The semisolid residue was extracted with boiling acetonitrile (5 × 10 ml.), and the extract evaporated to dryness under reduced pressure. The resulting white crystalline residue was triturated with 1 ml. of cold acetonitrile, collected and dried *in vacuo* over phosphorus pentoxide at room temperature: yield 358 mg. (69%), m.p. 166° dec.[26] Recrystallization of a 150-mg. sample from 30 ml. of acetonitrile afforded 66 mg. of analytically pure 2-aminoethyl 3,3-dimethyldithiocarbazate hydrobromide as colorless cubic crystals, m.p. 166° dec.,[26] 148° dec. (capillary, from 125°).

Anal. Calcd. for $C_5H_{13}N_3S_2{\cdot}HBr$: C, 23.07; H, 5.42; S, 24.64. Found: C, 23.38; H, 5.50; S, 24.40.

2,2'-Dithiobisethylamine dihydrochloride from the reaction of 2-aminoethanethiol hydrochloride and trichloromethanesulfenyl chloride. A solution of 172 g. (0.924 mole) of trichloromethanesulfenyl chloride[27] in 750 ml. of absolute ethyl alcohol was added dropwise to a cooled, vigorously stirred solution of 100 g. (0.882 mole) of 2-aminoethanethiol hydrochloride[35] in 750 ml. of absolute ethyl alcohol, the rate of addition being such that the temperature of the mixture did not exceed 50°. A precipitate formed, and the reaction mixture was stirred for 1 hr. after the addition was complete. Then 1 l. of anhydrous ethyl ether was added, and the mixture was chilled for 2 hr. The precipitated solid was collected, washed with 200 ml. of ethyl ether, and dried *in vacuo* over phosphorus pentoxide at 80° for 17 hr.; m.p. 200°.[26] The crude product was dissolved in 1 l. of boiling methyl alcohol, and the solution was treated with Norit, filtered, cooled, and then treated with 1 l. of ethyl ether. After 1 hr., the resulting precipitate was collected and dried as described above; yield 88.5 g. (89%) of 2,2'-dithiobisethylamine dihydrochloride as a white crystalline powder, m.p. 211°.[26,36]

Anal. Calcd. for $C_4H_{12}N_2S_2.2HCl$: C, 21.07; H, 6.24; S, 28.60. Found: C, 20.97; H, 6.27; S, 28.48.

Acknowledgment. The authors are indebted to Mr. Carl R. Stringfellow, Jr., for technical assistance, and to members of the Analytical Section of Southern Research Institute, who, under the direction of Dr. W. J. Barrett, performed the microanalyses reported herein.

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[35] Evans Chemetics, Inc., 250 East 43rd St., New York, 17, N. Y.

[36] The disulfide that was isolated from a preliminary run in which equimolar quantities of reactants and a reversed order of addition were used had a m.p. of 216°[26]; reported melting points for the dihydrochloride range from 203° [W. Coblentz and S. Gabriel, *Ber.*, **24**, 1122 (1891)] to 217° [A. H. Nathan and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 2361 (1941)].

[CONTRIBUTION FROM THE CENTRAL RESEARCH DIVISION, STAMFORD RESEARCH LABORATORIES, AMERICAN CYANAMID CO.]

Preparation and Reactions of 1-Cyanoformimidic Acid Hydrazide

KEN MATSUDA AND LUCILLE T. MORIN

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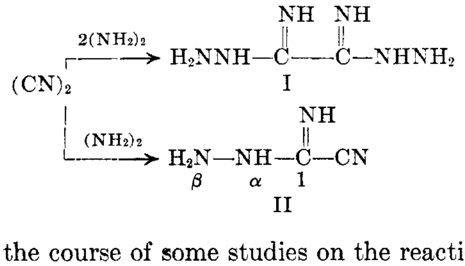
1-Cyanoformimidic acid hydrazide [$NH_2NHC({=}NH)CN$] has been synthesized in good yield by the reaction of cyanogen and hydrazine. The chemistry of this new compound has been investigated and a number of derivatives have been prepared. These include the β-alkylidene, β-acyl, β-carbamoyl, and β-phenylcarbamoyl derivatives; substituted *as*-triazine-3-carbonitriles; substituted *s*-triazole-3-carbonitriles; substituted 1,3,4-oxadiazoles; and tetrazole-5-carbonitrile.

The reaction of cyanogen with two moles of hydrazine to form oxalimidic acid dihydrazide (I) has been known for over sixty years.[1-3] 1-Cyanoformimidic acid hydrazide (II), the product from equimolar amounts of cyanogen and hydrazine, however, has not been reported.



$$(CN)_2 \xrightarrow{2(NH_2)_2} H_2NNH{-}\overset{NH}{\overset{\|}{C}}{-}\overset{NH}{\overset{\|}{C}}{-}NHNH_2 \quad \text{I}$$

$$(CN)_2 \xrightarrow{(NH_2)_2} \underset{\beta}{H_2N}{-}\underset{\alpha}{NH}{-}\underset{1}{\overset{NH}{\overset{\|}{C}}}{-}CN \quad \text{II}$$

In the course of some studies on the reactions of cyanogen with hydrazine we isolated, in addition to a large quantity of oxalimidic acid dihydrazide, a small amount of a second solid material. From its elemental analysis, molecular weight, and infrared spectrum we determined that 1-cyanoformimidic acid hydrazide had been obtained. With this material in hand we were able to study its solubility characteristics and thereby devise a suitable synthesis. We believe that the major reason that this material had eluded discovery is that, under the conditions employed heretofore, the marked insolubility of oxalimidic acid dihydrazide in most solvents tended to favor its formation and isolation almost exclusively.[4] It was therefore necessary to find conditions under which 1-cyanoformimidic acid hydrazide would form readily and then precipitate immediately from solution to render it unavailable for further reaction.

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[1] A. Angeli, *Gazz. chim. ital.*, **23**, II, 101–4 (1893).

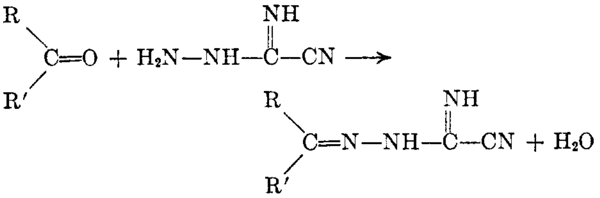
[2] T. Curtius, *J. prakt. Chem.*, [2], **52**, 272 (1895).

[3] G. Dedichen, *Avhandl, Norske Videnskaps-Akad. Oslo, I, Mat.-Naturv., Kl.*, **1936**, No. 5, pp. 161–7.

[4] We have found that procedures which would normally be expected to favor our desired reaction are inadequate. Thus the slow addition of hydrazine to a stirred ethanolic solution of cyanogen (equimolar with the hydrazine or in threefold excess) produces little or no 1-cyanoformimidic acid hydrazide.

After a number of unsuccessful preliminary trials, the procedure finally devised to produce 1-cyanoformimidic acid hydrazide in 70–80% yield is the slow addition of hydrazine in 10:1 dioxane-methanol to a stirred dioxane solution of cyanogen at 5°. 1-Cyanoformimidic acid hydrazide is a white crystalline solid melting at 84–86° with decomposition. It is highly soluble in water, alcohol, and ether but insoluble in cold dioxane, benzene, or hexane.

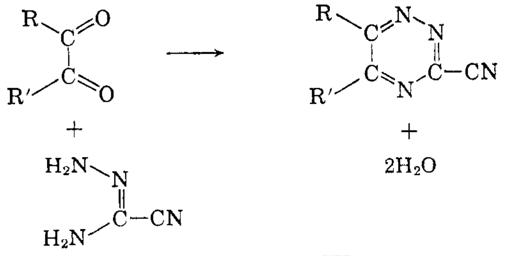
When it was found that 1-cyanoformimidic acid hydrazide could be prepared readily, it was of interest to study some of its reactions. The reaction with aldehydes and ketones proceeded smoothly to yield 1-cyanoformimidic acid alkylidenehydrazides. With the exception of 1-cyanoformimidic acid (1-methylheptylidene)hydrazide (VII), these derivatives were isolated as crystalline solids. The simple aliphatic and aromatic aldehydes and ketones underwent the condensation in yields of 60–90% when an alcoholic solution of the reactants, acidified with a few drops of acetic acid, was heated on a steam bath. Benzophenone was unreactive under these conditions, while acrolein, even in the presence of hydroquinone, yielded a yellow polymeric solid.



$$\mathrm{RR'C{=}O} + \mathrm{H_2N{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}CN} \longrightarrow \mathrm{RR'C{=}N{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}CN} + \mathrm{H_2O}$$

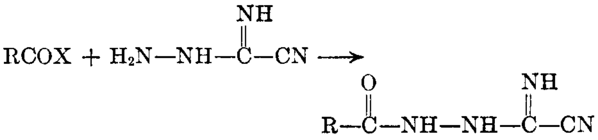
III. R = CH_3, R′ = H.
IV. R = C_6H_5, R′ = H.
V. R = o-HO-C_6H_4, R′ = H.
VI. R = CH_3, R′ = CH_3.
VII. R = n-C_6H_{13}, R′ = CH_3.
VIII. R = C_6H_5, R′ = CH_3.

With α-dicarbonyl compounds such as biacetyl and benzil, a disubstituted *as*-triazine was the final product. The reaction of glyoxal with 1-cyanoformimidic acid hydrazide did not yield the expected *as*-triazine-3-carbonitrile but gave a mixture consisting of a brittle black polymeric product and a yellow solid which darkened slowly above 150°.



IX. R = CH_3, R′ = CH_3.
X. R = C_6H_5, R′ = C_6H_5.

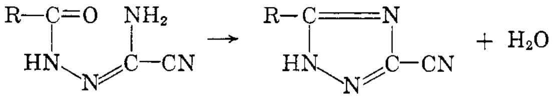
A few β-acyl derivatives of 1-cyanoformimidic acid hydrazide were prepared in 75–95% yield by treatment of the latter with an acid anhydride or acid chloride. The acetylation with acetic anhydride was best effected in a solvent such as benzene with equimolar quantities of the reagents. In the acyl chloride reactions it was found that the simultaneous dropwise addition of the acyl chloride and aqueous sodium hydroxide in equimolar amounts to a well stirred aqueous solution of 1-cyanoformimidic acid hydrazide gave the highest yields. These acyl derivatives are white crystalline solids which decompose at their melting points.



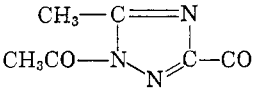
$$\mathrm{RCOX} + \mathrm{H_2N{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}CN} \longrightarrow \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}NH{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}CN}$$

XI. R = CH_3, X = CH_3COO.
XII. R = $CH_2{=}CH$, X = Cl.
XIII. R = C_6H_5, X = Cl.
XIV. R = p-Cl-C_6H_4, X = Cl.

It was difficult to convert these β-acyl derivatives of 1-cyanoformimidic acid hydrazide into *s*-triazole-3-carbonitriles by cyclodehydration, but the acetyl and benzoyl compounds did produce low yields of the triazoles. The 5-methyl derivative (XV) was obtained in 25% yield together with the acetylated and hydrolyzed by-products XVII and XVIII when 1-cyanoformimidic acid β-acetylhydrazide (XI) was heated with acetic anhydride alone or with acetic anhydride in pyridine solution. Heating the β-acetyl derivative in the absence of acetic anhydride in various solvents did not cause cyclization.

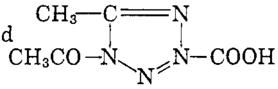


XV. R = CH_3.
XVI. R = C_6H_5.



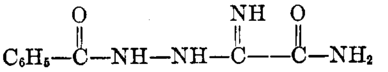
XVII

and



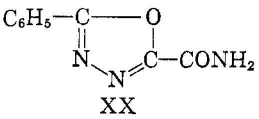
XVIII

Numerous attempts were made to cyclize the β-benzoyl derivative (XIII) by heating in various solvents without catalyst and in the presence of acidic and basic catalysts. Extensive decomposition occurred when strong acids or bases such as *p*-toluenesulfonic acid or sodium hydroxide were employed. Refluxing in pyridine solvent with a trace of acetic acid gave a 75% yield of the amide of the benzoylhydrazide (XIX). When the benzoyl derivative (XIII) was heated at reflux in acetic acid, a low yield of the expected 5-phenyl-*s*-triazole-3-carbonitrile (XVI) was obtained, in addition to a substantial amount of 5-phenyl-1,3,4-oxadiazole-2-carboxamide (XX).



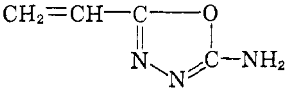
$$\mathrm{C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}NH{-}NH{-}\overset{NH}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}NH_2}$$

XIX



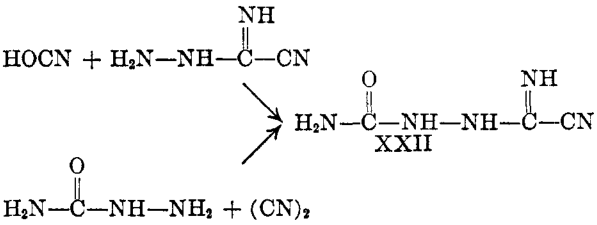
XX

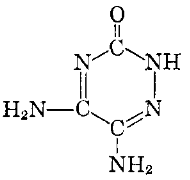
Several attempts to cyclodehydrate the β-acryloylhydrazide of 1-cyanoformimidic acid (XII) resulted either in polymerization, or in elimination of hydrogen cyanide to produce 2-amino-5-vinyl-1,3,4-oxadiazole (XXI)



XXI

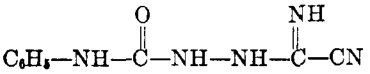
When an acidified aqueous solution of 1-cyanoformimidic acid hydrazide was treated with potassium cyanate, the β-carbamoyl derivative (XXII), a white solid which did not melt at 300°, was obtained in 55% yield. This material has been prepared by Thiele[5] by the treatment of cyanogen with semicarbazide. The infrared spectrum of our product showed, in addition to the expected carbonyl absorption peak at 1665 cm.$^{-1}$, a second carbonyl peak at 1745 cm.$^{-1}$ These peaks also existed in the spectrum of the semicarbazide-cyanogen product which was prepared by us for comparison. Since the analysis for the material was consistent with the formula $C_3H_5N_5O$, a second material having the same empirical formula was present. This material is believed to be the cyclic derivative XXIII. From the relative heights of the two carbonyl peaks in the infrared it was estimated that the cyclic material comprised about 30% of the crude product mixture. Repeated recrystallizations failed to reduce the amount of this impurity below an estimated 20%.





XXIII

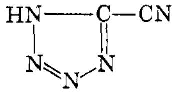
1-Cyanoformimidic acid β-phenylcarbamoylhydrazide (XXIV) was prepared in 68% yield by treatment of 1-cyanoformimidic acid hydrazide with phenyl isocyanate. This material exhibited a single carbonyl absorption peak at 1700 cm.$^{-1}$



$C_6H_5-NH-\overset{\overset{O}{\|}}{C}-NH-NH-\overset{\overset{NH}{\|}}{C}-CN$

XXIV

The treatment of 1-cyanoformimidic acid hydrazide with nitrous acid resulted in the formation of tetrazole-5-carbonitrile (XXV) in 45% yield.



XXV

This product has also been prepared from the reaction of cyanogen with hydrazoic acid.[6]

EXPERIMENTAL[7]

Materials. Cyanogen was prepared by the vapor phase thermal reaction of chlorine and hydrogen cyanide[8] and purified by low-temperature distillation. All reagents were purchased from Distillation Products Industries and were used without purification. The acryloyl chloride was prepared by a published procedure[9] from acrylic acid and benzoyl chloride.

1-Cyanoformimidic acid hydrazide (II). To a stirred solution, maintained at 5°, of 156 g. (3.0 moles) of cyanogen in 850 ml. of dioxane was added during 2.5 hr., a solution of 100 g. (3.0 moles) of hydrazine in 330 ml. of a 10:1 (by volume) mixture of dioxane and methanol. The mixture was stirred for an additional 0.5 hr., and then was filtered to give 178 g. (70% yield) of a pink solid, m.p. 74–79°. This material was dissolved in 600 ml. of hot isopropyl alcohol, treated with charcoal, and cooled to 50°. Hexane was added until a cloudiness appeared and the mixture was then cooled and filtered to give 132 g. of yellow plates, m.p. 82–86°. A portion, recrystallized from benzene, gave white crystals, m.p. 84–86°.

Anal. Calcd. for $C_2H_4N_4$: C, 28.57; H, 4.80; N, 66.64; mol. wt., 84. Found: C, 29.26, 29.56; H, 4.97; N, 65.73; mol. wt., 86.

Reactions with aldehydes and ketones. (a) *1-Cyanoformimidic acid ethylidenehydrazide* (III) *from acetaldehyde.* A cold solution of 4.2 g. (0.05 mole) of II in 50 ml. of ethanol was added to a solution of 4.0 g. (0.09 mole) of acetaldehyde in 50 ml. of alcohol, while the temperature was maintained below 10°. The temperature was maintained at 5° for 0.5 hr. and then at room temperature for 2.5 hr. Evaporation of the solvent under vacuum left a yellow oil which solidified on trituration with hexane to give 4.5 g. (82% yield) of a yellow solid, m.p. 49–55°. Two recrystallizations from hexane produced a white solid, m.p. 62–64°.

Anal. Calcd. for $C_4H_6N_4$: C, 43.63; H, 5.49; N, 50.88; mol. wt., 110. Found: C, 43.33; H, 5.41; N, 50.81; mol. wt., 107.

(b) *1-Cyanoformimidic acid benzylidenehydrazide* (IV) *from benzaldehyde.* A weakly acidic solution of 5.3 g. (0.05

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(5) J. Thiele and K. Schleussner, *Ann.*, 295, 129–72 (1897).

(6) E. Oliveri-Mandalà and T. Passalacqua, *Gazz. chim. ital.*, 41, II, 430–5 (1911).

(7) Melting points and boiling points are uncorrected. Molecular weights were determined ebullioscopically in benzene, acetone, chloroform, methanol, or ethanol; or cryoscopically in water or benzene. Oxygen was determined by a modified Unterzaucher procedure [J. Holowchak and G. E. C. Wear, *Anal. Chem.*, 23, 1404 (1951)].

(8) B. S. Lacy, H. A. Bond, and W. S. Hinegardner, U. S. Patent 2,399,361 (1946).

(9) G. H. Stempel, Jr., R. P. Cross, and R. P. Mariella, *J. Am. Chem. Soc.*, 72, 2299–300 (1950).

mole) of benzaldehyde and 4.2 g. (0.05 mole) of II in 75 ml. of ethanol was heated on the steam bath for 0.5 hr. The solvent was then evaporated to leave 7.0 g. (81% yield) of a yellow solid, m.p. 123–126°. After two recrystallizations from carbon tetrachloride, the product was obtained as pale yellow crystals, m.p. 127–128°.

Anal. Calcd. for $C_9H_8N_4$: C, 62.77; H, 4.68; N, 32.54; mol. wt., 172. Found: C, 62.63; H, 4.95; N, 32.30; mol. wt., 170.

(c) *1-Cyanoformimidic acid salicylidenehydrazide* (V) *from salicylaldehyde.* The product was prepared by the method described above using 7.2 g. (0.059 mole) of salicylaldehyde and 5.0 g. (0.059 mole) of II. On cooling the reaction mixture there was obtained 10.5 g. (93% yield) of a solid, m.p. 179° dec. Two recrystallizations from benzene yielded pale yellow needles, m.p. 180–181° dec.

Anal. Calcd. for $C_9H_8N_4O$: C, 57.44; H, 4.29; N, 29.77; O, 8.50; mol. wt., 188. Found: C, 57.72; H, 4.26; N, 29.36; O, 9.39; mol. wt., 189.

(d) *1-Cyanoformimidic acid isopropylidenehydrazide* (VI) *from acetone.* Twenty grams (0.24 mole) of II was dissolved in an excess of acetone acidified with a few drops of acetic acid. After being heated for 0.5 hr. on the steam bath the red solution was treated with charcoal and partially evaporated to leave 21 g. (71% yield) of a pink solid. Recrystallization from hexane gave white needles, m.p. 112–114°.

Anal. Calcd. for $C_5H_8N_4$: C, 48.37; H, 6.50; N, 45.13; mol. wt., 124. Found: C, 48.31; H, 6.53; N, 45.23; mol. wt., 123.

(e) *1-Cyanoformimidic acid (1-methylheptylidene)hydrazide* (VII) *from 2-octanone.* Treatment of 21 g. (0.25 mole) of II with 32 g. (0.25 mole) of 2-octanone as described above yielded 48 g. of an orange liquid upon evaporation of the solvent. This liquid was extracted with hexane to leave 1.0 g. of unchanged II. Evaporation of the hexane left 46 g. (95% yield) of an orange liquid whose infrared spectrum is similar to that of the acetone derivative. The product decomposes on standing but can be distilled under vacuum, b.p. 124–127°/1 mm.

(f) *1-Cyanoformimidic acid (α-methylbenzylidene)hydrazide* (VIII) *from acetophenone.* An acidified alcoholic solution of 12 g. (0.10 mole) of acetophenone and 8.4 g. (0.10 mole) of II was refluxed for 3 hr. It was then treated with charcoal and the solvent was evaporated to leave 15.6 g. of an oily yellow solid. This was washed with water and dried to give 10.6 g. (57% yield) of a yellow solid which, upon recrystallization from hexane, gave yellow needles, m.p. 99.5–101°.

Anal. Calcd. for $C_{10}H_{10}N_4$: C, 64.50; H, 5.41; N, 30.09. Found: C, 63.90; H, 5.45; N, 31.03.

Reaction with α-dicarbonyl compounds. (a) *5,6-Dimethyl-as-triazine-3-carbonitrile* (IX) *from biacetyl.* A solution of 17.2 g. (0.20 mole) of biacetyl, 8.4 g. (0.10 mole) of II and a few drops of acetic acid in 500 ml. of dry benzene was heated under reflux in a flask fitted with a Dean-Stark trap. After 1 hr., 3.6 ml. (theoretical) of water was collected, but the refluxing was continued for an additional hour. The benzene was evaporated under vacuum to leave 11.7 g. of an oily brown residue. This material was dissolved in 60 ml. of ether, treated with charcoal, and cooled in a Dry Ice–acetone bath to give 7.4 g. (55% yield) of a light tan solid, m.p. 38–42°. It was recrystallized three times from ether to give a pale yellow solid, m.p. 41–43°.

Anal. Calcd. for $C_6H_6N_4$: C, 53.72; H, 4.51; N, 41.77; mol. wt., 134. Found: C, 53.81; H, 4.64; N, 42.06; mol. wt., 129.

(b) *5,6-Diphenyl-as-triazine-3-carbonitrile* (X) *from benzil.* A mixture of 21 g. (0.10 mole) of benzil and 8.4 g. (0.10 mole) of II was refluxed for 17 hr. in the manner just described. A total of 1.4 ml. of water (39%) was collected during this time. Two drops of concd. hydrochloric acid was added and the mixture was refluxed for 24 hr. The amount of water collected was increased to 2.0 ml. (55%). The benzene solvent was evaporated under vacuum leaving 23 g. of a yellow solid, m.p. 70–105°. This was washed thoroughly with ether and filtered to give 12 g. (46% yield) of product, m.p. 145–151°. Recrystallization from isopropyl alcohol raised the m.p. to 154–155°.

Anal. Calcd. for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.70; mol. wt., 258. Found: C, 74.63; H, 3.86; N, 21.90; mol. wt., 256.

Reaction with acid chlorides and anhydrides. (a) *1-Cyanoformimidic acid β-acetylhydrazide* (XI) *from acetic anhydride.* With stirring and cooling, 8.4 g. (0.10 mole) of II was added in small portions to a solution of 12.0 g. (0.12 mole) of acetic anhydride dissolved in 100 ml. of benzene. A white solid began to precipitate shortly after the addition was started. The product was filtered and washed with ether to give 12.5 g. (99% yield) of a solid, m.p. 213° dec. Recrystallization from acetone yielded white crystals, m.p. 217° dec.

Anal. Calcd. for $C_4H_6N_4O$: C, 38.09; H, 4.80; N, 44.43; O, 12.69 mol. wt., 126. Found: C, 38.43; H, 4.78; N, 44.29; O, 13.37; mol. wt., 133.

(b) *1-Cyanoformimidic Acid β-acryloylhydrazide* (XII) *from acryloyl chloride.* A small amount of hydroquinone and 42 g. (0.5 mole) of II were dissolved in 300 ml. of water and cooled to 10°. With stirring, 45.2 g. (0.5 mole) of acryloyl chloride and 100 g. of 20% sodium hydroxide (0.5 mole) were added separately and dropwise. The mixture was then stirred for 1 hr. and filtered to give 48 g. (70% yield) of a tan solid. Recrystallization from alcohol gave a white crystalline solid which did not melt to 300° but darkened slowly on heating.

Anal. Calcd. for $C_5H_6N_4O$: C, 43.47; H, 4.38; N, 40.56; O, 11.58; mol. wt., 138. Found: C, 43.53; H, 4.43; N, 40.52; O, 11.64; mol. wt., 141.

(c) *1-Cyanoformimidic acid β-benzoylhydrazide* (XIII) *from benzoyl chloride.* To a solution of 8.4 g. (0.10 mole) of II and 40 ml. of 10% sodium hydroxide (*ca.* 0.10 mole) in 150 ml. of water was added 14.0 g. (0.10 mole) of benzoyl chloride in small portions with shaking, while the temperature was maintained below 30°. Precipitation of a tan solid began shortly after addition of the benzoyl chloride was started. The mixture was cooled and filtered to give 13.7 g. (73% yield) of a solid product, m.p. 197° dec. Recrystallization from acetonitrile yielded a white solid, m.p. 207° dec.

Anal. Calcd. for $C_9H_8N_4O$: C, 57.44; H, 4.28; N, 29.77; O, 8.50; mol. wt., 188. Found: C, 57.28; H, 4.34; N, 29.84; O, 8.54; mol. wt., 184.

(d) *1-Cyanoformimidic acid β-p-chlorobenzoylhydrazide* (XIV) *from p-chlorobenzoyl chloride.* The procedure just described was repeated with *p*-chlorobenzoyl chloride using 0.05 mole of each reactant. The crude tan product (10.5 g.) was washed with water, dried, and then washed with ether to give 8.5 g. (76% yield) of solid, m.p. 220° dec. After two recrystallizations from acetonitrile the product was a white solid, m.p. 238–239° dec.

Anal. Calcd. for $C_9H_7N_4OCl$: C, 48.54; H, 3.17; N, 25.16; O, 7.18; Cl, 15.94; mol. wt., 223. Found: C, 48.40; H, 3.41; N, 25.32; O, 8.08; Cl, 15.76; mol. wt., 220.

Cyclization of 1-cyanoformimidic acid β-acylhydrazides. (a) *5-Methyl-s-triazole-3-carbonitrile* (XV) *from 1-cyanoformimidic acid β-acetylhydrazide.* The β-acetylhydrazide (XI) was prepared *in situ* by adding 5 g. (0.059 mole) of II in small amounts and with stirring to 70 ml. of acetic anhydride. The acetylhydrazide precipitated immediately. The mixture was refluxed for 15 min. to give a clear yellow solution. Upon evaporation of the acetic anhydride under vacuum, there remained a white oily solid, which was washed with benzene to give 1.5 g. of a white solid, m.p. 178–185°. Recrystallization from benzene gave white crystals, m.p. 186–187°. The infrared spectrum showed no nitrile but indicated the presence of a triazole ring. The analyses are such that the product appears to be a mixture of the acetylated amide XVII (60%) and the acid XVIII (40%).

Anal. Calcd. for $C_6H_8N_4O_2$ (XIX): C, 42.85; H, 4.80; N, 33.32; O, 19.03; mol. wt., 168. Calcd. for $C_6H_7N_3O_3$

(XX): C, 42.60; H, 4.17; N, 24.85; O, 28.38; mol. wt., 169. Found: C, 42.88; H, 5.13; N, 30.06; mol. wt., 162.

The benzene filtrate from above was evaporated to leave an orange oil. This was triturated with water to give 2.0 g. of a white oily solid, m.p. 60–65°. The solid was dissolved in water and extracted with ether. Upon evaporation of the ether there was obtained 1.5 g. of a white solid, m.p. 132–134°. Recrystallization from toluene gave white crystals, m.p. 135–136°. The infrared spectrum was consistent with the structure of 5-methyl-s-triazole-3-carbonitrile (XV).

Anal. Calcd. for $C_4H_4N_4$: C, 44.44; H, 3.73; N, 51.83; mol. wt., 108. Found: C, 44.16; H, 4.13; N, 51.95; mol. wt., 105.

(b) *5-Phenyl-s-triazole-3-carbonitrile* (XVI) *from 1-cyanoformimidic acid β-benzoylhydrazide.* A solution of 5 g. of the β-benzoylhydrazide (XIII) in 150 ml. of acetic acid was heated under reflux for 2.5 hr., and then evaporated to give 8 g. of a brown oil. This was dissolved in acetonitrile and filtered. Evaporation of the acetonitrile left 6 g. of an orange oil which was dissolved in ethyl acetate, filtered, and evaporated. The remaining oil was extracted with water and the water was evaporated to leave a yellow oil. This was then extracted with 0.1N sodium hydroxide and the solution was acidified to precipitate 1 g. of a solid, m.p. 60–90°. Recrystallization from water gave white crystals, m.p. 123–124°, whose infrared spectrum showed the presence of phenyl, nitrile, and heterocyclic —C=N— groups consistent with the desired 5-phenyl-s-triazole-3-carbonitrile. The analyses were poor, indicating the presence of an impurity which is suspected to be benzoic acid. The latter could not be removed completely.

Anal. Calcd. for $C_9H_6N_4$: C, 63.52; H, 3.55; N, 32.93; mol. wt., 170. Found: C, 64.10; H, 3.93; N, 26.21; mol. wt., 162.

The reaction was repeated using 8 g. of the β-benzoylhydrazide (XIII) in 200 ml. of acetic acid. The brown oil left upon evaporation of the solvent was dissolved in ethyl acetate, filtered, and the filtrate was treated with charcoal and evaporated to give a yellow oil. Trituration with water gave 2.5 g. of a yellow solid, m.p. 145–165°. Three recrystallizations from benzene followed by two recrystallizations from water gave a white solid, m.p. 163–168°. The infrared spectrum, which showed phenyl (690, 712 cm.$^{-1}$), amide (1690 cm.$^{-1}$), and cyclic C=N (1560 cm.$^{-1}$) absorptions, and the analyses were consistent with the structure of 5-phenyl-1,3,4-oxadiazole-2-carboxamide (XX).

Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.14; H, 3.73; N, 22.21; O, 16.92. Found: C, 57.30; H, 3.81; N, 22.05; O, 17.08.

1-Carbamoylformimidic acid β-benzoylhydrazide (XIX) was obtained in the following manner: two grams of the 2-benzoylhydrazide (XIII) and a few drops of glacial acetic acid in 150 ml. of pyridine were heated under reflux for 3 hr. Upon filtration there was obtained 0.7 g. of a tan solid, m.p. 235° dec. The filtrate was heated under reflux for an additional 6 hr., cooled, and filtered to give 0.8 g. of a solid, m.p. 240° dec. Recrystallization of the combined solids from toluene gave a white solid, m.p. 238–239° dec.

Anal. Calcd. for $C_9H_{10}N_4O_2$: C, 52.42; H, 4.89; N, 27.17; O, 15.52; mol. wt., 206. Found: C, 52.14; H, 5.03; N, 27.04; O, 16.15; mol. wt., 197.

(c) *Preparation of 2-amino-5-vinyl-1,3,4-oxadiazole* (XXI) *from 1-cyanoformimidic acid β-acryloylhydrazide.* A solution of 5 g. of the acryloylhydrazide (XII) and a small amount of hydroquinone in 100 ml. of pyridine was heated under reflux for 18 hr. The mixture was filtered to remove a small amount of insoluble material, and the filtrate was evaporated to give a tacky brown material. This material was dissolved in alcohol, filtered, and the alcohol was evaporated. The residue was treated in the same manner with acetone as the solvent. An orange solid, m.p. 120–140°, was obtained at this stage. Three recrystallizations from toluene gave a white solid, m.p. 162–163°. The infrared spectrum of this solid indicated the presence of a vinyl group (1843, 1605, 990, 930 cm.$^{-1}$), a cyclic C=N (1605, 1550 cm.$^{-1}$), an amide or melamine type NH_2 (3280, 3120, 1665 cm.$^{-1}$); and the absence of nitrile or strained ring carbonyl groups. This information, together with the analysis, is accommodated by the structure of 2-amino-5-vinyl-1,3,4-oxadiazole.

Anal. Calcd. for $C_4H_5N_3O$: C, 43.23; H, 4.54; N, 37.81; O, 14.39; mol. wt., 111. Found: C, 43.70; H, 4.45; N, 37.28; O, 14.60; mol. wt., 121.

Reaction with isocyanates. (a) *1-Cyanoformimidic acid β-carbamoylhydrazide* (XXII) *from potassium cyanate.* A solution of 2.1 g. (0.026 mole) of potassium cyanate in a small amount of water was added to a solution of 2.1 g. (0.025 mole) of II in 25 ml. of 1N hydrochloric acid. The precipitate which formed immediately was filtered and washed with cold water and then with alcohol to leave 2.5 g. of a pale yellow solid which did not melt to 300° but darkened slowly. Several recrystallizations from water gave a white solid with no melting point to 300°.

Anal. Calcd. for $C_3H_5N_5O$: C, 28.35; H, 3.97; N, 55.10; O, 12.59. Found: C, 28.39; H, 4.16; N, 55.31; O, 12.38.

(b) *1-Cyanoformimidic acid β-phenylcarbamoylhydrazide* (XXIV) *from phenyl isocyanate.* To a solution of 2.1 g. (0.025 mole) of II in 75 ml. of anhydrous ether was added 3.0 g. (0.025 mole) of phenyl isocyanate. After the exothermic reaction had subsided the mixture was cooled and filtered to give 3.5 g. of a pale yellow solid, m.p. 175–180° dec. Two recrystallizations from alcohol gave white needles, m.p. 199–200° dec.

Anal. Calcd. for $C_9H_9N_5O$: C, 53.19; H, 4.46; N, 34.47; O, 7.87; mol. wt., 203. Found: C, 53.03; H, 4.72; N, 34.19; O, 8.20; mol. wt., 206.

Reaction with nitrous acid to yield tetrazole-5-carbonitrile (XXV). Twenty milliliters of dilute nitric acid was added to a solution of 2.0 g. (0.024 mole) of II in 50 ml. of water. This solution was cooled to 5° and 4.0 g. (0.024 mole) of silver nitrate was added. The white precipitate was dissolved by adding 50 ml. of water and 15 ml. of concd. nitric acid. To this solution, cooled to 0°, was added dropwise with stirring, a solution of 1.7 g. (0.024 mole) of sodium nitrite in 20 ml. of water. The solid which formed was filtered and washed thoroughly with water. It was then suspended in 100 ml. of warm water and treated with hydrogen sulfide until no more silver sulfide precipitated. The latter was removed by filtration and the filtrate was evaporated under vacuum to leave 1 g. (45% yield) of a light orange solid. Recrystallization from benzene gave white hygroscopic crystals which turned red at about 95° and melted at 103–104° dec. (lit.,[6] light pink at 70°, red-brown liquid at 99°).

Anal. Calcd. for C_2HN_5: C, 25.27; H, 1.06; N, 73.67; mol. wt., 95. Found: C, 25.00; H, 1.27; N, 73.96; mol. wt., 94.

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