# The Evidence for Generation of Dimethylaminocyanocarbene in the Thermolysis of Dimethylaminomalononitrile. The Dimethylamino(dicyano- and cyano)methyl Radicals, Carbon Analogues of the Nitroxides[1]

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**Abstract:** Neat dimethylaminomalononitrile (**1**) decomposes at ambient temperature to give the very persistent dimethylaminodicyanomethyl radical (**5**). The *g* value and the hyperfine splitting constants, determined by computer simulation of the ESR spectrum, are consistent with this structure. The structure of **5** is confirmed by its thermal generation from the monodeuterio analogue of **1** and by its alternative generation through hydrogen atom abstraction from **1** by the *tert*-butoxy radical. In dilute solution thermal generation of **5** requires prior heating to 140 °C but occurs almost instantaneously at room temperature upon UV irradiation of solutions containing added di-*tert*-butyl peroxide. Hydrogen cyanide and the dimethylaminocyanomethyl radical (**4**) are also formed. This is inferred from the isolated thermolysis (60 °C) products, 1-dimethylamino-2-aminomaleonitrile (**3**), the product of addition of hydrogen cyanide to **1**, and dimethylglycinonitrile (**6**), the product of hydrogen abstraction from **1** by the radical **4**. The generation of hydrogen cyanide is also directly demonstrated by mass spectroscopy. The radicals **4** and **5** account for the formation of two additional thermolysis products, 1-amino-2,3-bis(dimethylamino)-1,3-dicyanopropene (**9**) and 1,4-bis(dimethylamino)-1,2,4-tricyano-3-aza-1,3-butadiene (**12**). It is proposed that **9** originates from dimerization of **4**, followed by addition of hydrogen cyanide and subsequent rearrangement. Formation of **12** may result from combination of the radicals **4** and **5** to give a ketenimine, subsequent addition of hydrogen cyanide, and final dehydrogenation. $\alpha$-Elimination of hydrogen cyanide from **1** in a symmetry-allowed $[\sigma^{2s} + \sigma^{2a}]$ nonlinear cheletropic fragmentation is postulated to give dimethylaminocyanocarbene, which abstracts a hydrogen atom from **1** to give the radicals **4** and **5**. Thermolysis of **1** in benzene produces in addition to **3** and **9** the Thorpe dimer of **1**, 1,3-bis(dimethylamino)-2-amino-1,3,3-tricyanopropene (**15**). This is the main product when **1** is treated with triethylamine at room temperature. Possible implications in the prebiotic synthesis of polypeptides and purines are discussed.

Two preceding papers presented evidence for the generation of *tert*-octylaminocyanocarbene from *tert*-octylaminomalononitrile in basic media[2] and by thermolysis.[3] The mechanism involves $\alpha$-elimination of hydrogen cyanide; $\beta$-elimination to give *tert*-octyliminoacetonitrile, formally an alternative, was rejected upon theoretical grounds.

The analogous reactions of dimethylaminomalononitrile (**1**) are of special interest because formation of hydrogen cyanide must occur by $\alpha$-elimination. If this is a unimolecular process, it constitutes proof for the generation of dimethylaminocyanocarbene (**2**).

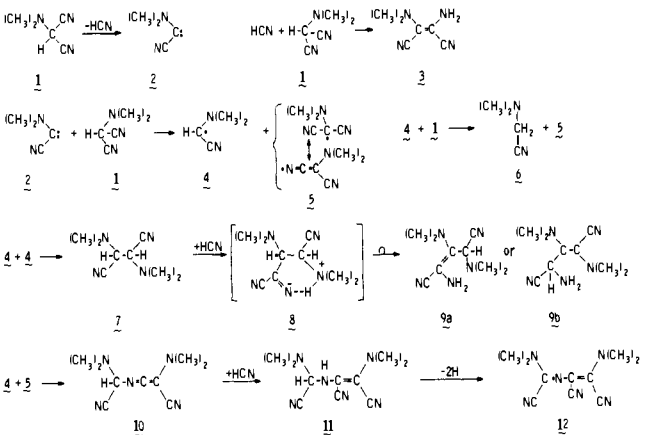
## Results and Discussion

**Evidence for Radical Formation.** At 60 °C under a nitrogen blanket, neat dimethylaminomalononitrile (**1**) gradually darkens and becomes extremely viscous. During this process, hydrogen cyanide is eliminated (vide infra) and radicals are formed as is evident from the observation of an intense ESR spectrum which arises even when **1** is allowed to stand for some time at ambient temperatures (Figure 1A).

The evidence points to the concerted elimination of hydrogen cyanide with formation of dimethylaminocyanocarbene (**2**) (vide infra). The earlier work[2,3] suggests that *tert*-octylaminocyanocarbene is primarily a hydrogen-abstracting species. By analogy **2** abstracts a hydrogen atom from the aminomalononitrile **1** to produce simultaneously the dimethylglycinonitrile radical **4** and the dimethylaminodicyanomethyl radical **5** (Chart I). The ESR spectrum is assigned to the dimethylaminodicyanomethyl radical (**5**) on the following grounds.

1. At ambient temperature (4 h), **1** and its monodeuterio analogue produce the same spectrum (Figure 1A), proving that the radical lacks the hydrogen attached to the central carbon atom.

**Chart I**



2. In dilute solutions of **1**, emergence of the spectrum requires prior heating to 140 °C for 30 min but also occurs at ambient temperature by 30-s irradiation of a 5% solution of **1** in benzene/di-*tert*-butyl peroxide (95:5) (Figures 1C and E). Under these conditions, the *tert*-butoxy radical abstracts the central hydrogen atom from **1**, giving rise to radical **5**.

The hyperfine splitting constant for the amino nitrogen (10.25 G) in radical **5** is almost twice that for the $\alpha$-dimethylaminoethyl radical [$a$(N) $CH_3\dot{C}HN(CH_2CH_2)_2$ = 5.2 G][4] and more than half that for the dimethylaminium radical [$a$(N) $H^+\dot{N}(CH_3)_2$ = 19.28 G].[5] This indicates that the lone electron is appreciably delocalized onto nitrogen. Charge-separated forms such as $(CH_3)_2{}^+\dot{N}\bar{C}(CN)_2$ evidently contribute to the stabilization of radical **5** (metostabilization[6]) and, hence, **5** can be seen as a carbon analogue of dimethyl nitroxide which has an analogous principal resonance form, $(CH_3)_2\dot{N}^+O^-$.[7] The stability of radical **5** is, therefore, an additional example of the analogy between O and $C(CN)_2$ which

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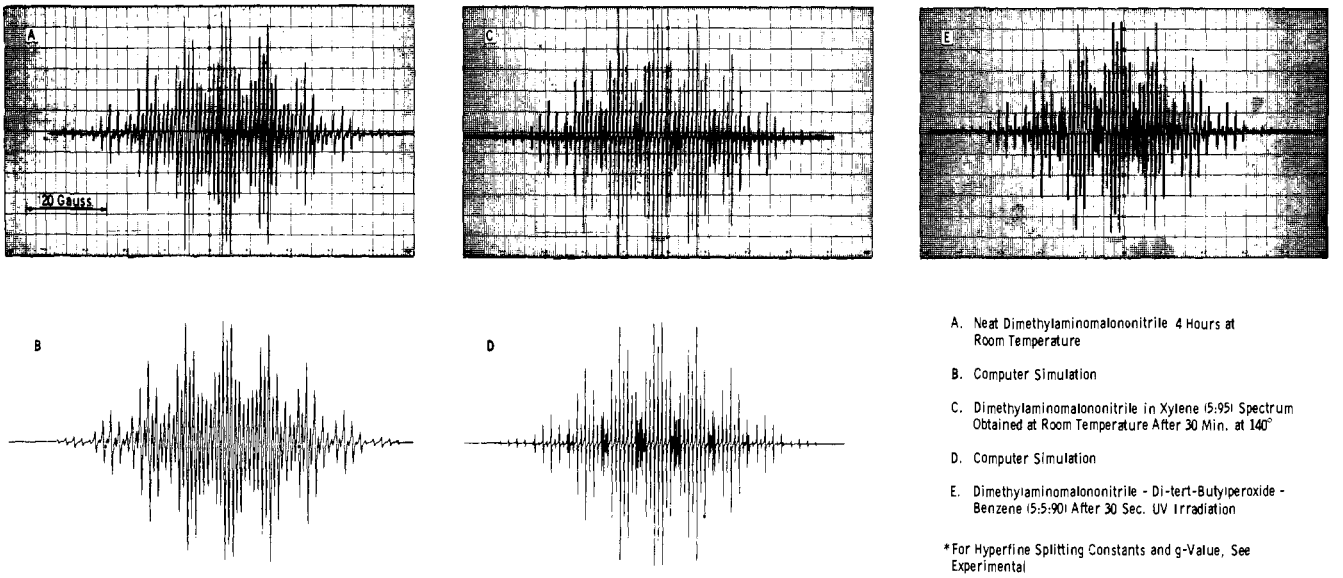



**Figure 1.** ESR spectra of dimethylaminodicyanomethyl radical (**3**)*.

was recently pointed out by Wallenfels et al.[8] For a dilute xylene solution of **1**, the hyperfine splitting constants for the amino nitrogen and the methyl hydrogens are lower than for the neat compound. This is consistent with the expected lesser importance of charge-separated forms in the less polar xylene medium.

To a diminished extent, the same factors are probably operative for the less stable dimethylaminocyanomethyl radical (**4**). This radical is expected to be much less persistent than **5** because it is less sterically hindered and has only a single nitrile group.[9] Direct evidence for the generation of **4** is lacking since it is not detected by ESR spectroscopy; however, its generation is inferred from the isolated thermolysis products (vide infra).

**Thermolysis Products.** Mass spectral evidence shows that hydrogen cyanide is generated in the thermolysis of dimethylaminomalononitrile (**1**). A peak at mass 27 in the spectrum of **1** is consistent with hydrogen cyanide formation as the result of a mass spectral fragmentation process. Generation of hydrogen cyanide during thermolysis of **1** is, however, indicated by the fivefold increase in relative intensity of this peak in the spectrum of a sample that had been preheated in the probe at 60 °C for 20 min.

Thermolysis of **1** at 60 °C for 48 h produces as a main isolated product an intractable, dark brown, resinous material. In addition, the crystalline products 1-dimethylamino-2-aminomaleonitrile (**3**) and 1-amino-2,3-bis(dimethylamino)-1,3-dicyanopropene (**9**) are isolated in substantial yield and 1,4-bis(dimethylamino)-1,2,4-tricyano-3-aza-1,3-butadiene (**12**) in low yield.

Compound **3** was identical with an authentic sample prepared by the addition of cyanide to dimethylaminomalononitrile. The formation of **3** confirms the generation of hydrogen cyanide in the thermolysis of **1** and infers the concomitant formation of dimethylaminocyanocarbene **2** as the other fragment.

The compositions of **9** ($C_9H_{15}N_5$) and **12** ($C_{10}H_{12}N_6$), established by elemental analysis and mass spectra, are anomalous. It would appear that **12** originates from two molecules of dimethylaminomalononitrile ($C_5H_6N_3$) with loss of two hydrogen atoms and **9** from two molecules of **1** with loss of one molecule of hydrogen cyanide and the gain of two hydrogen atoms.

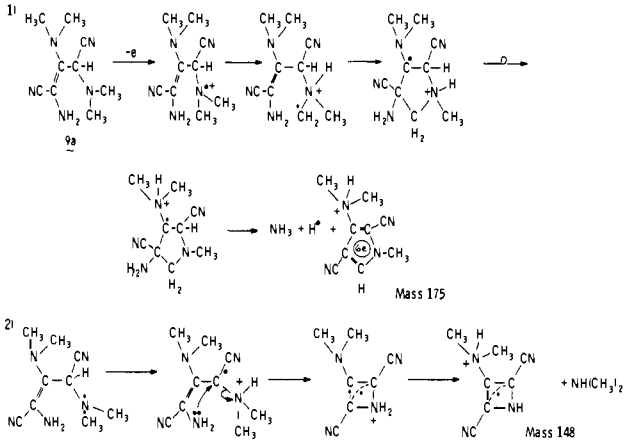
**Structure Proof of 9.** According to the spectral evidence **9** is 1-amino-2,3-bis(dimethylamino)-1,3-dicyanopropene (**9a**). An enamino nitrile moiety is indicated by an anomalously low nitrile frequency at 2175 $cm^{-1}$ and an olefinic stretching mode at 1645 $cm^{-1}$, and also by a UV band at 267 nm.[10] Two IR bands in the NH stretching region (3352 and 3465 $cm^{-1}$) and an NH deformation mode at 1560 $cm^{-1}$ are evidence for a primary amino group. These bands shift to the correspondingly lower frequencies upon exchange with $D_2O$. Two Raman bands indicate two nonequivalent nitrile groups. One corresponds to the single IR band, the other to the nitrile group that is attached to the dimethylamino-substituted saturated carbon atom. The IR inactivity of this nitrile group is consistent with this assignment as nitrile bands in dimethylaminomalononitrile[11] and in dimethylaminoacetonitrile (see Experimental Section) are either absent or extremely weak.

The $^1H$ NMR and the decoupled $^{13}C$ NMR spectra each show two resonances corresponding to the two dimethylamino groups. The $^{13}C$ NMR spectrum—before decoupling—shows these signals as partially superimposed 1,3,3,1 quartets. The two NH protons give rise to a broad $^1H$ NMR signal, disappearing upon exchange with $D_2O$. The methine hydrogen, acidic because of the $\alpha$-nitrile group,[12] gives a sharp one-proton resonance which disappears upon exchange with LiOD-$D_2O$. This assignment is confirmed by the $^{13}C$ NMR spectrum where the corresponding carbon atom gives rise to a doublet ($J$ = 143 Hz), collapsing to a singlet upon decoupling.

In the mass spectrum the major fragmentation path involves the loss of mass 18 from the molecular ion. Exact mass measurements show that this is due to the loss of $NH_3$ and H·. First the $NH_3$ is expelled relatively slowly and then the hydrogen atom very rapidly. This follows from the observation of two metastable ions,[13] one for the combined loss of both fragments and one for the loss of $NH_3$ alone. The remarkably facile expulsion of the hydrogen atom suggests that the fragment of mass 175 is highly stabilized and accordingly probably aromatic. A mechanism that rationalizes such a fragmentation for structure **9a** is shown in Chart II, path 1. This mechanism is consistent with the mass spectra of the di- and trideuterio compounds. In each case, all the deuterium is lost to give the same fragment of mass 175 and the corresponding metastable ions are observed. A similar rationalization is not feasible for the isomeric structure **9b** and therefore **9a** is preferred. The primary enamine moiety in **9a** does not rearrange to the imino tautomer, because the double bond is part of a resonance-stabilized enamino nitrile system.[10] Formation of the second major fragment of mass 148 is rationalized in Chart II, path 2.

**Structure Proof of 12.** The structure of **12** is 1,4-bis(di-

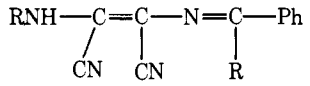
Chart II.
Proposed Mass Spectral Fragmentation Paths of 9




methylamino)-1,2,4-tricyano-3-aza-1,3-butadiene. This assignment is based on the following spectral evidence (for details see Experimental Section).

The absence of NH is shown by IR spectroscopy and by the absence of a deuteration-sensitive $^1H$ NMR signal. Three Raman bands in the 2100–2200-$cm^{-1}$ region correspond to three nonequivalent nitrile groups. The $^1H$ NMR spectrum consists of two resonances of equal area representing the two dimethylamino groups. The $^{13}C$ NMR spectrum shows eight lines; the two most intense, at highest field, represent the carbons in the two dimethylamino groups.

The conjugated azadiene–aminonitrile assignment is supported by two deuteration-insensitive IR bands at 1603 and 1573 $cm^{-1}$ that are also Raman active and by three strong bands in the visible and UV spectra. The UV spectrum is consistent with the proposed azabutadienaminonitrile structure



as the system gives rise to three similarly intense bands in the range 260–400 nm.[14]

**Mechanism of the Formation of 9 and 12.** It is proposed that the radicals **4** and **5** provide the key to the formation of **9** and **12** as shown in Chart I.

Dimerization of the dimethylglycinonitrile radical (**4**) to 1,2-bis(dimethylamino)succinonitrile (**7**), then addition of a molecule of hydrogen cyanide, gives the dicyanotriaminopropane **9.** The postulated dimerization of the dimethylglycinonitrile radical (**4**) is in accord with earlier mass spectral evidence that the *tert*-octylglycinonitrile radical forms an analogous dimer (compound **11,** Scheme I and ref 30, both in ref 2).

Formation of the intramolecularly hydrogen-bonded intermediate **8** could account for the implied unusually facile addition of hydrogen cyanide to the diaminosuccinonitrile **7.** In this intermediate the ammonium proton may help to solvate the negative charge developing on the imino nitrogen as a result of addition of a cyanide ion to the nitrile group. Drastically increased rates of nitrile group hydrolysis have been observed in cases where similar "intramolecular solvation" by a proton[16,17] or a metal ion[17a] is possible (factors of $10^4$ and $10^9$, respectively). The dimethylaminocyanomethyl radical (**4**) and the dimethylaminodicyanomethyl radical (**5**) also provide an explanation of the formation of the azabutadiene **12.** Combination of these two radicals gives the ketenimine **11.** Ketenimines are formed in most thermal and photochemical decompositions of azonitriles,[18] and the combination of two 2-cyano-2-propyl radicals to give a ketenimine has been reported.[19]

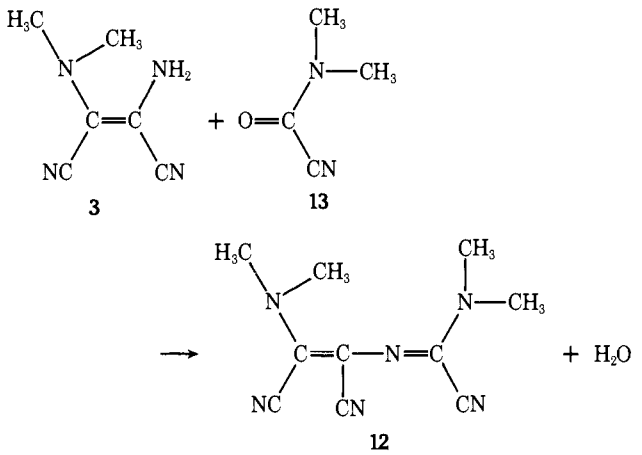
Addition of hydrogen cyanide to the ketenimine **10** gives the diaminomaleonitrile **11.** Dehydrogenation of **11,** either by autoxidation in the workup or by the aminocyanocarbene **2,** gives the azabutadiene **12**[20] (Chart I).

By means of preparative GLC, two minor thermolysis products were isolated in addition to **3, 9,** and **12.** The more volatile was *N,N*-dimethylglycinonitrile (**6**) (Chart I). Its formation indicates that the dimethylglycinonitrile radical **4** is capable of some hydrogen abstraction, i.e., **4** + **1** → $(CH_3)_2NCH_2CN$ (**6**) + **5.**

The other product is dimethylcarbamoylcyanide (**13**). The structure follows from elemental analysis and from mass and infrared spectral evidence. GLC shows the presence of **13** as an impurity in the original dimethylaminomalononitrile. This material is hard to remove. It could originate during distillation. Partial thermolysis of **1** may give the aminocyanocarbene **2** which—as reported for other carbenes[22]—may autoxidize to give **13** owing to adventitious access of atmospheric oxygen. The carbamoyl cyanide **13** is probably responsible for the prominent anomalous band at 1680 $cm^{-1}$ in the published IR spectrum of **1.**[11]

The isolation of **13** suggests a route to the azabutadiene **12** which does not involve the aminocyanocarbene **2.** The relatively abundant thermolysis product 1-dimethylamino-2-aminomaleonitrile (**3**) could condense with dimethylcarbamoyl cyanide (**13**) to give **12** (Scheme II).

Scheme II

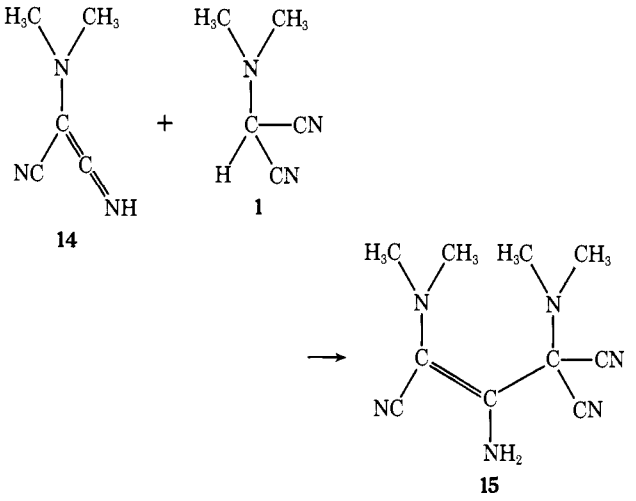


The facile condensation of diaminomaleonitrile with aldehydes to give products with an azabutadiene structure analogous to **12** is known.[15] However, aldehydes with electronegative substituents require acid catalysis and condensation with amides requires phosphorus oxychloride. Compound **13** can be considered an amide with an electronegative nitrile substituent; hence, its uncatalyzed condensation with **3** appears improbable.

The products discussed thus far originate from the thermolysis of neat dimethylaminomalononitrile **1.** Thermolysis of **1** in refluxing benzene gives a different product mixture. Only two crystalline products are isolated: the triaminodicyanopropene **9** and a product, obtained in small yield, which is not isolated in the thermolysis of neat **1.** This compound is 1,3-bis(dimethylamino)-2-amino-1,3,3-tricyanopropene (**15**), the Thorpe dimer of dimethylaminomalononitrile (Scheme III). Elemental analysis and mass spectra show the formula to be $C_{10}H_{14}N_6$ and all spectral evidence (IR, Raman, UV, $^1H$ NMR, and $^{13}C$ NMR) is consistent with this assignment. The aminocyanoketenimine **14** is a tautomeric form of **1.**

Treatment of **1** with triethylamine at room temperature gives **15** as the main product; no **3, 9,** or **12** is isolated. The dimethylaminomalononitrile anion is assumed to be the intermediate.

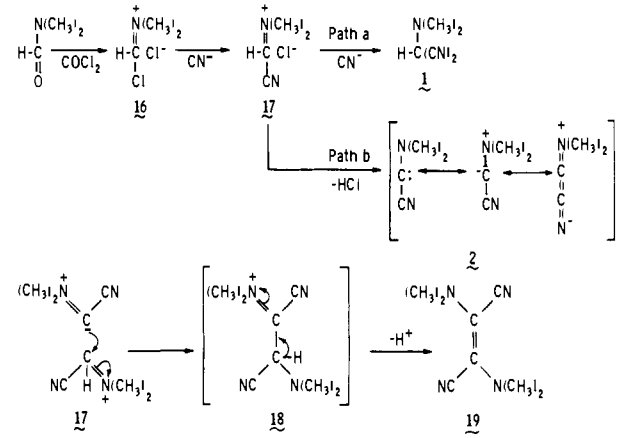
**Scheme III**



Neither bis(dimethylamino)maleo- nor fumaronitrile **19** is among the thermolysis products of **1**, suggesting that dimethylaminocyanocarbene (**2**) does not dimerize. The same conclusion was reached in the analogous case of *tert*-octylaminocyanocarbene.[3] Even though dimerization of **2** would be expected to be highly exothermic, Coulombic repulsion between the carbene carbon atoms may be prohibitively high in the transition state since these carbon atoms carry a partial negative charge.[23] Also dimerization is unlikely because the concentration of **2** is probably very low under the reaction conditions (see below).

Bis(dimethylamino)fumaronitrile (**19**) is, however, obtained by modification of a published procedure for the preparation of dimethylaminomalononitrile (**1**)[11] (path a in Chart III). In

**Chart III**

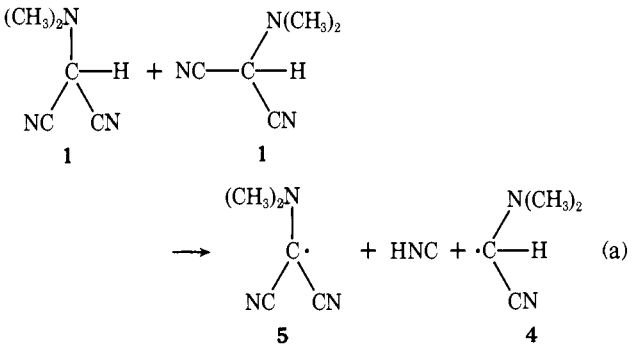


this procedure, cyanide ion is allowed to react with chlorodimethylformiminium chloride (**16**). Dimethylaminomalononitrile (**1**) is the product obtained when the ether-insoluble salts (including **16** and the cyanoformiminium chloride **17**) are extracted into water before heating during the final distillation. However, when, prior to water extraction, the product, which includes the salts **16** and **17**, is heated to 100 °C, no **1** is obtained, probably owing to thermolysis at this temperature. Instead, the main product is bis(dimethylamino)fumaronitrile (**19**), identified by elemental analysis and by physical and spectral properties.[15]

It is proposed that in a first fast step chlorodimethylformiminium chloride (**16**) reacts with cyanide ion to give cyanodimethylformiminium chloride (**17**). Reaction of **17** with a second cyanide ion at room temperature gives dimethylaminomalononitrile (**1**, path a).

At an elevated temperature though, the aminocyanocarbene **2** may be formed either by thermolysis of **1** or by deprotonation of **17** (path b). In dimethylformamide both $Cl^-$ and $CN^-$ are powerful bases[24] so that either could abstract a proton from **17**. These conditions favor formation of the diaminofumaronitrile **19**. The carbene **2** (shown in the ylide form, with a negatively charged central carbon) attacks the abundantly available immonium ion **17** to give a new imminium ion **18**. Loss of a proton gives **19**. A similar mechanism has been proposed for the formation of tetraaminoethylenes from "halves".[25]

**Mechanistic Considerations.** In the thermolysis of dimethylaminomalononitrile, generation of the radicals **4** and **5** can account for the formation of all the observed products. As stated above, the preferred mechanism for the generation of these radicals involves $\alpha$-elimination of HCN from **1** to give the aminocyanocarbene **2**, which abstracts a hydrogen from **1** to give **4** and **5**. However, a priori these radicals could also originate from an alternate molecule-assisted homolysis (MAH) reaction,[26] which avoids the intermediacy of the carbene **2**:



(a)

$$HNC \xrightarrow{\Delta} HCN; \Delta H = -9.8 \text{ kcal}^{27} \qquad \text{(b)}$$

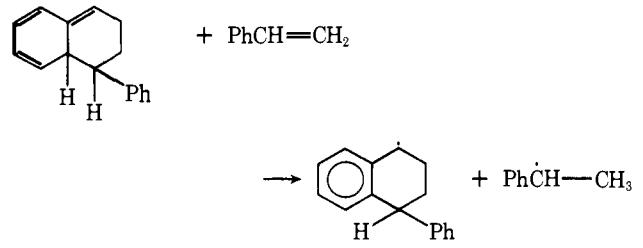
Some processes which may proceed by an MAH mechanism are (1) the direct fluorination of hydrocarbons:[28]

$$RH + F - F \rightarrow R\cdot + HF + F\cdot$$

(2) the initiation of styrene polymerization by *tert*-butyl hypochlorite:[29]

$$t\text{-BuOCl} + CH_2{=}\underset{H}{C}{-}Ph \longrightarrow t\text{-BuO}\cdot + ClCH_2{-}\dot{C}HPh$$

(3) the self-initiation of styrene polymerization via its Diels–Alder dimer:[30]



(4) the "bimolecular" decomposition of allylic hydroperoxides:[31]

$$2ROOH \rightarrow RO\cdot + H_2O + ROO\cdot$$

The general mechanistic pattern involves attack at a moderately weak covalent bond (O–O, O–Cl, Cl–Cl, F–F, a weak C–H bond, etc.) by a species—usually somewhat nucleophilic in character—which can complex or, in the limiting case, react with an incipient radical in a transition leading to a radical pair which is stabilized by this specific solvation.[26b] These reactions are energetically favorable and often exothermic as in reactions 2 and 1 where conditions are exceptionally favored owing to the combination of the very high dissociation energy of HF

(135 kcal) and the very low dissociation energy of $F_2$ (37 kcal).[28]

Similarly reaction 4 is about 30 kcal less endothermic than the unimolecular generation of RO· and OH·.[32] Hydrogen bonding appears essential since at lower concentrations the unimolecular process prevails.[31]

However, even in these energetically favorable cases, an MAH mechanism remains often in doubt. Questionable examples are reaction 1[33] and specifically reaction 4, for which a compelling alternative to the bimolecular mechanism has recently been presented.[34] Considering these reactions, the improbability of an MAH reaction of dimethylaminomalononitrile becomes clear.

Complexing (hydrogen bonding) of a C–H hydrogen—if at all possible—would preferentially involve a basic dimethylamino—rather than a neutral nitrile—nitrogen, an arrangement unsuitable for elimination of HCN. However, assuming complexation of a C–H to a nitrile group, the nitrile nitrogen rather than the carbon atom would be preferred. Apart from the absence of nonbonding electrons on the carbon atom, the needed interpenetration of the two molecules of **1** would require a prohibitively crowded transition state. Accordingly, HNC rather than HCN would be formed as shown in reaction a.

In the self-initiation of styrene polymerization according to reaction 2, the Diels–Alder dimer is an exceptionally active hydrogen transfer agent, which upon loss of a hydrogen atom gains aromatic resonance stabilization. Nothing comparable applies to **1.** Moreover, its potentially transferable hydrogen lacks a multiple bond which it can attack with formation of a stabilized radical. The nitrile group is singularly resistant against radical attack.[35]

Compared to bimolecular ROOH decomposition, **1** lacks a manifestly weak bond such as O–O (44 kcal[33]). The C–CN bond in **1** is expected to be weaker than the corresponding bond in acetonitrile (121 kcal[36]) by the radical stabilization energy of a nitrile group (5–7 kcal[37]) plus an additional unknown amount due to "merostabilization" by the α-amino group.[13] Clearly this will not suffice to allow unimolecular homolysis at room temperature. To the objections already raised against an MAH mechanism, i.e., absence of a weak bond in **1** and the improbability of suitable complexing, this adds the requirement that this process must be concerted, a special feature without clear precedent.

Finally, when an MAH process is postulated, this path has usually a marked thermochemical advantage over alternate routes for radical generation.[26] However, as a route to the radicals **4** and **5,** the preferred carbene mechanism (reaction e) is energetically favored over a concerted MAH process (reaction a) by $\Delta H$ (reaction b) = 9.8 kcal.

**The Dimethylaminocyanocarbene Mechanism (See Chart 1).** The elimination of hydrocyanic acid in reaction c can a priori be either concerted or nonconcerted.

$$\mathbf{1} \leftrightharpoons \mathbf{2} + \mathrm{HCN} \qquad \text{(c)}$$

$$\mathbf{2} + \mathbf{1} \rightarrow \mathbf{4} + \mathbf{5} \qquad \text{(d)}$$

$$\mathbf{1} + \mathbf{1} \rightarrow \mathbf{4} + \mathbf{5} + \mathrm{HCN} \qquad \text{(e) (= c + d)}$$

**Nonconcerted Processes. Homolytic.** Both processes below are improbable as each requires the unprecedented generation of a carbene from two radicals.

$$\mathbf{1} \rightarrow \mathbf{4} + \mathrm{CN}\cdot;\ \mathrm{CN}\cdot + \mathbf{4} \rightarrow \mathbf{2} + \mathrm{HCN} \text{ or}$$

$$\mathbf{1} \rightarrow \mathbf{5} + \mathrm{H}\cdot;\ \mathrm{H}\cdot + \mathbf{5} \rightarrow \mathbf{2} + \mathrm{HCN}$$

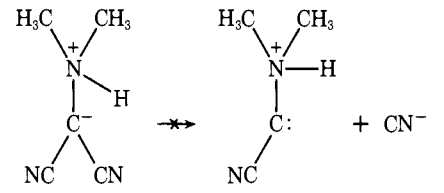
Moreover, unimolecular homolysis of the C–CN (vide supra) or C–H bond is not feasible at room temperature. Unimolecular homolysis of a C–H bond to form a hydrogen atom is unprecedented even when a highly stable radical fragment would result. Triphenylmethane does not thermolyze; and the highly stable nitroxides, which are structural analogues of **5** (see above), are obtained from the corresponding N,N-disubstituted hydroxylamines only by oxidation ($Cu^{2+}$ or $Ag^+$, etc.) and not by thermolysis of the O–H bond. Some substituted aryl-*tert*-butylhydroxylamines are stable at melting points as high as 149 °C.[38]

**Heterolytic.** The rate of the process below is dependent upon the thermodynamic stability of the immonium ion that is formed. The nitrile substituent on the immonium ion derived from **1** destabilizes it relative to the immonium ions derived

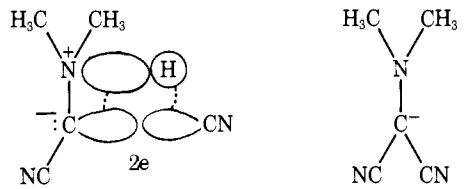
$$\underset{\mathbf{1}}{(\mathrm{CH_3})_2\mathrm{NCH(CN)_2}} \longrightarrow \mathrm{CN^-} + (\mathrm{CH_3})_2\overset{+}{\mathrm{N}}{=}\mathrm{CHCN}$$

from dimethyl- or diethylaminoacetonitrile. Both compounds are stable at their boiling points (137 and 170 °C, respectively). This is consistent with the extreme sluggishness of cyanide as a leaving group[37b] and rules out heterolysis of the C–CN bond in **1** as the initial step in generation of **2.**

Base-catalyzed α-elimination is a well-established route to some carbenes. A priori the generation of **2** could be initiated by either an intra- or intermolecular proton abstraction by the dimethylamino group of **1.** Neither process is likely, however. The intramolecular route requires expulsion of a cyanide ion from **20** and then proton abstraction by the leaving cyanide ion. These steps cannot be concerted since that would be a forbidden [$\sigma^{2s} + \sigma^{2s}$] pericyclic process (**22**).



**20** **21**



**22** **23**

The energy requirements of the nonconcerted intramolecular route would be prohibitive because cyanide ion is a very poor leaving group[37b] and the intermediate carbene **21,** as the conjugate acid of **2,** lacks the stabilization which in **2** is provided by the nonbonding electrons on the neighboring amino nitrogen. (See below and ref 2, especially pp 2607 and 2608.) Moreover, intramolecular rearrangement of **21** to the dimethylaminocyanomethylimmonium ion is expected to be much faster than proton abstraction by $CN^-$.

Intermolecular proton abstraction would produce the dimethylaminodicyanomethyl anion **23,** which could expel a cyanide ion to give the carbene **2** as there is strong evidence for the analogous generation of *tert*-octylaminocyanocarbene from *tert*-octylaminomalononitrile under basic conditions.[2] However, treatment of **1** with triethylamine gives the Thorpe dimer **15** as the main product and none of the products **3, 9,** or **12** which are indicative of generation of the carbene **2** is isolated (see above). Apparently, the anion **23** adds to **1** much faster than it expels a cyanide ion to give **2.**

In conclusion, concerted α-elimination of hydrogen cyanide, proceeding via the aminocyanocarbene **2,** appears the most probable route to the radicals **4** and **5** and to the isolated products **3, 9,** and **12.** The energy of formation of the H–CN

bond (129 kcal)[36] offsets, in large part, the breaking of the C-CN bond. Additionally, the activation energy of such a reaction is likely to be moderate or even low because aminocyanocarbenes—while fairly energetic species—are expected to be uniquely stabilized relative to carbenes with only amino or cyano substituents.[2] The electron-withdrawing and supplying substituents on the carbene carbon atom, as in **2**, allow stabilization by ylidelike, charge-separated forms[23] (see Chart III) regardless of multiplicity.

Even though reaction c is assumed to be endothermic and reversible, it is driven to completion because both the hydrogen cyanide and the carbene **2** are rapidly consumed in reactions with **1** (reactions f and d)

$$\mathbf{1} + \mathrm{HCN} \rightarrow \mathbf{3} \qquad \text{(f)}$$

and in the subsequent reactions of the radicals **4** and **5** (see Chart I). Hence the carbene **2** is expected to be present in a small steady-state concentration only. Unfortunately, direct experimental proof of the unimolecular generation of hydrogen cyanide is lacking because of the obvious difficulties in measuring its rate of evolution due to reaction c in a medium where it reacts rapidly with starting material (reaction f).

Kinetic electron spin resonance, applied to radical **5**, is equally complicated. Apart from the difficulties inherent in this method, avoidance of meaningless pseudo-zero-order kinetics requires dilute solutions and, therefore, elevated temperatures. Under these conditions, the bimolecular reaction d may become rate determining and the carbene process may show second- or mixed-order kinetics. Moreover, **1** is consumed by at least three paths shown in Chart I and additionally by formation of the Thorpe dimer **15** (see above). Radical **5** is also likely to disappear by a number of paths, one of which is shown in Chart I.

It now remains to examine the mechanism of reaction c in more detail. Consider the microscopic reverse, i.e., the insertion of the aminocyanocarbene **2** in the H-CN bond to give the aminomalononitrile **1**. Recent calculations show that the insertion of singlet methylene in a methane C-H bond is a concerted process in which the carbene initially approaches the hydrogen atom with its empty p orbital.[39] Such "leading" with the unoccupied electrophilic orbital appears to be general. It has also been postulated for the additions of methylene and of sulfur dioxide to ethylene,[40] and it probably applies as well to the insertion of singlet aminocyanocarbene. The proposed mechanism is shown in Figure 2. It is assumed that the carbene **2** is linear as Jameson and Yang[23a] claim for the unsubstituted analogue, on the basis of INDO calculations.

Initially (Figure 2a) the vacant p orbital of the carbene interacts with the H-CN bond to form a two-electron, three-center bond. This is analogous to a proposal by Seyferth et al.[41] to account for the concerted insertion of dichlorocarbene in the benzylic C-H bond. As the hydrogen and the cyano group move farther apart, the situation is better represented by Figure 2b. The proton's orbital overlaps increasingly with the filled $\omega$ orbital, while the cyano carbon's filled sp orbital overlaps more and more with the vacant $\omega$ orbital. Still later, each of those two entities becomes bonded to one of the p orbitals on the "carbene" carbon atom; and finally rehybridization and bond angle adjustment complete the process. Since symmetry is lacking, a correlation diagram cannot be constructed; but the generalized rules for pericyclic processes should still be applicable.[42] If Figure 2b represents the transition state, the reaction is seen to be of the allowed $[\sigma^{2s} + \omega^{2a}]$ type.

Thermal $\alpha$-elimination of hydrogen cyanide from **1** gives singlet dimethylaminocyanocarbene as a consequence of spin conservation. It is the reverse of the insertion reaction and can now be pictured as a nonlinear cheletropic fragmentation.

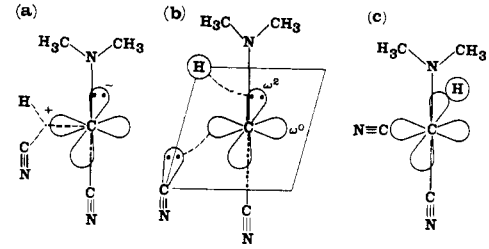



Figure 2.

The reaction is initiated by spreading of an $(H_3C)_2N$-C-CN angle with concomitant rehybridization at the central carbon atom. As the two orbitals involved in these bonds acquire more s character, the other two orbitals which bind the hydrogen and the second cyano group become more p-like. While the C-H and C-CN bonds thus weaken, the angle between them decreases so that the hydrogen and the cyano group move closer together until eventually the situation shown in Figure 2c is reached. Disengagement of the hydrogen and the cyano group (Figures 2b and a) can now occur, but not necessarily at equal rates, so that the transition state may have dipolar character. Such an "unsymmetrical" concerted process in which rupture of the carbon-hydrogen bond proceeds faster is essentially equivalent to the mechanism proposed earlier in a valence bond description for the thermal generation of *tert*-octylaminocyanocarbene from *tert*-octylaminomalononitrile.[3]

**Prebiological Implications.** Aminocyanocarbene has been suggested as a possible intermediate in the prebiotic synthesis of polypeptides and purines.[43] However, its direct formation by rearrangement of iminoacetonitrile—the hydrogen cyanide dimer—is improbable.[44] The present work suggests that aminocyanocarbene may have originated via a circuitous route, i.e., the thermolysis of aminomalononitrile, the trimer of hydrogen cyanide. Polymerization of aminocyanocarbene to give polypeptides may have occurred via the $HN^+{=}C{=}C{=}\bar{N}$ form[45] or through the corresponding diradical.[23a] It is attractive to speculate that the analogous polymerization of dimethylaminocyanocarbene accounts for an intractable amber-colored polymeric material, which constitutes the major thermolysis product of **1**. It could be the product of reaction of the ketenimine moieties in a polymer of **2** with the hydrogen cyanide generated during the thermolysis of **1** and/or with the water used in the workup.

## Experimental Section

**Equipment.** The following instruments were used: a Perkin-Elmer 621 double-beam grating IR spectrometer, a laser-Raman Carey 81 spectrometer, and a Varian T-60 NMR spectrometer. GLC analysis of mixtures was by the coinjection technique, which identifies a component through the increased intensity of a specific peak upon injection of a mixture modified by addition of an authentic compound.

**Materials.** Hydrogen cyanide was from Fumico Inc. Dimethylaminomalononitrile was prepared by a modification of the procedure of Gold and Bayer.[46] Dimethylcarbamoyl chloride was from Aldrich Chemical Co.

**Tetramethylformamidinium Chloride.**[47] Dimethylcarbamoyl chloride (535 g, 462 mL, 5 mol) in dimethylformamide (730 g, 775 mL, 1 mol) was heated with stirring at 120 °C for 6 h. Evolution of carbon dioxide started when the temperature reached 90 °C. After cooling to room temperature, the crystalline product was collected by filtration and washed with acetone (400 mL). A sheet rubber dam was used during the filtration to protect the hygroscopic product from atmospheric moisture. After drying at 25 °C and 0.04 mm for 10 h, the yield was 327 g (48%), mp 143–143.5 °C. Concentration of the mother liquors in vacuo yielded a second, less pure crop of 110 g. Anal. C, H, N. Cl.

**Dimethylaminomalononitrile (1).** Tetramethylformamidinium chloride (327 g, 2.39 mol) was dissolved in hydrogen cyanide (383 mL,

268.3 g, 9.91 mol) at 0–10 °C and set aside overnight at room temperature. Excess hydrogen cyanide was distilled into a receiver containing potassium hydroxide (560 g) in water (1000 mL). An oil bath at 50 ± 1 °C was used and a slight nitrogen sparge. Sparging with nitrogen at 50 °C was continued for 3 h, after which a vacuum of 120 mm was applied for an additional 1 h. The residue was diluted with 300 mL of ether, stirred for 30 min, and filtered. The precipitate of dimethylamine hydrochloride was washed with 300 mL of ether. The filtrate and washings were combined, and the ether was evaporated at 35 °C and 100 mm. Distillation of the residue in vacuo at a bath temperature not exceeding 50 °C and using a receiver cooled to −78 °C yielded 231.3 g (88.7%) of **1** as a colorless oil: bp 39–40 °C (0.4 mm); NMR ($CDCl_3$) $\delta$ 2.47 [6 H, $N(CH_3)_2$], 4.76 ppm (1 H, CH, disappears upon deuteration). The compound was stored at −30 °C. Anal. C, H, N.

**Thermolysis of 1. Isolation of 1-Amino-2,3-bis(dimethylamino)-1,3-dicyanopropene (9), 1,4-Bis(dimethylamino)-1,2,4-tricyano-3-aza-1,3-butadiene (12), and 1-Dimethylamino-2-aminomaleonitrile (3).** Neat **1** (43.12 g, 0.395 mol) was stirred at 60 °C under a nitrogen blanket for 48 h. The tarry thermolysis product was diluted with tetrahydrofuran (30 mL) and poured into ether (900 mL). The reaction flask was rinsed with 10 mL of warm tetrahydrofuran, and the rinsings were added to the ether solution. This solution was heated to reflux and filtered to give 3.2 g of tarry, acetone-soluble black solids. Extraction of the filtrate with 5% aqueous hydrochloric acid (2 × 175 mL) gave an organic phase and a combined aqueous phase. Upon cooling to −5 °C, the aqueous extracts deposited colorless, crystalline hydrochloric acid salt of **9**. This salt was collected by filtration and treated with an excess of a concentrated solution of sodium bicarbonate, and the mixture was extracted with ether. The ether extracts were dried ($MgSO_4$), treated with Norit, filtered, and concentrated to 50 mL. Filtration after 4 h at −15 °C yielded a precipitate which was recrystallized at −10 °C from benzene–hexane (1:1) to give 6.95 g (19.1%) of **9**: mp 91.0–91.8 °C; UV max (MeOH) 267 nm (log $\epsilon$ 4.10); IR ($CHCl_3$) 3475, 3360 (vs, $NH_2$), 2180 (vs, C≡N), 1645 (vs, C=C), 1556 $cm^{-1}$ (m, $NH_2$ def, shifts upon treatment with $D_2O$); Raman (crystal) 2226 (m, C≡N), 2169 (vs, C≡N), 1618 $cm^{-1}$ (vs, C=C); $^1H$ NMR ($CDCl_3$) $\delta$ 2.37, 2.41 [each 6 H, $N(CH_3)_2$], 4.18 (1 H, CH, disappears upon deuteration with $D_2O$); $^{13}C$ NMR (decoupled) $\delta$ 41.9, 42.8 (superimposed quartets before decoupling, two $N(CH_3)_2$ groups), 58.33 (CH, doublet before decoupling), 99.35 [$(CH_3)_2NC$=C], 114.2, 114.6 (both C≡N), 145.9 ppm [$H_2N(NC)C$=C<]; mass spectrum (70 eV) *m/e* 193 ($M^+$), 178 ($M^+ - CH_3$), 175 ($M^+ - NH_3$-H·), 166 ($M^+$ − HCN), 164.17 (metastable for $193^+ \rightarrow 178^+ + 15$), 158.70 (metastable for $193^+ \rightarrow 175^+ + 18$), 160.50 (metastable for $193^+ \rightarrow 176^+ + 17$), 148 [$M^+ - HN(CH_3)_2$]. Mass spectrum of **9** ($D_2$), obtained by deuteration with $D_2O$: *m/e* 195 ($M^+$), 175 ($M^+ - NHD_2$), 150 [$M^+ - HN(CH_3)_2$]. Mass spectrum of **9** ($D_3$), obtained by deuteration with LiOD–$D_2O$ (LiH dissolved in $D_2O$): *m/e* 196 ($M^+$), 175 ($M^+ - NHD_3$), 150 [$M^+ - DN(CH_3)_2$]. Anal. C, H, N.

The ether–tetrahydrofuran phase, remaining after the aqueous hydrochloric acid extraction, was washed with concentrated aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated in vacuo to 200 mL. Bright yellow needles started to precipitate. After 2 h at −15 °C filtration yielded 1.5 g (1.8%) of **12**: mp 114.0–115.0 °C; UV max (MeOH) 393, 315, 277 nm (log $\epsilon$ 4.472, 4.076, 4.279); IR ($CHCl_3$) 2180, 2220 (m, both C≡N), 1602, 1573 $cm^{-1}$ (vs >C=CN=C<); Raman (crystal) 2190 (w), 2220 (m), 2230 (w, all three C≡N), 1603 (vs), 1573 $cm^{-1}$ (ms, both >C=CN=C<); $^1H$ NMR ($CDCl_3$) $\delta$ 3.11, 3.24 ppm [equal area, each $N(CH_3)_2$]; $^{13}C$ NMR (decoupled) $\delta$ 133.8 [-N=$C$(CN)$N(CH_3)_2$)], 124.8, 115.1, 114.2 (all three C≡N), 107.3, 103.3 [NC(>N)$C$=$C$(N=)CN], 42.88, 38.5 [both $N(CH_3)_2$]; mass spectrum (70 eV) *m/e* 216 ($M^+$), 201 ($M^+ - CH_3$). Anal. ($C_{10}H_{12}N_6$) C, H, N.

The mother liquors of **12** were reduced to 18 mL and refrigerated at −15 °C for 2 h. Filtration yielded a colorless, crystalline solid. Recrystallization from benzene–hexane (1:1) gave **3**: 3.90 g (2.8%); mp 72.5–73.5 °C (lit.[11] 74–74.5 °C); IR ($CHCl_3$) 3475, 3360 (vs, both $NH_2$), 3135 (w, overtone of 1620 $cm^{-1}$), 2240 (m), 2190 (s, C≡N), 1620 vs, 1575 m (>NC=C-C≡N); mass spectrum (70 eV) *m/e* 136 ($M^+$), 121 ($M^+ - CH_3$), 94 ($M^+ - CH_3$ − HCN). Anal. ($C_6H_8N_4$) C, H, N.

**Identification of Dimethylaminoacetonitrile (6) and Dimethylcarbamoyl Cyanide (13) in the Thermolysis Mixture.** The mother liquors of **3** were freed of solvent. Vacuum distillation of the residue in a microstill yielded a small, colorless fraction (0.48 g), distilling at 80 °C (0.3 mm). Two components were isolated from this fraction by preparative GLC. The more volatile of these was shown to be **6** by means of the coinjection technique using authentic dimethylaminoacetonitrile (Aldrich Chemical Co.) by identity of IR spectra and by elemental analysis. Anal. ($C_4H_4N_2$) C, H, N.

Identification of the other component as **13**, isolated in very small amount, is based on IR[48] ($CHCl_3$) 1670 $cm^{-1}$ (vs, C=O) and mass spectrum (70 eV): *m/e* 98 ($M^+$), 83 ($M^+ - CH_3$), 72 ($M^+$ − CN), 54 [$M^+ - N(CH_3)_2$]. Anal. ($C_4H_6NO$) C, H, N.

**Authentic 3 from 1 and Sodium Cyanide.** **1** (1.5 g, 0.014 mol) was added to sodium cyanide (1 g) in water (3 mL), stirred for 45 min at room temperature under a nitrogen blanket, and filtered. The crystalline precipitate was dissolved in hot chloroform–carbon tetrachloride (1:1). The solution was dried ($MgSO_4$), treated with Norit, and chilled (−15 °C) to give 1.1 g (63%) of **3**, identical with the product from thermolysis of **1** (IR spectra and mixture melting point).

**Intractable Polymeric Residue.** The pot residue (11.51 g) remaining after recovery of **6** and **13** constitutes the balance of the thermolysis product of **1**. It is an apparently intractable, viscous, amber-colored material.

**Thermolysis of 1 in Refluxing Benzene. Isolation of 1,3-Bis(dimethylamino)-2-amino-1,3,3-tricyanopropene (15).** **1** (31.7 g, 0.29 mol) in benzene (100 mL) was stirred at reflux under a nitrogen blanket for 36 h. The benzene was removed in vacuo and the black residue extracted with ether (2 × 200 mL at reflux). An insoluble black gum (3.20 g) was not identified. The ether extract was treated with Norit, filtered, and extracted with 5% aqueous hydrochloric acid (3 × 80 mL). Upon cooling to 0 °C, the aqueous acidic extracts deposited the hydrochloric acid salt of **9**, which was collected by filtration. From this salt 1.63 g (2.9%) of **9** was recovered as described above. Identity with the earlier product was proven by IR spectra and mixture melting point.

The acid-extracted ether solution was extracted with aqueous sodium bicarbonate, dried ($MgSO_4$), treated with Norit, and evaporated to give a syrupy residue which partially crystallized during 2 days in the refrigerator. The crystals were collected by filtration, dissolved in benzene (10 mL), treated with Norit, filtered, and diluted with hexane (25 mL). The crystalline precipitate formed after 10 h at −15 °C, was recrystallized from benzene–hexane (1:3) to yield 0.72 g (1.1%) of **15**: mp 119.5 °C dec; UV max (MeOH) 273 nm (log $\epsilon$ 3.93); IR (KBr pellet) 3422, 3318 (vs, $NH_2$), 2224 (vw), 2184 (s, both C≡N), 1640 (vs, C=C), 1586 $cm^{-1}$ (s, $NH_2$ def); Raman (crystal) 2253 (m), 2225 (m), 2180 (s, all three C≡N), 1645 (s, NC=CCN), 1585 $cm^{-1}$ (w, $NH_2$ def); $^1H$ NMR ($CDCl_3$) $\delta$ 2.54 [12 H, two $N(CH_3)_2$], 5.00 ppm (2 H, $NH_2$); mass spectrum (70 eV) *m/e* 218 ($M^+$), 203 ($M^+ - CH_3$), 174 [$M^+ - N(CH_3)_2$], 147 [$M^+ - N(CH_3)_2$ − HCN]. Anal. ($C_{10}H_{14}N_6$) C, H, N.

The brown liquid residue from the mother liquors of **15** (8.1 g) constituted the main thermolysis product. The components of this mixture were, however, not identified since they could not be crystallized.

**Formation of 15 by Dimerization of 1 in Triethylamine.** **1** (30 g, 0.275 mol) in triethylamine (80 mL) was kept at room temperature under a nitrogen blanket for 19 h. The triethylamine was evaporated in vacuo. The residue was dissolved in ether (250 mL) and extracted with 5% aqueous hydrochloric acid (3 × 100 mL). Cooling of the aqueous extracts to 0 °C did not cause precipitation of the hydrochloric acid salt of **9**. Neither was **9** isolated when the aqueous extracts were neutralized with sodium bicarbonate, then extracted with ether, and the ether extracts were concentrated and chilled.

The original ether solution was washed with saturated aqueous bicarbonate to neutralize any hydrochloric acid, dried ($MgSO_4$), treated with Norit, and concentrated to 50 mL. After 4 h at −15 °C filtration yielded a copious, crystalline precipitate which was further purified by two recrystallizations (from ether–pentane (5:3), 160 mL) to give colorless crystals of **15** (9.68 g, 16.1%), identical by IR spectra and mixture melting point, with the product obtained from thermolysis of **1** in refluxing benzene. The combined mother liquors provided an additional 4.41 g (7.3%) of **15** after condensation, chilling, filtration, and two recrystallizations from ether–pentane (2:1), using Norit each time.

**Bis(dimethylamino)fumaronitrile (19).** A suspension of powdered sodium cyanide (35.3 g, 0.72 mol) in dimethylformamide (104 mL) was stirred at 0 °C. Consecutively, phosgene (19.7 g, 14.2 mL at 0 °C,

0.20 mol) and hydrogen cyanide (19.55 g, 28.4 mL, 0.72 mol) were introduced by distillation. The ice cooling was discontinued, and the reaction was allowed to proceed overnight at room temperature with stirring. Benzene (450 mL) was added, and excess hydrogen cyanide was removed by sparging with nitrogen (4 h). The mixture was filtered through Celite, and the benzene removed through a spinning band column at 5 mm (bath temperature 70 °C). The bath temperature was then raised to 80–100 °C, and the dimethylformamide removed at 2.7 mm. The residue was extracted with ether and filtered, leaving a considerable amount of a crystalline precipitate which was not identified. The filtrate was evaporated in vacuo and the residue distilled through a short-path column at a bath temperature of 90–97 °C, to give 6.5 g of crude **19**, bp 82–88 °C (0.12–0.15 mm) [lit.[15] 89 °C (0.25 mm)], which crystallized upon cooling. Two crystallizations from ether–hexane gave **19**, mp 46.5–47 °C (lit.[15] 46–47.5 °C). Anal. ($C_8H_{12}N_4$) C, H, N. IR ($CHCl_3$) 2215 m and 2165 s (C≡N), 1585 $cm^{-1}$ vs (C=C); NMR ($CDCl_3$) $\delta$ 2.88 ppm ($NCH_3$); mass spectrum (70 eV) *m/e* 164 ($M^+$), 149 ($M^+ - CH_3$), 122 ($M^+ - CH_3 - HCN$), 120 [$M^+ - N(CH_3)_2$].

**Preparation of Samples for ESR Spectra.** For the ESR experiments, an aliquot of **1** was redistilled through a short-path column prior to use. Bath temperature was held at less than 45 °C to minimize decomposition, and the receiver was cooled in dry ice–acetone. The distillate was stored at −78 °C. Under these conditions, the only possible contaminants are traces of hydrogen cyanide and dimethylglycinonitrile. GLC showed only a single peak for **1**. In a nitrogen atmosphere ESR tubes, maintained at −78 °C, were filled with neat **1**, a 5% solution of **1** in xylene, or a 5% solution of **1** in xylene–di-*tert*-butyl peroxide (95:5). In an additional set of tubes, **1** was replaced by its monodeuterio analogue, obtained by vigorously shaking freshly distilled **1** with excess $D_2O$ at 0 °C, repeating this operation twice, and each time discarding the aqueous layer.

The tubes were degassed by three freeze–thaw cycles. This removes hydrogen cyanide, and dimethylglycinonitrile—if at all present—is inert in the ESR experiment. The tubes were sealed and stored at −78 °C.

**ESR Spectra of the Dimethylaminodicyanomethyl Radical (5) and Computer Simulation.** Tubes with neat **1** or with deuterated **1** were allowed to stand at room temperature for 4 h before recording the ESR spectra. The spectra were identical for both compounds (Figure 1A). Computer simulation (Figure 1B) *a* values: 6H[$N(CH_3)_2$], 9.19 G; 1N[$N(CH_3)_2$], 10.25 G; 2N(C≡N), 1.99 G; $g$ = 2.0030.

The tubes containing 5% solutions of **1** or its monodeuterio analogue in xylene were heated for 30 min at 140 °C. ESR spectra, identical for both compounds, were obtained after allowing the tubes to cool to room temperature (Figure IC). Computer simulation (Figure ID) *a* values: 6H[$N(CH_3)_2$], 8.61 G; 1N[$N(CH_3)_2$], 9.61 G; 2N(C≡N), 2.04 G.

The tube containing a 5% solution of **1** in benzene–di-*tert*-butyl peroxide (95:5) gave no ESR spectrum at room temperature; but, after 30 s UV irradiation, an extremely strong spectrum resulted that was identical with Figure 1C upon reducing the receiver gain by a factor of $10^2$ (Figure 1E).

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