

lowered, and the cyanide resonance sharpens considerably because of reduced nitrogen quadrupolar broadening at the lower temperatures, but no new resonances or splitting of peaks were observed. This behavior is consistent with the presence of only one geometric isomer in solution, but rapid interconversion of isomers at -47° cannot be excluded. The assignments of resonances indicated in Table VII are consistent with the relative ^{13}C chemical shift values quoted for other cyano and cyanide metal complexes.^{40,40a} The data for potassium octacyanomolybdate(IV) in aqueous solution (Table VII and ref 39) are more suggestive of fluxional behavior,³⁹ but again a unique interpretation is not yet possible. Recently, stereochemical nonrigidity was conclusively demonstrated for

(40) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971).

(40a) NOTE ADDED IN PROOF. The identification of the cyanide resonance, made on the basis of the quadrupolar broadening cited above, must be regarded as tentative. Recent studies of $\text{Mo}(\text{CNR})_6\text{I}^+$ in solution suggest the assignment of $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{NR}$ resonances in Table VII may have to be reversed.

related molecules, $\text{MoH}_4(\text{PR}_3)_4$, although a topological mechanism was not established.^{41,42}

Acknowledgments. We are indebted to the National Science Foundation for support of this research under Grant No. GP 27239X, to Dr. Bernard Bulkin of Hunter College for kindly providing the Raman spectra, to Bruker Scientific Co. for the variable-temperature Fourier-transform ^{13}C nmr spectra, to Professor H. B. Gray for a stimulating discussion, and to the Alfred P. Sloan Foundation for a research fellowship to S. J. L. (1968–1970).

(41) (a) J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.*, **93**, 5261 (1971); (b) B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *Chem. Commun.*, 1617 (1971).

(42) As indicated previously,¹ the X-ray structure of $(\text{CH}_3\text{NC})\text{Mo}(\text{CN})_4$ was determined early last year. Publication of the results was delayed pending completion of the chemical and spectroscopic studies reported here. At the time when this paper was being submitted, a completely independent investigation of the $(\text{CH}_3\text{NC})_4\text{Mo}(\text{CN})_4$ crystal structure appeared as a preliminary communication.⁴³ The two structural determinations are in good agreement.

(43) F. H. Cano and D. W. J. Cruickshank, *Chem. Commun.*, 1617 (1971).

The Mechanism of the Oligomerization of Hydrogen Cyanide and Its Possible Role in the Origins of Life¹

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Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. Received February 8, 1972

Abstract: Addition of HCN to $\text{RN}=\text{CHCN}$ (VIII) ($\text{R} = (\text{CH}_3)_3\text{C}$, $(\text{CH}_3)_2\text{CH}$, C_6H_{11} , C_2H_5) yielded $\text{RNHCH}(\text{CN})\text{C}(\text{NHR})(\text{CN})_2$ (XI) and $(\text{RNH})(\text{NC})\text{C}=\text{C}(\text{CN})(\text{NH}_2)$ (X). The formation of X and not $(\text{RNH})(\text{NC})\text{C}=\text{C}(\text{CN})(\text{NHR})$ (XII) demonstrates that the oligomerization of HCN proceeds by stepwise addition of cyanide to cyanide oligomers, $\text{HCN} + \text{HCN} \rightarrow \text{I}$, $\text{I} + \text{HCN} \rightarrow \text{VI}$, $\text{VI} + \text{HCN} \rightarrow \text{III}$, and not by the dimerization of $\text{I} \rightarrow \text{III}$. These results show that I does not exhibit the properties of a carbene. Furthermore, the mechanism of the oligomerization process demonstrates that the so-called "HCN polymer" must be a mixture of low molecular weight compounds. Since it had previously been shown that these compounds do not contain amide links a reinvestigation of the role of HCN in the chemical evolution of amino acids and other biological monomers is warranted.

Hydrogen cyanide may have played an important role in prebiological chemistry.² It is known to self-condense to form "polymers." Amino acids and heterocyclic bases are released from these "polymers" on hydrolysis.³

Matthews and coworkers⁴ first suggested that the dimeric species I was the direct precursor to the "HCN polymer." They suggested that I has the properties of a carbene (II) and that this carbene dimerized to III and polymerized to the "HCN polymer" IV. It was further suggested that mild hydrolysis of IV yielded peptides V, while it was known that vigorous hydrolysis of IV yields amino acids (Scheme I).

(1) Chemical Evolution. IX. For the previous paper in this series see J. P. Ferris, D. B. Donner, and W. Lotz, *Bioorg. Chem.*, in press.

(2) For a recent review see R. M. Lemmon, *Chem. Rev.*, **70**, 95 (1970).

(3) C. V. Lowe, M. W. Rees, and R. Markham, *Nature (London)*, **199**, 219 (1963).

(4) C. N. Matthews and R. E. Moser, *Proc. Nat. Acad. Sci. U. S.*, **56**, 1087 (1966); C. N. Matthews and R. E. Moser, *Nature (London)*, **215**, 1230 (1967).

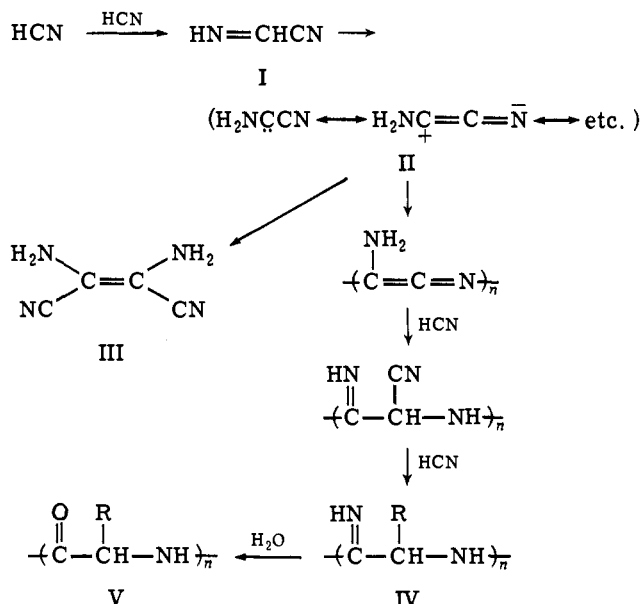
The assignment of structure V is based, principally, on the observation that amino acids are released on acid or base hydrolysis. However, glycine is released on hydrolysis of III, a substance which does not contain an amide linkage.⁵ Hydrolytic release of amino acids from a compound, or mixture of compounds, does not constitute evidence for the presence of a peptide bond.

The only experimental evidence presented to indicate that the HCN dimer I has the properties of carbene II is the uv-visible spectrum of a yellow substance prepared photochemically at -196° from the lithium salt of 1-cyanofornamide *p*-toluenesulfonylhydrazone.⁶ Compounds I or II were not isolated but, instead, III was the only substance obtained in this investigation. In considering the methods used for the generation of carbenes it would appear highly improbable that such a

(5) R. A. Sanchez, J. P. Ferris, and L. E. Orgel, *J. Mol. Biol.*, **30**, 223 (1967).

(6) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Amer. Chem. Soc.*, **89**, 5673 (1967).

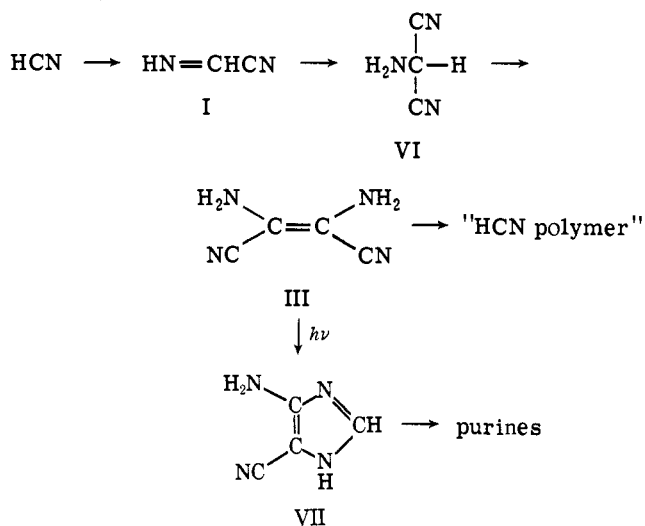
Scheme I



carbene would be formed in condensations of cyanide conducted in aqueous alkaline media.

In an alternative scheme it was proposed that compounds I, VI, and III are discrete intermediates in the "polymerization" of hydrogen cyanide. It was shown that VI will react with cyanide to produce III.⁵ The photochemical conversion of III to VII was extensively studied⁷ and the conversion of VII to purines was demonstrated.⁸ These results are summarized in Scheme II.

Scheme II

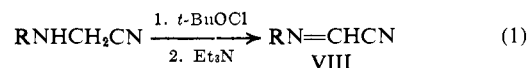


The present studies were undertaken with the goal of differentiating between the alternative reaction pathways proposed in Schemes I and II. In particular we felt that the carbenoid structure postulate (structure II) remained unproven and that it was highly unlikely that a carbene intermediate would be formed in the course of the condensation of cyanide in aqueous solution. Furthermore we found the evidence for structure IV postulated for the "HCN polymer" to be unconvincing and inconsistent with the known chemistry of hydrogen

cyanide. An investigation of the proposal that iminoacetonitrile (I) has the properties of carbene II is the subject of this paper.⁹

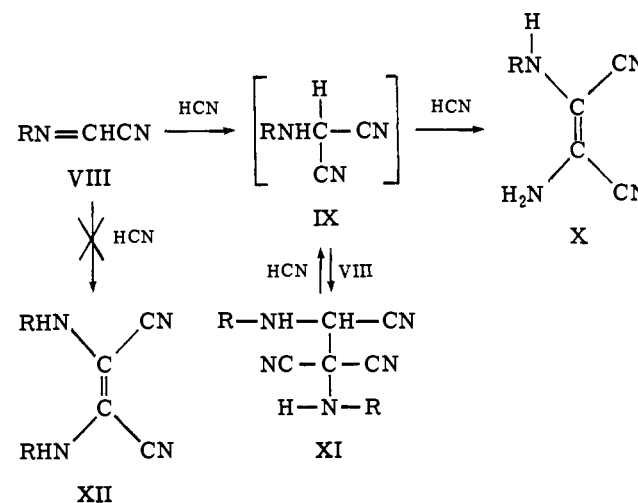
Results and Discussion

The reported synthesis of *N-tert*-butyliminoacetonitrile (VIII, R = *t*-Bu)¹⁰ suggested a way of elucidating the reactions involved in the oligomerization of hydrogen cyanide (eq 1). A series of *N*-alkyliminoaceto-



nitriles was prepared (VIII, R = *tert*-butyl, isopropyl, cyclohexyl, and ethyl) and the reactions of these compounds with hydrogen cyanide and potassium hydroxide were investigated (Scheme III). It was thought

Scheme III



that the chemistry of the *N*-alkyliminoacetonitriles (VIII) might be similar to that of the unsubstituted iminoacetonitrile (I).

All of the *N*-alkyliminoacetonitriles (VIII) are stable, colorless compounds which do not exhibit the uv-visible absorption bands attributed to the carbene II.⁶ Our data clearly demonstrate that the absorption spectral properties reported by Moser, *et al.*,⁶ cannot be due to the ground state of I. These compounds exhibit infrared bands at 1620 (C=N) and 2250 cm⁻¹ (C≡N) consistent with structure VIII. Furthermore, all these compounds are sufficiently stable so that complete characterization was possible. Consequently, there is no basis for assigning carbene structure II to iminoacetonitrile (I).

The reactions of these *N*-alkyliminoacetonitriles were investigated to further elucidate the pathway for the oligomerization of HCN. These compounds react with hydrogen cyanide to yield 1,1,2-tricyano-1,2-diaminoalkylethanes (XI) and *N*-alkyldiaminomaleonitriles (X). Compound XI (R = *t*-Bu) was formed on attempted chromatography of VIII (R = *t*-Bu).¹⁰ Attempted conversion of XII to XI by reaction with HCN was not successful.¹¹ These reactions are summarized in Scheme III.

(9) For a preliminary communication of some of these data see ref 1 and D. B. Donner, A. P. Lobo, J. D. Wos, and J. P. Ferris, *Biol. Bull.*, **139**, 419 (1970).

(10) J. H. Boyer and H. Dabek, *Chem. Commun.*, 1204 (1970).

(11) Unpublished work of Dr. T. Ryan.

(7) J. P. Ferris and J. E. Kuder, *ibid.*, **92**, 2527 (1970).

(8) R. A. Sanchez, J. P. Ferris, and L. E. Orgel, *J. Mol. Biol.*, **38**, 121 (1968).

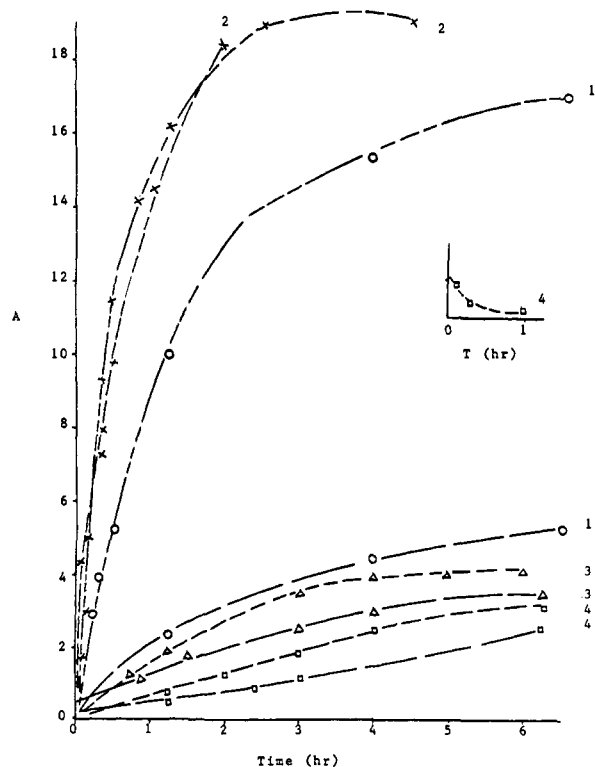


Figure 1. The reactions of *N*-isopropyliminoacetonitrile with sodium cyanide and potassium hydroxide. (1) *N*-isopropyliminoacetonitrile (about 10^{-3} *M*) and sodium cyanide (about 10^{-3} *M*) at pH 10: (---○---), the rate of appearance of 1,1,2-tricyano-*N,N'*-diisopropyl-1,2-diaminoethane monitored at 240 nm; (—○—), the rate of appearance of *N*-isopropylidiaminomaleonitrile monitored at 310 nm. (2) *N*-isopropyliminoacetonitrile (about 10^{-3} *M*) and sodium cyanide (about 5×10^{-4} *M*) at pH 9.2: (---×---), the rate of appearance of 1,1,2-tricyano-*N,N'*-diisopropyl-1,2-diaminoethane monitored at 237 nm; (-×-), the rate of appearance of *N*-isopropylidiaminomaleonitrile monitored at 310 nm. (3) *N*-isopropyliminoacetonitrile (about 10^{-3} *M*) treated with potassium hydroxide at pH 9.2: (-Δ-), the rate of appearance of *N,N'*-diisopropylaminomaleonitrile monitored at 323 nm; (—Δ—), the rate of appearance of 1,1,2-tricyano-*N,N'*-diisopropyl-1,2-diaminoethane monitored at 237 nm. (4) *N*-isopropyliminoacetonitrile (about 10^{-3} *M*) in ethanol-water solution at pH 7-8: (—□—), the rate of appearance of 1,1,2-tricyano-*N,N'*-diisopropyl-1,2-diaminoethane monitored at 238 nm; (-□-), rate of appearance of *N,N'*-diisopropylaminomaleonitrile monitored at 325 nm; (-□-), the rate of disappearance of *N*-isopropyliminoacetonitrile monitored at 272 nm (inset).

The chemistry outlined in Scheme III is analogous with the stepwise addition of cyanide to form oligomers as suggested in Scheme II. Of particular significance is the observation that only the monoalkyldiaminomaleonitrile (X) was produced when cyanide was added to VIII and none of the corresponding dialkylaminomaleonitrile (XII) was observed. The absence of XII could be ascertained by the absence of the characteristic ultraviolet absorption maximum at 325 nm. An intense absorption maximum at 306 nm characteristic of X developed during the course of the reaction and subsequently X was isolated from the reaction mixture. These results clearly demonstrate that nucleophilic addition of cyanide to I takes place rather than a dimerization of the carbenoid form II. As a consequence it is possible to conclude that I and not II is the structure of dimeric HCN.

The formation of XI was unexpected because the corresponding compound (XI, R = H) has not been

isolated as a product of the oligomerization of HCN. However, the formation of XI in significant amounts in our syntheses is due to the use of equimolar amounts of hydrogen cyanide and VIII in the reaction mixture. It has been shown that the steady-state concentration of VI in 1 *M* hydrogen cyanide at pH 9.3 is 10^{-5} – 10^{-6} *M*. The observed reactivity of VIII demonstrates that the concentration of the hydrogen analog I should be equally low or lower. Therefore, the bimolecular reaction of I and VI to form XI (R = H) is not likely to be observed in aqueous cyanide.

The formation of oligomeric adducts of VIII (e.g., XI and X) is not suggestive of eventual polymer formation in the hydrogen cyanide system; to the contrary, it appears that the oligomerization reactions eventually reach an equilibrium. It was found possible to convert 1,1,2-tricyano-1,2-diaminoalkylethanes (XI) to the corresponding *N*-alkyldiaminomaleonitriles (X) by longer reaction time. This result, coupled with the reaction rates suggested in Figure 1 comparing the rates of formation of both species, indicates that these compounds are formed competitively. Compounds of structure X appear to be thermodynamically stable whereas those of structure XI are kinetically favored.

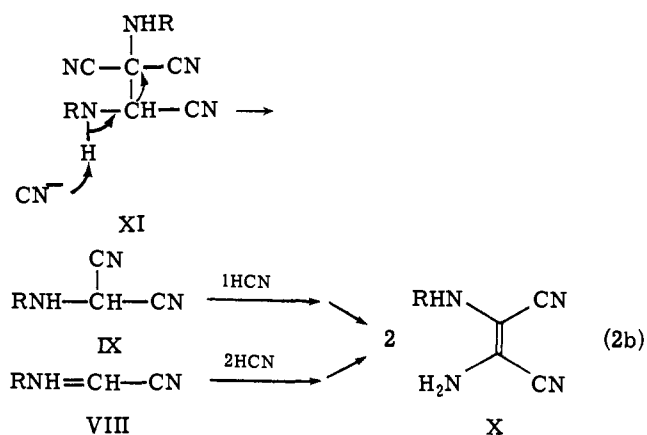
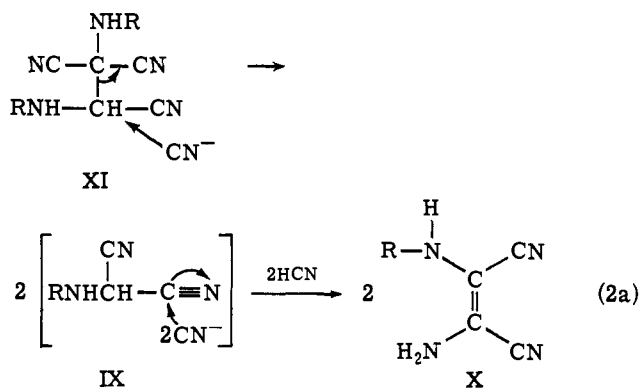
Attempts were made to form higher molecular weight oligomeric species by the reaction of cyanide with III and X (R = isopropyl). No reaction was observed in acid solution and brown substances of unknown structure were produced on prolonged reaction. Similar brown substances were also formed using aqueous base alone suggesting that these are decomposition products of X. Furthermore, cyanide ion was detected when III or X was allowed to stand in basic medium. The brown substances formed in basic medium are undoubtedly decomposition products of III. These data support the contention that the diaminomaleonitrile (III) is the thermodynamically favored product of cyanide oligomerization and that this substance does not react further to form higher molecular weight compounds.

Further support for this argument is the finding that the same end products are obtained by allowing solutions of HCN to stand at pH 9.2 as are obtained when diaminomaleonitrile (III) is permitted to stand under the same reaction conditions. These data, to be reported separately, suggest that a series of equilibria are established between HCN and III (Scheme II).⁹ Hydrolytic or oxidation-reduction reactions of the compounds I, VI, and III account for the final products obtained in the HCN or diaminomaleonitrile oligomerizations.

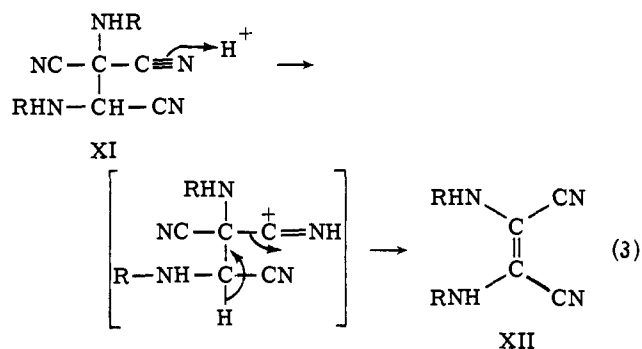
It was possible to effect the conversion of compound XI to the monoalkyldiaminomaleonitrile at pH 9.2 in the presence of 3 molar equiv of cyanide. When 1 molar equiv of cyanide was utilized, only decomposition of XI was observed. These data may be rationalized by either eq 2a or 2b.¹²

The product obtained on acidic treatment of XI (in the presence of 3 molar equiv of hydrogen cyanide) exhibited a uv maximum at 325 nm. It was not possible to isolate this substance; however, the dialkylaminomaleonitrile structure XII is tentatively assigned to the product on the basis of the uv spectrum. Monoalkyldiaminomaleonitriles exhibit a uv maximum at about 306 nm while the dialkylaminomaleonitriles ex-

(12) We thank a referee for suggesting eq 2b.



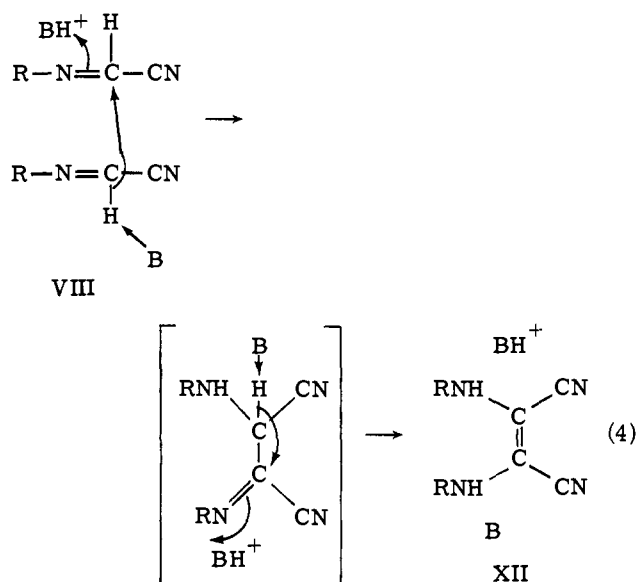
hibit a uv maximum at about 325 nm. The formation of the dialkylaminomaleonitriles (XII) is rationalized in eq 3.



Although the *N*-alkyliminoacetone nitriles (VIII) were stable, neat, and in nonhydroxylic solvents, these substances did dimerize in the absence of cyanide in hydroxylic solvents to the *N,N'*-dialkylaminomaleonitriles (XII). The mechanism of the reaction is not clear although a base-catalyzed reaction is possible since the dimerization was observed at pH 7–9 (eq 4). Attempted reaction in strongly acidic or basic solution resulted in the immediate decomposition of VIII. The absence of a dimerization reaction in nonhydroxylic solvents mediates against a carbenoid mechanism.⁴ Furthermore it was concluded from quantum mechanical calculations that the ground state of I does not have carbenoid character.¹³

It was possible to synthesize the cyclohexyl and isopropyl analogs of XII; however, attempts to isolate the *tert*-butyl adduct of XII were unsuccessful and instead the formation of 1,1,2-tricyano-*N,N'*-di-*tert*-butyl-1,2-

(13) G. H. Loew and S. Chang, *Tetrahedron*, **27**, 3069 (1971); G. H. Loew, *J. Theor. Biol.*, **33**, 171 (1971).

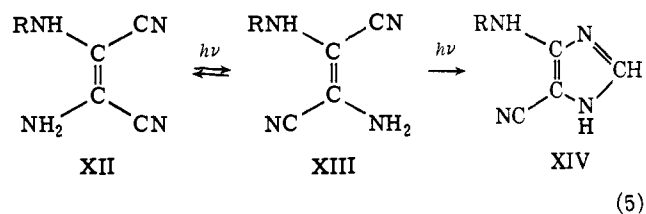


diaminoethane (XI, R = *t*-Bu) and *N-tert*-butyldiaminomaleonitrile (X, R = *t*-Bu) was observed. These products were probably formed by the hydrolytic release of cyanide from some of the iminoacetone nitrile (I, R = *t*-Bu) and the subsequent reaction of this cyanide with I as outlined in Scheme III.

Figure 1 shows the rate of formation of dialkylaminomaleonitrile XII in alkaline media. The fact that formation of XI is always observed when VIII (R = isopropyl, cyclohexyl, and *t*-Bu) is dissolved in aqueous medium at pH 7–9 suggests that some hydrolysis of X to liberate cyanide occurs in each instance.

Apparently the *cis* geometry of the reactants in the transition state is necessary for dimerization to occur and the steric requirements of two *cis tert*-butyl groups are such as to preclude reaction. This steric argument is consistent with the isolation of a greater yield (38%) of the *N,N'*-diisopropylaminomaleonitrile (XII, R = isopropyl) than the *N,N'*-dicyclohexylaminomaleonitrile (XII, R = cyclohexyl) (18%).

Irradiation of all of the *N*-alkyldiaminomaleonitriles and *N,N'*-dialkylaminomaleonitriles resulted in a rapid decrease and shift in the uv absorbance maximum to longer wavelength. This shift was followed by slow development of a uv maximum in the 250–260-nm region. A similar effect has been observed for the unsubstituted diaminomaleonitrile and is due to the rapid photochemical conversion of the *cis* isomer (XII) to the *trans* isomer (XIII) followed by a slower conversion to the imidazole XIV (eq 5, R = H).⁵ The *trans-N-tert*-



butyldiaminomaleonitrile (XIII, R = (CH₃)₃C) was isolated and partially characterized. The corresponding imidazole (XIV, R = *t*-Bu) was obtained as the toluenesulfonic acid salt. The location of the *tert*-butyl grouping in XIV was provisionally assigned on the basis of formation of an intense red color with the

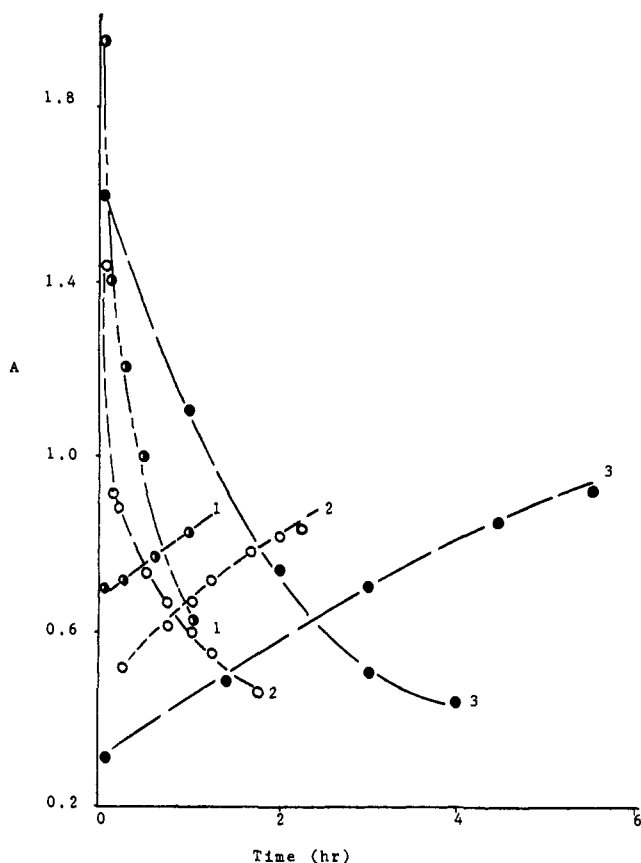


Figure 2. The photolysis of diaminomaleonitrile, *N,N'*-dicyclohexylaminomaleonitrile, and *N*-cyclohexyldiaminomaleonitrile. (1) Photolysis of *N,N'*-dicyclohexylaminomaleonitrile monitored at 301 nm to study decomposition of starting material and at 281 nm to study the increase in product as a function of time. (2) The photolysis of *N*-cyclohexyldiaminomaleonitrile monitored at 318 nm to study the decomposition of starting material and at 258 nm to study the increase in product as a function of time. (3) The photolysis of diaminomaleonitrile monitored at 296 nm to study the rate of decrease of the starting material and at 245 nm to study the rate of appearance of the photoproduct. This experiment was performed by Mr. Frank Antonucci.

Pauly reagent. The corresponding dialkylimidazoles (XIV, $N_1-H = N_1-R$) give only pale yellow colors with this reagent. The similarity in the photochemical reaction rates between the alkylated and unsubstituted diaminomaleonitriles (Figure 2) provides further support to the contention that the same transformations are observed in each instance.

Conclusions

We have shown that a series of simple cyanide addition products are formed in the reaction of iminoacetonitriles with aqueous alkaline cyanide. The iminoacetonitriles did not exhibit any of the properties of a carbene. We conclude from these data that mildly alkaline solutions of cyanide condense to oligomers by an ionic mechanism and that carbenoid species are not involved.

The stepwise reactions outlined in Scheme I suggest that the so-called "HCN polymer" is a mixture of low molecular weight compounds. Cyanide condensations only occur under mildly alkaline conditions where the concentrations of initiator (CN^-) and monomer (HCN) are similar.⁵ Addition polymers are generally formed by a chain process involving a small amount of initiator.

A high concentration of initiator relative to monomer will result in the formation of low molecular weight compounds.¹⁴ Furthermore, the detection of significant amounts of diaminomaleonitrile in the cyanide oligomerization proves that the reaction does not proceed rapidly to polymeric products.⁵ The oligomeric products such as diaminomaleonitrile and the other oligomers shown in Scheme I are susceptible to competing hydrolytic side reactions so that one would not expect to observe efficient condensation to high polymers. It would appear that the term "HCN polymer" is a misnomer.⁹

Experimental Section^{15,16}

Preparation of *N*-Alkyliminoacetonitriles (I). *tert*-Butyl hypochlorite (55.4 g, 60.8 ml, 0.51 mol) was added dropwise, with stirring (temperature maintained at 0–2° in the absence of light), to a cold solution of *N*-alkyl-substituted aminoacetonitrile^{16–18} ($RNH-CH_2CN$, 0.5 mol) in 400 ml of ether. After stirring in the dark for 1.5 hr at 2–3°, triethylamine (55.6 g, 76 ml, 0.55 mol) was added to the solution dropwise over a 30-min period. The temperature was maintained below 3°. The solution was stirred for 2 hr, in the dark, and then permitted to rise to room temperature. The ether was removed by rotary evaporation and the product distilled.

The procedure described above yielded 12.1 g (23%) of *N*-ethyliminoacetonitrile: bp 38° (70 mm); n_D^{20} 1.4169; uv max (CH_2CN) 283 nm (ϵ 155); ir (neat) 2975, 2850 (alkyl), 2250 (CN), 1620 ($C=N$) cm^{-1} ; nmr ($CDCl_3$) δ 1.38 (t, 3, CH_3), 3.84 (d of q, 2, CH_2), 7.40 (t, 1, CH); irradiation at δ 7.40 caused the doublet of quartets at 3.84 to collapse to a quartet; irradiation at δ 3.84 caused the triplet at 7.40 to collapse to a singlet. Anal. Calcd for $C_4H_8N_2$: C, 58.52; H, 7.36; N, 34.12. Found: C, 58.18; H, 7.44; N, 33.75.

The procedure described above yielded 25 g (52.5%) of *N*-isopropyliminoacetonitrile: bp 38–39° (10 mm); n_D^{20} 1.4212; uv max (CH_2CN) 288.5 nm (ϵ 90); ir (neat) 2975, 2850 (alkyl), 2250 (CN), 1620 ($C=N$) cm^{-1} ; nmr ($CDCl_3$) δ 1.44 (d, 6, CH_3), 3.84 (heptet, 1, CH), 7.62 (s, 1, CH). Anal. Calcd for $C_6H_{12}N_2$: C, 62.47; H, 8.39; N, 29.14. Found: C, 62.71; H, 8.21; N, 28.60.

The procedure described above yielded 37.8 g (55.6%) of *N*-cyclohexyliminoacetonitrile: bp 86.5° (12 mm); mp 46°; n_D^{20} 1.4762; uv max (CH_2CN) 282 nm (ϵ 150), 228 nm (200); uv max (EtOH) 276 nm; uv max (80% EtOH, pH 5.5) 272 nm; in alkaline media no uv maxima were observed, apparently due to the rapid reaction of the imine with hydroxide ion; ir (neat) 2975, 2850 (alkyl), 2250 (CN), 1620 ($C=N$) cm^{-1} ; nmr ($CDCl_3$) δ 1.98 (br, 10, cyclohexyl), 3.70 (br, 1, CH cyclohexyl), 7.50 (d, 1, CH). Anal. Calcd for $C_8H_{12}N_2$: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.60; H, 8.93; N, 20.44.

The procedure described above yielded 28 g (51%) of *N*-*tert*-butyliminoacetonitrile: bp 25° (2.5–3.0 mm) (lit.¹⁰ bp 28–29°) (3 mm); ir (neat) 2975 (alkyl), 2250 (CN), 1620 ($C=N$) cm^{-1} . It was not possible to prepare iminoacetonitrile (I) by this procedure.¹⁶

Preparation of 1,1,2-Tricyano-1,2-diaminoalkylethanes (XI). **a. General Procedure.** $RN=CHCN$ (0.1 mol) was dissolved in ab-

(14) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953; G. Odian, "Principles of Polymerization," McGraw-Hill, New York, N. Y., 1970.

(15) The infrared spectral data were recorded on a Perkin-Elmer Model 137 sodium chloride spectrophotometer. The nmr spectra of solutions, in deuteriochloroform with TMS as an internal standard or with the spectrometer calibrated to an external TMS standard, were recorded on a Varian Model T-60 spectrophotometer. Ultraviolet spectra were recorded on a Unicam Model SP 800A spectrophotometer. Mass spectra were obtained using a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. Elemental analyses were carried out at Intranal Laboratory, Inc. (Rensselaer, N. Y.). Photolyses were carried out in a Rayonet photochemical reactor using lamps with principal emission at either 300 or 254.7 nm. A Mettler Type H 15 analytical balance was used to obtain all weights. Compounds were visualized with a 254-nm uv light source in all cases where a spray reagent was not used. Melting points are uncorrected.

(16) Further experimental details and mass spectra of the compounds described in this work may be found in the Ph.D. Thesis of D. B. Donner, Rensselaer Polytechnic Institute, 1972.

(17) E. Knovenagel and E. Mercklin, *Chem. Ber.*, **37**, 4087 (1904).

(18) A. Cook and S. Cox, *J. Chem. Soc.*, 2334 (1949).

solute ethanol (200 ml) and added to 1 l. of water. Freshly distilled HCN¹⁹ (8 ml) was added to this solution. After 10 min a white precipitate formed which was filtered under vacuum and recrystallized from hexane.

b. Procedure for the Preparation of 1,1,2-Tricyano-*N,N'*-di-*tert*-butyl-1,2-diaminoethane. *tert*-Butyliminoacetonitrile (11.0 g, 0.1 mol) was dissolved in ice cold acetonitrile (-2°). Freshly distilled HCN¹⁹ (3.0 g, 4.35 ml, 0.11 mol) was added to this solution. The solution was stirred and the temperature permitted to rise to room temperature over a period of several hours. After standing overnight, the solution was poured into water and the product, which was precipitated, was recrystallized from hexane.

Attempted preparation of 1,1,2-tricyano-*N,N'*-diethyl-1,2-diaminoethane by procedure a yielded only *N*-ethylidiaminomaleonitrile.

Procedure a yielded 1.5 g (20%) of 1,1,2-tricyano-*N,N'*-diisopropyl-1,2-diaminoethane in a 0.5-mol preparation: mp 50° ; uv max (CH₃CN) 228 nm (ϵ 240); ir (KBr) 3350 (NH), 2950 (alkyl), 2250 (CN) cm⁻¹; nmr (CDCl₃) δ 1.30 (d, 6, CH₃), 1.40 (d, 6, CH₃), 1.8–2.3 (br, 2, NH, exchanged with D₂O), 3.14 (heptet, 2, CH), 4.05 (d, 1, CH). *Anal.* Calcd for C₁₁H₁₇N₅ (mol wt 219): C, 60.25; H, 7.81; N, 31.94. Found: C, 60.11; H, 7.88; N, 31.95; mol wt by isothermal distillation in benzene, 205.

Procedure a yielded 2.7 g (46%) of 1,1,2-tricyano-*N,N'*-dicyclohexyl-1,2-diaminoethane in a 0.04-mol preparation: mp 113° dec; uv max (CH₃CN) 228.5 nm (ϵ 344); ir (KBr) 3350 (NH), 2975 (alkyl), 2250 (CN) cm⁻¹; nmr (CDCl₃) δ 1–2 (br, 20, cyclohexyl), 2.1 (br, 2, NH, exchanged with D₂O), 2.90 (br, 2, cyclohexyl), 4.05 (d, 1, CH). *Anal.* Calcd for C₁₇H₂₅N₅ (mol wt 299): C, 68.20; H, 8.42; N, 23.39. Found: C, 68.30; H, 8.53; N, 23.43; mol wt by isothermal distillation in benzene, 306.

Procedure a yielded 7 g (57%) and procedure b yielded 10 g (81%) of 1,1,2-tricyano-*N,N'*-di-*tert*-butyl-1,2-diaminoethane: mp 122.5–123.5 $^{\circ}$; uv max (CH₃CN) 228.5 nm (ϵ 315); ir (KBr) 3350 (NH), 2975 (alkyl), 2250 (CN) cm⁻¹; nmr (CDCl₃) δ 1.30 (s, 9, CH₃), 1.64 (s, 9, CH₃), 2.0 (br, 2, NH, exchanged with D₂O), 4.04 (d, 1, CH). *Anal.* Calcd for C₁₃H₂₁N₅ (mol wt 242): C, 63.13; H, 8.56; N, 28.31. Found: C, 63.02; H, 8.57; N, 28.31; mol wt by isothermal distillation in benzene, 250.

Preparation of *N*-Alkyldiaminomaleonitriles (X). The *N*-alkyliminoacetonitrile was dissolved in 20 ml of ice-cold acetonitrile and to this was added a 1 molar equiv of freshly distilled HCN.¹⁹ The reaction was permitted to stand 24 hr and was then concentrated to an oil. The oil was crystallized from hexane and then recrystallized from hexane or from hexane with a small amount of added benzene. In some instances the final product was then sublimed.

The procedure described above yielded 40 mg (0.5%) of *N*-ethylidiaminomaleonitrile from a reaction conducted on a 0.094 mol scale: mp 105° ; uv max (CH₃CN) 311 (ϵ 1.3×10^4), 228.5 nm (ϵ 2.32×10^3); ir (KBr) 3450, 3350 (NH, NH₂), 2950 (alkyl), 2250 (CN), 1640 (C=C) cm⁻¹; nmr (CDCl₃) δ 1.26 (t, 3, CH₃), 3.10 (br, 3, NH, NH₂, exchanged with D₂O), 3.38 (q, 2, CH₂). *Anal.* Calcd for C₆H₈N₄: C, 52.93; H, 5.92; N, 41.15. Found: C, 53.06; H, 5.80; N, 41.11.

The procedure described above yielded 4.3 g (27%) of *N*-isopropylidiaminomaleonitrile from a reaction conducted on a 0.185 mol scale: mp 86.5–87.5 $^{\circ}$; uv max (CH₃CN) 310.5 (ϵ 1.31×10^4), 229 nm (ϵ 2.23×10^3); ir (KBr) 3450, 3350 (NH, NH₂), 2950 (alkyl), 2250 (CN), 1650 (C=C) cm⁻¹; nmr (CDCl₃) δ 1.37 (d, 6, CH₃), 3.38 (br, 3, NH, NH₂, exchanged with D₂O), 3.68 (heptet, 1, CH). *Anal.* Calcd for C₇H₁₀N₄: C, 55.98; H, 6.71; N, 37.31. Found: C, 55.90; H, 6.69; N, 37.27.

The procedure described above yielded 4.6 g (63%) of *N*-cyclohexyldiaminomaleonitrile from a reaction conducted on a 0.077 mol scale: mp 120.5–121.5 $^{\circ}$; uv max (CH₃CN) 313 (ϵ 1.39×10^4), 228.5 nm (ϵ 2.7×10^3); ir (KBr) 3450, 3350 (NH, NH₂), 2975, 2850 (alkyl), 2250 (CN), 1640 (C=C) cm⁻¹; nmr (CDCl₃) δ 1–2 (br, 10, cyclohexyl), 3.40 (br, 4, NH, NH₂, CHNH, three protons exchanged with D₂O). *Anal.* Calcd for C₁₀H₁₄N₄: C, 63.13; H, 7.42; N, 29.45. Found: C, 63.10; H, 7.40; N, 29.50.

The procedure described above yielded 0.6 g (14%) of *N*-*tert*-butyldiaminomaleonitrile from a reaction conducted on a 0.05 mol scale: mp 130–131 $^{\circ}$; uv max (CH₃CN) 306.5 (ϵ 1.15×10^4), 232 nm (ϵ 2.28×10^3); ir (KBr) 3400, 3375 (NH, NH₂), 2950 (alkyl), 2250 (CN), 1640 (C=C) cm⁻¹; nmr (CDCl₃) δ 1.40 (s, 9, CH₃), 2.0

(br, 3, NH, NH₂, exchanged with D₂O). *Anal.* Calcd for C₉H₁₂N₄: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.17; H, 7.31; N, 33.75.

Preparation of *N,N'*-Dialkyldiaminomaleonitriles (XII). The *N*-alkyliminoacetonitrile was dissolved in water–ethanol (about 100 ml) and this solution was permitted to stand at room temperature for 24 hr. At the end of this time the solution was extracted with ether, dried over calcium chloride, and concentrated. The residue, a brown oil, was eluted from a silica gel column with chloroform. The desired product was first eluted. The product was purified by recrystallization from hexane–benzene solution.

The procedure described above yielded 1.0 g (38%) of *N,N'*-diisopropylidiaminomaleonitrile from a reaction conducted on a 0.028 mol scale: mp 89–90 $^{\circ}$; uv max (CH₃CN) 324.5 (ϵ 1.12×10^4), 226.5 nm (ϵ 1.3×10^4); ir (KBr) 3350 (NH), 2950 (alkyl), 2250 (CN), 1630 (C=C) cm⁻¹; nmr (CDCl₃) δ 1.45 (d, 12, CH₃), 2–3 (br, 2, NH, exchanged with D₂O), 3.68 (heptet, 2, CH). *Anal.* Calcd for C₁₀H₁₆N₄: C, 62.47; H, 8.39; N, 29.14. Found: C, 62.37; H, 8.28; N, 29.14.

The procedure described above yielded 0.6 g (17.5%) of *N,N'*-dicyclohexyldiaminomaleonitrile from a reaction conducted on a 0.025 mol scale: mp 134–135 $^{\circ}$; uv max (CH₃CN) 326.5 (ϵ 1.61×10^4), 226 nm (ϵ 1.15×10^4); ir (KBr) 3375 (NH), 2950 (alkyl), 2250 (CN), 1630 (C=C) cm⁻¹; nmr (CDCl₃) δ 1–2.2 (br, 20, cyclohexyl), 3.20 (br, 4, NH, CH, two protons exchanged with D₂O). *Anal.* Calcd for C₁₆H₂₄N₄: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.78; H, 8.87; N, 20.67.

Attempted Synthesis of *N,N'*-Di-*tert*-butylidiaminomaleonitrile (XII, R = *t*-Bu). a. *tert*-Butyliminoacetonitrile (4.1 g, 0.037 mol) was dissolved in 35 ml of ethanol and 50 ml of water. After 2.5 hr a white, crystalline precipitate formed which was filtered, dried over phosphorus pentoxide, and recrystallized from hexane. The product (2.33 g, 75%) was shown to be 1,1,2-tricyano-*N,N'*-di-*tert*-butyl-1,2-diaminoethane by the identity of the ir and nmr spectra, melting point (122.5–123.5 $^{\circ}$), and mixture melting point (119 $^{\circ}$ dec) with an authentic sample.

b. *tert*-Butyliminoacetonitrile (9.9 g, 0.09 mol) was dissolved in a mixture of 100 ml of water and 200 ml of ethanol and the solution was permitted to stand at room temperature for 41 hr. Since no product precipitated from solution, the ethanol was distilled and the product was extracted from the aqueous solution with ether and dried over calcium chloride. The oily residue which remained after distillation of the ether was eluted from a silica gel column with chloroform. The first fraction exhibited a uv maximum at 325 nm characteristic of the *N,N'*-dialkyldiaminomaleonitrile. However, there was not enough sample present to be isolated. The second fraction contained 0.5 g (10%) of a substance that was shown to be *N*-*tert*-butyldiaminomaleonitrile by the identity of its ir and uv spectra, melting point (130–131 $^{\circ}$), and mixture melting point (129.5–130.5 $^{\circ}$) with an authentic sample.

Preparation of *N*-Cyclohexyldiaminomaleonitrile from 1,1,2-Tricyano-*N,N'*-dicyclohexyl-1,2-diaminoethane. A solution of sodium cyanide¹⁹ (294 mg, 0.006 mol) in 5 ml of water was added to 1,1,2-tricyano-*N,N'*-dicyclohexyl-1,2-diaminoethane (599 mg, 0.002 mol) dissolved in 30 ml of ethanol. The pH of the solution was immediately adjusted to 2 with dilute hydrochloric acid. After standing at room temperature for 23 hr, the ethanol was removed by distillation and the solution extracted with ether. The ether extract was dried over calcium chloride and concentrated to yield a yellow oil. This oil was eluted from a silica gel column with chloroform. The first substance eluted from the column was shown to be *N*-cyclohexyldiaminomaleonitrile by the identity of the ir and uv spectra, melting point (120.5–121.5 $^{\circ}$), and mixture melting point (119–120 $^{\circ}$) with an authentic sample. This procedure yielded 14 mg (1.85%) of the desired product.

Preparation of *N*-*tert*-Butyldiaminomaleonitrile from 1,1,2-Tricyano-*N,N'*-di-*tert*-butyl-1,2-diaminoethane. A solution of sodium cyanide¹⁹ (147 mg, 0.003 mol) in 5 ml of water was added to a solution of 1,1,2-tricyano-*N,N'*-di-*tert*-butyl-1,2-diaminoethane (247 mg, 0.001 mol) in 15 ml of ethanol. The pH of the reaction solution was immediately adjusted to 4.8 using dilute hydrochloric acid. The resulting light yellow solution darkened slightly on standing for 20 hr at room temperature. The solution was poured into ether; the ether layer was washed with water and then dried over calcium chloride. The ether was evaporated and the material was then eluted from a silica gel column with chloroform. A yellow substance was eluted from the column which upon recrystallization from hexane yielded 63 mg (19%) of a white, crystalline material. This was shown to be *N*-*tert*-butyldiaminomaleonitrile by the identity of its ir and uv spectra, melting point (128–129 $^{\circ}$), and mix-

(19) HCN and NaCN are highly toxic compounds. HCN should be prepared and used in a good fume hood; L. F. Fieser and M. Fieser, "Reagents For Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, pp 454–455.

ture melting point (128–129°) with an authentic sample. When the same reaction was carried out at pH 2 a much lower yield of product was obtained.

Reaction of *N*-Isopropylaldiaminomaleonitrile with HCN. *N*-Isopropylaldiaminomaleonitrile (2.0 g, 0.013 mol) was dissolved in 30 ml of acetonitrile and the solution was cooled in an ice water bath. HCN¹⁹ (0.36 g, 0.525 ml, 0.013 mol) was added to this solution and the mixture was permitted to stand for 24 hr while the temperature was allowed to rise slowly to room temperature. Tlc on silica gel showed that no reaction had occurred and that the reactants were recovered unchanged.

Reaction of *N*-Isopropylaldiaminomaleonitrile with Sodium Cyanide. *N*-Isopropylaldiaminomaleonitrile (200 mg, 0.0013 mol) was dissolved in 200 ml of ethanol and to this was added sodium cyanide¹⁹ (66 mg, 0.0013 mol) dissolved in 4 ml of water. Over a period of 3 hr the solution, which initially was colorless, turned brown. The reaction was monitored by tlc for 6 hr; this showed that the starting material was the main component of the reaction mixture. There was no indication of the presence of *N*-isopropylaldiaminoacetoneitrile or 1,1,2-tricyano-*N,N'*-diisopropyl-1,2-diaminoethane. After 10 days the solution did not give a positive ninhydrin test and the test for the presence of acids using Bromocresol Green was also negative. A uv spectrum of the solution showed only a continuum. Acid hydrolysis of the solution yielded glycine as one component of the reaction system.

Decomposition of *N*-Isopropylaldiaminomaleonitrile in Base. *N*-Isopropylaldiaminomaleonitrile (10 mg, 6.6×10^{-5} M) was dissolved in 10 ml of ethanol and to this solution was added an excess of sodium hydroxide in ethanol. After 3 hr of reaction the *N*-isopropylaldiaminomaleonitrile was no longer detectable by uv or tlc. After 20 hr a test for cyanide (silver nitrate) showed that decomposition yielding free cyanide was occurring. The same reaction using diaminomaleonitrile yielded an identical result.

Reactions of *N*-Alkylaldiaminoacetoneitriles with Cyanide and Hydroxide. A stock solution of about 10^{-3} M *N*-alkylaldiaminoacetoneitrile was prepared in a 10:1 water-ethanol mixture. To an aliquot of this solution was added a 1 molar equiv of sodium cyanide¹⁹ and the pH was adjusted to 9.2 with dilute HCl (in some instances the amount of cyanide added was a 0.5 mol equiv). A second aliquot of the stock solution was treated with dilute potassium hydroxide by adjusting the pH of the solution to 9 with the base. A blank of the stock solution was maintained to follow the reaction of the *N*-alkylaldiaminoacetoneitrile in a nearly neutral solution (pH 7–8).

The reaction solutions were monitored by uv spectroscopy. The disappearance of *N*-alkylaldiaminoacetoneitrile was followed by the absorption maximum at 280 nm. The formation of 1,1,2-tricyano-1,2-diaminoalkylethane was monitored by its absorption maximum at about 240 nm, and the formation of *N*-alkyl- and *N,N'*-dialkylaldiaminomaleonitrile was monitored by their absorption maxima at about 310 and 325 nm, respectively. Figure 1 shows typical results obtained for such a reaction series using *N*-isopropylaldiaminoacetoneitrile. Similar results were obtained for the other *N*-alkylaldiaminoacetoneitriles.

Conversion of 1,1,2-Tricyano-*N,N'*-dialkyl-1,2-diaminoethanes to *N*-Alkylaldiaminomaleonitriles and to *N,N'*-Dialkylaldiaminomaleonitriles. A stock solution of about 10^{-4} M 1,1,2-tricyano-1,2-diaminoalkylethane in absolute ethanol was prepared. This solution was divided into two parts. To each fraction of the stock solution was added 1 equiv of 3 M sodium cyanide.¹⁹ The pH values of the solutions were then adjusted to 10.3 and 2.2 with dilute HCl.

The course of each reaction was monitored by uv spectroscopy. The formation of *N*-alkylaldiaminomaleonitrile was indicated by its absorption maximum at about 310 nm and the formation of *N,N'*-dialkylaldiaminomaleonitrile by its absorption maximum at about 325 nm. These experiments were carried out on XI (R = *t*-Bu and cyclohexyl) with similar results.

Irradiation of *N*-Alkylaldiaminomaleonitriles and *N,N'*-Dialkylaldiaminomaleonitriles. Solutions of both the *N*-alkylaldiaminomaleonitriles and the *N,N'*-dialkylaldiaminomaleonitriles (about 10^{-4} M) in purified acetonitrile were photolyzed at 300 nm in Pyrex cells. The uv maxima of these compounds decreased in intensity and shifted to longer wavelengths upon irradiation. This is consistent with initial cis geometry which is converted to the trans photochemically. Longer periods of photolysis (all samples being outgassed three times by freeze-pump-thaw technique on a vacuum line) resulted in the formation of a product which exhibited absorbance maxima between 250 and 280 nm. These compounds all gave a positive Pauly test characteristic of imidazoles after tlc in chloroform. As expected, the products formed from *N,N'*-dialkylaldiaminomaleonitriles gave only a faint yellow coloration since both amino functions are alkylated. The change in uv spectral properties with time is shown in Figure 2 for the cyclohexyl derivative. Similar data were obtained for all the other alkylated derivatives.

Photolysis of *N*-*tert*-Butylaldiaminomaleonitrile. *N*-*tert*-Butylaldiaminomaleonitrile (30 mg) was dissolved in 200 ml of purified acetonitrile in a quartz cell. The solution was subjected to outgassing through three freeze-pump-thaw cycles under vacuum and then photolyzed for $2\frac{2}{3}$ hr with a 300-nm light source. The solution was concentrated to yield a product which was then recrystallized from hexane-benzene. The product was shown to be different from the starting cis reactant by tlc in chloroform. The similarity of the uv and ir spectra of the starting material and product suggested that the trans isomer of *N*-*tert*-butylaldiaminomaleonitrile had been isolated: mp 103–104°; ir (KBr) 3350, 3300 (NH, NH₂), 2950 (alkyl), 2260, 2250 (CN), 1670 (C=C) cm⁻¹; uv (CH₃CN) 306 nm; uv (ethanol) 307 nm (the uv of the cis isomer in ethanol exhibited a maxima at 309 nm); mass spectrum (70 eV) *m/e* (rel intensity, which was virtually identical with that of the cis starting material): 164 (4), 108 (37), 81 (29), 57 (100), 41 (55), 39 (25), 29 (43), 28 (41), 27 (26).

Irradiation of a degassed acetonitrile solution (350 ml) of *N*-*tert*-butylaldiaminomaleonitrile (XIII) (50 mg) in a Pyrex cell for 3 days resulted in the formation of 4-*tert*-butylaminoimidazole-5-carbonitrile (XIV, R = *t*-Bu). The acetonitrile was concentrated to dryness and the product was taken up in 10 ml of ether. An ethereal solution of toluenesulfonic acid was added dropwise until no further precipitate formed. The product (as the tosylate salt) was filtered and recrystallized twice from 1-butanol: mp 215–215.5°; ir (KBr) 3450, 3350 (NH), 2900–2700 (alkyl), 2250 (CN), 1670 (C=C) cm⁻¹; nmr (CD₃CN + D₂O) δ 1.80 (s, 9, CH₃), 2.50 (s, 3, *p*-CH₃), 7.50 (q, 4, C₆H₄), 8.22 (s, 1, *im*-H).

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