ibid.*, **64**, 1985 (1942). See also E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 350 ff.

[12] For instance, acrylonitrile is readily hydrogenated to propionitrile [I. N. Kazarov and G. A. Shvekhgeimer, *Zh. Priklad. Khim.*, **32**, 1177 (1959)] and ethylidenemalononitrile to ethylmalononitrile (S. Trofimenko, unpublished results). In each case, hydrogen absorption ceases after one mole has been absorbed.

[13] One can envisage the formation of XIII directly from I by a 1,4-addition of hydrogen across the conjugated nitrile system, as has been pointed out by a referee. Although such an addition to α,β-unsaturated ketones has been reported [K. Hensler, P. Wieland, and A. Wettstein, *Helv. Chim. Acta*, **42**, 1586 (1959)], it would have no precedent in the nitrile case. Nevertheless, it may be considered as an alternative for lack of experimental data to the contrary.

[14] (a) H. Staudinger and E. Hauser, *ibid.*, **4**, 887 (1921); H. Staudinger and J. Meyer, *Ber.*, **53**, 72 (1920); (b) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657, (1953); **76**, 4398 (1954); (c) R. Dijkstra and J. Backer, *Rec. trav. chim.*, **72**, 813 (1963); **73**, 569, 575, 695 (1954); (d) M. S. Newman, F. Fukunaga, and T. Miwa, *J. Am. Chem. Soc.*, **82**, 873 (1960).

[15] The hydrogen atom is not only of low steric significance but is probably collinear with the C=C=N sequence [R. K. Bullough and P. J. Wheatley, *Acta Cryst.*, **10**, 233 (1957)].

Experimental

Reduction of Aquoethereal Cyanoform. 3-Amino-2-cyanoacrolein (V) and 3-Amino-2-cyanoacrylonitrile (IV). A.—Aquoethereal cyanoform was prepared as previously described.[16] According to Hantzsch and Osswald[17] the composition of aquoethereal cyanoform is $HC(CN)_3$–H_2O–ether in 1:10:10 ratio. Seventy-nine grams (0.079 mole) of this solution was mixed with 1 g. of 10% palladium on charcoal and 10 g. of acetic acid and was hydrogenated in a Parr apparatus at 40 p.s.i. Hydrogen absorption was rapid and ceased in about an hour. The reaction mixture contained a white solid which was filtered and purified by crystallization from boiling water to give 3.5 g. (47%) of fluffy needles of 3-amino-2-cyanoacrolein. After recrystallization from water, the material melted with decomposition at 215–216°.

Anal. Calcd. for $C_4H_4N_2O$: C, 50.0; H, 4.20; N, 29.2; mol. wt., 96.0. Found: C, 50.2; H, 4.06; N, 29.0; mol. wt., 91, 88 (ebullioscopic in acetone).

The infrared spectrum was 3.04, 3.20, 4.49, 5.89, 6.13, 6.23, 7.08, 7.26, 7.94, 9.60, 9.99, 12.20, and 13.67 μ. Evaporation of the mother liquor from the reduction mixture gave crude 3-amino-2-cyanoacrylonitrile.

B.—Aquoethereal cyanoform was prepared by dissolving 13 g. of potassium tricyanomethanide in 80 ml. of water, adding 250 ml. of ether, and acidifying carefully with 10 g. of concentrated sulfuric acid at 5–10°. The entire middle layer was combined with 0.4 g. of 10% palladium on charcoal and 4 ml. of acetic acid and hydrogenated as in the preceding section. The product was evaporated to dryness, and the residue crystallized from boiling water, the hot mixture being filtered to remove the catalyst. The yield of 3-amino-2-cyanoacrolein was 3.7 g. (40%).

Reaction of 3-Amino-2-cyanoacrolein with Amines. Compounds of the Type VIII.—The substituted amino derivatives of V were prepared by treating V with an excess of the appropriate amine either without a solvent or using an inert solvent such as tetrahydrofuran or glyme (1,2-dimethoxyethane). The solvent and excess amine were removed *in vacuo* and residue was purified by crystallization or sublimation. Most of the reactions were moderately exothermic and rapid. Data on compounds VIII are given in Table I.

With diethylamine ammonia was not evolved until the solution was heated to 90°; with diisopropylamine no reaction occurred even after heating for several hours, and the starting material was recovered unchanged.

Reaction of 3-Amino-2-cyanoacrylonitrile with Amines. Compounds of the Type IX.—Compounds of the type IX were prepared as outlined previously; their properties are summarized in Table II. The same materials were obtained when 3-ethoxy-2-cyanoacrylonitrile was used as the starting material.

Dimethylaminotricyanoethylene (X).—This compound was prepared in a manner similar to that reported for other tricyanovinylamines.[18] The material was purified by chromatography on alumina, then by sublimation *in vacuo;* m.p. 134–135°. A mixture of this material with 1,1-bis(dimethylamino)-2,2-dicyanoethylene (m.p. 134–135°) melted at 90–100°.

Anal. Calcd. for $C_7H_6N_4$: C, 57.5; H, 4.14; N, 38.3; mol. wt., 146. Found: C, 58.1; H, 4.41; N, 39.0; mol. wt., 152.

Treatment of this material with dimethylamine gave the known 1,1-bis(dimethylamino)-2,2-dicyanoethylene.[19]

4-Cyanopyrazole (VI).—To a slurry of 2.0 g. (0.02 mole) of 3-amino-2-cyanoacrolein in 30 ml. of ethanol was added 1.1 g. (0.02 mole) of hydrazine hydrate. The solid dissolved, and then a small amount of bright yellow precipitate separated. After stirring at room temperature for 2 hr. the mixture was filtered. The filtrate was evaporated to dryness and the residue extracted with methylene chloride. On evaporation of the methylene chloride there was obtained 1.2 g. (65%) of crude 4-cyanopyrazole, m.p. 77–81°. It was purified by chromatography on alumina using ether as eluent which raised the melting point to 86.5–87.5° and finally by sublimation. Pure 4-cyanopyrazole melts at 91–92°.

Anal. Calcd. for $C_4H_3N_3$: C, 51.6; H, 3.25; N, 45.1. Found: C, 51.6; H, 3.32; N, 45.1.

The infrared spectrum contains an NH band at 3.25 and a CN band at 4.49 μ.

Hydrolysis of 4-Cyanopyrazole. 4-Pyrazolecarboxylic Acid.—4-Cyanopyrazole (1.4 g.) was refluxed in 30 ml. of constant boiling hydrochloric acid for 2 hr. The solution was evaporated in an air stream, and the residue was stirred with 25 ml. of ice-water. The solid that separated was filtered, washed thoroughly with water, and air-dried; yield, 0.75 g. The infrared spectrum had bands at 3.05 (NH) and 6.0 μ (COOH carbonyl). The material melted with decomposition at 279–281°; the reported value for 4-pyrazolecarboxylic acid is 278–279° dec.[6]

Hydrolysis of 3-Amino-2-cyanoacrolein. Cyanomalonaldehyde Sodium Salt.—3-Amino-2-cyanoacrolein was suspended in water, and an equivalent amount of sodium hydroxide was added. Ammonia was evolved, and the material dissolved. The solution was evaporated *in vacuo* and the residue recrystallized from 90% ethanol to give crystals, m.p. 296–299° dec., of the monohydrate.

Anal. Calcd. for $C_4H_4O_3NNa$: C, 35.0; H, 2.94; N, 10.2. Found: C, 34.9; H, 3.37; N, 10.4.

The infrared spectrum has bands at 2.65, 2.79, 4.50, 6.02, 7.98, 8.04, 12.07, and 12.85 μ. The salt is quite soluble in water and gives no precipitate with silver or tetramethylammonium ion.

Cyanomalonaldehyde (VII).—A solution of 1.92 g. (0.02 mole) of 3-amino-2-cyanoacrolein was dissolved in 20 ml. of 1 *N* sodium hydroxide. After stirring for 38 min. at room temperature, the solution was run through an ion-exchange column (Amberlite IR-120), and the acidic effluent was evaporated *in vacuo*. Yield of the crude solid was 1.6 g. (84%). The material was purified by sublimation at 110° (20 mm.). It melts at 113–115° dec. and is water soluble (pH *ca.* 1). It decomposes slowly on storage.

The Monoanil of Cyanomalonaldehyde.—The sodium salt of the malonaldehyde was dissolved in water and stirred for 15 min. with excess aniline in 5% hydrochloric acid. The precipitate was recrystallized from ethanol to yield colorless crystals, m.p. 188.5–189.5°. The reported melting point for "2-cyano-2-formylethylideneaniline"[7] is 189–190°.

The ultraviolet spectrum of this material has λ_{max} 317 (4.75) and λ_{max} 228 mμ (log ϵ 4.70).

High-Pressure Reduction of 3-Amino-2-cyanoacrylonitrile. 2-Amino-3,5-dicyanopyridine (XI).—A mixture of 50 g. of 3-amino-2-cyanoacrylonitrile and 4 g. of 10% palladium on charcoal in 250 ml. of ethyl acetate was hydrogenated at 1000–1500 p.s.i. and 77° until about 1 mole equivalent of hydrogen was absorbed. The resulting solution was chromatographed on acid-washed alumina, using ethyl acetate as eluent. Only one solid fraction was obtained. Yield of the crude material was 21 g. (54%). It could not be conveniently recrystallized and was purified by sublimation at 190° (5 mm.). The product sinters when placed on a hot block at 200° and melts at 225–227° turning yellow.

Anal. Calcd. for $C_7H_4N_4$: C, 58.7; H, 2.80; N, 38.9; mol. wt., 144. Found: C, 58.7; H, 2.90; N, 39.5; mol. wt., 145 (ebullioscopic in acetone).

The infrared spectrum has bands at 2.8, 2.13, 4.50, 6.06, 6.30, 6.52, 6.72, 7.13, 7.40, 7.75, 7.94, 9.65, 10.42, 10.73, 12.41, 12.9, broad absorption around 13.5, and 14.3 μ. The ultraviolet spectrum has maxima at 332 (3.70), 270 (4.43), and 221 mμ (log ϵ 3.70).

2-Amino-3,5-dicyanopyridine is insoluble in water, dilute acid, or dilute base, but dissolves in 15% hydrochloric acid and can be recovered unchanged on neutralization.

2-Amino-3,5-pyridinedicarboxylic Acid and Its Pyrolysis.—One gram of 2-amino-3,5-dicyanopyridine was refluxed in constant-boiling hydrochloric acid for 30 hr. Making the solution basic resulted in the formation and redissolution of a precipitate. Maximum precipitation was obtained at pH 5–6. The solid was filtered and washed with water and alcohol, yielding 0.65 g. The infrared spectrum contained amino and carboxylic acid bands. The material was very insoluble in water, alcohol, or acetic acid and could not be recrystallized. It did not melt up to 320°.

The aforementioned acid (0.64 g.) was mixed intimately with an equal volume of copper powder. The mixture was heated in a sublimation tube at 340–345° (1 mm.). About 0.10 g. of a waxy sublimate was obtained. It melted at 56–57° as did authentic 2-aminopyridine and a mixture of the two. The infrared spectra of the two compounds were identical.

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(16) H. Schmidtmann, *Ber.*, **29**, 1171 (1896).

(17) A. Hantzsch and G. Osswald, *ibid.*, **32**, 641 (1899).

(18) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

(19) W. J. Middleton and V. A. Engelhardt, *ibid.*, **80**, 2788 (1958), report m.p. 129–130°.