A Stable Glycinonitrile Radical.   Evidence Suggesting Generation of Aminocyanocarbenes from Aminomalononitriles in Basic Media

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In basic media both dimethylaminomalononitrile (4) and *tert*-octylaminomalononitrile (1) decompose with generation of hydrogen cyanide.   In the case of 4, α elimination is indicated, implying formation of dimethylaminocyanocarbene (6).   Evidence is presented which suggests that in the decomposition of 1 analogous α elimination occurs to give *tert*-octylaminocyanocarbene (3).   A solution of 1 in triethylamine shows a strong 16-line esr signal which is assigned to the stable *N-tert*-octylglycinonitrile radical (7).   It is proposed that the carbene 3 abstracts a hydrogen from 1 to give 7 and the *N-tert*-octylaminomalononitrile radical (8).   Three products are identified corresponding to dimerization of 7, disproportionation of 8, and combination of 7 and 8.   There is no evidence for dimerization of the aminocyanocarbene 3 or for its addition to olefins.   However, 3 may add to 1 and to *tert*-octylaminocyanoketene-*N-tert*-octylimine (24) to give the corresponding aminoiminopropenes.   In aqueous base 4 gives dimethylamine.   Hydrolysis of the carbene 6 appears to be the indicated mechanism.   In the same medium 1 gives *tert*-octylamine, possibly owing to the analogous hydrolysis of *tert*-octylaminocyanocarbene (3).   A novel synthesis of 1 is described.
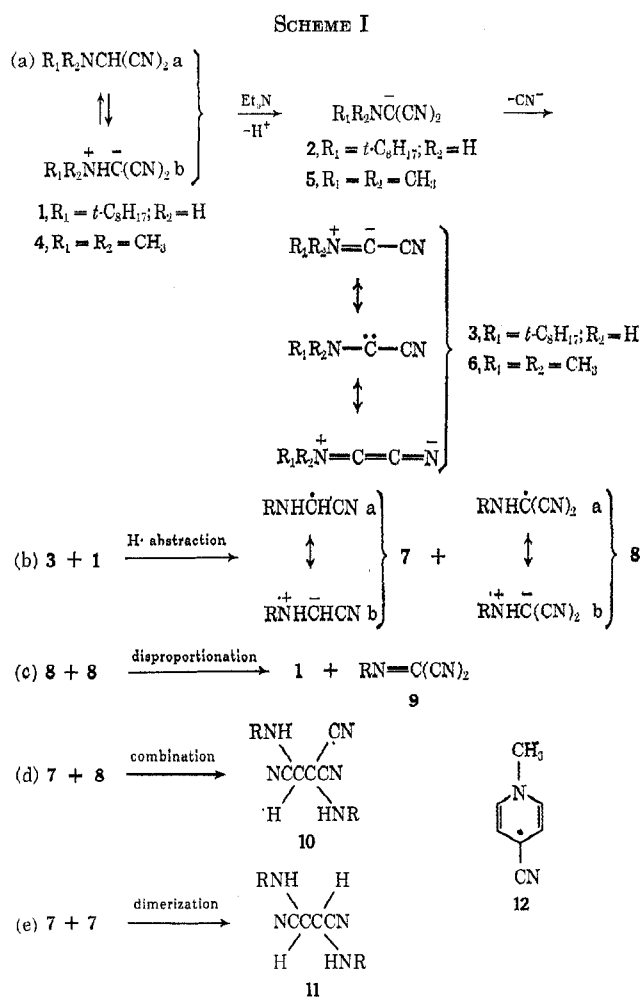
In an earlier article,[1] the reaction of 2,4,4-trimethylpentene-2 with hydrogen cyanide and hydrogen fluoride was shown to give *tert*-octylaminomalononitrile (1), *tert*-octylaminocyanoketene-*N-tert*-octylimine (23), and other products.   Also, it was suggested that *tert*-octylaminocyanocarbene (3) is generated when 1 is decomposed in basic media.   The following report presents further evidence pointing to carbene 3 as an intermediate.

Results and Discussion

Evidence for a Radical Intermediate.—An oxygen-free solution of 1 in triethylamine decomposes smoothly at room temperature.   Glpc shows that after 4 hr all 1 has disappeared.   During the decomposition, the solution generates a strong 16-line esr signal, which persists for several hours (Figure 1).   Computer simulation supports assignment of the observed spectrum to the *N-tert*-octylglycinonitrile radical 7[2] (Scheme I).   The high stability of this radical is not unexpected since the vinylogous 4-cyano-*N*-methylpyridyl radical (12) is reportedly stable for a week.[3]

Another radical with a closely related α-aminonitrile structure is the di-*tert*-octylaminomaleonitrile radical whose stability was reported earlier.[1]   The stability of the radical 7 is probably due to resonance involving a charge-separated canonical form 7b (Scheme I).

No conventional explanation seems to account for the formation of the glycinonitrile radical 7 from 1 under such mild conditions.   It is, therefore, proposed that initially α elimination of hydrogen cyanide occurs to give the aminocyanocarbene 3 (discussed in detail

SCHEME I

below).   Once formed, 3 abstracts a hydrogen atom from unreacted 1 (reaction b, Scheme I) to give 7.   In this process, the *tert*-octylaminomalononitrile radical 8 should be the second product.   This radical may be responsible for a very broad unstructured doublet that underlies the signal for radical 7.   The broadness and apparent lack of hyperfine structure can be ascribed to a very short relaxation time, which may result from two possible exchange processes.   These are electron exchange between the radical 8 and the aminomalononitrile anion 2 and possibly also hydrogen exchange be-
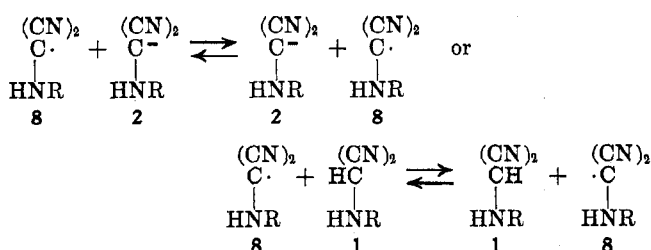
(1) L. deVries, *J. Org. Chem.*, **36**, 3442 (1971).

(2) Dr. J. Q. Adams has closely matched the observed hyperfine structure (Figure 1A) through computer simulation.   The odd electron is assumed to interact with two nitrogen atoms and two hydrogen atoms as in radical 7.   Hyperfine splitting constants and line width giving the best agreement (Figure 1c) follow: N_1, 2.77 G; N_2, 3.32 G; H_1, 12.84 G; H_2, 22.81 G; line width 1.38 G.   An even closer approach to the experimental spectrum results when a simple doublet is superimposed.   The doublet spectrum (hyperfine splitting constant 17.54 G; line width, 9.23 G) is shown in Figure 1D and the composite spectrum (1D + 1C) in Figure 1b.   It is probable that the doublet actually contains additional fine structure which is broadened owing to exchange processes discussed below.   As an alternate possibility, we considered interaction of the odd electron with one hydrogen atom and three nitrogen atoms (two of which are equivalent) as in radical 8 (Scheme I).   A satisfactory match could, however, not be obtained.

(3) M. Itoh and S. Nagakura, *Tetrahedron Lett.*, **No. 8**, 417 (1965).

tween the radical **8** and the aminomalononitrile **1**, *e.g.*

$$\begin{array}{c}(CN)_2 \\ C\cdot \\ HNR \\ 8\end{array} + \begin{array}{c}(CN)_2 \\ C^- \\ HNR \\ 2\end{array} \rightleftharpoons \begin{array}{c}(CN)_2 \\ C^- \\ HNR \\ 2\end{array} + \begin{array}{c}(CN)_2 \\ C\cdot \\ HNR \\ 8\end{array} \quad \text{or}$$

$$\begin{array}{c}(CN)_2 \\ C\cdot \\ HNR \\ 8\end{array} + \begin{array}{c}(CN)_2 \\ HC \\ HNR \\ 1\end{array} \rightleftharpoons \begin{array}{c}(CN)_2 \\ CH \\ HNR \\ 1\end{array} + \begin{array}{c}(CN)_2 \\ \cdot C \\ HNR \\ 8\end{array}$$

The stability of the radical **8** could be comparable to or even greater than that of the radical **7**. The doublet shape of the spectral envelope suggests that in **8** the largest hyperfine splitting constant is associated with the hydrogen atom.

Hydrogen abstraction by the aminocyanocarbene **3** is plausible if the structure of this carbene is similar to the structure recently proposed for unsubstituted aminocyanocarbene by Loew and Chang.[4] These authors postulate a bent singlet ground state resembling a spin-paired biradical in which slightly more than one electron is localized on the "methylene" carbon and somewhat less than one electron is delocalized throughout the π system. This results in a carbon atom which is more accurately described as trivalent and with greater kinship to a radical than a methylene carbon. According to Wagner and Hammond,[5] hydrogen abstraction by such a singlet biradical is no less probable than by a triplet, providing that the singlet has a sufficiently long lifetime.

It is, therefore, unnecessary to invoke for carbene **3** a triplet state which, moreover, is expected to be of higher energy than the singlet ground state.[4]

In a valence bond description **3** is represented by a resonance hybrid with a major contribution from an ylide form (Scheme I). Similar resonance-stabilized structures have been proposed for various so-called "nucleophilic" carbenes,[6] but the aminocyanocarbene structure is unique because the carbene carbon carries an electron-supplying amino group as well as an electron-withdrawing nitrile group. This substitution pattern should be conducive to maximum stabilization of carbenes.[7] One may, therefore, expect aminocyanocarbenes to exhibit an enhanced stability relative to carbenes with only amino or cyano substituents.

In the absence of data about carbene stabilities, such a postulate cannot be supported by calculation, nor has it been demonstrated experimentally. However, some stable compounds, such as carbon monoxide, the isonitriles, and fulminic acid derivatives, represent extremes of stabilization of divalent carbon by charge-separated forms. An important factor in the unusual stability of these compounds is that a highly electronegative sp orbital is available to accommodate the negative charge on carbon.

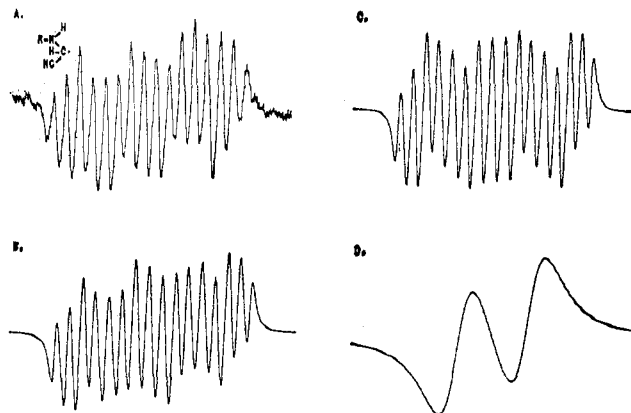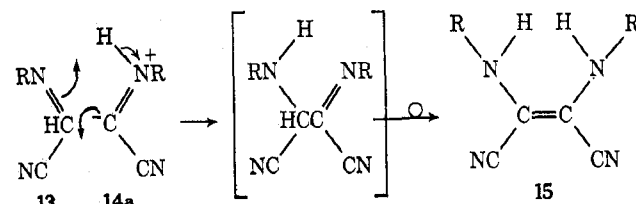The carbene **3** has not been reported, but Moser,

Figure 1.—Esr spectrum of **7** and computer simulation (width of spectra = 70 G): (A) experimental spectrum; (B) best computer match composite spectrum; (C) computed fine structure for **7** alone; (D) background doublet (amplitude magnified ∼40×).

et al.,[8] have claimed the generation of unsubstituted aminocyanocarbene by photolysis of aminodiazoacetonitrile in a 2-methyltetrahydrofuran glass at −196°. They postulate a singlet ground state similar to the one described above.

Three recent calculations compare the stabilities of aminocyanocarbene and the tautomeric iminoacetonitrile (NH=CHCN). Serre and Schneider[9] suggest that aminocyanocarbene should be the more stable isomer, but recently Loew and Chang[4] and later yet Jameson and Yang[10] have reached the opposite conclusion. Respectively, these authors arrive at energy differences of 76 and 56 kcal in favor of the iminoacetonitrile. The greater stability of the iminoacetonitrile tautomer is supported by recent work of Ferris, *et al.*,[11] who find alkyliminoacetonitriles to be relatively stable compounds which show no evidence of carbene character. On the other hand, iminoacetonitriles have recently been reported to dimerize upon heating to give the diaminomaleonitriles **15**.[12a] This suggests that the aminocyanocarbene may be present in a small equilibrium concentration and that dimer formation may result from attack of the carbene **14** (shown in the ylide form **14a**) on the iminoacetonitrile,[13] *i.e.*

$$\underset{13}{\underset{14a}{\begin{array}{c}H \\ RN \\ HC \\ NC \end{array}}} \rightarrow \left[\begin{array}{c}H \\ RN \quad NR \\ HCC \\ NC \quad CN \end{array}\right] \xrightarrow{\Omega} \underset{15}{\begin{array}{c}R \quad H \quad H \quad R \\ N \quad N \\ C=C \\ NC \quad CN\end{array}}$$

(4) G. H. Loew and S. Chang, *Tetrahedron*, **27**, 2989 (1971); G. H. Loew, *J. Theor. Biol.*, **33**, 121 (1971).

(5) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4009 (1965), especially footnote 12.

(6) (a) H. Quast and S. Hünig, *Chem. Ber.*, **99**, 2017 (1966); D. M. Lemal, R. A. Lovald, and K. J. Kawano, *J. Amer. Chem. Soc.*, **86**, 2518 (1964); (b) H. W. Wanzlick and F. Esser, *Angew. Chem.*, **76**, 614 (1964); **74**, 129 (1962); H. W. Wanzlick and H. Arens, *Chem. Ber.*, **97**, 2447 (1964).

(7) (a) W. Wilberg, *Angew. Chem.*, **80**, 809 (1968); (b) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, p 168ff.

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

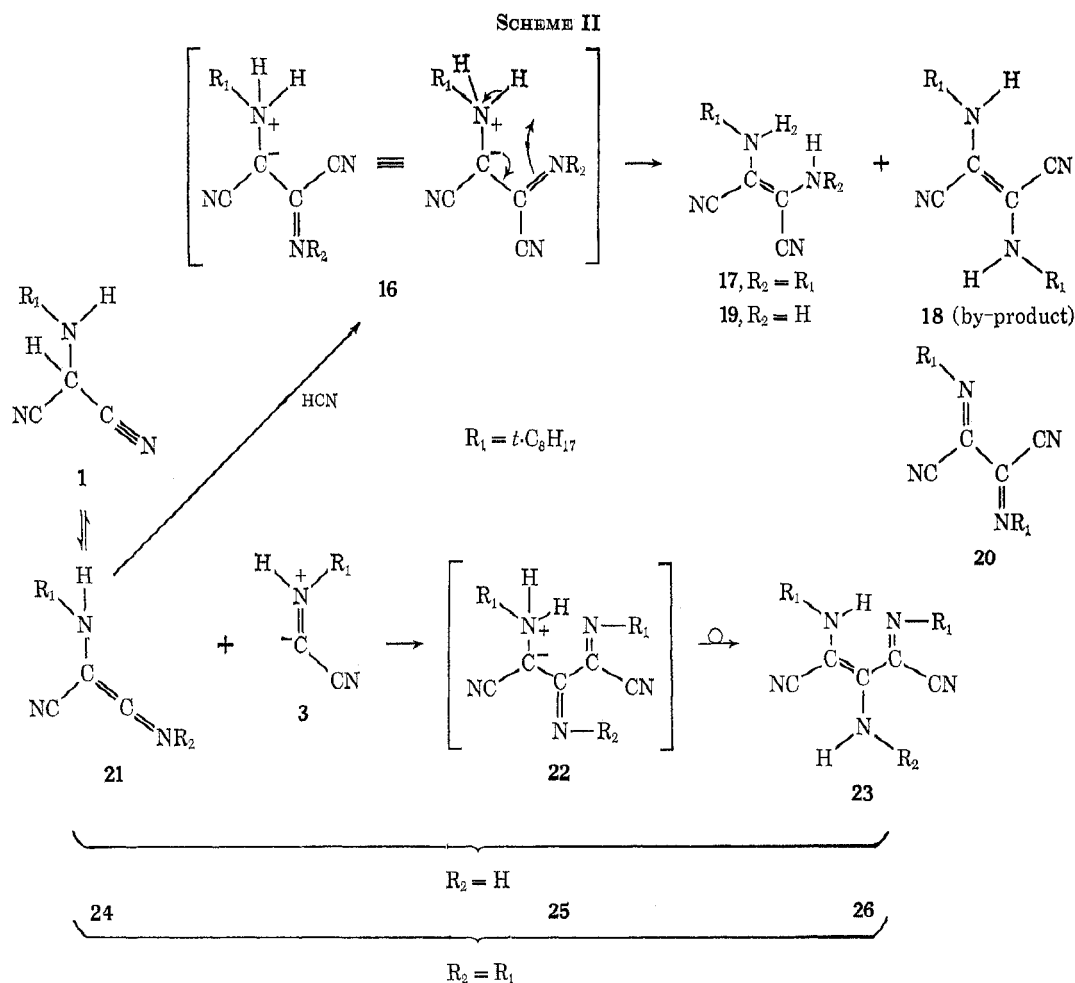(9) J. Serre and F. Schneider, *J. Chim. Phys.*, **60**, 1655 (1964).

(10) C. J. Jameson and W. Yang, *J. Theor. Biol.*, **35**, 247 (1972).

(11) J. P. Ferris, D. B. Donner, and W. Lotz, *J. Amer. Chem. Soc.*, **94**, 6968 (1972).

(12) (a) H. Dabek, R. Selvarajan, and J. H. Boyer, *Chem. Commun.*, 244 (1972); (b) J. H. Boyer and H. Dabek, *ibid.*, 1204 (1970).

(13) Direct dimerization of the aminocyanocarbene **14** is unlikely, since the carbene carbon is expected to carry a partial negative charge owing to a major contribution of the ylide structure **14a** to the resonance hybrid representing **14**. Therefore, Coulombic repulsion in the transition state is likely to result in a prohibitively high energy barrier to dimerization, although such a process is expected to be highly exothermic. Additionally, dimerization is unlikely because the concentration of **14** is probably very low. Balli[14] finds accordingly that nucleophilic carbenes alone do not produce dimers.

(14) H. Balli, *Angew. Chem., Int. Ed. Engl.*, **3**, 809 (1964).

SCHEME II

$R_1 = t\text{-}C_8H_{17}$

17, $R_2 = R_1$
19, $R_2 = H$

18 (by-product)

$R_2 = H$

24   25   26

$R_2 = R_1$

Evidence for α Elimination in Triethylamine Solution.—The hydrogen cyanide generated in the decomposition of 1 in triethylamine solution was identified by the glpc coinjection technique. Its formation was confirmed by the isolation of a crystalline product, shown by elemental analysis and spectral properties to be 1-*tert*-octylamino-2-aminomaleonitrile (**19**), the addition product of 1 and hydrogen cyanide[15] (Scheme II).

The generation of hydrogen cyanide is only then indicative of formation of the aminocyanocarbene **3** when α elimination can be demonstrated. Direct proof is complicated in the case of 1 because β elimination and a number of bimolecular mechanisms are alternative possibilities (Scheme III). Instead, indirect evidence pointing to α elimination and formation of the carbene comes from the investigation of three related compounds.

The first is dimethylaminomalononitrile[16] (**4**, Scheme I), which in triethylamine solution also generates hydrogen cyanide, though at a lower rate than 1. This was demonstrated by glpc, by high resolution mass spectroscopy, and also chemically. When **4** was treated with triethylamine in the presence of the amino-

cyanoketenimine **24**, the only identified product was bis-*tert*-octylaminomaleonitrile (**17**), which is the known[1] product of addition of hydrogen cyanide to **24**. (See Scheme II.)
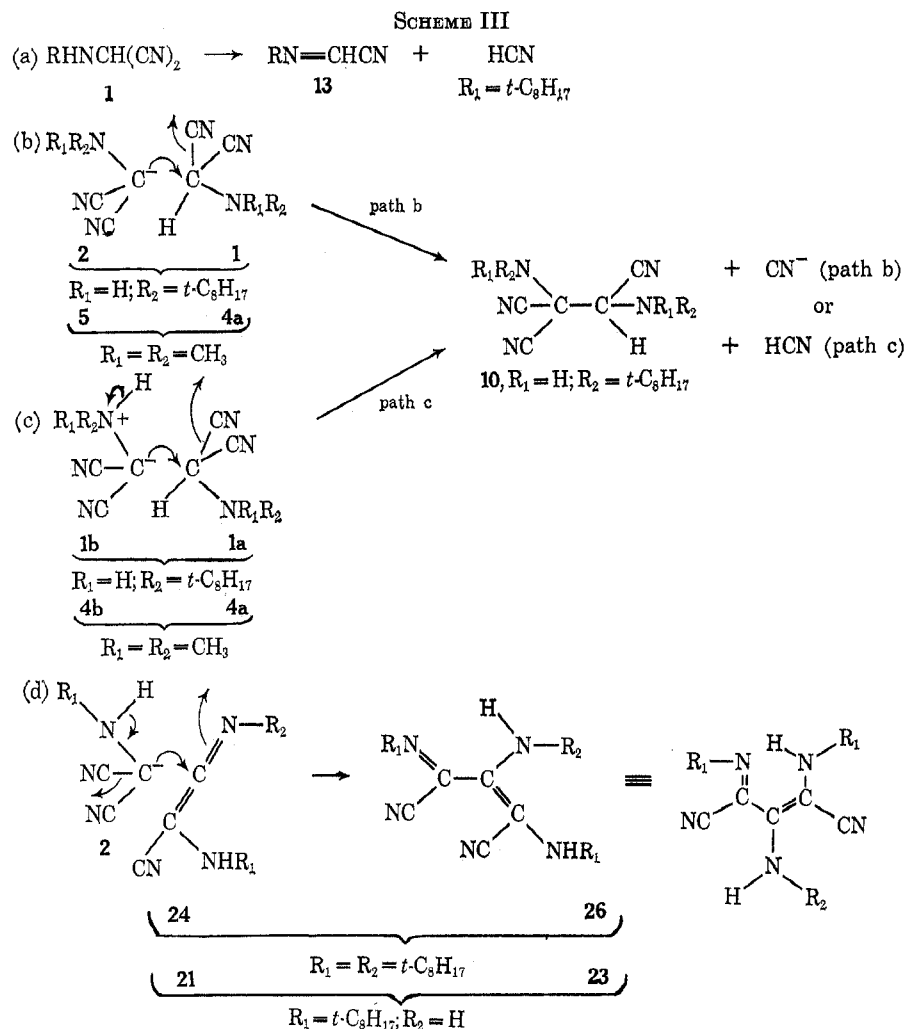
In the case of **4**, two reactions are ruled out which are alternatives to α elimination in the case of 1. These are β elimination of hydrogen cyanide and concerted elimination of cyanide ion owing to attack of the aminomalononitrile anion on the ketenimine tautomer (reactions a and d, Scheme III).

There appear to remain only two alternatives to α elimination. Both of these are bimolecular mechanisms.

(1) Nucleophilic displacement of cyanide ion from **4** by the aminomalononitrile anion **5** could occur (reaction b, Scheme III). This mechanism appears unlikely because the nucleophile, the substrate, and the product are all sterically crowded; moreover, the nitrile group is a very poor leaving group. There appears to be no precedent for its nucleophilic displacement in an S$_N$2 reaction unless it is assisted by a complexing metal.[18]

(2) Attack on the aminomalononitrile **4** by its ylide tautomer **4b** (reaction c, Scheme III) could occur. Such a cyclic mechanism implies independence on the medium and fails to explain why **4** is stable in nonbasic

(15) The reaction of 1 with hydrogen cyanide is analogous to the reported additions of hydrogen cyanide to dimethylaminomalononitrile to give 1-dimethylamino-2-aminomaleonitrile[16] and to aminomalononitrile to give diaminomaleonitrile.[17] These reactions can be explained by assuming that the aminomalononitrile reacts in the tautomeric aminocyanoketenimine form **21** (Scheme II).

(16) Z. Arnold, *Collect. Czech. Chem. Commun.*, **26**, 1113 (1961); see also H. Gold and O. Bayer, *Chem. Ber.*, **94**, 2594 (1961).

(17) J. P. Ferris and L. E. Orgel, *J. Amer. Chem. Soc.*, **88**, 3829 (1966).

(18) Y. Yoshimura, Y. Ohgo, and T. Sato, *Bull. Chem. Soc. Jap.*, **38**, 1809 (1965); M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice-Hall, Englewood Cliffs, N. J., 1954, Chapter 10.

SCHEME III

(a) $RHNCH(CN)_2 \longrightarrow RN=CHCN + HCN$

　　1　　　　　　　　**13**

　　　　　　　　　　　　$R_1 = t\text{-}C_8H_{17}$

(b) ...

path b

path c

$R_1R_2N\text{-}C\text{-}C\text{-}NR_1R_2 + CN^-$ (path b)

or

10, $R_1 = H$; $R_2 = t\text{-}C_8H_{17}$　　$+ HCN$ (path c)

(c) ...

$R_1 = H; R_2 = t\text{-}C_8H_{17}$

1b　　**1a**

$R_1 = H; R_2 = t\text{-}C_8H_{17}$

4b　　**4a**

$R_1 = R_2 = CH_3$

(d) ...

2

24　　　　　　　　　　　　**26**

21　　　　$R_1 = R_2 = t\text{-}C_8H_{17}$　　　　**23**

$R_1 = t\text{-}C_8H_{17}; R_2 = H$

solvents but decomposes in triethylamine or aqueous base (see below.)

Assuming that the two alternate mechanisms can thus be discounted, it appears that hydrogen cyanide evolution from **4** must occur by α elimination, resulting in the initial formation of the corresponding amino-cyanocarbene **6** (Scheme I).

The second model compound was *N-tert*-octylamino-*tert*-octylmalononitrile[19] (**37**). This compound was indefinitely stable in triethylamine, even at reflux. In

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(19) Compound **27** is the main product in the thermal rearrangement of *tert*-octylaminocyanoketen-*N-tert*-octylimine (**24**).

24　　　　　　**27**

$R = t\text{-}C_8H_{17}$
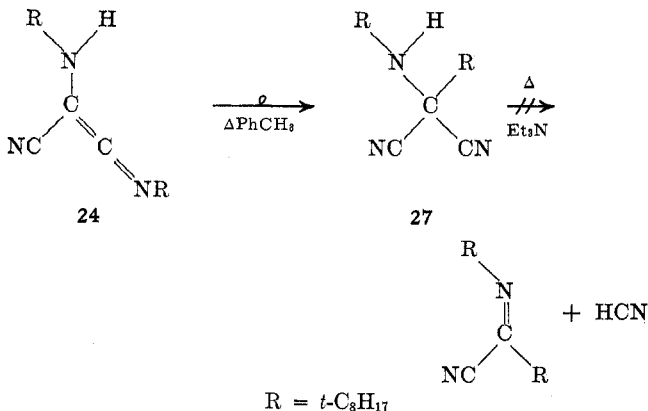
This thermolysis will be discussed in a separate article.

this case, α elimination of hydrogen cyanide is impossible, but β elimination does not appear to occur.

The third model compound was malononitrile. This compound is unstable in triethylamine solution; however, glpc showed that hydrogen cyanide is not produced.[20]

This thermolysis will be discussed in a separate article.

For all three compounds the initial proton-abstraction process is readily apparent: malononitrile is a known carbon acid, and nmr spectra show rapid deuterium exchange of the protons on both nitrogen and carbon for **1** and of the proton on carbon for **4** (see Experimental Section).
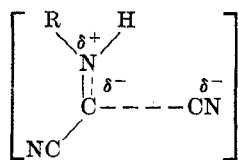
For the feasibility of the next step, the elimination of a cyanide ion from the resulting malononitrile anion, an amino substituent appears to be essential. Stabilization of the incipient aminocyanocarbene by an ylide form, as proposed above for **3**, allows the developing positive charge to be accommodated at the amino nitrogen while electron density increases at the neighboring "carbene" carbon. The resulting repulsion

(20) A small amount of hydrogen cyanide is generated when oxygen is not rigorously excluded. This is to be expected, since hydrogen cyanide forms when cyanoalkyl radicals react with oxygen.[21] The mechanism is probably analogous to that proposed by Russell[22] for the generation of nitrous acid in the autoxidation of 2-nitropropane.
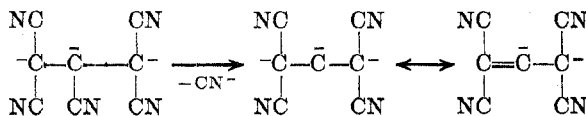
(21) M. Talât-Erben and N. Önol, *Can. J. Chem.*, **38**, 1154 (1960).

(22) G. A. Russell, *J. Amer. Chem. Soc.*, **76**, 1595 (1954).

could effectively promote departure of the cyanide ion, *i.e.*,

$$\left[\begin{array}{c} R \quad\quad H \\ {}^{\delta+}\!\!\diagdown N\diagup \\ \|\,{}^{\delta-} \quad\quad {}^{\delta-} \\ C\text{-----}CN \\ \diagup \\ NC \end{array}\right]$$

α elimination of a cyanide ion from an anion to give a carbene has been reported by Riegel, *et al.*,[23] *i.e.*,

$$\underset{NC\quad\ \ CN\quad CN}{\overset{NC\quad\ \ CN\quad CN}{-C-C-C-}} \xrightarrow{-CN^-} \underset{NC\quad\ \ CN\quad CN}{\overset{NC\quad\ \ CN\quad CN}{-C-C-C-}} \longleftrightarrow \underset{NC\quad\ \ CN}{\overset{NC\quad\ \ CN}{C=C-C-}}$$

In this case, stabilization is probably due to a decreased accumulation of negative charge and to resonance of the carbene form with two olefinic anion forms.

Formation of a carbene from an anion by α elimination of a group capable of stabilizing the negative charge has a well-established precedent: in the generation of difluorocarbene from difluoromethylphenyl sulfone,[24] α elimination of the benzenesulfinate ion occurs, *e.g.*,

$$PhSO_2CHF_2 + CH_3O^- \longrightarrow PhSO_2\bar{C}F_2 \xrightarrow{-PhSO_2^-} :CF_2$$
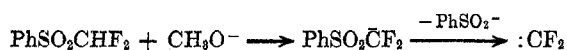
Difluoromethylene resembles **3** in two respects: it has a singlet ground state and it is unusually stable,[25] owing in part to contribution of such forms as $^+F{=}\bar{C}F$.

In summary, the evidence points to the conclusion that in triethylamine solution aminomalononitriles generate hydrogen cyanide by α but not by β elimination. The implied formation of the aminocyanocarbene **3** is consistent with the earlier, independent evidence for such an intermediate based on the observed generation of the radical **7** (see above).

Products.—Further evidence pointing to the formation of **3** and the radicals **7** and **8** comes from identification of a number of additional products in the decomposition of **1** in triethylamine. Three of these can be explained as combination or disproportionation products of the radicals **7** and **8** (reactions c, d, and e in Scheme I). Many such combination and disproportionation reactions of cyanoalkyl radicals have been reported.[26]

Disproportionation of the radical **8** according to reaction c may account for the formation of *tert*-octyliminomalononitrile (**9**), which is a decomposition product when **1** is treated with triethylamine. This
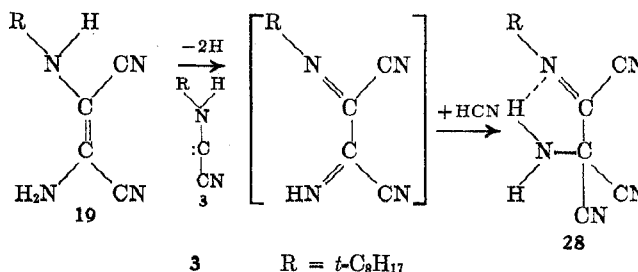
was demonstrated by glpc using authentic **9**[27] and also by coupled gas chromatography–mass spectroscopy.

A small amount of the diaminotricyanoethane (**10**) was isolated. The formation of **10** can be explained by combination of the radicals **7** and **8** (reaction d). This is equivalent to insertion of the carbene **3** in the C–H bond of the aminomalononitrile **1**.

It is, however, also possible that the radicals **7** and **8** are not involved in the formation of **10**. The carbene **3** may initially rearrange to the more stable *tert*-octyliminoacetonitrile (**13**, R = *t*-C$_8$H$_{17}$), to which **1** may add to give **10**.[29]
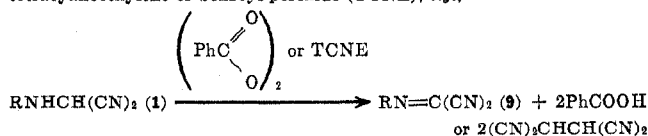
Mass spectra of the crude reaction product of **1** and triethylamine provide strong evidence for the presence of the diaminosuccinonitrile **11**,[30] which is the dimerization product of radical **7** (reaction e, Scheme I).

One additional product was isolated and identified as 1-*tert*-octylimino-2-*tert*-octylamino-1,2,2-tricyanoethane (**28**). It is assumed that the aminocyanocarbene **3** is responsible for the hydrogen abstraction which is implied in this structure. The following mechanism is tentatively suggested.

$$\underset{19}{\overset{R\ \ H}{\underset{H_2N\quad CN}{\diagup N\diagdown}}}\ \xrightarrow[R\ H]{-2H}\ \left[\ \ \right]\ \xrightarrow{+HCN}\ \underset{28}{\overset{R}{\ }}$$

3　　R = *t*-C$_8$H$_{17}$

It is significant that no evidence was found for either 1,2-di-*tert*-octylaminotetracyanoethane or *tert*-octylglycinonitrile (RNHCH$_2$CN).[32] The absence of the former compound may indicate that the radical **8** does not dimerize. This could reflect an important

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(23) P. H. Riegel, I. Bernal, W. H. Reinsmith, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963).

(24) J. H. Hine and J. J. Porter, *J. Amer. Chem. Soc.*, **82**, 6178 (1960).

(25) J. P. Simons, *J. Chem. Soc.*, 5406 (1965); *Nature (London)*, **192**, 943 (1961); J. H. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964, pp 40, 41, and 45.

(26) C. G. Overberger and A. Lebovits, *J. Amer. Chem. Soc.*, **76**, 2722 (1954); A. F. Bichel and W. A. Waters, *Recl. Trav. Chim. Pays-Bas*, **69**, 1490 (1950); G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, **77**, 3244 (1955); C. G. Overberger and M. B. Berenbaum, *ibid.*, **73**, 4883 (1951); **74**, 3293 (1952).

(27) Compound **9** is prepared in high yield by dehydrogenation of **1** with tetracyanoethylene or benzoyl peroxide (TCNE), *e.g.*,

$$RNHCH(CN)_2\ (1)\ \xrightarrow{\left(PhC\overset{O}{\underset{O}{\diagup\!\!\diagdown}}\right)_2\ or\ TCNE}\ RN{=}C(CN)_2\ (9)\ +\ 2PhCOOH$$
$$or\ 2(CN)_2CHCH(CN)_2$$

The analogous dehydrogenation of the diaminomaleonitrile **17** (Scheme II) by benzoyl peroxide was described in an earlier article.[1] The use of tetracyanoethylene in dehydrogenation has been reported.[48]

(28) D. T. Logone and G. L. Smith, *Tetrahedron Lett.*, 205 (1962).

(29) Authentic **10** was isolated as a product in the thermolyses of **1** and of the aminocyanoketenimine **26** (to be published). Boyer and Dabek[12b] and very recently Ferris, *et al.*,[11] have reported that reaction of *tert*-butyliminoacetonitrile (**13**, R = *t*-C$_4$H$_9$) with hydrogen cyanide gives 1,2-di-*tert*-butylamino-1,2,2-tricyanoethane, the *tert*-butyl analog of **10**. Ferris proposed that **13** adds hydrogen cyanide to give *tert*-butylaminomalononitrile, which adds to **13** to give the diaminotricyanoethane. The present author has observed the analogous addition of hydrogen cyanide to *tert*-octyliminoacetonitrile (**13**, R = *t*-C$_8$H$_{17}$) in an aprotic medium containing methanesulfonic acid. Under these conditions, the salt of *tert*-octylaminomalononitrile (**1**) precipitates. This reaction has been developed into a novel highyield synthesis of **1** (see Experimental Section).

(30) In an attempt to obtain unambiguous proof for the presence of **11**, its preparation was tried by various reduction methods, *i.e.*, catalytic hydrogenation of the diaminomaleonitrile **17** and of di-*tert*-octyliminosuccinonitrile[1] (**20**, Scheme II), as well as reduction of **20** with lithium aluminum hydride, sodium borohydride, or dimethylaminoborane, which is a specific reagent for the reduction of imines.[31] In each case, only **17** was formed, which could not be reduced further by any method tried.

(31) J. H. Billman and J. W. McDowell, *J. Org. Chem.*, **26**, 1437 (1961).

(32) An authentic sample of *tert*-octylglycinonitrile was prepared according to the method of Luskin, *et al.*[33]

(33) L. S. Luskin, M. L. Gulver, G. E. Gantert, W. E. Craig, and R. S. Cook, *J. Amer. Chem. Soc.*, **78**, 4042 (1956).

contribution of the charge-separated structure 8b (Scheme I). High charge density at the central carbon atom would give rise to Coulombic repulsion and consequently a high activation energy in dimerization. The absence of *tert*-octylglycinonitrile indicates that hydrogen abstraction by the glycinonitrile radical 7 does not occur. This is consistent with its high stability and with the relatively low nucleophilicity expected for this radical.

The evidence suggests that the aminocyanocarbene 3 is not a direct precursor for any of the products of the decomposition of 1 in triethylamine that have been described thus far. Rather, it suggests that their immediate precursors are the radicals 7 and 8, whose formation is proposed to involve 3 as an intermediate (see above).

From the decomposition mixture, one additional compound was isolated which could be derived directly from the carbene 3. Elemental analysis and spectral data show this to be 1-*tert*-octylamino-2-amino-3-*tert*-octylimino-1,3-dicyanopropene-1 (23, Scheme II) which formally is the product of addition of 3 to 1 (as the tautomeric aminocyanoketenimine 21).

Possibly 21 traps the carbene 3 to give an ylide intermediate 22 which, after a prototropic rearrangement, gives the enaminoimine 23. Such a mechanism appears consistent with the general pattern proposed for the addition reactions of the analogous *tert*-octyl-aminocyanoketen-*N*-*tert*-octylimine (24), specifically, the addition of hydrogen cyanide.[1] In that reaction, protonation of the *tert*-octylamino group of 24 and attack of cyanide ion at the imino carbon atom is proposed to give an ylide intermediate 16. A prototropic rearrangement of 16 then gives di-*tert*-octyl-aminomaleonitrile as the final product (17, Scheme II).

Additional support for involvement of the amino-cyanoketenimine tautomer 21 in the formation of 23 comes from the observation that reaction of the authentic aminocyanoketenimine 24 with 1 in basic media (the conditions for the proposed generation of aminocyanocarbene 3) gives an enaminoimine 26 (see below) which is a homolog of 23.

A mixture of 1 and the aminocyanoketenimine 24 in mole ratio 1:2 was treated with either triethylamine or aqueous potassium hydroxide at room temperature. Under both sets of conditions, an orange-red reaction product was obtained, mainly consisting of approximately equimolar amounts of two major components. These were separable through their different solubilities in hexane. The less soluble compound was colorless and was proved to be di-*tert*-octylamino-maleonitrile (17). The more soluble product 26 was orange-red. Elemental analysis and spectral data indicate that this compound is 1,2-di-*tert*-octylamino-3-*tert*-octylimino-1,3-dicyanopropene-1.[34] This is formally the product of addition of 3 to aminocyano-

ketenimine 24. It is proposed that the mechanism is analogous to that postulated for the formation of 23 from 1 in the absence of 24.

There is no direct evidence to exclude alternative routes for the formation of the enaminoimines 23 and 26. One such mechanism involving addition of the aminomalononitrile anion 2 and concerted elimination of cyanide ion is shown in Scheme III (reaction d). However, these alternatives fail to account for the formation of the radicals 7 and 8 and the decomposition products which evidently are derived from them. Economy of mechanism, therefore, favors the aminocyanocarbene route.

The aminoiminopropene 26 was also obtained directly from the reaction of 2,4,4-trimethylpentene-2 with hydrogen cyanide and hydrogen fluoride when the crude product was treated with triethylamine or with concentrated potassium hydroxide for a prolonged period of time. Under these conditions, the aminocyanoketenimine 24, which is the main reaction product, slowly decomposes. This is evident from the disappearance of the characteristic ketenimine band at 2025 cm^{-1}. The initial products apparently are 2,4,4-trimethylpentene-1 (demonstrated by glpc) and *tert*-octylaminomalononitrile (1). Formation of 26 can then occur as outlined above. The hydrogen cyanide which is the second product in the decomposition of 1 adds to 24 to give the diaminomaleonitrile 17 accompanied by a small amount of the tautomeric diaminofumaronitrile 18[35] (Scheme II). According to glpc, both compounds are absent in the product of decomposition of 1 in triethylamine. This suggests that dimerization of the aminocyanocarbene 3 to give 17 or 18 does not occur.

The above interpretation is supported by the isolation of the enaminoimine 26 as a minor product in the decomposition of pure 24 in refluxing triethylamine. The main product was 17, and the formation of 2,4,4-trimethylpentene-1 was demonstrated by glpc.

Evidence for α Elimination in Aqueous Base.—In the decomposition reactions of aminomalononitriles which have been discussed so far, triethylamine was the medium. Aminocyanocarbenes may also be formed in aqueous base. The aminomalononitriles 1 and 4 dissolve in aqueous potassium hydroxide to give initially colorless solutions. In these solutions the aminomalononitriles must occur as the corresponding anions 2 or 5[38] since immediate neutralization followed by solvent extraction allows their recovery in high yields.

A solution of 4 in aqueous potassium hydroxide

(34) The nmr spectrum of 26 shows the presence of two magnetically equivalent *tert*-octyl groups. This suggests that 26 occurs in a single configuration in which the terminal amino and imino groups are bridged by an intramolecular hydrogen bond through which very fast proton exchange occurs. The nmr spectrum of 23 is consistent with an equilibrium mixture of two conformational isomers A and B in approximately equimolar proportions. The two *tert*-octyl groups are equivalent in A and nonequivalent in B. The equivalence in A is ascribed to the occurrence of very fast proton exchange as postulated for 26. The nonequivalence in B implies the absence of such exchange. The structures of 26 and 23 are the subject of a forthcoming article.

(35) Compound 18 is apparently in thermodynamic equilibrium with the diaminomaleonitrile 17. Small amounts of 18 are formed when 17 is treated with bases (KOH or Et₃N) for a prolonged period and also when 17 is prepared by catalytic hydrogenation of di-*tert*-octyliminosuccinonitrile[1] (20, Scheme II) or by addition of hydrogen cyanide to the aminocyanoketenimine 24 (Scheme II). The diaminofumaronitrile structure of 18 is proven by its acid-catalyzed conversion to 17 at room temperature (see Experimental Section). This is similar to the acid-catalyzed cis–trans isomerization of enamino esters[36] and of unsubstituted diaminofumaronitrile.[37] The structure of 18 is confirmed by elemental analysis and spectral data. The ir activity of the C=C stretching band at 1575 cm^{-1} seems unexpected for a symmetrical structure, but the analogous band was also observed for unsubstituted diaminofumaronitrile.[37]
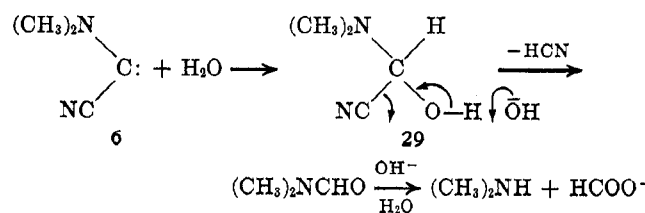
(36) K. Herbig, R. Huisgen, and H. Huber, *Chem. Ber.*, 99, 2546 (1966).
(37) Y. Yamada, N. Nagashima, Y. Iwashita, A. Nakamura, and T. Kumashiro, *Tetrahedron Lett.*, 43, 4529 (1968).
(38) Ferris and Orgel[39] showed similarly that bromomalononitrile dissolves in aqueous potassium hydroxide as the anion.
(39) J. P. Ferris and L. E. Orgel, *J. Org. Chem.*, 30, 2365 (1965).

evolves dimethylamine essentially at once as shown by its characteristic odor, by glpc, and by mass spectra. A possible explanation is that the dimethylamine originates from hydrolysis of the carbene **6**. Pre-

$$(CH_3)_2N \diagdown C: + H_2O \longrightarrow (CH_3)_2N \diagdown C \diagup H \xrightarrow{-HCN}$$
$$NC \diagup \qquad\qquad NC \diagup O-H \diagdown OH$$
$$\mathbf{6} \qquad\qquad \mathbf{29}$$

$$(CH_3)_2NCHO \xrightarrow[H_2O]{OH^-} (CH_3)_2NH + HCOO^-$$

cedents for such a reaction are the reported methanolyses of the related resonance-stabilized carbenes, cyanophenylcarbene[40] and diphenylcarbene,[41] to give the corresponding ethers.

Analogously, dimethylaminocyanocarbinol (**29**) is expected to be the initial hydrolysis product of dimethylaminocyanocarbene. In the basic medium **29** can eliminate hydrogen cyanide to give dimethylformamide, whose further hydrolysis gives dimethylamine.

Conceivably, ionization of **4** to give the cyanoimmonium cyanide $[(CH_3)_2N=CHCN]^+(CN)^-$, followed by hydrolysis, could account for the formation of **29** and finally dimethylamine. This mechanism does not involve the aminocyanocarbene **6**. It is, however, unlikely for the following reasons. Firstly, ionization of **4** and subsequent hydrolysis should proceed about as well in neutral as in basic aqueous solution, but **4** is found to be insoluble in neutral water and to be stable in its presence.

Furthermore, ionization of cyanide ion in aminomalononitriles is inductively opposed by the second nitrile group and should be far slower than in diaminoacetonitriles, where a highly stabilized amidinium counterion can be formed. Aminoacetonitriles are expected to be intermediate in this respect. Of these three classes of compounds only the diaminoacetonitriles show some evidence of ionization. Dipiperidinoacetonitrile[42] is a distillable compound which partially ionizes in the highly polar solvent phenol but is un-ionized in aprotic solvents.

Aminoacetonitriles split off a nitrile group only when treated with a Grignard reagent which aids the elimination through complexation.[18] In aqueous base the nitrile group hydrolyzes instead,[43a] demonstrating the lack of ionization even in this highly ionizing medium. *tert*-Octylglycinonitrile gives *tert*-octylglycine in high yield.[43b]

The hydrolysis of **1** is markedly analogous to the above-described hydrolysis of **4**. From an initially homogeneous solution of **1** in aqueous potassium hydroxide, a second phase separates upon standing. The major part of this phase is pentane soluble and is identified by ir and glpc as *tert*-octylamine of higher than 80% purity. The major component of the pentane-insoluble part is the diaminomaleonitrile **19**

(Scheme II), which was identified by glpc. Since **19** results from the addition of hydrogen cyanide to **1**, this is proof of the generation of hydrogen cyanide.

In the hydrolysis of **1** in strong aqueous base, initial loss of hydrogen cyanide could, conceivably, occur by β elimination. Further hydrolysis of the resulting *tert*-octyliminonitrile (**13**, R = *t*-C$_8$H$_{17}$) could account for the observed formation of *tert*-octylamine. There is no specific evidence to disprove this route, which does not require the aminocyanocarbene **3** as an intermediate. However, the analogy with the case of **4**, where similar alternatives do not exist, suggests that the carbene mechanism is operative in the case of **1** as well.

Evidence is available that the radicals **7** and **8** and probably the aminocyanocarbene **3** are also intermediates in the thermolyses of the aminocyanoketenimine **24** and of the aminomalononitrile **1**.

Additionally, it has been found that a modification of the published[16] reaction conditions for the formation of dimethylaminomalononitrile yields a bisdimethylaminodicyanoethylene as the main product. Dimethylaminocyanocarbene is a possible intermediate. These reactions will be discussed in forthcoming publications.

Experimental Section

Equipment and Technique.—The following instruments were used: a Perkin-Elmer 621 double-beam grating ir spectrometer, a Laser-Raman Carey 81 spectrometer, and a Varian HA-100 nmr spectrometer.

In analyzing the composition of mixtures, frequent use is made of the glpc coinjection technique. This technique identifies a mixture component through the increased intensity of a specific peak when a new mixture containing an added authentic compound is injected. In all glpc work the support was 5% silicone SE-30 (General Electric Co.) on Chromosorb W (Johns-Manville). In each case injection was followed by a 4-min period at 40°. After this the temperature was raised to 250° using a 15°/min program.

Materials.—*tert*-Octylaminocyanoketen-*N*-*tert*-octylimine (**24**) was prepared as described previously.[1]

Using a novel method, *N*-*tert*-octylaminomalononitrile (**1**) was prepared in high overall yield from *N*-*tert*-octylglycinonitrile via *N*-*tert*-octyliminoacetonitrile (**13**, R = *t*-C$_8$H$_{17}$).

N-*tert*-Octylglycinonitrile was prepared in high yield from *tert*-octylamine and glycolonitrile (available from J. T. Baker) according to Luskin, *et al.*[38]

tert-Butyl hypochlorite, used in the preparation of **13**, is available from K & K Laboratories, Inc.

N-*tert*-Octyliminoacetonitrile (**13**) from *N*-*tert*-Octylglycinonitrile[44]—A 13.6-g (0.162 mol) quantity of finely ground sodium bicarbonate was suspended in a solution of 131 g (0.778 mol) of *N*-*tert*-octylglycinonitrile in 1400 ml of ether. The stirred solution was cooled to 10° in an ice bath, and under exclusion of light 106.4 g (0.98 mol) of *tert*-butyl hypochlorite was added over a 25 min period. Stirring at 10° was continued for 1 hr. The inorganic salts were removed by filtration. Under continued exclusion of light 200 g (1.97 mol) of triethylamine was added. Precipitation of triethylammonium chloride started at once. After 19 hr at room temperature, the solids were removed by filtration and triturated with 300 ml of ether. The extracts were combined with the filtrate, and the ether was removed *in vacuo*. Distillation of the residue gave 103.4 g (0.621 mol, 80%) of *tert*-octyliminoacetonitrile (**13**), bp 61–63° (0.2 mm), n^{20}D 1.4519.

Anal. Calcd for C$_{10}$H$_{18}$N$_2$: C, 72.22; H, 10.93; N, 16.85. Found: C, 72.13; H, 10.90; N, 16.78.

Ir (CCl$_4$) 2220 (w, C≡N), 1618 cm^{-1} (m, C=N).

Methanesulfonic Acid Salt of *tert*-Octylaminomalononitrile

(40) P. C. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Amer. Chem. Soc.*, **89**, 1967 (1967).

(41) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **666**, 9 (1963).

(42) M. Seefelder, *Chem. Ber.*, **99**, 2678 (1966).

(43) (a) H. Zahn and H. Wilhelm, *Justus Liebigs Abn. Chem.*, **579**, 1 (1953); (b) J. S. Strong, U. S. Patent 2,787,640 (April 2, 1957); *Chem. Abstr.*, **51**, 13909a (1957).

(44) This is an adaptation of the method of Boyer and Dabek;[12b] see also Ferris, Donner, and Lodge.[11]

(1 CH₃SO₃H) from 13, HCN, and CH₃SO₃H.—The above product (103.4 g) was dissolved in 1000 ml of ether. The solution was stirred and cooled to 0° in an ice bath, and 70 g (2.59 mol) of hydrogen cyanide was introduced by distillation using an ice-cooled condenser. After completion of the addition, 63 g (0.652 mol) of methanesulfonic acid was added from an addition funnel over a 5-min period. A precipitate started to form at once. Stirring at 0° was continued for 45 min. The solution was allowed to warm to room temperature, and the precipitate was collected by filtration. (Caution: excess HCN present.)

After washing with 200 ml of ether, the product was dried *in vacuo* at room temperature for 30 min and then stored in the refrigerator, yield 136.6 g (76%) of colorless 1 CH₃SO₃H.

The combined filtrate and washings were concentrated *in vacuo* at room temperature and allowed to stand for 17 hr. Filtration yielded an orange-colored precipitate which was largely decolorized upon trituration with 60 ml of acetonitrile. The washed precipitate was dried *in vacuo* at room temperature to give an additional 27.8 g of slightly impure (faintly orange colored) 1 CH₃SO₃H.

tert-Octylaminomalononitrile (1) from the Methanesulfonic Acid Salt.—Treatment of 1 CH₃SO₃H with potassium bicarbonate solution as described in ref 1 gave 1, mp 35.0–35.5°, which was spectrally identical with 1 prepared according to that reference. Statisfactory elemental analyses were obtained for both 1 and its methanesulfonic acid salt.

The *tert*-Octylglycinonitrile Radical (7) from Decomposition of *tert*-Octylmalononitrile (1) in Triethylamine.—To a vacuum line system were attached an esr tube containing 0.1 g of 1 (freshly recrystallized from pentane) and a tube containing 2 ml of triply distilled triethylamine. The triethylamine was frozen in liquid nitrogen, the system was evacuated, and the triethylamine was degassed by repeated (three) freezing–pumping cycles. The epr tube was then cooled to −76° and the triethylamine was transferred into it by distillation. The cold epr tube was closed and detached from the vacuum system. When it reached room temperature, it was inserted into the esr spectrometer. As soon as 1 dissolved in the triethylamine, the solution became reddish orange and the spectrum of 7 emerged.

Products from Decomposition of *tert*-Octylaminomalononitrile (1) in Triethylamine.—Under strict exclusion of oxygen, 12.2 g of 1 (twice recrystallized from pentane) was dissolved in 50 ml of freshly distilled triethylamine. The solution was stirred at room temperature for 3 hr in a nitrogen atmosphere. The triethylamine and the volatile products were removed by distillation *in vacuo* (distillate A). The residue was extracted with 250 ml of refluxing pentane to give an insoluble precipitate (B) and a pentane extract (C).

Isolation of 1-*tert*-Octylimino-2-amino-1,2,2-tricyanoethane (28).—The pentane insoluble fraction B (see above) was dissolved in 250 ml of refluxing ether. After treatment with 5 g of Norit the filtered ether solution was concentrated to a 25 ml volume. Crystallization started and was completed in the refrigerator. After one additional crystallization from ether, 0.35 g of 28 was obtained, mp 138.5–139.5°.

Anal. Calcd for C₁₃H₁₉N₅: C, 63.63; H, 7.82; N, 28.56. Found: C, 63.86; H, 7.96; N, 28.67. Mass spectrum (70 eV) *m/e* parent 245; ir (CHCl₃) 3472 (m), 3380 (ms), 3325 (m), 3220 (m), 3170 (sh) (all NH stretch, bonded and free), 2270 (sh, vw), 2220 (vs) (C≡N); 1625 (s, C≡N), 1552 cm⁻¹ (ms, NH₂ def); nmr (CDCl₃) δ 0.88 [9 H, C(CH₃)₃], 1.90 [6 H, C(CH₃)₂], 2.01 (2 H, CH₂), 3.77 ppm (2 H, NH₂).

Isolation of 1-*tert*-Octylamino-2-aminomaleonitrile (19).—The ether mother liquors of 28 were freed of solvent *in vacuo*. The residue was dissolved in 25 ml of benzene. The solution was treated with Norit, filtered, concentrated to a 3-ml volume *in vacuo*, and finally diluted with 3 ml of hexane.

After 3 hr at −10°, the crystalline precipitate was collected by filtration and recrystallized from benzene–hexane, yield 0.076 g of 19, identified by mixture melting point determination and by identity of ir spectra, using an authentic sample of 19 (see below).

Isolation of 1-*tert*-Octylamino-2-amino-3-*tert*-octylimino-1,3-dicyanopropene-1 (23).—The pentane extract C, obtained from decomposition of 1 in triethylamine, was treated with Norit, filtered, and then concentrated to a 50-ml volume. After 12 hr at −10°, a crystalline precipitate was obtained. One recrystallization from hot hexane gave after 3 hr at −10° 4.07 g of 23 as yellow needles, mp 79.0–79.5°.

Anal. Calcd for C₂₁H₃₇N₅: C, 70.12; H, 10.40; N, 19.48. Found: C, 70.43; H, 10.61; N, 19.44.

Mass spectrum (70 eV) *m/e* parent 359; uv max (isooctane) 400.0, 234.0 nm (log ε 3.747, 3.922); ir (KBr pellet) 3466 (m), 3438 (s), 3292 (m), (NH), 2182 (sh), 2175 (s, C≡N), 1598 (vs), 1537 cm⁻¹ (s), (C=CC=N); ir (CCl₄) 3476 (m), 3360 (m) (NH), 2212 (m), 2192 (m), 2183 (sh) (C≡N), 1598 (sh), 1580 (s), 1522 cm⁻¹ (s) (C=CC=N); Raman (cryst) 2221 (mw), 2176 (s) (C≡N), 1592 (vs), 1537 cm⁻¹ (s) (C=CC=N); nmr (CCl₄) δ 1.017 [2 C(CH₃)₃, A + C(CH₃)₃ B],[45] 1.100 [C(CH₃)₃ B], total 18 H, 1.386 [C(CH₃)₂ B], 1.474 [2 C(CH₃)₂ A], 1.586 [(C(CH₃)₂ B], total 12 H, 1.693 (CH₂ B), 1.860 (2 CH₂ A), 1.920 (CH₂ B), total 4 H, 3.636, 4.800, 7.650 ppm (NH₂ A + B and NH A + B), total 3 H.

Isolation of 1,2-Di-*tert*-octylamino-1,2,2-tricyanoethane (10).—The pentane and hexane mother liquors of 23 were combined and concentrated to a 30-ml volume *in vacuo*. The solution was cooled to −10° and crystallization was initiated by seeding with authentic 10.[29] After 12 hr at −10°, the precipitate was collected by filtration. Recrystallization from hexane yielded 0.224 g of 10 identified by ir spectrum and mixture melting point determination, using a sample of authentic 10.[29]

Identification of *tert*-Octyliminomalononitrile (9).—The mother liquors of 10 were chromatographed through a silica column. In the oily residue, recovered from the pentane–ether (95:5) eluate, 9 was identified as a major component by mass spectrum, ir spectrum, and the glpc coinjection technique using authentic 9 (see below).

Preparation of *tert*-Octylamino-*tert*-octylmalononitrile (27) by Thermal Rearrangement of *tert*-Octylaminocyanoketen-*N*-*tert*-octylimine (24).—An 11.4-g (0.037 mol) quantity of 24 was dissolved in 75 ml of toluene, and the solution was heated at reflux in a nitrogen atmosphere for 14 hr. The toluene and the volatile reaction products were collected by distillation *in vacuo*. The residue was diluted with 20 ml of pentane, chilled to −10°, and filtered to give 6.5 g of a crystalline product. With the exception of a small residue, this product could be redissolved in cold pentane. After three recrystallizations from this solvent at −10° (including a treatment with Norit), 4.1 g of pure 27 was recovered, mp 67.0–67.5°.

Anal. Calcd for C₁₉H₃₅N₃: C, 74.69; H, 11.54; N, 13.75. Found: C, 74.61; H, 11.63; N, 13.84.

Ir (CCl₄) 3405, 3360 (w) (NH), 2235 cm⁻¹ (vw) (C≡N);[46] nmr (CCl₄) δ 0.97, 1.01 [18 H, 2 C(CH₃)₃], 1.26, 1.41 [each 6 H, C(CH₃)₂], 1.46, 1.54 ppm (each 2 H, CH₂); mass spectrum (70 eV) *m/e* parent 305; mol wt 303 (Thermonam).

Stability of 27 in Triethylamine.—A solution of 0.5 g of 27 in 10 ml of triethylamine was heated at reflux under a nitrogen blanket for 12 hr. The slightly yellow solution was freed of triethylamine *in vacuo*. The crystalline residue was recrystallized from hot hexane. Cooling to −10° gave 0.461 g of unchanged 27, identified by ir spectrum and mixture melting point determination.

Glpc Analysis of the Reaction Product of 1 and Triethylamine.—Glpc analysis (coinjection technique) of the crude reaction product of 1 and triethylamine showed that hydrogen cyanide is developed copiously within the first minutes of the reaction. It also showed the presence of *tert*-octyliminomalononitrile (9) and the absence of di-*tert*-octylaminomaleonitrile (17),[1] di-*tert*-octylaminofumaronitrile (18), and N-*tert*-octylglycinonitrile.[33] The preparation of 17 was reported earlier,[1] and the preparation of 18 and 9 is described below.

Mass Spectral Analysis of the Reaction Product of 1 and Triethylamine. Evidence for the Formation of 1,2-Di-*tert*-octylaminosuccinonitrile (11).—An aliquot of the mother liquors from the crystallization of 23 was freed of solvent *in vacuo*. The mass spectrum of the residue showed the presence of a parent compound of mass 334. This is consistent with C₂₀H₃₈N₄ (11); attempts to synthesize 11 are described below.

Analysis of the crude reaction product of 1 and triethylamine by combined gas chromatography–mass spectrometry was consistent with the glpc results. It showed the presence of a fraction (mass 191) with a mass spectrum identical with that of *tert*-octyliminomalononitrile (9) (see below); compounds of higher mass were not observed owing to decomposition in the instrument.

1-*tert*-Octylamino-2-aminomaleonitrile (19).—A 0.7-g quantity of 1 was dissolved in 3 ml of benzene. A 5-ml quantity of a

(45) A and B refer to the two conformational isomers of **23**.

(46) Extremely weak C≡N bands are the rule in aminomalononitriles.[1]

concentrated aqueous solution of sodium cyanide was added, and the mixture was stirred under nitrogen at room temperature for 24 hr. The organic layer, in which a crystalline precipitate had formed, was diluted with 10 ml of pentane, separated from the aqueous layer, and filtered to give 0.4 g of crude **19**. After two recrystallizations from benzene, the melting point was 136–137°:

Anal. Calcd for $C_{12}H_{20}N_4$: C, 65.45; H, 9.09; N, 25.46. Found: C, 65.37; H, 9.34; N, 25.47.

Ir (CHCl₃) 3475 (w), 3350 (s), 3315 (sh) (all NH), 2210 (sh), 2180 (s) (C≡N), 1610 (s), 1590 cm⁻¹ sh (C=C); nmr (CDCl₃) δ 1.04 [9 H, C(CH₃)₃], 1.40 [6 H, C(CH₃)₂], 1.70 (2 H, CH₂), 3.26 (1 H, NH), 3.60 ppm (2 H, NH₂); mass spectrum (70 eV) *m/e* parent 220; mol wt, 221 (Thermonam).

Compound **19** was also formed from **1** and hydrogen cyanide in triethylamine solution. This was demonstrated by glpc.

Preparation of *tert*-Octyliminomalononitrile (9). A. From 1 and Tetracyanoethylene.—A 1.13-g (0.006 mol) quantity of **1** and 0.75 g (0.006 mol) of tetracyanoethylene were dissolved in 20 ml of tetrahydrofuran. The solution was left at room temperature overnight and then filtered. The solvent was evaporated from the filtrate *in vacuo*, and the residue was extracted with pentane. After Norit treatment, the pentane was removed *in vacuo*. This left 0.73 g (65%) of **9** as a colorless oil: bp (determined by differential thermal analysis) 237–238° (760 mm), 100° (7 mm); n^{20}D 1.4569.

Anal. Calcd for $C_{11}H_{17}N_3$: C, 69.02; H, 8.97; N, 22.00. Found: C, 68.93; H, 8.79; N, 21.88.

Ir (CCl₄) 2210 (m) (C≡N), 1595 cm⁻¹ (m) (C=N); nmr (CDCl₃) δ 1.01 [9 H, C(CH₃)₃], 1.54 [6 H, C(CH₃)₂], 1.66 ppm (2 H, CH₂); mass spectrum (70 eV) *m/e* 191 (parent, weak), 176 (parent − CH₃), 150 (176 − CN), 120 (parent − C₅H₁₁, strong).

B. From 1 and Benzoyl Peroxide.—A 1.0-g (0.005 mol) quantity of **1** and 1.21 g (0.005 mol) of benzoyl peroxide were dissolved in 15 ml of benzene. The solution was allowed to stand at room temperature for 24 hr. The benzene solvent was then removed *in vacuo*. The residue was extracted with pentane. The pentane-insoluble part was pure benzoic acid identified by ir spectrum and mixture melting point determination using an authentic sample. The pentane extract was washed with a concentrated solution of sodium bicarbonate to remove any dissolved benzoic acid. The washed pentane extract was treated with Norit, and the pentane solvent was removed *in vacuo* to leave a colorless oil (0.74 g, 77%), which was identified as essentially pure **9** by identity of ir spectrum and by glpc (coinjection technique).

Di-*tert*-octylaminofumaronitrile (18). A. From Di-*tert*-octylaminomaleonitrile (17) and Triethylamine.—A solution of 10 g of **17** in 50 ml of triethylamine was stirred magnetically and kept at reflux overnight. The triethylamine was removed *in vacuo*. The solid residue, consisting mainly of **17**, was extracted with 25 ml of pentane. The pentane extract was kept at −15° overnight and gave upon filtration a precipitate which consisted of pure **17** according to ir spectrum and mixture melting point determination. The pentane mother liquors were chromatographed through a silica column. From the pentane–1% ether eluate a crystalline residue was obtained which was recrystallized three times from pentane at −30°, yield *0.32 g of 18 as colorless* crystals, mp 55.5–56.5°.

Anal. Calcd for $C_{20}H_{36}N_4$: C, 72.24; H, 10.91; N, 16.85. Found: C, 72.28; H, 11.13; N, 16.98.

Uv max (isooctane or MeOH) 340 nm (log ε 4.05); ir (CCl₄) 3380 (m, NH), 2195 (m) with shoulders at 2160 and 2210 (C≡N), 1575 cm⁻¹ (m, C=C); nmr (CDCl₃) δ 1.05 [18 H, 2 C(CH₃)₃], 1.37 [12 H, 2 C(CH₃)₂], 3.50 ppm (2 H, 2 NH), disappears upon deuteration; mass spectrum (70 eV) *m/e* parent 332.

B. From *tert*-Octylaminocyanoketen-*N*-*tert*-octylimine[1] (24) and Hydrogen Cyanide.—A 10-g quantity of **24** was dissolved in 20 ml of triethylamine, and 3 g of hydrogen cyanide was introduced by distillation. After 2 hr, all volatiles were removed by sparging with nitrogen. The residue, consisting mainly of **17**, was extracted with 25 ml of pentane. From this pentane extract 0.43 g of **18** was obtained by the procedure described above for the preparation of **18** from **17** and triethylamine. Compound **18** was identified by ir spectrum and mixture melting point determination.

C. From Catalytic Hydrogenation of Di-*tert*-octyliminosuccinonitrile[1] (20).—A 2-g quantity of **20** in ethyl acetate solution was hydrogenated using 75 mg of a 5% palladium on carbon

catalyst. When 1 equiv of hydrogen had been absorbed, the hydrogen uptake virtually stopped. After removal of the catalyst by filtration and of the solvent by evaporation *in vacuo*, a crystalline residue remained which, according to the ir spectrum, consisted mainly of **17**. This residue was extracted with 25 ml of pentane. The pentane extract was treated by the procedure described above to give 0.075 g of **18**, identified by ir spectrum and mixture melting point determination.

Rearrangement of 18 to Give 17.—A 0.20-g quantity of **18** was dissolved in 10 ml of ether. A 0.050-g quantity of methanesulfonic acid dissolved in 5 ml of ether was added. After standing at room temperature for 2 hr, the solution was extracted with aqueous sodium bicarbonate to remove the methanesulfonic acid. The ether layer was dried (MgSO₄) and the solvent was evaporated *in vacuo* to leave a crystalline residue which was recrystallized from hexane, yield 0.180 g of **17**, identified by ir spectrum and mixture melting point determination.

Attempts to Prepare 1,2-Di-*tert*-octylaminosuccinonitrile (11). A. By Catalytic Hydrogenation of 20.—Catalytic hydrogenation of **20** (5% Pd/C) gave a product which was **17**, containing some **18**, according to ir spectrum, mixture melting point determination, and glpc analysis.

B. By Catalytic Hydrogenation of 17.—Hydrogenation of **17** using a 5% palladium on carbon catalyst was unsuccessful since even at reflux of the ethyl acetate solvent no hydrogen was taken up. With a 5% rhodium on alumina catalyst, hydrogen was absorbed at room temperature, but the product was dark colored, and chromatography through a silica column did not yield an identifiable pure compound.

C. By Lithium Aluminum Hydride Reduction of 20.—Lithium aluminum hydride reduction of 1 g of **20** in ether by the usual procedure gave a product that was pentane soluble except for a small amount of **17**, identified by ir spectrum. Chromatography through a silica column did not yield a pure, identifiable product.

D. By Dimethylamine Borane Reduction of 20.—A 2-g quantity of **20** was treated with 1.59 g of dimethylamine borane in glacial acetic acid according to the method of Billman and McDowell.[31] The product appeared to consist exclusively of a mixture of **17** and unreacted **20**; no other compound could be isolated.

E. By Sodium Borohydride in Dimethylformamide (DMF).—Treatment of **20** with a twofold molar excess of sodium borohydride in DMF followed by decomposition with water gave a product from which only **17** could be isolated. Chromatography of the mother liquors through a silica column yielded some additional **17** (pentane–5% ether eluent) and some starting material (pentane–2% ether eluent) but no other identifiable compound.

Malononitrile and Triethylamine.—Under strict exclusion of oxygen, a 1-g quantity of malononitrile was dissolved in 20 ml of freshly distilled triethylamine at room temperature. After 30 min, the solution had become dark colored. Glpc (coinjection technique using authentic hydrogen cyanide) demonstrated the absence of hydrogen cyanide. When oxygen was not excluded, hydrogen cyanide was shown to be present in small amount.

***tert*-Octylamine and 19 from 1 and Potassium Hydroxide.**—A 1-g quantity of the methanesulfonic acid salt of **1** was dissolved in 10 ml of 25% aqueous potassium hydroxide to give a clear, colorless solution. After 24 hr of stirring at room temperature in a nitrogen atmosphere, a second, orange-colored layer had formed. This layer dissolved in added benzene and was separated from the aqueous layer. The benzene solvent was removed *in vacuo*, and the residue was extracted with pentane. Evaporation of the pentane from this extract left 0.43 g of an oil. The ir spectrum of this oil was essentially identical with that of authentic *tert*-octylamine. Glpc (coinjection technique) showed the oil to be *tert*-octylamine of >80% purity.

The pentane-insoluble part of the residue was recrystallized (after Norit treatment) from a 50:50 mixture of benzene and hexane to give 0.067 g of **19**, identified by ir spectrum and mixture melting point determination.

1,2-Di-*tert*-octylamino-3-*tert*-octylimino-1,3-dicyanopropene-1 (26). A. From Reaction of 24 and 1 in Triethylamine.—A solution of 2.75 g (0.009 mol) of **24** and 0.87 g (0.0045 mol) of **1** in a mixture of 3 ml of triethylamine and 10 ml of benzene was allowed to stand at room temperature for 48 hr. The benzene and triethylamine were then removed *in vacuo*. The deep orange residue was dissolved in 40 ml of pentane, chilled to −15°, and filtered to give a crystalline precipitate and an orange filtrate.

The precipitate was recrystallized from hot hexane to give 1.06 g of colorless crystals, identified as 17 by mixture melting point determination and identity of ir spectra.

The filtrate was concentrated *in vacuo* to a volume of 5 ml and chilled. Filtration of this solution after 12 hr at −15° gave orange-colored crystals. After one additional crystallization from pentane, 0.67 g of pure 26 was obtained, mp 93.4–94.3°. Chromatography of the mother liquors through an alumina column yielded an additional 0.55 g of 26 from the pentane eluate.

Anal. Calcd for $C_{29}H_{53}N_5$: C, 73.70; H, 11.33; N, 14.95. Found: C, 73.48; H, 11.22; N, 14.97.

Ir (CCl₄) 3385, 3335, 3180 (vw) (NH), 2220 (w), 2180 (vvw) (C≡N), 1575, 1530 cm⁻¹ (s) (N=CC=C); nmr (CDCl₃) δ 0.97 [18 H, 2 C(CH₃)₃], 1.06 [9 H, C(CH₃)₃], 1.10 [6 H, C(CH₃)₂], 1.42 [12 H, 2 C(CH₃)₂], 1.54 (2 H, CH₂), 1.79 (4 H, 2 CH₂), 2.68 and 9.88 ppm (2 H, NH, disappear on deuteration); mass spectrum (70 eV) *m/e* parent 471; mol wt, 474 (Thermonam).

B. From Reaction of 1 and 24 in Aqueous KOH.—To 5 ml of 25% aqueous KOH were added 0.8 g of 1 and 2.5 g of 24, and the mixture was stirred under a nitrogen blanket at room temperature for 12 hr. The organic layer in which crystals had formed was diluted with pentane, separated from the aqueous layer, chilled to −15°, and filtered to give a crystalline precipitate and a deeply orange-colored filtrate. The precipitate was twice recrystallized from hot hexane to give 0.45 g of colorless crystals identified as 17 by mixture melting point determination and identity of ir spectra.

The orange-colored filtrate was concentrated *in vacuo* to a volume of 5 ml and chilled. After 12 hr at −15°, the solution was filtered to give 0.35 g of orange-yellow crystals identified as 26 by mixture melting point determination and identity of ir spectra. Chromatography of the mother liquors through a silica column yielded an additional 0.25 g of 26 eluted with pentane containing 2% ether.

C. Directly from Reaction of 2,4,4-Trimethylpentene-2 (TMP) with HF and HCN. Isolation of Di-*tert*-octylamino-fumaronitrile (18).—A polyethylene reactor with a polyethylene condenser and magnetic stirrer was charged with 150 g (1.34 mol) of TMP (freshly distilled and dried over CaH₂) and 250 ml of dichloromethane (dried over CaH₂). At 0° 155 ml (108.6 g, 4.01 mol) of HCN was distilled in, followed by 81 ml (80.15 g, 4.04 mol) of HF. The reaction mixture was stirred at room temperature for 2 hr. The solvent and unreacted HCN and HF were removed by sparging with nitrogen. The residue was diluted with 350 ml of fresh dichloromethane, and stirring at room temperature was continued overnight. The reaction mixture was then poured into a stirred slurry of 300 g of KOH, 300 g of water, and 600 g of crushed ice. Upon reaching room temperature, the mixture was filtered through a sintered glass funnel. A 12.8 g quantity of 4-cyano-5-*tert*-octylaminoimidazole[1] was collected, identified by its ir spectrum and mixture melting point with authentic compound.

The filtrate (organic as well as aqueous layers) was stirred under a nitrogen blanket at room temperature. After 96 hr, the ir spectrum proved the absence of 24 (initially a major component) through disappearance of the characteristic ketenimine band at 2025 cm⁻¹. The organic layer was separated, the dichloromethane was removed *in vacuo*, and the residue was diluted with 200 ml of pentane.

After cooling at −20° overnight, the solution was filtered to yield 38.5 g of crude 17, identified by ir spectrum and mixture melting point.[1]

The mother liquor was chromatographed through a silica column (solvent-free substrate to SiO₂ ratio 1:30). The initial pentane eluate contained an unidentified oil. Later pentane fractions, which were bright orange, yielded 7.42 g (after two recrystallizations from pentane at −20°) of 26, identified through ir spectrum and mixture melting point.

From the subsequent pentane-ether (98:2) eluate, 3.2 g of an impure crystalline product was obtained. Rechromatography of this product through a silica column yielded from the pentane eluate 0.47 g of 26. The residue from the subsequent pentane-ether (99:1) eluate was recrystallized three times from pentane at −30° (using decolorizing carbon the first time), yield 1.96 g of colorless crystals, mp 55.5–56.5°. This compound was identified as 18 by its ir spectrum and by mixture melting point determination.

D. From 24 and Triethylamine.—An 11.0-g quantity of 24 in 200 ml of triethylamine was kept at reflux in a nitrogen at-

mosphere for 32 hr. The triethylamine was removed *in vacuo*, and the residue was dissolved in 160 ml of pentane. Filtration after 14 hr at −10° yielded 2.4 g of a crystalline precipitate which was identified as 17 by ir spectrum and mixture melting point determination. After concentration, the mother liquors were chromatographed through a silica column (500 g of SiO₂). From the pentane-2% ether eluate an orange-yellow residue was obtained. After one recrystallization from 3 ml of pentane at −30°, 0.62 g of orange-yellow crystals were recovered which were identified as 26 by ir spectrum and mixture melting point determination.

Preparation of Dimethylaminomalononitrile (4).—This compound was prepared according to Arnold,[16] nmr (CDCl₃) δ 2.47 [6 H, N(CH₃)₂], 4.76 ppm (1 H, CH), disappears upon deuteration.

Hydrogen Cyanide from Dimethylaminomalononitrile (4) and Triethylamine.—A 500-mg quantity of 4 was dissolved in 3 ml of triethylamine at room temperature in a nitrogen atmosphere. After the solution had stood for 20 min, the presence of hydrogen cyanide was demonstrated by the glpc coinjection method. The amount continued to increase over a 4-hr period.

The generation of hydrogen cyanide was also confirmed by high-resolution mass spectrometry. A solution of 4 in triethylamine, blanketed with nitrogen, was allowed to stand in the probe for 30 min at room temperature. The solution was then frozen in liquid nitrogen and a mass spectrum was obtained of the vapors. The presence of hydrogen cyanide was proven by a peak at mass 27.01097 (calcd 27.01090).

17 from 4, 24, and Triethylamine.—A mixture consisting of 10 ml of benzene, 6.1 g (0.02 mol) of 24, 1.1 g (0.0067 mol) of 4, and 10 ml of triethylamine was kept at room temperature in a nitrogen atmosphere for 36 hr. The benzene and triethylamine were then removed, and the residue was dissolved in 35 ml of pentane. After 12 hr in the refrigerator, a precipitate had formed which was collected and recrystallized from hot hexane. A 0.95-g yield of colorless crystals was obtained, shown to be 17 through identity of ir spectra and by mixture melting point determination. From the mother liquors, an additional 0.63 g of 17 was recovered. The reaction product which had not crystallized was chromatographed through a silica column, but no pure identifiable compound was isolated.

Dimethylamine from 4 and Aqueous Potassium Hydroxide.—A 1-g quantity of 4, dissolved in 5 ml of benzene, and 10 ml of 25% aqueous potassium hydroxide was stirred at room temperature in a nitrogen atmosphere. An aliquot drawn after 5-min reaction time evolved basic vapors with a strong amine odor. Glpc analysis (coinjection technique) of a sample of the benzene layer, drawn after 2-hr reaction time, showed dimethylamine to be the main product in that layer.

The generation of dimethylamine was also confirmed by mass spectroscopy. A solution of 4 in aqueous potassium hydroxide was allowed to stand in the probe for 30 min at room temperature. The solution was then frozen in liquid nitrogen and a mass spectrum was obtained of the vapors. A large peak at mass 44 (M⁺ − H) and a smaller peak at mass 45 (M⁺) proved the presence of dimethylamine.