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Cyanoguanyl Azide Chemistry[1]

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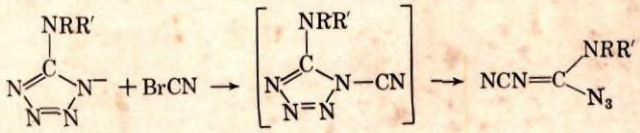
Several cyanoguanyl azides were prepared. Infrared and ultraviolet spectral data indicate that the structure, NC—N=C(N_3)NHR (where R = H, alkyl, aryl), is the dominant tautomer. The actions of bases on cyanoguanyl azide (**1**) fall into four categories: (1) cyclization to 5-cyaniminotetrazoline salts, (2) displacement of azide, (3) addition to the cyano group, and (4) simple complex formation. Diazomethane acts as a cyclizing and methylating agent on **1** and N-cyano-N′-methylguanyl azide (**2**) yielding 1,4-dimethyl-5-cyaniminotetrazoline (**7**). The role of base in the cyclization of guanyl azides, in general, is discussed. The structures and chemistry of the 5-cyaniminotetrazolines were investigated. Potassium 5-(N-cyano-N-methylamino)tetrazole (**4**), a member of a new tetrazole series, was isolated, derivatives were prepared, and structures were established.

Cyanoguanyl azide (**1**) was reported and characterized by Hart[2] in 1928, but the chemistry was not investigated further. This paper deals in more detail with the structure and chemistry of **1** and some of its derivatives.

N-Cyano-N′-methylguanyl azide (**2**) and N-cyano-N′,N′-dimethylguanyl azide (**3**) were prepared by Hart's procedure using the potassium salts of 5-methylaminotetrazole and 5-dimethylaminotetrazole, respectively, and cyanogen bromide. One coproduct in the preparation of **2** was potassium 5-(N-cyano-N-methylamino)tetrazole (**4**); in this case the cyano group attacked the 5-methylamino position. Cyanoguanyl azide formation proceeds through the intermediate formation of a 1-cyano-5-aminotetrazole. Arenesulfonyl halides and 5-aminotetrazole, in the presence of base, proceed similarly to produce arenesulfonylguanyl



1, R = R′ = H
2, R = CH_3; R′ = H
3, R = R′ = CH_3

(1) Presented at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.
(2) C. V. Hart, *J. Am. Chem. Soc.*, **50**, 1922 (1928).

azides.[3-5] The instability of a tetrazole with an electronegative group in the 1-position also can be inferred from the failure of imidoazides, X—N=C(N$_3$)—N$_3$ (where X is in electronegative group), to form tetrazoles.[6,7]

N-Cyano-N′-phenylguanyl azide (**5**)[2] and N,N-(1,4-phenylene)bis(N′-cyanoguanyl azide) (**6**) were prepared by the reaction of aniline and 1,4-phenylenediamine, respectively, with N-cyanimidocarbonyl azide.

$$2NC-N=C(N_3)-N_3 + 1,4\text{-}C_6H_4(NH_2)_2 \longrightarrow 1,4\text{-}C_6H_4(NH-C(N_3)=NCN)_2 + 2HN_3$$

6

There is now quite general agreement that electronegatively substituted guanidines have the structure X—N=C(NHR)$_2$, where X is acyl, nitro, or cyano and R is H or alkyl.[8-12] The tautomer with the proton on the more basic nitrogen would be expected to predominate. It is reasonable to assign a similar structure to cyanoguanyl azide and its derivatives, neglecting the additional resonance structures involving charge separation. In the case of **3** the two methyl groups on the amino nitrogen fix the structure in this configuration. The ultraviolet absorption spectra (Table I) of **1**, **2**, and **3** show marked similarities indicating that **1** and **2** are structurally similar to **3**. There is a regular bathochromic shift of the maxima in the spectra as methyl groups are added. A similar effect was noted by McKay with nitroguanidines.[13] 1,4-Dimethyl-5-cyaniminotetrazoline (**7**) absorbs in the 220–230-mμ region as do **1**, **2**, and **3** and with about the same intensity. In each case an imino group in conjugation with a nitrile group may be the chromophore responsible for this band. 1-Methyl-5-cyaniminotetrazoline (**8**) and its diisopropylammonium salt (**9**) also absorb in this region.

The infrared spectra of **1**, **2**, and **3** offer additional evidence that the cyano group is in conjugation with the imino group. The unconjugated nitrile group of dimethylcyanamide absorbs at 4.52 μ, and the nitrile group (unconjugated) of 2-methyl-5-(N-cyano-N-methylamino)tetrazole (**10**) absorbs at 4.47 μ. The nitrile absorptions of **1**, **2**, and **3** (Table II) are all shifted to longer wave lengths as would be expected for a conjugated system. Similarly the >C=N— absorption frequency, which occurs at 5.98 to 6.01 μ in unconjugated systems,[14] occurs at 6.06, 6.17, and 6.23 μ, respectively, in **1**, **2**, and **3**, which indicates conjugation of the >C=N— group with the cyano group and possibly the azido group.

TABLE I

ULTRAVIOLET SPECTRA OF CYANOGUANYL AZIDES AND TETRAZOLINES[a,b]

Compound	λ_{max}, mμ	(ϵ)
Cyanoguanyl azide (**1**)	219	(10,400)
	242	(7950)
N-Cyano-N′-methylguanyl azide (**2**)	224	(11,500)
	247	(7800)
N-Cyano-N′,N′-dimethylguanyl azide (**3**)	231	(9560)
	253	(9300)
1,4-Dimethyl-5-cyaniminotetrazoline (**7**)	226	(14,000)
1-Methyl-5-cyaniminotetrazoline (**8**)	221	(9500)
Bisdiisopropylammonium 5-cyaniminotetrazoline (**32**)	end absorption	
Diisopropylammonium 1-methyl-5-cyaniminotetrazoline (**9**)	218	(11,000)
1-Phenyl-5-cyaniminotetrazoline (**22**)	273	(10,000)

[a] The solvent used was 95% ethanol. [b] Spectra were recorded on a Model 11 Cary spectrophotometer.

Sodium iodide in trifluoroacetic acid[15] reacts immediately with **1**, **2**, and **3** to release iodine showing the presence of the azido group.[16] Triphenylphosphine reacts with guanyl azides to give the phosphinimides shown in Table III. In general a bright yellow color develops upon combining the two reagents followed by rapid evolution of nitrogen and disappearance of color. In the case of **3**, the initial bright yellow adduct, P,P,P-triphenyl-N-(N-cyano-N′,N′-dimethylguanyl)phosphazide, crystallized from solution and was comparatively stable. Phosphazides have been isolated before, but more often than not they decompose at room temperature or below.[17,18]

Guanyl azides isomerize to 5-aminotetrazoles with greater or lesser ease depending upon the substituents present.[19] The cyanoguanyl azides are similar to the arenesulfonylguanyl azides[3] and nitroguanyl azide[20] in that a base is required to effect the cyclization to the isomeric tetrazole. *t*-Butylamine, diisopropylamine, 1,4-dimethyl-5-iminotetrazoline, and dilute aqueous sodium hydroxide at 25° convert **1** into the corresponding dicationic salts of 5-cyaniminotetrazoline; the salts can be converted to free 5-cyaniminotetrazoline (**11**) by acidification. Certain other bases and **1**

(3) H. K. Nagy, A. J. Tomson, and J. P. Horwitz, *J. Am. Chem. Soc.*, **82**, 1609 (1960).

(4) K. A. Jensen and C. Pedersen, *Acta. Chem. Scand.*, **15**, 991 (1961).

(5) 5-Alkylamino- or 5-arylaminotetrazoles and acetic anhydride react in the presence of base to give compounds which rearrange, when heated, to 1-alkyl (or aryl)-5-acetamidotetrazoles [R. M. Herbst and W. L. Garbrecht, *J. Org. Chem.*, **18**, 1283 (1953); R. M. Herbst and J. E. Klingbeil, *J. Org. Chem.*, **23**, 1912 (1958)]. Here again the reaction proceeds by attack on the 1-position of the tetrazole ring. These reactions and the previous ones, all involving 5-aminotetrazole and derivatives, are to be contrasted with the reactions of 5-phenyltetrazole with acylating agents in which attack appears to occur exclusively at the 2-position [R. Husigen, J. Sauer, H. J. Sturm, and J. H. Markgraf, *Chem. Ber.*, **93**, 2106 (1960); R. M. Herbst, *J. Org. Chem.*, **26**, 2372 (1961)].

(6) F. Eloy, *ibid.*, **26**, 952 (1961).

(7) G. A. Reynolds, J. A. VanAllan, and J. F. Tinker, *ibid.*, **24**, 1205 (1959).

(8) R. Greenhalgh and R. A. B. Bannard, *Can. J. Chem.*, **39**, 1017 (1961).

(9) W. D. Kumler, *J. Org. Chem.*, **20**, 700 (1955).

(10) W. D. Kumler and P. P. T. Sah, *ibid.*, **18**, 669 (1953).

(11) S. S. Barton, H. Hall, and G. F Wright, *J. Am. Chem. Soc.*, **73**, 2201 (1951).

(12) X-ray crystallographic studies on nitroguanidine [J. H. Bryden, L. A. Burkardt, and E. W. Hughes, *Acta. Cryst.*, **9**, 573 (1956)] and cyanoguanidine [E. W. Hughes, *J. Am. Chem. Soc.*, **62**, 1258 (1940)] show that all three guanidine carbon–nitrogen bond lengths are approximately equal in each compound indicating that various resonance forms involving charge separations contribute substantially, and all the carbon–nitrogen bonds have some double bond character.

(13) A. F. McKay, J. P. Picard, and P. E. Brunet, *Can. J. Chem.*, **29**, 746 (1951).

(14) F. H. Suydam, *Anal. Chem.*, **35**, 193 (1963).

(15) This convenient reagent was devised by Dr. W. R. Carpenter of this laboratory.

(16) Hydrogen iodide reacts with azides to give I_2 [P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951)].

(17) H. Staudinger and E. Hauser, *Helv. Chim. Acta.*, **4**, 861 (1921).

(18) J. E. Leffler, U. Honsberg, Y. Tsuno, and I. Forsbald, *J. Org. Chem.*, **26**, 4810 (1961).

(19) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **77**, 2264 (1955).

(20) E. Lieber, E. Sherman, R. A. Henry, and J. Cohen, *ibid.*, **73**, 2327 (1951).

TABLE II

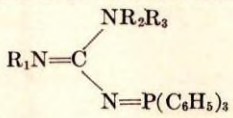
INFRARED SPECTRA OF CYANOGUANYL AZIDES, TETRAZOLINES, AND TETRAZOLES IN THE 4.4–6.5-μ REGION[a,b]

Compound	λmax, μ				
Cyanoguanyl azide (1)	4.55	4.60, 4.62	6.06 6.17		
N-Cyano-N′-methylguanyl azide (2)					
N-Cyano-N′,N′-dimethylguanyl azide (3)	4.58	4.68	6.23		
N-Cyano-N′-phenylguanyl azide (5)	4.58	4.62	6.16	6.35[c]	
5-Cyaniminotetrazoline (11)	4.59		6.17		
Monosodium 5-cyaniminotetrazoline (37)	4.60		6.19		
Disodium 5-cyaniminotetrazoline (28)	4.58		6.12		
Bisdiisopropylammonium 5-cyaniminotetrazoline (32)	4.73		6.09	6.21	6.34[d]
Bis-*t*-butylammonium 5-cyaniminotetrazoline (35)	4.48[e]	4.67	6.09		
1-Methyl-5-cyaniminotetrazoline (8)	4.59		6.13		
Diisopropylammonium 1-methyl-5-cyaniminotetrazoline (9)	4.62		6.22	6.42[d]	
1-Phenyl-5-cyaniminotetrazoline (22)	4.58		6.10	6.35[c]	
Hydrazinium 1-phenyl-5-cyaniminotetrazoline (38)	4.58		6.19	6.35[c]	
Bisdiisopropylammonium 1,4-bis(5-cyanimino-1-tetrazolinyl)-benzene (41)	4.62		6.22	6.47[e]	
1,4-Dimethyl-5-cyaniminotetrazoline (7)	4.58		6.18		
5-(N-Cyano-N-methylamino)tetrazole (33)	4.43			6.48	
Potassium 5-(N-cyano-N-methylamino)tetrazole (4)	4.51			6.58	
2-Methyl-5-(N-cyano-N-methylamino)tetrazole (10)	4.48			6.50	

[a] The spectra were determined on a Perkin-Elmer Infracord spectrophotometer employing potassium bromide as the medium. [b] The peaks reported in this range are only the moderately strong to strong. [c] Probably associated with the phenyl group. [d] Probably due to the diisopropylammonium group. Diisopropylammonium chloride has a moderately strong absorption at 6.32 μ. [e] Probably due to the *t*-butylammonium ion. *t*-Butylammonium 5-bromotetrazole has a band of medium intensity at 4.52 μ.

TABLE III

PREPARATION OF SUBSTITUTED GUANYLTRIPHENYLPHOSPHINIMIDES



Compound[a]				Analysis, %					
				Carbon		Hydrogen		Nitrogen	
R_1	R_2	R_3	M.p., °C.	Calcd.	Found	Calcd.	Found	Calcd.	Found
CN	H	H[b]	222–223	69.75	70.28	4.98	4.94	16.27	16.56
CN	CH_3	H[c]	229–230	70.38	70.08	5.34	5.25	15.63	15.68
CN	CH_3	CH_3[d]	159–160	70.95	70.91	5.68	5.30	15.05	15.20
CN	C_6H_5	H	200–202					13.33	13.28
NO_2	H	H	178.5–179.5	62.63	62.68	4.70	4.21	15.38	15.60
C_6H_5	H	H[e]	194–195	75.93	74.46	5.61	5.64	10.63	9.89
4-$NO_2C_6H_4SO_2$	H	H[f]	232–233	59.52	59.90	4.20	4.04	11.11	11.18

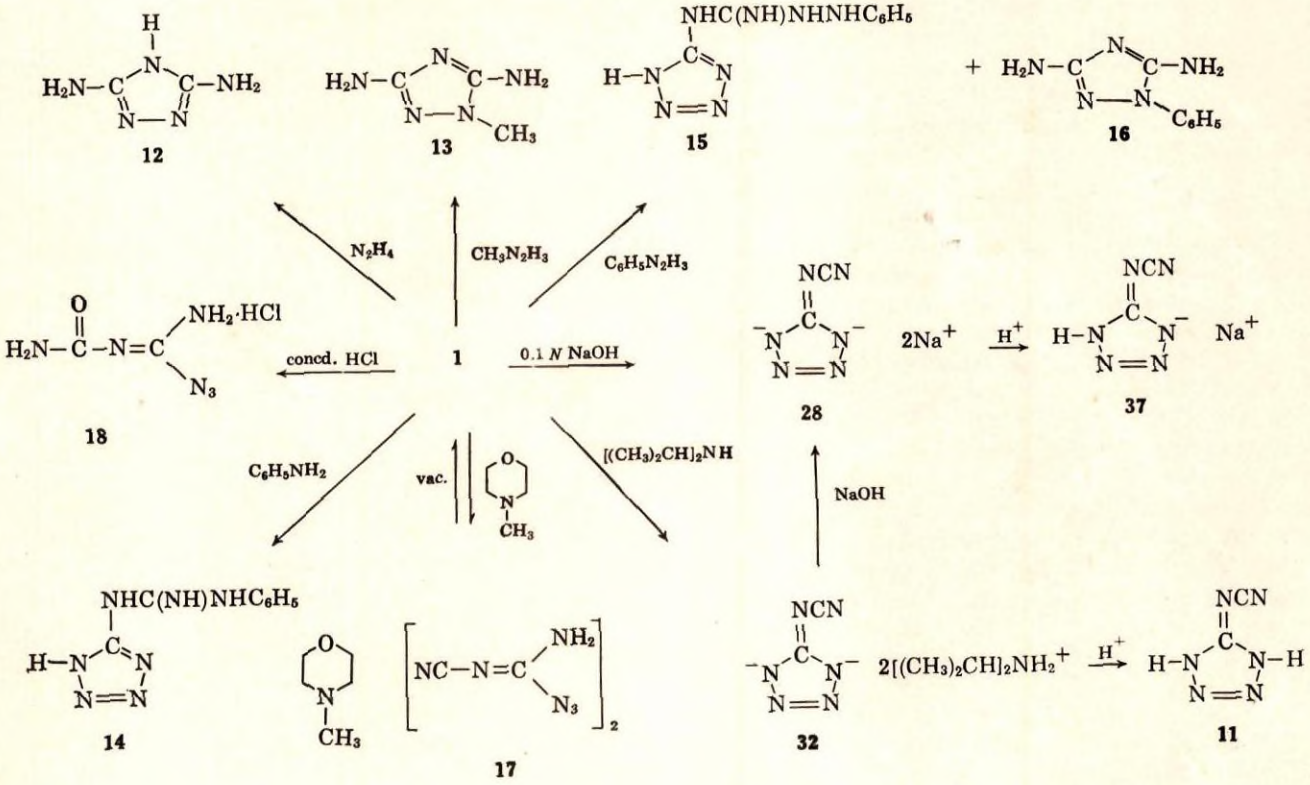
[a] The products were crystallized from benzene except where R_1 = C_6H_5 when ethanol was used. [b] Product which crystallized contained 1 mole of C_6H_6: *Anal.* Calcd. for $C_{20}H_{17}N_4P \cdot C_6H_6$: C, 73.93; H, 5.49; N, 13.26; C_6H_6, 18.5. Found: C, 73.22; H, 5.27; N, 13.57; C_6H_6, 18.5. It was desolvated by heating for 6 hr. at 100°. This same phosphinimide was obtained from either $N_3C(NH_2)$-NCN or $(N_3)_2C$=NCN. [c] Calcd.: P, 8.64. Found: P, 8.90. [d] Calcd.: P, 8.32. Found: P, 8.56. [e] This compound was prepared by heating 0.8 g. of 1-phenyl-5-aminotetrazole with 1.3 g. of triphenylphosphine for 9 hr. at 165–180°; gas was evolved. The glassy solid residue was dissolved in benzene, and the product precipitated with hexane. [f] Calcd.: S, 6.35. Found: S, 6.49.

react differently. Hydrazine and methylhydrazine, being weaker bases and better nucleophiles than the above organic bases,[21a] displace azide[21b] to give the intermediate aminocyanoguanidines which cyclize immediately to the corresponding triazoles, **12** and **13**. The structure of **13** was verified by synthesizing it from methylhydrazinium sulfate and sodium dicyanamide. Aniline and phenylhydrazine, which are weak bases and relatively poor nucleophiles, do not react with **1** at 25°, but in refluxing ethanol they add to the cyano group and cyclization occurs (not necessarily in that order) to give 1-phenyl-2-(5-tetrazolyl)guanidine (**14**) and 1-anilino-2-(5-tetrazolyl)guanidine (**15**), respectively. In addition, some azide displacement occurs with phenylhydrazine to give 1-phenyl-3,5-diamino-1,2,4-triazole (**16**). The structure of **16** was established by independent synthesis; the structure of **15** was inferred from analytical data and the failure of the compound to react with benzaldehyde, which indicates the absence of an >N–NH_2 group. N-Methylmorpholine, a relatively weak aliphatic amine, and **1** form a 1:2 complex (**17**) from which **1** may be recovered unchanged. Gummy precipitates which contain azide ion but which were not further characterized were obtained from either methylamine or triethylamine and **1** in diethyl ether. (See Chart I.)

The effect of acid on **1** was investigated only briefly. Cold concentrated hydrochloric acid and **1** react to give a compound which Hart[2] designated as the hydrate of

(21)(a) In the reaction, $H_2\overset{+}{N}{=}CNH_2(OC_2H_5) + BH \rightarrow H_2\overset{+}{N}{=}CNH_2$(B) + C_2H_5OH, in water at 25° the relative second-order rate constants, where BH = hydrazine, methylamine, isopropylamine, ammonia, and diethylamine, are 100, 89, 1.3, 1.0, and 0.050, respectively (unpublished work by R. A. Henry and W. R. McBride of this laboratory); (b) under certain conditions azide displacement by hydrazine from guanyl azide and nitroguanyl azide has been observed [F. L. Scott, D. G. O'Donovan, and J. Reilly, *J. Appl. Chem.* (London) **2**, 368 (1952); T. E. O'Connor, K. Horgan, and J. Reilly, *ibid.*, **1**, 91 (1951); F. L. Scott, F. C. Britten, and J. Reilly, *J. Org. Chem.*, **21**, 1519 (1956)].

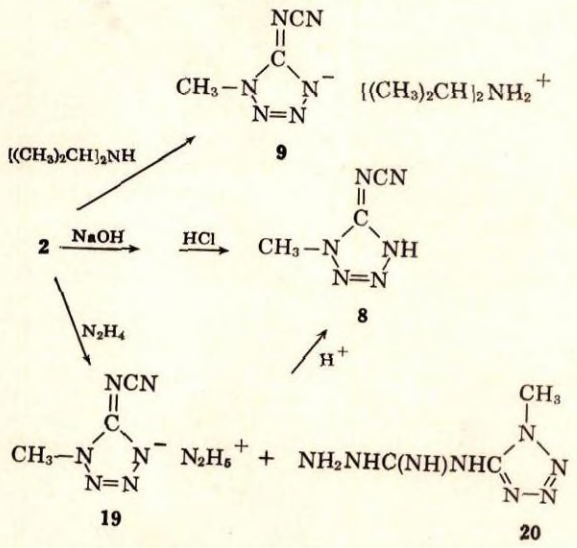
CHART I



cyanoguanyl azide hydrochloride on the basis of chloride analysis. It gives a positive test for the azido group and shows a strong carbonyl absorption band, 5.72 μ, indicating that the nitrile group has probably added water to form carbamoylguanylazide hydrochloride (**18**).

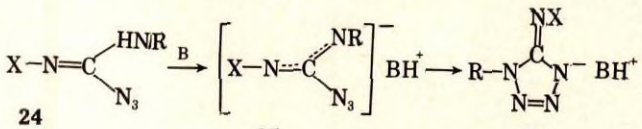
N-Cyano-N′-methylguanyl azide (**2**) forms the sodium, diisopropylammonium (**9**), and hydrazinium (**19**) salts of 1-methyl-5-cyaninotetrazoline when treated with respective bases. With hydrazine some 1-amino-2-(1-methyl-5-tetrazolyl)guanidine (**20**) (see Chart II) also is formed. Benzaldehyde reacts with the picrate of **20** to give the corresponding benzal hydrazone picrate. Since **3** cannot cyclize to a tetrazole or a tetra-

CHART II



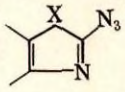
zoline, hydrazine again displaces azide ion and the intermediate, 1-amino-2-cyano-3,3-dimethylguanidine, ring closes to 3-amino-5-dimethylamino-1,2,4-triazole (**21**). N-Cyano-N′-phenylguanyl azide (**5**) resembles **2** since diisopropylamine and hydrazine convert it to salts of 1-phenyl-5-cyaniminotetrazoline (**22**). N,N-(1,4-Phenylene)bis(N′-cyanoguanyl azide) (**6**) reacts with diisopropylamine and sodium hydroxide to give the corresponding salts of 1,4-bis(5-cyanimino-1-tetrazolinyl)-benzene (**23**).

The function of base in the cyclization of electronegatively substituted guanyl azides (**24**) is to increase the electron density of the system by removal of a proton to give an intermediate (**25**) which then ring closes to **26**.



X = $ArSO_2$, NO_2, CN
R = H, CH_3, C_6H_5

Alternatively, a concerted process of proton removal and ring closure may occur, converting **24** to **26** directly.[22] Qualitatively this hypothesis is consistent with the facts. Nitroguanyl azide, with the most electronegative group and, therefore, the most acidic protons, requires only a very weak base such as acetate or amines to convert it to salts of 5-nitraminotetrazole[20]; arenesulfonylguanyl azides require aqueous sodium hydroxide or hot sodium carbonate solution for cyclization, pyridine being ineffective[3]; and cyanoguanyl

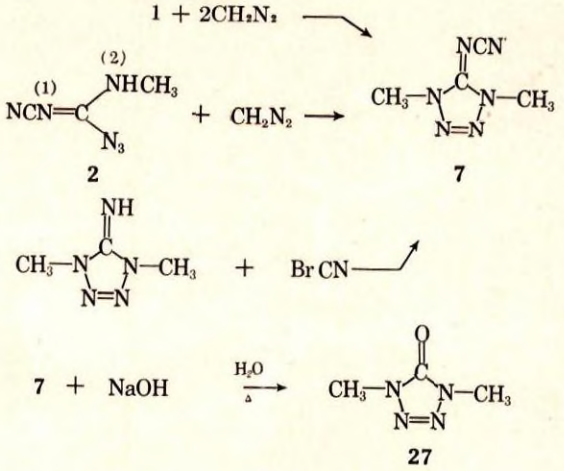
(22) Reynolds, VanAllan, and Tinker (ref. 7) put forth a similar argument to explain the effect of electron availability on tetrazole formation or lack thereof, in the system  where X is varied.

azide undergoes cyclization at room temperature with sodium hydroxide, 1,4-dimethyl-5-iminotetrazoline, diisopropylamine, and *t*-butylamine but not with weaker bases such as N-methylmorpholine and aniline. N-Cyano-N′-phenylguanyl azide (**5**) would be expected to have a more acidic proton than cyanoguanyl azide and require a weaker base. This seems to be the case because attempts to prepare **5** from sodium 5-anilinotetrazole and cyanogen bromide always gives 1-phenyl-5-cyaniminotetrazoline (**22**) rather than the acyclic guanyl azide, presumably with sodium 5-anilinotetrazole acting as the base. Guanyl azide does not require the assistance of external base to effect cyclization since the electron density is sufficiently high in the neutral molecule to permit its rapid isomerization to 5-aminotetrazole. The same is true of phenylguanyl azide and other similar systems.[19] The effectiveness of the bases, diisopropylamine, *t*-butylamine, and 1,4-dimethyl-5-iminotetrazoline, in cyclizing **1** may have been due, in part, to their bulk which would not affect the base strength much but would greatly inhibit nucleophilic attack on the imidoyl carbon. This may explain why methylamine and triethylamine apparently failed to give salts of 5-cyaniminotetrazoline when reacted with compound **1**.

Diazomethane and either **1** or **2** react slowly to give 1,4-dimethyl-5-cyaniminotetrazoline (**7**); a small amount of 2-methyl-5-(N-cyano-N-methylamino)tetrazole (**10**) also is formed in the first reaction.[23] The structure of **7** was established by its synthesis from 1,4-dimethyl-5-iminotetrazoline and cyanogen bromide and by its hydrolysis to 1,4-dimethyltetrazolone (**27**).[24] Methyl iodide and disodium 5-cyaniminotetrazoline (**28**) likewise give a mixture of **7** and **10**. The conversion of **2** to **7** with diazomethane involves a cyclization of the guanyl azide and a methylation, in that order, because methylation at N-(2) would give **3** and methylation at N-(1) followed by cyclization would give 1-methyl-5-(N-cyano-N-methylamino)tetrazole, materials which were not detected in this reaction. The latter two processes could, but apparently do not, compete with the first process since carbamyl azide reacts slowly with diazomethane to give N-methylcarbamyl azide. The base required for the cyclization must be diazomethane, a reagent which has been found to be an effective catalyst for transesterifications.[25,26] In the case of cyanoguanyl azide, monomethylation of the amino group followed by cyclization and further methylation may occur or cyclization may occur first, followed by dimethylation. Either route could lead to **7**. (See Chart III.)

Potassium 5-(N-cyano-N-methylamino)tetrazole (**4**) and methyl iodide react to give chiefly **10**; a small amount of the 1-methyl isomer is undoubtedly formed too, but it was not detected. The structure of **10** was established by basic hydrolysis to the known 2-methyl-5-methylaminotetrazole; the nitrile group is readily hydrated to give (2-methyl-5-tetrazolyl)urea (**29**), but the latter is hydrolyzed only with difficulty. The activated cyano group of **4** and azide ion readily condense to give N-methyl-N,N-bis(5-tetrazolyl)amine (**30**). Similarly, N,N-bis(5-tetrazolyl)amine hydrate (**31**) can be prepared in good yield from bisdiisopropylammonium 5-cyaniminotetrazoline (**32**), sodium dicyanamide, or potassium dicyanoguanidine, and trimethylammonium azide (see Chart IV following) in refluxing aqueous solution. Potassium dicyanoguanidine in hot aqueous solution must be in equilibrium with cyanamide and potassium dicyanamide, thus accounting for formation of **31** in the reaction (Chart IV). Cyanoguanidine behaves in a similar fashion, dissociating to cyanamide and reacting with hydrazoic acid to give 5-aminotetrazole.[27]

CHART III



The assignment of the 5-cyaniminotetrazoline structure in lieu of a 5-cyanaminotetrazole structure to some of the compounds reported here is based on infrared spectral data. The structures of **4**, **7**, and **10**, and **33** have been firmly established by chemical means. A comparison of the infrared spectrum of **7**, which is a tetrazoline, with the spectra of the others, which are tetrazoles, reveals some significant differences (Table II). The tetrazoles show absorption at 6.50–6.58 μ (possibly due to endocyclic >C=N–)[28] and 4.45 to 4.52 μ (unconjugated –C≡N). Dimethyl cyanamide shows –C≡N absorption at 4.52 μ. The exocyclic >C=N– of **7** absorbs at 6.18 μ and the conjugated –C≡N at 4.58 μ. The spectra of the other compounds named as 5-cyaniminotetrazoline derivatives correspond closely with that of **7** in these two particular regions of the spectrum.

Experimental

Reaction of 5-Methylaminotetrazole with Cyanogen Bromide.—5-Methylaminotetrazole, 9.9 g. (0.10 mole), was suspended in 20 ml. of water and neutralized to a phenolphthalein endpoint with potassium hydroxide. Ethanol (20 ml.) was added, the mixture was cooled to 0°, and 12.6 g. (0.12 mole) of cyanogen bromide was added. Potassium hydroxide (50% solution) was added dropwise to keep the reaction system at about pH 9 until all the cyanogen bromide had dissolved. The reaction mixture was stirred an additional 15 min. during which time a white

(23) The sluggish reaction of diazomethane with **1** and **2** is in marked contrast to its vigorous reaction with nitroguanyl azide. The principal product of the latter reaction is 2-methyl-5-(N-methyl-N-nitroamino)-tetrazole with a little 1-methyl isomer. The combined infrared spectra of these two compounds accounts for all the bands present in the spectrum of the product.

(24) K. Hattori, E. Lieber, and J. P. Horwitz, *J. Am. Chem. Soc.*, **78**, 411 (1956).

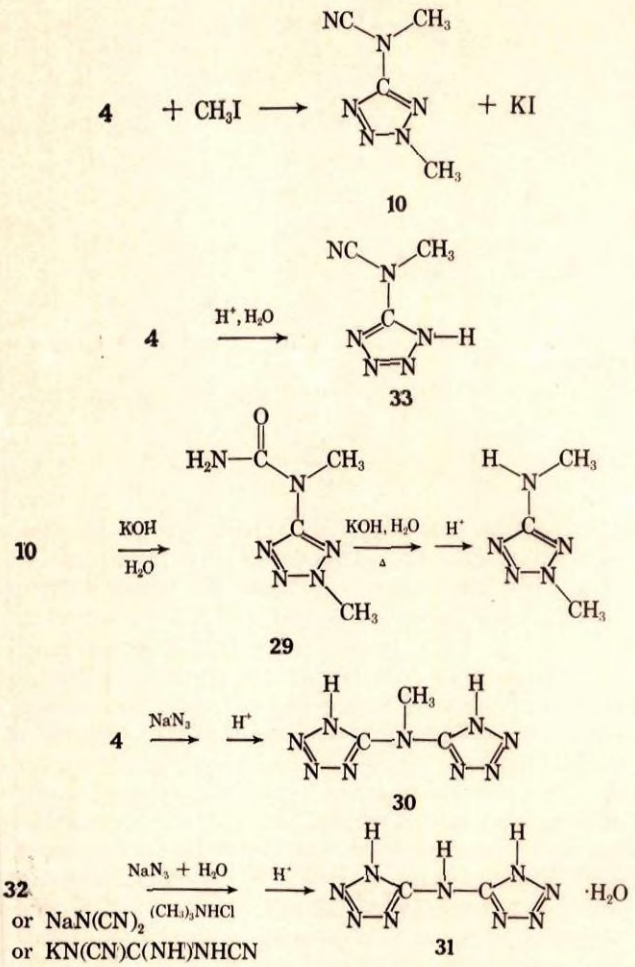
(25) T. Wieland and R. K. Rothhaupt, *Chem. Ber.*, **89**, 1176 (1956).

(26) H. Bredereck, R. Sieber, L. Hamphenkel, and R. Bamberger, *ibid.*, **89**, 1169 (1956).

(27) R. Stolle, *Ber.*, **62**, 1118 (1929)

(28) 5-Trifluoromethyltetrazoles absorb in this narrow band width also [W. P. Norris, *J. Org. Chem.*, **27**, 3248 (1962)].

CHART IV



precipitate formed. The solvent was removed under reduced pressure, and the solid residue was extracted with 50 ml. of boiling methylene chloride. Concentration and cooling to 0° gave 2.5 g. (20% yield) of N-cyano-N′-methylguanyl azide (**2**), m.p. 118–121° dec. Recrystallization from carbon tetrachloride raised the melting point to 122–123° dec. Exposure to light in the laboratory caused the solid to turn pink. This compound causes immediate liberation of iodine from a solution of sodium iodide in trifluoroacetic acid.

Anal. Calcd. for $C_3H_4N_6$: C, 29.03; H, 3.25; N, 67.72. Found: C, 28.61; H, 3.37; N, 67.92.

The methylene chloride insoluble residue from the above reaction was extracted with 700 ml. of boiling acetonitrile. The solution was filtered and cooled, depositing 0.70 g. of potassium 1-methyl-5-cyaniminotetrazoline (**34**), m.p. 290° dec., as fine white needles. Concentration of the filtrate and cooling gave 3.5 g. of large white needles of potassium 5-(N-cyano-N-methylamino)tetrazole (**4**), m.p. 210° dec. Further concentration and cooling gave alternately additional quantities of the 290 and 210° melting point materials. A total of 1.2 g. (7% yield) of **34** was obtained. Recrystallization from acetonitrile raised the decomposition point to 300°. The sample for analysis was dried at 100° (0.01 mm.) for 16 hr.

Anal. Calcd. for $C_3H_3KN_6$: C, 22.21; H, 1.86; K, 24.11; N, 51.82. Found: C, 22.30; H, 2.21; K, 24.09; N, 51.81.

A total of 4.0 g. (25% yield) of **4** was recovered. After recrystallization from acetonitrile the decomposition temperature remained at 210°. The sample for analysis was dried at 100° (0.01 mm.) for 16 hr.

Anal. Calcd. for $C_3H_3KN_6$: C, 22.21; H, 1.86; K, 24.11; N, 51.82. Found: C, 21.99; H, 2.43; K, 23.65; N, 51.27.

Neither of the latter compounds caused liberation of iodine from the sodium iodide–trifluoroacetic acid reagent.

N-Cyano-N′,N′-dimethylguanyl Azide (3).—5-Dimethylaminotetrazole (6.7 g., 0.058 mole) was suspended in 15 ml. of water and neutralized to a phenolphthalein end point with potassium hydroxide. Ethanol (15 ml.) was added followed by 6.2 g. (0.058 mole) of cyanogen bromide. The reaction mixture was stirred, maintaining a temperature of 30° until the cyanogen bromide dissolved. After 1 hr. the solvent was removed under reduced pressure. The residue was extracted with three 100-ml. portions of boiling ether. The ether solutions were combined and concentrated to 20 ml. Four grams of solid separated. This was chromatographed on a Celite–silicic acid column using benzene as the eluent. There was recovered 3.5 g. (44% yield) of **3**, m.p. 74–76°. Recrystallization from ether–methylene chloride solution gave 1.3 g. of material, m.p. 75–76°. Exposure to light in the laboratory caused this compound to turn pink. The compound causes immediate liberation of iodine from a solution of sodium iodide in trifluoroacetic acid.

Anal. Calcd. for $C_4H_6N_6$: C, 34.78; H, 4.38; N, 60.84. Found: C, 35.06; H, 4.48; N, 60.72.

General Procedure for Preparation of Guanyl-P,P,P-triphenylphosphinimides.—One millimole each of guanyl azide and triphenylphosphine were combined and heated at reflux, if necessary, in 5 ml. of benzene until the initially intense yellow color had disappeared. Upon cooling the phosphinimide crystallized from solution in high purity. In most cases the compound was recrystallized before analysis. Table III gives melting points and elemental analyses for the products. In the instance of **3** and triphenylphosphine, an intensely yellow solution formed at 25° from which an 88% yield of bright yellow crystals of the initial adduct, P,P,P-triphenyl-N-(N-cyano-N′,N′-dimethylguanyl)-phosphazide, m.p. 119° dec., separated.

Anal. Calcd. for $C_{22}H_{21}N_4P$: C, 65.99; H, 5.29; N, 20.99; P, 7.74. Found: C, 67.03; H, 5.18; N, 20.34; P, 7.73.

N-Carbamyl-P,P,P-triphenylphosphinimide from carbamyl azide and triphenylphosphine melted at 183.5–184.5° after two recrystallizations from benzene.

Anal. Calcd. for $C_{19}H_{17}N_2OP$: C, 71.24; H, 5.35; N, 8.75. Found: C, 71.51; H, 5.67; N, 8.78.

Bis-*t*-butylammonium Salt of 5-Cyaniminotetrazoline (35).—Cyanoguanyl azide (1.1 g., 0.01 mole) was dissolved in 125 ml. of diethyl ether and treated with 1.5 g. (0.02 mole) of *t*-butylamine in 75 ml. of ether. A turbidity developed immediately and in a few minutes a flocculent precipitate began to separate. After standing for 16 hr., the solid was removed and washed several times with ether; the yield of dried material was 1.75 g. (68%). It was recrystallized by dissolving in ethanol, filtering, and adding ether. The melting point is indefinite although a change of character occurs at 150–155°. The same compound resulted in lower yield when equimolar amounts of reactants were employed. This salt did not react with triphenylphosphine in ethanol (no yellow color, no gas evolution) and did not give a positive test for azide with sodium iodide and trifluoroacetic acid.

Anal. Calcd. for $C_{10}H_{24}N_8$: C, 45.85; H, 9.44; N, 43.71. Found: C, 45.88; H, 9.27; N, 43.73, 43.45.

Bisdiisopropylammonium salt of 5-cyaniminotetrazoline (32) was prepared in the same manner; the recrystallization was effected as before except that a few drops of diisopropylamine were added to the ethanol before the addition of ether. The salt can also be recrystallized, wastefully, from absolute ethanol. The salt begins to lose amine about 125° and decomposes 133–136°.

Anal. Calcd. for $C_{14}H_{32}N_8$: C, 53.81; H, 10.32; N, 35.86. Found: C, 53.89; H, 10.23; N, 36.04.

When an ethanolic solution of the salt was treated with picric acid, diisopropylammonium picrate could be recovered; after two recrystallizations from benzene the melting point was 148–149°; admixed with an authentic sample, the melting point was undepressed.

Anal. Calcd. for $C_{12}H_{18}N_4O_9$: N, 16.96. Found: N, 17.01.

An aqueous solution of the salt was treated with excess hydrochloric acid. The water was removed under reduced pressure and the gummy residue was extracted with ether and then dissolved in acetonitrile. Upon cooling, diisopropylammonium chloride, m.p. 211–213°, crystallized from solution. The melting point was not depressed by admixture with an authentic sample of diisopropylammonium chloride.

The salt (**32**) in ethanol did not react with triphenylphosphine; furthermore, no reaction occurred when such a solution was acidified, yet the addition of cyanoguanylazide to this same solution caused an immediate reaction. The salt also was recovered unchanged after being refluxed in tetrahydrofuran for 46 hr.

A more rapid alternate procedure is as follows: 3.3. g. of **1** is slurried in 35 ml. of absolute ethanol, 7.5 g. of diisopropylamine is added all at once, and the solution is allowed to warm spontane-

ously. The azide dissolves, then some of the white crystalline salt begins to separate; when the exothermic reaction is over, 100 ml. of diethyl ether is added, the mixture is cooled to 5°, and the product is removed by filtration. Washing with ether and drying furnishes 7.32 g. (95.5%) of **32**.

If equimolar quantities of 1 and diisopropylamine are refluxed in absolute ethanol, a yellow gelatinous precipitate, similar to that obtained with triethylamine (see below), is formed. Some of **32** in absolute ethanol was refluxed for 4 hr. with an excess of phenyl isothiocyanate; yellow plates began to separate after 2 hr. It was necessary to protect the reaction vessel from light otherwise the product became purple in color. After the heating period, the solid was removed from the hot solution by filtration and washed with ethanol until free of isothiocyanate. The dried product did not melt up to 250°; it was insoluble in water or aqueous base and was essentially insoluble in hot ethanol. The dried solid was also photosensitive and rapidly turned purple unless kept in the dark. A sample of the unrecrystallized material was analyzed. The structure is unknown.

Anal. Calcd. for $C_{10}H_9N_7S$: C, 46.32; H, 3.49; N, 37.82; S, 12.36. Found: C, 46.28; H, 3.46; N, 37.82; S, 12.50.

Bis-1,4-dimethyl-5-iminotetrazoline Salt of 5-Cyaniminotetrazoline (36).—This salt was made in absolute ethanol, precipitated with diethyl ether, and recrystallized from absolute ethanol, m.p. 140–141° dec.

Anal. Calcd. for $C_8H_{16}N_{16}$: C, 28.57; H, 4.80; N, 66.64. Found: C, 28.24; H, 4.58; N, 66.97.

Monosodium Salt of 5-Cyaniminotetrazoline (37).—To a solution of sodium hydroxide (0.8 g., 0.02 mole) in 20 ml. of water at 5° was added all at once 3.2 g. (0.02 mole) of recrystallized **32**. This solution was then evaporated to one-half volume at ambient temperature under reduced pressure in order to remove the diisopropylamine, cooled to 5°, and acidified with concentrated hydrochloric acid to the bromophenol blue end-point. The white plates which separated were removed and washed with a small volume of ice–water; the yield of dried product was 1.0 g. This monosodium salt, m.p. above 300°, was recrystallized, wastefully, by dissolving in 10 ml. of water at 35°, filtering, and chilling to 0°; the white felted needles were dried at 100° before analysis.

Anal. Calcd. for C_2HN_6Na: C, 18.19; H, 0.76; N, 63.64; Na, 17.42. Found: C, 17.63; H, 0.97; N, 63.30; Na, 16.90.

The monosodium salt also was prepared directly from **1**. **1** (1.1 g., 0.010 mole) was added to 200 ml. of 0.10 *N* sodium hydroxide. The solution was basic to phenolphthalein indicator. The water was removed under reduced pressure to leave a white powder. The powder was dissolved in 5 ml. of water and acidified with 6 *N* hydrochloric acid to give 1.1 g. of **37** with properties identical with those of the compound made in the preceding experiment. An excess of acid or base converts the monosodium salt to the more soluble diacidic or dibasic forms.

5-Cyaniminotetrazoline (11) was isolated in poor yield and in an impure state by dissolving 3.1 g. of **32** in 5 ml. of ice–water, adding 3.4 ml. of cold 6 *N* hydrochloric acid, and cooling overnight at −18°. A mixture of amorphous and crystalline material separated; the amorphous product, which was removed by swirling the solution and decantation, was very poorly soluble in water but was soluble in base. It decomposed at about 240° when plunged into a hot bath. The remaining crystalline fraction was washed with a small volume of ice–water and dried; it was soluble in water giving a strongly acidic solution. When heated from ambient the compound did not melt up to 155°. When plunged into a hot bath at 120°, however, it decomposed explosively. The infrared spectrum was distinctly different from that for the isomeric cyanoguanyl azide. When an aqueous solution of the free acid stood at 0°, an amorphous white solid, which decomposed about 240° when plunged into a preheated bath, was formed. The nitrogen content was about 67%.

Anal. Calcd. for $C_2H_2N_6 \cdot 0.5H_2O$: N, 70.57. Found: N, 71.58.

3,5-Diamino-1,2,4-triazole (12).—Cyanoguanyl azide (1) (3.3 g., 0.03 mole) was slurried in 30 ml. of absolute ethanol, cooled to 5°, and treated with 1.1 g. (0.033 mole) of 96% hydrazine in 30 ml. of cold ethanol. There was a complete and rapid solution of all solid; some gas was evolved. The solution was refluxed for 2 hr., then cooled to 5°; the white solid was removed by filtration, washed with diethyl ether, and dried (2.0 g., 66%). It recrystallized from absolute ethanol upon the addition of ether as felted needles, m.p. 201–202°, with wetting and shrinking at 190–195°.

Anal. Calcd. for $C_2H_5N_5$: C, 24.24; H, 5.09; N, 70.68. Found: C, 24.10; H, 5.20; N, 70.75.

This compound furnished a picrate decomposing at 248–249° after recrystallization from water; admixture with authentic 3,5-diamino-1,2,4-triazole picrate did not depress the melting point.

The pale yellow dibenzal derivative, made by refluxing some of the compound in ethanol with benzaldehyde and piperidine, decomposed at 203–204° after recrystallization from benzene in which it is only sparingly soluble.

Anal. Calcd. for $C_{16}H_{13}N_5$: C, 69.80; H, 4.76; N, 25.44. Found: C, 69.45; H, 5.30; N, 24.83.

In one experiment a small amount of a compound, poorly soluble in alcohol, was recovered from the initial reaction. This unknown, which was water soluble, was fractionally precipitated from 75% ethanol with diethyl ether. The early crops were amorphous and were discarded; finally a crystalline fraction was obtained which did not melt up to 300° although it became tan colored about 240–250°. This material might possibly be either impure dihydrazinium 5-cyaniminotetrazoline or the isomeric hydrazinium 1-amino-2-(5-tetrazolyl)guanidine.

Anal. Calcd. for $C_2H_{10}N_{10}$: C, 13.79; H, 5.79; N, 80.42. Found: C, 14.39; H, 3.73; N, 81.95.

3,5-Diamino-1-methyl-1,2,4-triazole (13).—A solution of methylhydrazine (0.08 g.) and **1** (1.85 g.) in 40 ml. of absolute ethanol, after standing at room temperature for 1 hr., was refluxed for 2 hr.; gas was evolved. When the solution was cooled, a small amount (0.05 g.) of white flocculent solid with an indefinite melting point separated and was removed. The ethanol solution was evaporated under reduced pressure to leave a viscous oil which was redissolved in 20 ml. of ethanol. One-half of this solution was treated with excess picric acid; there was an immediate precipitation of the yellow monopicrate (rosettes of fine needles) which decomposed at 273–274° after two recrystallizations from 95% ethanol.

Anal. Calcd. for $C_9H_{10}N_8O_7$: C, 31.58; H, 2.95; N, 32.74. Found: C, 31.52; H, 2.83; N, 31.97, 32.04.

The other half of the ethanolic solution was adjusted to the bromophenol blue endpoint with concentrated hydrochloric acid and treated with 10 ml. of ether. The white crystalline solid was removed and washed well with more ether, 0.95 g. (75%). After recrystallization from ethanol–diethyl ether this hydrochloride decomposed at 188–190°.

Anal. Calcd. for $3(C_3H_7N_5) \cdot 2HCl$: N, 50.95; Cl, 17.20. Found: N, 50.59; Cl, 16.99.

The monohydrochloride decomposed at 218–220° and was obtained by recrystallizing some of the initial hydrochloride from absolute ethanol which contained a few drops of concentrated hydrochloric acid.

Anal. Calcd. for $C_3H_7N_5 \cdot HCl$: N, 46.82; Cl, 23.70. Found: N, 46.24; Cl, 23.36.

3,5-Diamino-1-methyl-1,2,4-triazole (13), characterized as its picrate, was made in 96.5% yield by heating 0.04 mole of methylhydrazinium sulfate ($CH_3NHNH_2 \cdot 0.5H_2SO_4$) with 0.04 mole of sodium dicyanamide in 25 ml. of water for 2 hr.[29]

Phenylhydrazine with 1.—Cyanoguanyl azide (2.2 g., 0.02 mole) and phenylhydrazine (2.2 g., 0.02 mole) were dissolved in 50 ml. of absolute ethanol. There was no evidence of reaction at ambient temperature. The solution was refluxed for 2 hr., then cooled at 5° for several days. The white solid (0.7 g., 16%) was removed, washed with cold ethanol, and recrystallized twice from ethanol, m.p. 221–222° dec., darkening about 210°. The compound, which was slightly soluble in hot water and readily soluble in cold, dilute sodium hydroxide solution, showed neither nitrile nor azido function in its infrared spectrum; it did not react with benzaldehyde. These properties suggest 1-anilino-2-(5-tetrazolyl)guanidine (15).

Anal. Calcd. for $C_8H_{10}N_8$: C, 44.03; H, 4.62; N, 51.35. Found: C, 43.90; H, 4.93; N, 51.19.

That the product might be the hydroazide of 3,5-diamino-1-phenyl-1,2,4-triazole (16) is excluded on the basis of the infrared spectrum; that it might be the latter triazole is excluded on the basis of its analyses.

Evaporation of the original alcoholic mother liquors gave a red-brown gum which was converted to a picrate, m.p. about 220° dec. After one recrystallization from a large volume of 95% ethanol, the melting point of the orange needles was raised to 228–230° dec.[30]; admixture with an authentic sample of **16**

(29) M. B. Frankel, E. A. Burns, J. C. Butler, and E. R. Wilson, *J. Org. Chem.*, **28**, 2428 (1963).

picrate did not depress the melting point. The infrared spectrum for this picrate revealed no nitrile or azido function and was identical with that for **16** picrate.

Anal. Calcd. for $C_{14}H_{12}N_8O_7$: N, 27.72. Found: N, 27.58.

3,5-Diamino-1-phenyl-1,2,4-triazole can be made also by refluxing an aqueous solution of equimolar quantities of phenylhydrazine hydrochloride and sodium dicyanamide; the picrate decomposed at 233–234°.

Anal. Calcd. for $C_{14}H_{12}N_8O_7$: C, 41.59; H, 2.99; N, 27.72. Found: C, 42.07; H, 2.97; N, 27.95.

1-Phenyl-2-(5-tetrazolyl)guanidine (14).—Cyanoguanyl azide (1.1 g., 0.01 mole), 1.0 g. of aniline, and 25 ml. of absolute ethanol were refluxed for 16 hr. The microcrystalline solid, which gradually separated, was removed from the solution after cooling, washed with cold ethanol, and dried, yielding 0.95 g. (50.2%). It can be recrystallized from a large volume of acetonitrile, or purified by dissolution in dilute aqueous sodium hydroxide, followed by filtration and acidification. The melting point, which was somewhat dependent on the heating rate, was 271–273° dec.; phenyl isocyanide was generated during the decomposition. Absorption bands corresponding to nitrile and azido function were absent in the infrared spectrum.

Anal. Calcd. for $C_8H_9N_7$: C, 47.28; H, 4.46; N, 48.26. Found: C, 47.27; H, 4.62; N, 48.90.

No reaction occurred when the reactants in a 1:2 molar ratio in diethyl ether were allowed to stand at ambient temperature for 4 days.

Cyanoguanyl Azide–N-Methylmorpholine (2:1) Complex (17).—When **1** (1.1 g., 0.01 mole) in 125 ml. of diethyl ether was treated with 2.1 g. (0.02 mole) of dried N-methylmorpholine, no crystalline salt separated even after several days. The addition of 25 ml. of benzene did not cause any precipitation. The solution was evaporated to one-third volume under reduced pressure at ambient temperature; the white solid which appeared was then redissolved by gently warming the solution. Upon cooling the solution to 0°, colorless, clear prisms crystallized; these were removed and washed with a small volume of cold benzene. This compound was very soluble in water and, if dried for only a few minutes in a vacuum desiccator, decomposed at 98–100°.

Anal. Calcd. for $C_9H_{15}N_{13}O$: C, 33.64; H, 4.71; N, 56.67. Found: C, 33.53; H, 4.95; N, 56.45.

In contrast to the behavior of the salts obtained with *t*-butylamine or diisopropylamine, **17** reacted immediately with triphenylphosphine in ether, evolving gas and developing a yellow color. Furthermore, the infrared spectrum of this complex showed absorption peaks characteristic of both nitrile and azido groups (similar to **1**), whereas the salts show only a single strong absorption at 4.6–4.7 μ, characteristic of the cyanimino group. Additional evidence that this was only a complex of **1** and N-methylmorpholine was the fact that prolonged pumping at 20 mm. and room temperature caused the clear prisms to disintegrate to a white powder, m.p. 149.5–150.5° dec., whose infrared spectrum was identical with that of **1**.

Triethylamine and 1.—The latter compound (1.1 g., 0.01 mole) in 150 ml. of diethyl ether was treated with 1.0 g. of triethylamine (0.01 mole). No turbidity developed and no gradual precipitation of a crystalline solid occurred. After 15 days at ambient temperature, 1.6 g. of a yellow gum had separated. This gum was only partially soluble in absolute ethanol or in water; the insoluble fraction was swollen by water to a viscous, gelatinous mass. Evaporation of the ethereal mother liquors left a white, crystalline solid, m.p. 75–80°, which was very soluble in water, evolved triethylamine when made basic, and gave a strong, qualitative test for azide ion; the evidence suggests triethylammonium azide.

Similar results were obtained with monomethylamine.

Diisopropylammonium Salt of 1-Methyl-5-cyaniminotetrazoline (9).—This salt separated as clear needles when 0.12 g. (0.001 mole) of **2** in 20 ml. of diethyl ether was treated with 0.25 g. (0.002 mole) of diisopropylamine in ether. The ether-washed product melted at 136–137° (without decomposition) after vacuum drying; it gave no qualitative test for azido function.

Anal. Calcd. for $C_9H_{19}N_7$: C, 47.97; H, 8.50; N, 43.52. Found: C, 48.18; H, 8.35; N, 43.57.

1-Methyl-5-cyaniminotetrazoline (8).—N-Cyano-N′-methylguanyl azide (0.43 g., 0.0035 mole) was dissolved in 35 ml. of 0.10 *N* sodium hydroxide, then 35 ml. of 0.10 *N* hydrochloric acid was added. The solution was extracted with ether to remove 50 mg. of starting material. The water was then removed under reduced pressure and the solids were extracted eight times with ether. The ether was evaporated to leave 0.25 g. of solid, m.p. 160° dec. Recrystallization from tetrahydrofuran gave 0.12 g. of **8**, m.p. 162° dec. This compound does not give an azide test with triphenylphosphine.

Anal. Calcd. for $C_3H_4N_6$: C, 29.03; H, 3.25; N, 67.72. Found: C, 29.28; H, 3.15; N, 67.65.

1-Methyl-5-cyaniminotetrazoline (8) and 1-Amino-2-(1-methyl-5-tetrazolyl)guanidine (20).—N-Cyano-N′-methylguanyl azide (0.74 g.) and 95% hydrazine (0.2 g.), each dissolved in 5 ml. of cold absolute ethanol, were mixed. The slurry was kept in an ice–water bath until gas evolution had ceased and the azide had dissolved completely (about 20 min.); the solution was heated to boiling and then evaporated to dryness under reduced pressure. The residue was dissolved in 5 ml. of water, acidified with 7 drops of concentrated hydrochloric acid, and chilled to 5°. The 1-methyl-5-cyaniminotetrazoline which separated (0.17 g., 23%) was removed and recrystallized from water as rosettes of white needles. An aqueous solution of the compound is strongly acidic.

Anal. Calcd. for $C_3H_4N_6$: C, 29.03; H, 3.25; N, 67.72. Found: C, 28.66; H, 3.24; N, 68.54.

If the alcoholic reaction mixture is treated with an equal volume of diethyl ether, instead of being worked up as outlined above, then hydrazinium 1-methyl-5-cyaniminotetrazoline (**19**) separates as white pills. The melting point of **19** is indefinite. The above compound changes character at about 100°, then decomposes at 220–225°; when plunged into a hot bath at 210°, it melts, decomposes, then resolidifies; when plunged into a hot bath at 140–145°, it swells during dehydrazination or reaction, then resolidifies.

Anal. Calcd. for $C_3H_8N_8$: N, 71.76. Found: N, 70.90.

The aqueous solution remaining after the removal of **8** was made basic to phenolphthalein with sodium hydroxide and evaporated to dryness. The residue was extracted with 15 ml. of boiling 95% ethanol, and the hot extract was treated with 1 g. of picric acid. The picrate (0.6 g.), which crystallized, melted between 180–190°. Several recrystallizations from 95% ethanol gave flat, yellow needles which decomposed 195–196°. The analyses are consistent with those required for the picrate of **20**.

Anal. Calcd. for $C_9H_{11}N_{11}O_7$: C, 28.06; H, 2.88; N, 39.99. Found: C, 28.11; H, 2.85; N, 39.38.

When some of the above picrate was dissolved in hot 95% ethanol and treated with benzaldehyde, the **benzal hydrazone picrate** separated as dagger-shaped plates, m.p. 239–240° dec., after another recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{15}N_{11}O_7$: C, 40.59; H, 3.19; N, 32.55. Found: C, 40.22; H, 3.23; N, 32.78, 32.60.

In another experiment a small amount of a picrate, m.p. 231–232° dec., after two recrystallizations from ethanol, also was recovered; this may have been the picrate of 3-amino-5-methylamino-1,2,4-triazole but it was not analyzed.

3-Amino-5-dimethylamino-1,2,4-triazole (21).—N-Cyano-N′,-N′-dimethylguanyl azide and hydrazine (molar equivalents) reacted exothermically in absolute ethanol with gas evolution. After 5 hr. at ambient temperature, the solution was stripped to dryness under reduced pressure and the residue was converted to a picrate. After three recrystallizations from 95% ethanol, the melting point was 206.5–207.5°.

Anal. Calcd. for $C_{10}H_{12}N_8O_7$: C, 33.71; H, 3.40; N, 31.45. Found: C, 33.69; H, 3.44; N, 31.43.

Hydrazine Salt of 1-Phenyl-5-cyaniminotetrazoline (38).—When equimolar quantities of **5** and 95% hydrazine were mixed in a small volume of absolute ethanol, the azido compound rapidly dissolved but no gas was evolved; white, felted needles of the salt gradually crystallized, m.p. 110–111° dec. This salt, which tends to lose hydrazine upon recrystallization or upon vacuum drying, is water soluble and gives **22** upon acidification (identical infrared spectra).

Anal. Calcd. for $C_8H_{10}N_8$: C, 44.03; H, 4.62; N, 51.35. Found: C, 44.23; H, 4.90; N, 51.09.

The diisopropylammonium salt of 1-phenyl-5-cyaniminotetrazoline (39) was made from **5** in the same manner as described above for the other salts. Recrystallization from ethanol–ether gave large, brilliant, clear prisms, which melted at 142–143° without decomposition.

(30) G. Cohn [*J. prakt. Chem.*, [2]**84**, 396 (1911)] reported m.p. 225°. Repetition of his procedure, however, gave a base whose picrate decomposed at 233–235° after recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_{21}N_7$: C, 58.51; H, 7.37; N, 34.12. Found: C, 57.82, 58.01; H, 7.35, 7.42; N, 34.71.

When some of the above salt in a minimum volume of cold water was acidified with concentrated hydrochloric acid, a white powdery solid separated. After recrystallization from a small volume of absolute ethanol, the rosettes of fine needles partially melted and slumped, then resolidified when plunged into a preheated bath at 150–155°. If heated from room temperature, there was no visible change in the sample up to higher temperatures. The infrared spectrum of this compound was identical with **22** made by the following procedure.

Anal. Calcd. for $C_8H_6N_6$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.49; H, 3.41; N, 45.20.

1-Phenyl-5-cyaniminotetrazoline (22).—5-Anilinotetrazole (3.0 g., 0.019 mole) was dissolved in 40 ml. of 50% aqueous acetone, neutralized to the phenolphthalein endpoint with aqueous sodium hydroxide, cooled to 5°, and treated with 2.0 g. of cyanogen bromide. The mixture was stirred for 1.5 hr. and complete solution was attained. After about 4 hr. solid began to separate; after the solution had stood for 3 days at 5°, the solid was removed and washed with 10 ml. of cold 50% aqueous acetone. Approximately 0.5 g. of starting anilinotetrazole was recovered from this solid which also contained a material not immediately soluble in aqueous base and which decomposed about 145°. (This base-insoluble fraction, which was very soluble in acetonitrile and ethyl acetate but insoluble in benzene, was not investigated further, although it is suggested that it might have been phenylcyanoguanyl azide.) The cold original mother liquors plus the aqueous acetone washings were acidified; the white solid which separated was removed and washed with two 25-ml. portions of cold water. The yield of dried product was 1.1 g. in one experiment, 1.4 g. in another. This material melted and resolidified at about 150–155° when plunged into a hot bath, then decomposed at 240–241°. If the compound were recrystallized rapidly from acetonitrile, it was obtained as white needles showing the same melting behavior as the starting material. It was base-soluble, gave no test for azido function with potassium iodide in trifluoroacetic acid, and showed =NCN absorption (4.6 μ) in its infrared spectrum; these properties are consistent with those expected for **22**.

Anal. Calcd. for $C_8H_6N_6$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.45; H, 3.45; N, 45.11.

There was no evolution of gas and no development of a yellow color (further confirming the absence of an azido group) when 0.2 g. of the compound and 0.3 g. of triphenylphosphine were dissolved in 50 ml. of ethanol–benzene (1:1). When this solution was refluxed for 4 hr., there was recovered a sparingly soluble compound whose infrared spectrum no longer showed a –CN group. An identical compound was obtained when **22** was refluxed in acetonitrile. Recrystallization from absolute ethanol gave white clusters of crystals which decomposed at 273–277° with evolution of phenyl isocyanide. The properties and analyses of this compound suggest that it is probably a triazine derivative.

Anal. Calcd. for $(C_8H_6N_6)_3$: C, 51.61; H, 3.25; N, 45.14. Found: C, 51.36, 51,90; H, 3.25, 3.31; N, 45.05, 44.97.

1,4-Bis(5-cyanimino-1-tetrazolinyl)benzene (23).—Crude N,N-(1,4-phenylene)bis(N′-cyanoguanyl azide) (**40**), which was prepared from 1,4-diaminobenzene and $(N_3)_2C{=}NCN$[2] in absolute ethanol, was slurried in cold water and treated with excess cold 0.1 *N* sodium hydroxide solution. An appreciable amount of gelatinous material remained undissolved and was removed by filtration. When the clear, cold filtrate was carefully acidified with dilute hydrochloric acid, a light gray powder separated. It was filtered, washed well with cold water, and vacuum dried at 20 mm., first at ambient temperature, then at 80°. The compound decomposed explosively when plunged into a bath preheated to 220° but did not when plunged into a bath at 215°. When heated from ambient, the compound did not decompose visibly or melt up to 250°. The infrared spectrum shows a strong, single absorption at 4.55 μ.

Anal. Calcd. for $C_{10}H_6N_{12}$: C, 40.82; H, 2.06; N, 57.13. Found: C, 39.53, 40.72; H, 2.48, 3.06; N, 57.59.

Bisdiisopropylammonium 1,4-bis(5-cyanimino-1-tetrazolinyl)-benzene (41) was made as follows. Crude diazide (**40**, 1.87 g.) was slurried in 50 ml. of absolute ethanol and treated with 1.5 g. of diisopropylamine. There was an immediate reaction with heat evolution, a partial solution of solids, then a reprecipitation. After 4 hr. at room temperature the salt was brought into solution amorphous, insoluble material remained and was removed by filtration after the solution had been chilled to 5°. An equal volume of diethyl ether now was added slowly to the filtrate; an almost white crystalline solid separated, which was filtered and washed first with ethanol–ether (1:2), then with ether. The yield of dried salt, which melted above 300°, was 1.17 g.; this product is readily and completely soluble in cold water.

Anal. Calcd. for $C_{22}H_{36}N_{14}$: C, 53.20; H, 7.31; N, 39.49. Found: C, 52.97; H, 7.31; N, 39.75.

Reaction of 1 with Diazomethane.—Cyanoguanyl azide (1.4 g., 0.013 mole) was dissolved in 100 ml. of ether and added to an ether solution of diazomethane (0.013 mole). The diazomethane color was not discharged rapidly, and there was no visible nitrogen evolution. After standing for 72 hr. in the dark at 25°, the yellow color of diazomethane was gone. The ether was evaporated, and the residue was dissolved in methylene chloride and then chromatographed on a silicic acid–Celite column using methylene chloride as the eluting solvent. The first solid recovered was 1,4-dimethylcyaniminotetrazoline (**7**) which amounted to 0.45 g., m.p. 110–111° (with softening at 108°). This compound does not liberate iodine from a saturated solution of sodium iodide in trifluoroacetic acid.

Anal. Calcd. for $C_4H_6N_6$: C, 34.78; H, 4.38; N, 60.84. Found: C, 34.94; H, 4.33; N, 61.00.

Approximately 0.5 g. of **1** subsequently was eluted from the column with ether.

In another experiment 0.14 mole of **1** and 0.34 mole of diazomethane were used. The per cent yield of **7** was approximately the same. In addition, a small amount of oil was isolated. Its infrared spectrum showed absorption bands at 4.47 and 6.48 μ, characteristic of **10**, and at 4.58 and 6.12 μ, characteristic of **7**, indicating a mixture of the two.

Reaction of 2 with Diazomethane.—N-Cyano-N′-methylguanyl azide (0.75 g., 0.0060 mole) was dissolved in 75 ml. of ether containing 0.007 mole of diazomethane. The reaction was worked up in the same manner as in the previous experiment to give 0.60 g. (72% yield) of **7**, m.p. 110–112°, after recrystallization from carbon tetrachloride.

Methylation of 28.—Bisdiisopropylammonium salt of 5-cyaniminotetrazoline (0.70 g., 0.0022 mole) was dissolved in 15 ml. of methanol and added to 10 ml. of methanol containing 0.0045 mole of sodium methoxide. The volatiles were removed under reduced pressure leaving a powdery white residue. The salt was suspended in 35 ml. of acetonitrile containing 2 ml. of methyl iodide and was refluxed until the solid had disappeared. The solvent was removed under reduced pressure and the gummy residue was triturated with ether. Evaporation of the ether left 0.25 g. of oil. An infrared spectrum of the oil showed it to consist of about equal proportions of **7** and **10**.

1,4-Dimethyl-5-cyaniminotetrazoline (7).—A solution of 1,4-dimethyl-5-iminotetrazole (0.53 g.) and triethylamine (0.5 g.) in 30 ml. of diethyl ether–benzene (2:1) was cooled in an ice–water bath. Cyanogen bromide (0.5 g.) in 10 ml. of cold ether was added to the first solution; immediately a white flocculent precipitate formed. After 3 days, the triethylammonium bromide was removed and washed with ether. The combined ethereal solutions were evaporated to dryness, and the residue was recrystallized from carbon tetrachloride, yielding 0.2 g., m.p. 112–113°. The infrared spectrum of this compound was identical with **7** obtained by the previous procedures.

Hydrolysis of 7.—1,4-Dimethyl-5-cyaniminotetrazoline (0.30 g., 0.0022 mole) was added to 0.26 g. (0.0065 mole) of sodium hydroxide in 5 ml. of water and was heated for 15 min. on a steam bath. The cooled solution was extracted with three 15-ml. portions of ether. The ether was evaporated and the residue sublimed at 100° (0.1 mm.) to give 0.10 g. (40% yield) of **27**, m.p. 117–118°. The melting point was not depressed when mixed with an authentic sample of 1,4-dimethyltetrazalone-5 and the infrared spectrum of **27** was identical with that of the latter compound.

Monomethylation of Carbamyl Azide.—The latter compound reacted very slowly at ambient temperature with an ethereal solution of diazomethane (excess); several days were required to discharge the yellow color completely. The solution was filtered and evaporated to dryness; the remaining oil gradually crystallized. Recrystallization from hexane gave white plates, m.p. 47–48°, which sublimed rapidly at 25 mm. and room temperature. The melting point for N-methylcarbamyl azide (**42**) is reported[31] to be 46–47°.

Anal. Calcd. for $C_2H_4N_4O$: N, 55.98. Found: N, 55.57, 55.40.

The infrared spectrum showed that the azido function was still present; this was confirmed by reaction with triphenylphosphine. After two recrystallizations from benzene, the resulting phosphinimide decomposed 160–162°.

Anal. Calcd. for $C_{20}H_{19}N_2OP$: C, 71.82; H, 5.73; N, 8.38. Found: C, 71.65; H, 5.71; N, 8.22.

Some of **42** was refluxed for 30 min. with aniline in absolute ethanol; the solvent was then removed, and the oily residue was triturated several times with hot hexane. The white crystalline solid which remained melted at 148–149°; the melting point of *N-methyl-N'-phenylurea is* 151–152°. *Admixture with* N,N'-diphenylguanidine (m.p. 147–148°), the most likely product if the methylated carbamyl azide had been $NH{=}C(OCH_3)N_3$, was 110–115°.

Reaction of Diazomethane with Nitroguanyl Azide.—Diazomethane, 0.138 mole, in 135 ml. of ether was added to 7.3 g. (0.056 mole) of nitroguanyl azide in ether solution. The yellow color of diazomethane was discharged rapidly with vigorous evolution of gas. The solution was filtered and the ether was evaporated to leave 8.0 g. of viscous, light yellow liquid. The infrared spectrum of the crude material indicated that it was a mixture of starting material (azide band at 4.63 μ) and 1- and 2-methyl-5-(N-methyl-N-nitroamino)tetrazoles. All the absorption bands in the product could be accounted for from these three spectra.

1-Methyl-5-(N-methyl-N-nitroamino)tetrazole.—1-Methyl-5-methylaminotetrazole (22.6 g.) was added portionwise with stirring to 50 ml. of concentrated sulfuric acid at 15–20°. The solution was cooled to and maintained at 10° while 15 ml. of 90% nitric acid was added during 20 min. After 10 min. the nitration mixture was poured over 300 g. of crushed ice; the precipitated nitramine was removed by filtration and washed with four 50-ml. portions of ice–water; the yield of dried product, m.p. 55°, was 22.5 g. The melting point of the white needles was raised to 57.5–58.5° by recrystallization from 2-propanol. The compound is very soluble in methylene chloride, benzene, methanol, and ethyl acetate, moderately soluble in diethyl ether, and poorly soluble in cyclohexane.

Anal. Calcd. for $C_3H_6N_6O_2$: C, 22.79; H, 3.83; N, 53.15. Found: C, 22.70; H, 3.87; N, 52.92.

1-Ethyl-5-(N-ethyl-N-nitroamino)tetrazole, prepared similarly, melted at 48–49° after recrystallization from diethyl ether at −80°.

2-Methyl-5-(N-methyl-N-nitroamino)tetrazole.—One milliliter of 100% nitric acid was added dropwise to 0.50 g. of 2-methyl-5-methylaminotetrazole dissolved in 3 ml. of 95% sulfuric acid keeping the temperature below 20°. After completion of addition the mixture was poured onto ice and the whole was extracted with three 25-ml. portions of ether. The ether was evaporated and the oily residue was distilled from an Emick tube at *0.1* mm. *to give three drops of clear liquid,* $n^{25}D$ *1.5027.*

Anal. Calcd. for $C_3H_6N_6O_2$: C, 22.79; H, 3.83; N, 53.15. Found: C, 24.07; H, 3.76; N, 52.46.

Methylation of potassium 5-nitroaminotetrazole with excess methyl iodide in refluxing aqueous acetone gave a liquid product which exploded on the hot plate and whose infrared spectrum was essentially the same as that for 2-methyl-5-(N-methyl-N-nitroamino)tetrazole. An ethereal solution of this liquid gave no crystalline salt when treated with 2-aminopyridine and suggested the absence of monomethyl derivatives; Garrison and Herbst[32] characterized 1-methyl-5-nitroaminotetrazole and 5-(N-methyl-N-nitroamino)tetrazole in this manner. Treating 5-nitroaminotetrazole with an excess of diazomethane also gave a liquid dimethylated product (Found: N, 53.7. Theory: N, 53.2.).

2-Methyl-5-(N-cyano-N-methylamino)tetrazole (10).—**4** (2.1 g., 0.013 mole) and methyl iodide (1.8 g., 0.013 mole) were combined with 25 ml. of acetonitrile and stirred for 16 hr. at 25°. The solid was filtered off, and the solvent was evaporated; the residue was dissolved in ether and extracted with aqueous sodium thiosulfate. The ether was evaporated, and the colorless liquid was distilled at 115–125° (0.5 mm.) to give 0.87 g. (48% yield) of **10**, m.p. 30–35°. Recrystallization from ether raised the melting point to 35–37°.

Anal. Calcd. for $C_4H_6N_6$: C, 34.78; H, 4.38; N, 60.84. Found: C, 34.86; H, 4.47; N, 60.67.

Hydrolysis of 10.—Potassium hydroxide, 50% solution (0.5 ml.), was added to 1.0 g. (0.0072 mole) of **10** dissolved in 5.0 ml. of water. After 30 min. at 25°, 0.90 g. (80% yield) of N-methyl-N-(2-methyl-5-tetrazolyl)urea (**29**), m.p. 190–195°, was filtered off and washed with distilled water. After recrystallization from water the melting point was 197–200°. The infrared spectrum shows absorption bands at 5.92 (>C=O) and 6.52 μ (>C=N−).

Anal. Calcd. for $C_4H_8N_6O$: C, 30.76; H, 5.16; N, 53.83. Found: C, 30.90; H, 5.21; N, 53.89.

Hydrolysis of **29** with excess hot ethanolic potassium hydroxide *followed by acidification yielded some impure* 2-methyl-5-methylaminotetrazole, m.p. 42–45°, lit.[33] m.p. 48°, whose infrared spectrum, except of a small carbonyl absorption, was identical with that of an authentic sample. This result establishes the 2-position for the ring methyl group.

5-(N-Cyano-N-methylamino)tetrazole (33).—**4** (0.5 g.) was dissolved in 10 ml. of water and acidified with 6 *N* hydrochloric acid. The solution was extracted with three 25-ml. portions of ether. The ether was evaporated and the solid was dissolved in chloroform–ether solvent, filtered, concentrated, and cooled to give 0.2 g. of **33**, m.p. 129° dec. Recrystallization from ether–chloroform solution did not change the melting point.

Anal. Calcd. for $C_3H_4N_6$: C, 29.03; H, 3.25; N, 67.72; neut. equiv., 124.1. Found: C, 29.61; H, 4.34; N, 65.93; neut. equiv., 125.1.

N-Methyl-N,N-bis(5-tetrazolyl)amine (30).—**4** (0.4 g., 0.0025 mole) and sodium azide (0.0032 mole) were dissolved in 10 ml. of water and heated on the steam bath for 4 hr. When the cooled solution was acidified with 6 *N* hydrochloric acid, 0.30 g. (72% yield) of product, m.p. 210° dec., was precipitated. Recrystallization from water gave **30**, m.p. 211° dec.

Anal. Calcd. for $C_3H_5N_9$: C, 21.56; H, 3.02; N, 75.43. Found: C, 21.69; H, 3.61; N, 74.85.

Bis(5-tetrazolyl)amine (31). A.—Cyanoguanyl azide (11.0 g., 0.1 mole) was slurried with 50 ml. of cold water and treated with 10.1 g. (0.1 mole) of diisopropylamine in 5 ml. of water. Essentially all of the azido compound dissolved. Sodium azide (7.2 g., 0.11 mole) and 10.6 g. (0.11 mole) of trimethylammonium chloride were added, and the solution was refluxed for 18 hr. During the early stages of heating, copious amounts of trimethylamine were evolved. The almost neutral solution was cooled to room temperature, filtered from a small quantity of gelatinous material, and acidified with 20 ml. of concentrated hydrochloric acid. A white granular precipitate formed immediately; it was removed by filtration after the solution had been cooled to 0° and washed once with a small volume of cold water. The yield of air-dried product, **31** monohydrate, was 13.3 g. (78%). Its infrared spectrum was identical with that of the acid made by the following method.

B.—Sodium dicyanamide (8.9 g., 0.1 mole), 14.3 g. of sodium azide (0.22 mole), 21.2 g. of trimethylammonium chloride (0.22 mole), and 100 ml. of water were refluxed for 23 hr. The hot, neutral solution was filtered and cooled to 5°; rosettes of white needles crystallized slowly. This product was removed by filtration, washed with cold water, and vacuum dried; the mother liquors and washings were retained. The yield of hydrated, acid sodium salt was 3.8 g. (10%); for analysis a portion was recrystallized from water.

Anal. Calcd. for $C_4H_5N_{18}Na\cdot 3H_2O$: H_2O, 14.1. Found: H_2O, 13.5, 14.3. Calcd. for $C_4H_5N_{18}Na$: C, 14.64; H, 1.54; N, 76.82; Na, 7.01. Found: C, 14.64; H, 1.60; N, 76.51; Na, 7.25.

The aqueous mother liquors were heated to 80° and treated with 25 ml. of concentrated hydrochloric acid. The white granular solid was removed and washed with cold water after the solution had been cooled to 5°; the yield of dried **31** monohydrate was 11.5 g. (67%). It can be recrystallized from a large volume of water; this compound darkens between 270–280°, but does not melt or decompose up to 300°.

Anal. Calcd. for $C_2H_3N_9\cdot H_2O$: C, 14.04; H, 2.95; N, 73.67; H_2O, 10.53. Found: C, 14.14; H, 3.17; N, 73.20, 73.14; H_2O, 10.6. Calcd. for $C_2H_3N_9$: N, 82.34. Found: N, 83.01.

The diammonium salt crystallizes from water as white, felted needles which are not hydrated.

(31) E. Oliveri-Mandala and E. Calderano, *Gazz. chim. ital.*, **43I**, 539 (1913).

(32) J. A. Garrison and R. M. Herbst, *J. Org. Chem.*, **22**, 278 (1957).

(33) R. A. Henry and W. G. Finnegan, *J. Am. Chem. Soc.*, **76**, 923 (1954).

Anal. Calcd. for $C_2H_9N_{11}$: C, 12.83; H, 4.85; N, 82.32. Found: C, 12.87; H, 3.57; N, 83.07.

C.—Procedure B was followed except that 14.7 g. (0.1 mole) of potassium dicyanoguanidine was used instead of the sodium dicyanamide and the filtered, hot solution immediately was acidified with 25 ml. of hydrochloric acid. The product was removed after the solution had cooled to 25°, washed with cold water, and air-dried; the yield was 11.6 g. (67%). Recrystallization from water gave rosettes of coarse, white needles, whose infrared spectrum was identical with that for **31** monohydrate made by methods A or B.

Anal. Calcd. for $C_2H_3N_9 \cdot H_2O$: C, 14.04; H, 2.95; N, 73.67. Found: C, 14.00, 14.23; H, 2.90, 2.95; N, 73.36, 73.72.

N-(1-Methyl-5-tetrazolyl)-N-(5-tetrazolyl)amine.—A solution consisting of 0.95 g. of **34**, 0.42 g. of sodium azide, and 0.62 g. of trimethylammonium chloride in 10 ml. of water was heated overnight on the steam bath, acidified with 3 ml. of concentrated hydrochloric acid, and cooled to 0°. The yield of precipitated solid after filtration, washing, and drying was 0.5 g. Only 35 mg. of the title compound was recovered, as the less-soluble fraction, after fractional crystallization from water; the bulk of the material proved to be **8**. Recrystallization from water gave rosettes of white needles, decomposing at 242–243°.

Anal. Calcd. for $C_3H_5N_9$: C, 21.56; H, 3.02; N, 75.43. Found: C, 21.51; H, 3.56; N, 74.94.