Method B.—A mixture of 4.4 g. of 1-phenyl-3-amino-5-pyrazolone, 4 ml. of ethyl acetoacetate and 50 ml. of ethanol, in which was dissolved 0.5 g. of sodium, was heated under reflux and stirred for 1 hour. The reaction mixture, which contained a cream-colored precipitate, was cooled, diluted with ether and filtered. The collected solid was dissolved in 50 ml. of water and the *p*H adjusted to 4–5 with acetic acid. Filtration then yielded 3.4 g. (56%) of a colorless solid, which darkened above 295° and melted at 305–307° with decomposition.

Acetylation of the product from method A above with a 1:1 mixture of acetic acid and acetic anhydride yielded a colorless acetyl derivative, m.p. 145–146°, identical with the acetyl derivative prepared in a similar manner from the product of method B above.

PRINCETON, N. J.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Reaction of Malononitrile with Hydrazine[1,2]

BY EDWARD C. TAYLOR AND KLAUS S. HARTKE[3]

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The reaction of malononitrile or malononitrile dimer (1,1,3-tricyano-2-aminopropene-1) with hydrazine has been shown to give 3-cyanomethyl-4-cyano-5-aminopyrazole (I). A number of reactions of I are described which illustrate its versatility as an intermediate for the synthesis of condensed pyrazole heterocycles.

The reaction of malononitrile with hydrazine is reported[4] to yield a dark brown oil to which the structure 3,5-diaminopyrazole was assigned. Support for this structure consisted of a nitrogen determination on a poorly cyrstalline benzal derivative, since the parent substance could neither be crystallized nor purified. A picrate of "3,5-diaminopyrazole" was prepared but not analyzed, since it was formed only in very poor yield. Ten years later, Knorr[5] claimed an independent synthesis of 3,5-diaminopyrazole, which he described as a honey-yellow sirup, by a Curtius degradation sequence from pyrazole-3,5-dicarboxylic acid. The product proved to be too unstable to purify, but a nitrogen determination on the crude material was approximately in agreement with the calculated value for 3,5-diaminopyrazole. A dibenzoyl and a dibenzal derivative were prepared but not analyzed. Further details on the intermediates in the Curtius degradation and on the nature of the final product were promised but have not appeared.

Our attention was drawn to this work because of the unusual physical characteristics claimed for "3,5-diaminopyrazole." 5-Amino-3-pyrazolone is a high melting solid (m.p. 204° dec.) rather than a sirup, and indeed, all simple di-and poly-amino substituted nitrogen heterocycles are high melting solids as a result of strong intermolecularly hydrogen bonded crystal lattices. We therefore reinvestigated the reaction of malononitrile with hydrazine, and the present communication describes our results.

The reaction of equivalent amounts of malononitrile and hydrazine in ethanol solution, as described by von Rothenburg,[4] resulted in a mildly exothermic reaction to give a dark oil with properties similar to those previously reported. Apparently von Rothenburg failed to notice that the reaction was accompanied by the evolution of ammonia. However, crystallization of this oil from glacial acetic acid yielded a colorless, crystalline solid, m.p. 198°, which was shown to have the molecular formula $C_6H_5N_5$ by microanalysis and by a molecular weight determination. Upon mixing malononitrile and hydrazine in a smaller volume of ethanol, the reaction proceeded so exothermically that it boiled without external heating within a few minutes, with concomitant vigorous ammonia evolution, and cooling of the reaction mixture resulted in the separation of the compound $C_6H_5N_5$ as a mass of tan crystals. On the basis of the above observations, it appeared that the product was formed from two moles of malononitrile and one mole of hydrazine, with loss of one mole of ammonia, according to the equation

$$2NCCH_2CN + H_2NNH_2 \longrightarrow C_6H_5N_5 + NH_3$$

and combination of the reactants in this proportion indeed led to the expected product in increased yield and in a higher state of purity.

The product $C_6H_5N_5$ formed a monoacetyl derivative, m.p. 215°, and an unstable monobenzal derivative, m.p. ~168°, apparently identical with the product claimed by von Rothenburg to be the dibenzal derivative of 3,5-diaminopyrazole. The difference of 1.5% in the nitrogen value found by von Rothenburg as compared with that calculated for the monobenzal derivative of $C_6H_5N_5$ may be ascribed either to the recognized unreliability of nitrogen determinations on such nitrogen-containing heterocycles, or to the presence of impurities in the admittedly crude sample which was analyzed. The infrared spectrum of the product $C_6H_5N_5$ showed strong N–H bonds at 2.98, 3.04 and 3.20 μ, and two sharp nitrile bands, one at 4.45 (unconjugated) and one at 4.55 μ (conjugated). The ultraviolet absorption spectrum showed only decreasing absorption with increasing wave length with no maximum above 220 mμ. It was recovered unchanged after heating for long periods in ethanol solution in the presence of sodium ethoxide. Thus, of the three structures (I, II and III) which could reasonably be con-

(1) This work was supported in part by a grant (C-2551) to Princeton University from the National Cancer Institute of the National Institutes of Health, Public Health Service.

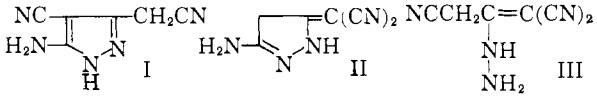
(2) Presented before the Division of Organic Chemistry at the 2nd Delaware Valley Meeting of the A.C.S., February 5, 1958, in Philadelphia, Pa., and before the Division of Organic Chemistry at the 133rd Annual A.C.S. Meeting, April 13–18, 1958, in San Francisco, Calif.

(3) Visiting Scholar from the University of Marburg, sponsored by Der Stifterverband für die Deutsche Wissenschaft.

(4) R. von Rothenburg, *Ber.*, **27**, 685 (1894).

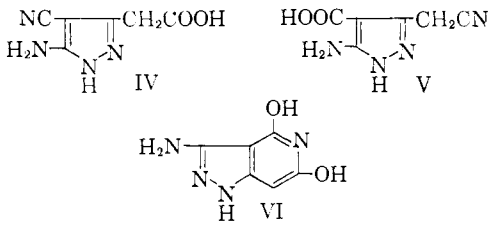
(5) L. Knorr, *ibid.*, **37**, 3520 (1904).

sidered for the product $C_6H_5N_5$, only I, 3-cyanomethyl-4-cyano-5-aminopyrazole, is consistent with all of the foregoing observations.

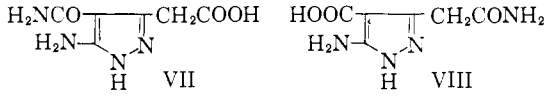


It seems probable that the formation of I from malononitrile and hydrazine was a result of an initial dimerization of malononitrile under the influence of the strongly basic hydrazine, followed by reaction of the latter with the dimer, with evolution of ammonia, to give I. Strong support for this view was afforded by the observation that compound I could be formed independently and in greatly improved yield by the reaction of hydrazine with the dimer of malononitrile (1,1,3-tricyano-2-aminopropene-1) formed by the action of sodium ethoxide on malononitrile.[6]

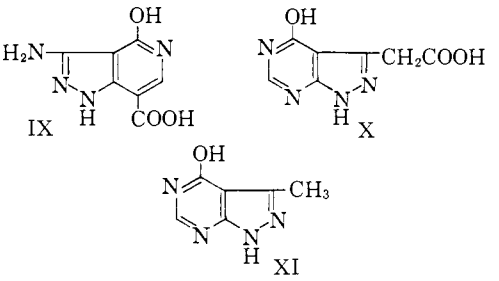
Treatment of I with hydrochloric, sulfuric or polyphosphoric acid yielded a compound $C_6H_6N_4O_2$, for which these structures may be considered:



Structures IV and V were readily eliminated, since the product did not undergo reactions characteristic of a carboxylic acid and did not possess a nitrile group (infrared). Furthermore, the product VI exhibited an ultraviolet absorption spectrum completely different from I and of a character indicating the presence of a bicyclic system. Alkaline hydrolysis of VI yielded a compound $C_6H_8N_4O_3$, identical in all respects with the product of alkaline hydrolysis of I. This product is assigned structure VII, and not VIII, on the basis of an independent observation that pyrazole-4-carboxylic acids related to VIII are too unstable to be isolated.[7] This conclusion is entirely consistent with the expectation that the more sterically hindered aromatic nitrile group of I should be more resistent to complete hydrolysis than the less hindered aliphatic nitrile group. VII could be reconverted to VI either by treatment with methanolic hydrogen chloride, presumably *via* the intermediate methyl ester, or by heating above its melting point.

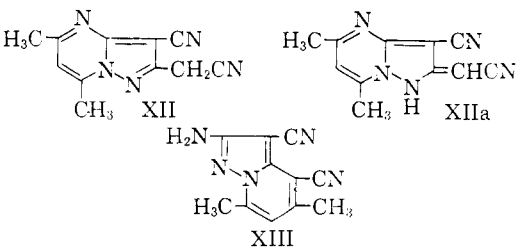


Treatment of VII with a mixture of acetic anhydride and ethyl orthoformate gave 3-amino-4-hydroxy-7-carboxypyrazolo(4,3-c)pyridine (IX). Cyclization across the *o*-aminocarboxamide functions of VII would have given an isomeric compound, 3-carboxymethyl-4-hydroxypyrazolo(3,4-d)-pyrimidine (X), but this possibility was eliminated



by comparison of the ultraviolet absorption spectrum of IX with that of 3-methyl-4-hydroxypyrazolo(3,4-d)pyrimidine (XI), prepared as a model for X. Furthermore, the infrared spectrum of IX revealed the same N–H bands as were present in the spectrum of VII, as well as a conjugated carboxyl group.

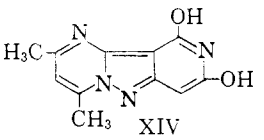
Reaction of I with acetylacetone in the presence of potassium ethoxide yielded two isomeric products with the molecular formula $C_{11}H_9N_5$. The lower melting (m.p. 226–227°), more soluble isomer was shown to be 2-cyanomethyl-3-cyano-5,7-dimethylpyrazolo(2,3-a)pyrimidine (XII), since its infrared spectrum showed both an unconjugated (4.45 μ) and a conjugated (4.51 μ) nitrile band, and only a slight N–H band (3.31 μ), presumably due to the presence of some of the tautomer XIIa. The higher melting (m.p.~370° dec.),

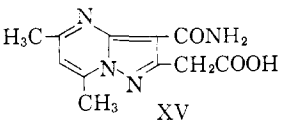


less soluble isomer is assigned the structure XIII, since its infrared spectrum indicated the presence of two conjugated nitrile groups (4.49 and 4.51 μ) and strong N–H bands (2.95, 3.00 and 3.14 μ). Hydrolysis of XII in concentrated hydrochloric acid yielded 2,4-dimethyl-7,9-dihydroxypyrimido-(1,2-b)pyrido(4,5-d)pyrazole (XIV), which in turn was converted to 2-carboxymethyl-3-carboxamido-5,7-dimethylpyrazolo(2,3-a)pyrimidine (XV) by alkaline hydrolysis; XV could also be prepared by direct alkaline hydrolysis of XII. Reconversion of XV to XIV could be effected in concentrated hydrochloric acid, but an attempt to carry out this reaction in methanolic hydrogen chloride (under conditions analogous to those used in the conversion of VII to VI) led only to the methyl ester XVI, which proved to be stable even to high temperature vacuum sublimation. The resistance of this

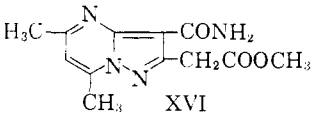
(6) Following the completion and initial presentation (see ref. 2) of this work, two independent reports of the preparation of the dimer of malononitrile came to our attention (W. J. Middleton to E. I. du Pont de Nemours and Co., U. S. Patent 2,790,806, April, 1957; and German Patent 922,531, Jan. 17, 1955 (*C. A.*, **52**, 2059 (1958)), M. Coenen to Farbenfabriken Bayer A.G.). The reaction of malononitrile dimer with hydrazine to give a product presumed to be 3-cyanomethyl-4-cyano-5-aminopyrazole (I) has more recently been described by the du Pont group (R. A. Carboni, D. D. Coffman and E. G. Howard, THIS JOURNAL, **80**, 2838 (1958)), but no structural evidence in support of this tentative conclusion was advanced.

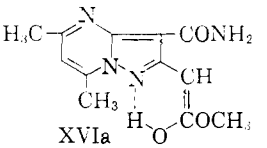
(7) E. C. Taylor and K. S. Hartke, THIS JOURNAL, **80**, 2456 (1959).


XIV

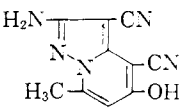

XV

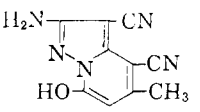
methyl ester to cyclization is most reasonably explained in terms of a cyclic hydrogen-bonded enol system (XVIa).


XVI


XVIa

Condensation of I with ethyl acetoacetate yielded an extremely insoluble, high melting product, whose infrared spectrum revealed the same strong N–H bands (2.98, 3.04 and 3.15 μ) as the starting material, and one very strong conjugated nitrile band (4.51 μ). The product would thus appear to be a pyrazolo(2,3-a)pyridine of structure XVII or XVIII, but no attempt was made to distinguish between these alternative structures.


XVII


XVIII

Experimental[8]

3-Cyanomethyl-4-cyano-5-aminopyrazole (I). Method A.—To a solution of 33.0 g. (0.5 mole) of malononitrile in 85 ml. of ethanol was added 4.0 g. of 85% hydrazine hydrate and the mixture carefully heated to boiling. An additional 12.0 g. of 85% hydrazine hydrate (total, 0.25 mole) was then added at such a rate that the reaction mixture continued to boil without external heating. Ammonia was continually evolved during this time. After all the hydrazine had been added, the reaction mixture was boiled for an additional 5 minutes and then quickly cooled to 0°. The light reddish tan crystals which had separated were collected by filtration and immediately recrystallized from glacial acetic acid with the addition of charcoal. A further recrystallization from water yielded 14.5 g. (40%) of colorless needles, m.p. 197–198°.

Anal. Calcd. for $C_6H_5N_5$: C, 49.0; H, 3.4; N, 47.6. Found: C, 48.6; H, 3.6; N, 48.0.

Method B.—To a solution of 26.4 g. (0.2 mole) of 1,1,3-tricyano-2-aminopropene-1 (malononitrile dimer) in 200 ml. of boiling ethanol was added 13.2 g. (0.22 mole) of 85% hydrazine hydrate at such a rate that the reaction mixture continued to boil without external heating. The strongly exothermic reaction was accompanied by a vigorous evolution of ammonia. After addition of the hydrazine hydrate was completed, the reaction mixture was heated under reflux for an additional 15 minutes and then allowed to cool slowly to room temperature. It was then chilled and filtered, and the collected product recrystallized from water to give 21.0 g. (71.5%) of colorless needles, m.p. 198°, identical with the product obtained by method A above.

1,1,3-Tricyano-2-aminopropene-1 (Malononitrile Dimer).—In a three-necked flask fitted with a stirrer, reflux condenser and a dropping funnel was placed a solution of sodium ethoxide prepared from 5.75 g. (0.25 mole) of sodium and 105 ml. of absolute ethanol. The flask was immersed in an ice-bath, the contents cooled to 0°, and a solution of 33.0 g. (0.5 mole) of malononitrile in 45 ml. of absolute ethanol added dropwise. After a few minutes, a vigorous exothermic reaction took place with the simultaneous separation of a white solid. The rate of addition of the malononitrile solution was adjusted so that the temperature of the reaction mixture did not rise above 30–40°. After all the malononitrile had been added, the mixture was heated under reflux for one hour on a water-bath and then cooled. Filtration yielded the white sodium salt of malononitrile dimer, which was washed with ethanol and dried in a vacuum oven at 50°; yield 33.0 g.

A solution of 4.0 g. of the sodium salt dissolved in 15 ml. of water was adjusted to *p*H 4 with concentrated hydrochloric acid, and the precipitated white solid collected by filtration, washed with ice-water and dried in a vacuum oven at 50° to give 3.3 g. (82.5%, based on malononitrile). Recrystallization from water yielded long, colorless needles, m.p. 172–173°.

Anal. Calcd. for $C_6H_4N_4$: C, 54.4; H, 3.1; N, 42.4. Found: C, 54.5; H, 3.1; N, 42.6.

Acetyl Derivative of 3-Cyanomethyl-4-cyano-5-aminopyrazole.—A mixture of 1.0 g. of 3-cyanomethyl-4-cyano-5-aminopyrazole in 10 ml. of acetic anhydride was heated under reflux for 30 minutes. Cooling yielded a white crystalline solid which was collected by filtration and recrystallized from nitromethane; yield 0.65 g. (50.5%) of white needles, m.p. 215°.

Anal. Calcd. for $C_8H_7N_5O$: C, 50.8; H, 3.7; N, 37.0. Found: C, 50.9; H, 3.9; N, 37.1.

3-Amino-4,6-dihydroxypyrazolo(4,3-c)pyridine (VI). Method A.—A mixture of 1.47 g. of 3-cyanomethyl-4-cyano-5-aminopyrazole and 15 ml. of concentrated hydrochloric acid was warmed gently until solution was complete and then heated to boiling for 10 minutes. During this period a white precipitate separated from the reaction mixture. Cooling and filtering yielded 1.45 g. (87%) of light yellow crystals which were recrystallized from water; m.p. >360°, $\lambda_{max}^{H_2O}$ 277 mμ, log ϵ 3.70.

Anal. Calcd. for $C_6H_6N_4O_2$: C, 43.4; H, 3.6; N, 33.7. Found: C, 43.2; H, 3.6; N, 34.1.

Method B.—A stream of dry hydrogen chloride gas was bubbled slowly through an ice-cold suspension of 1.0 g. of 3-carboxymethyl-4-carboxamido-5-aminopyrazole (VII) in 25 ml. of absolute methanol. Complete solution took place within a few minutes. After the methanol had been saturated with hydrogen chloride, the clear light yellow reaction mixture was heated on a water-bath for 30 minutes. During this period a light yellow crystalline precipitate slowly separated. Cooling and filtering yielded 0.85 g. (94.5%) of product, m.p. >360°, shown to be identical with the product obtained by method A above by comparison of infrared spectra.

3-Carboxymethyl-4-carboxamido-5-aminopyrazole (VII). Method A.—A mixture of 1.85 g. of sodium hydroxide, 2.94 g. of 3-cyanomethyl-4-cyano-5-aminopyrazole and 25 ml. of water was heated under reflux for 3 hours. Copious ammonia evolution took place during this time. The cooled reaction mixture was acidified to *p*H 5–6 with concentrated hydrochloric acid and then added to a suspension of 2.05 g. of finely powdered copper acetate monohydrate in 60 ml. of water. The gray-green solid which separated was collected by filtration, washed carefully with water and suspended in 75 ml. of boiling water. This mixture was then saturated with hydrogen sulfide and filtered hot. From the filtrate on cooling separated 2.1 g. (57%) of colorless needles which were recrystallized from water; m.p. 210° dec.

Anal. Calcd. for $C_6H_8N_4O_3$: C, 39.1; H, 4.4; N, 30.4. Found: C, 39.3; H, 4.4; N, 30.4.

Method B.—A mixture of 1.85 g. of sodium hydroxide, 3.32 g. of 3-amino-4,6-dihydroxypyrazolo(4,3-c)pyridine and 25 ml. of water was heated under reflux for 2.5 hours, and then worked up as described above to give 2.5 g. (68%) of colorless needles, m.p. 210° dec., which were identical with the product obtained by method A, as evidenced by a comparison of infrared spectra and by a mixture melting point determination.

3-Amino-4-hydroxy-7-carboxypyrazolo(4,3-c)pyridine (IX).—A mixture of 1.0 g. of 3-carboxymethyl-4-carboxamido-5-aminopyrazole, 20 ml. of ethyl orthoformate and 20 ml. of acetic anhydride was heated under reflux for 3 hours and then evaporated under reduced pressure. Ethanol was added to the residual oil and the mixture was again evaporated under reduced pressure. This process was re-

(8) We are indebted for the microanalyses to Dr. Joseph F. Alicino, Metuchen, N. J., and to Drs. G. Weiler and F. B. Strauss, Oxford, England. All melting points are corrected.

peated until the last traces of acetic acid had been removed. The residual solid was then collected by filtration and washed with water to give 1.1 g. of crude product. It was purified by dissolution in dilute sodium hydroxide solution followed by reprecipitation with dilute acetic acid, and was obtained as light tan needles, m.p. >350°; $\lambda_{max}^{0.1\ N\ NaOH}$ 237–238(shoulder), 328 mμ; log ε 4.19, 4.15.

Anal. Calcd. for $C_7H_8N_4O_3 \cdot H_2O$: C, 39.6; H, 3.8; N, 26.4. Found: C, 39.5; H, 4.0; N, 26.1.

3-Methyl-4-hydroxypyrazolo(3,4-d)pyrimidine (XI).—To 18 ml. of cold concentrated sulfuric acid was added, with stirring, 4.5 g. of finely powdered 3-methyl-4-cyano-5-aminopyrazole[9] at such a rate that the temperature of the acid did not rise above 15–20°. The resulting clear solution was stirred for 2 hours and then poured over 500 g. of ice. Neutralization and cooling caused the separation of 3-methyl-4-carboxamido-5-aminopyrazole as a white solid. It was collected by filtration, washed with water and dried at 80° *in vacuo* to give 4.9 g. (95%), m.p. 206–207°.

A mixture of 4.2 g. of 3-methyl-4-carboxamido-5-aminopyrazole and 25 ml. of formamide was heated under reflux for 1 hour and then evaporated under reduced pressure. Trituration of the residual gummy residue with a mixture of benzene and heptane yielded a dark solid which was purified first by reprecipitation from dilute potassium hydroxide solution with acetic acid and then by recrystallization from water to give colorless needles, m.p. 335–336°, yield 3.8 g. (85%); $\lambda_{max}^{0.1\ N\ NaOH}$ 255, 273(sh) mμ; log ε 3.84, 3.74.

Anal. Calcd. for $C_6H_6N_4O$: C, 48.3; H, 3.4; N, 37.6. Found: C, 48.6; H, 3.3; N, 37.6.

2-Cyanomethyl-3-cyano-5,7-dimethylpyrazolo(2,3-a)pyrimidine (XII).—A solution of 1.4 g. (0.04 mole) of potassium in 100 ml. of absolute ethanol was warmed to 30° and 4.0 g. (0.04 mole) of acetylacetone added. The temperature was maintained at 30°, and, after 10 minutes, 5.88 g. (0.04 mole) of finely powdered 3-cyanomethyl-4-cyano-5-aminopyrazole was added in small portions, so that the total time required for the addition was approximately 15 minutes. During this time a white precipitate started to separate from the reaction mixture. Approximately 35 minutes after the first addition of the pyrazole, an additional 4.0 g. (0.04 mole) of acetylacetone was added and the reaction mixture was stirred at 30° for 3.5 hours. The precipitated solid was then collected by filtration, washed well with water and dried in a vacuum oven at 50° to give 7.7 g. (91%) of a mixture of XII and XIII.

The collected solid was suspended in 60 ml. of nitromethane and the mixture heated to boiling and filtered. The filtrate was treated with charcoal, refiltered and the filtrate allowed to cool slowly to yield 3.4 g. (40%) of white needles, m.p. 226°; $\lambda_{max}^{H_2O}$ 228, 299 mμ; log ε 4.63, 3.66.

Anal. Calcd. for $C_{11}H_9N_5$: C, 62.6; H, 4.3; N, 33.2. Found: C, 62.7; H, 4.5; N, 33.1.

2-Amino-3,4-dicyano-5,7-dimethylpyrazolo(2,3-a)pyridine (XIII).—The residue from the nitromethane extraction above was recrystallized from dimethylformamide with the use of charcoal to give 1.7 g. (20%) of white needles, m.p. ~370° dec.; $\lambda_{max}^{cellosolve}$ 265, 350 mμ; log ε 4.59, 3.69.

Anal. Calcd. for $C_{11}H_9N_5$: C, 62.6; H, 4.3; N, 33.2. Found: C, 62.8; H, 4.3; N, 33.0.

2,4-Dimethyl-7,9-dihydroxypyrimido(1,2-b)pyrido(4,5-d)pyrazole (XIV). Method A.—A mixture of 2.0 g. of 2-cyanomethyl-3-cyano-5,7-dimethylpyrazolo(2,3-a)pyrimidine and 40 ml. of concentrated hydrochloric acid was heated under reflux for 45 minutes and filtered hot from a small amount of suspended solid. The filtrate was evaporated to dryness under reduced pressure to give 1.95 g. (89%) of crude product which was recrystallized from water to yield white needles, m.p. 325–330° dec.; $\lambda_{max}^{H_2O}$ 229, 256, 303 mμ; log ε 4.46, 4.05, 3.95.

Anal. Calcd. for $C_{11}H_{10}N_4O_2$: C, 57.4; H, 4.4; N, 24.3. Found: C, 57.5; H, 4.6; N, 24.0.

Method B.—Treatment of 2-carboxymethyl-3-carboxamido-5,7-dimethylpyrazolo(2,3-a)pyrimidine (XV) with concentrated hydrochloric acid according to the procedure given above yielded XIV in 86% yield. A mixture melting point determination and a comparison of infrared spectra showed the products from methods A and B to be identical.

2-Carboxymethyl-3-carboxamido-5,7-dimethylpyrazolo-(2,3-a)pyrimidine (XV). Method A.—A mixture of 2.0 g. of 2-cyanomethyl-3-cyano-5,7-dimethylpyrazolo(2,3-a)pyrimidine, 1.6 g. of sodium hydroxide and 40 ml. of water was heated under reflux for 6 hours, by which time ammonia evolution had ceased. The reaction mixture was filtered from a small amount of suspended solid, the filtrate acidified with hydrochloric acid and the precipitated solid collected by filtration to give 1.45 g. (62%). The extreme insolubility of the product necessitated purification by dissolution in dilute sodium hydroxide solution followed by reprecipitation with acetic acid. The product was thus obtained in the form of white needles, m.p. 275–285° dec. (depending on the rate of heating); $\lambda_{max}^{0.1\ N\ NaOH}$ 229, 281(shoulder), 305 mμ; log ε 4.49, 3.59, 3.65.

Anal. Calcd. for $C_{11}H_{12}N_4O_3$: C, 53.2; H, 4.9; N, 22.6. Found: C, 53.4; H, 4.7; N, 22.1.

Method B.—Hydrolysis of 2,4-dimethyl-7,9-dihydroxypyrimido(1,2-b)pyrido(4,5-d)pyrazole (XIV) with dilute sodium hydroxide for 3 hours, followed by isolation of the product as described above, yielded XV in 79% yield. The products from method A and B were shown to be identical by a mixture melting point determination and by comparison of infrared spectra.

2-Carbomethoxymethyl-3-carboxamido-5,7-dimethylpyrazolo(2,3-a)pyrimidine (XVI).—A dry stream of hydrogen chloride gas was bubbled for 45 minutes through an ice-cold suspension of 1.0 g. of finely powdered 2-carboxymethyl-3-carboxamido-5,7-dimethylpyrazolo(2,3-a)pyrimidine in 25 ml. of absolute methanol. The clear reaction mixture was then heated under reflux on a water-bath for 45 minutes and evaporated to dryness under reduced pressure. Methanol was added to the residue, and the mixture again evaporated to dryness. Recrystallization of the residue from a large volume of water yielded 0.55 g. (52%) of yellow needles, m.p. 247–249° dec.; $\lambda_{max}^{H_2O}$ 228, 276, 303 mμ; log ε 4.45, 3.67, 3.78.

Anal. Calcd. for $C_{12}H_{14}N_4O_3$: C, 55.0; H, 5.4; N, 21.4. Found: C, 55.4; H, 5.3; N, 21.2.

Condensation of 3-Cyanomethyl-4-cyano-5-aminopyrazole with Ethyl Acetoacetate.—To a solution of 1.6 g. (0.04 mole) of potassium in 60 ml. of absolute ethanol at room temperature was added 3.6 g. (0.028 mole) of ethyl acetoacetate. The mixture was stirred for 5 minutes, and then 2.94 g. (0.02 mole) of finely powdered 3-cyanomethyl-4-cyano-5-aminopyrazole was added in small portions. The reaction mixture was stirred at room temperature for one hour following the addition of the last portion of the pyrazole. Filtration yielded 5.95 g. of a solid potassium salt which was dissolved in a small amount of water. Acidification to *p*H 5–6 precipitated 3.4 g. (80%) of product, which was recrystallized from a small amount of dimethylformamide to yield white needles, m.p. >350°; $\lambda_{max}^{H_2O}$ 248, 300-(shoulder), 332 mμ; log ε 4.23, 4.08, 4.26.

Anal. Calcd. for $C_{10}H_7N_5O$: C, 56.3; H, 3.3; N, 32.9. Found: C, 56.7; H, 3.3; N, 33.3.

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