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Thermal Transformations of an Aminomalononitrile and of an Aminocyanoketenimine. Evidence for Homolysis and Heterolysis and for Aminocyanocarbenes

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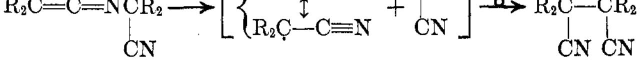
In refluxing toluene *N-tert*-octylaminocyanoketen-*N-tert*-octylimine (**3**) and *tert*-octylaminomalononitrile (**1**) both thermolyze. Additionally, **3** rearranges to give *tert*-octylamino-*tert*-octylmalononitrile (**10**). It is proposed that in each case the initial intermediate is a hybrid ion pair–radical pair in a solvent cage. This intermediate may either proceed directly to products or may—with increasing solvent separation—diverge into distinct ion and radical pairs. In the case of **3**, combination or disproportionation reactions can account for the formation of all identified products with the exception of *tert*-octylimino-*tert*-octylacetonitrile (**12**) and of di-*tert*-octylaminomaleonitrile (**16**). Stoichiometrically, these compounds are related to **3** as the products of elimination and addition of hydrogen cyanide. With β-cis elimination ruled out by MO-symmetry considerations, it is proposed that cyanide ion is generated by α elimination from the *tert*-octylaminomalononitrile anion which is the anionic component in the proposed ion pairs. Combination of the resulting *tert*-octylaminocyanocarbene (**11**) with the *tert*-octyl cation—the cationic component—and subsequent elimination of a proton gives **12**. In the case of **1**, Thorpe-type dimerization appears to compete with thermolysis since a triaminotricyanopyroline, **22**, was isolated. Formation of this compound may involve addition of hydrogen cyanide to an iminopyroline resulting from cyclization of the initial Thorpe dimer. Also obtained was an enaminoimine **23** which formally corresponds to the product of elimination of hydrogen cyanide from the dimer, but which may originate from insertion of the aminocyanocarbene **11** in the C–H bond of **1**. From the thermolysis of neat **1** a dehydrogenation product of the Thorpe dimer was isolated. It is proposed that **11** is responsible for the hydrogen abstraction.

In an earlier paper[1] the reactions of *tert*-octylaminomalononitrile (**1**) and of *N-tert*-octylaminocyanoketen-*N-tert*-octylimine (**3**) in basic media are described.

Esr evidence shows that under these conditions **1** gives the relatively stable *tert*-octylglycinonitrile radical (**18**). Additionally, the formation of the *tert*-octylaminomalononitrile radical (**5**) is indicated. The evidence points to initial α elimination of hydrogen cyanide from **1** to give the *tert*-octylaminocyanocarbene (**11**);[1] however, competing β elimination to give the tautomeric *tert*-octyliminoacetonitrile (**13**) is difficult to rule out.

Therefore, the uncatalyzed thermolysis of **1** and **3** became of interest. Under these conditions β elimination can be virtually ruled out. Concerted β-cis elimination is forbidden by the MO symmetry rules,[2,3] and the alternative nonconcerted β-trans elimination should be a high-energy process because it implies ionization without solvation. Moreover, as previously pointed out,[1] heterolysis of aminomalononitriles such as **1** is unlikely even in a solvating medium. These predictions are experimentally confirmed (see below). Homolytic paths are likely in the thermolysis of **3**, since a number of thermal rearrangements of ketenimines have been reported to involve the formation and recombination of radicals. Examples are R = CH_3,[5] $R_2 = -(CH_2)_5-$.[6]



$$R_2C{=}C{=}NCR_2(CN) \longrightarrow \left[\begin{Bmatrix} R_2C{=}C{=}N\cdot \\ \updownarrow \\ R_2\dot{C}{-}C{\equiv}N \end{Bmatrix} + \dot{C}R_2(CN)\right] \longrightarrow R_2C(CN){-}CR_2(CN)$$

Results and Discussion

Thermolysis of the Aminocyanoketenimine 3.—In the thermolysis of **3** (Scheme I) the major isolated products are 2,4,4-trimethylpentene-1 (**7**), 2,4,4-trimethylpentane (**8**), *tert*-octylimino-*tert*-octylaminomalononitrile (**10**), and *tert*-octylimino-*tert*-octylacetonitrile (**12**). Minor isolated products are di-*tert*-octylaminotricyanoethane (**19**), di-*tert*-octylaminomaleonitrile (**16**), and di-*tert*-octyliminosuccinonitrile (**25**). Additionally,

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[1] L. de Vries, *J. Org. Chem.*, **38**, 2604 (1973).

[2] R. Hoffmann and R. B. Woodward, *Science*, **167**, 825 (1970).

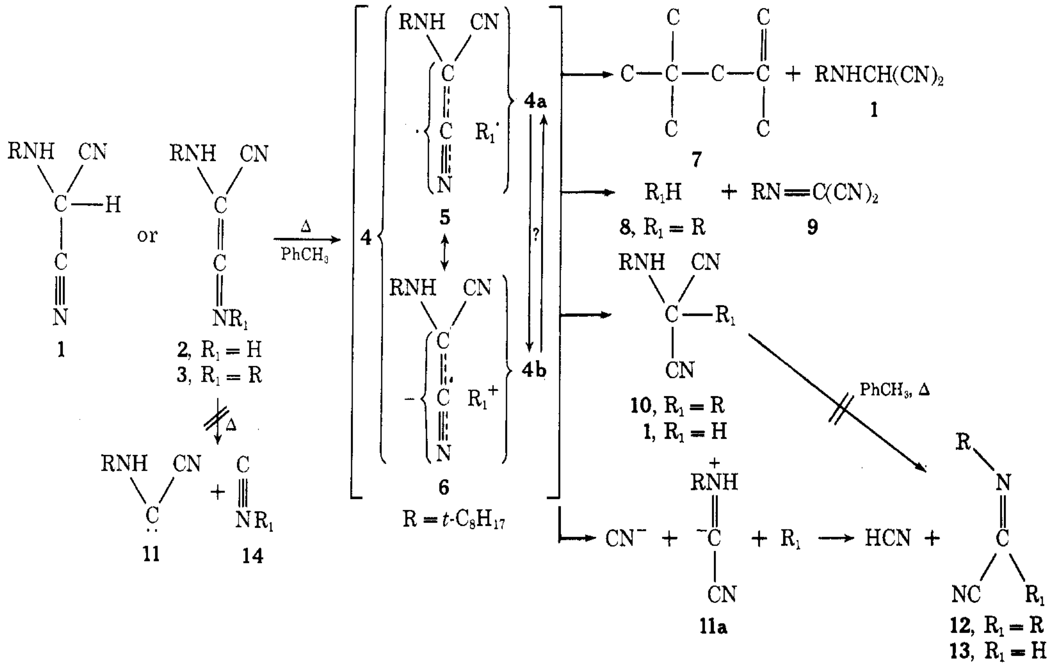
[3] It has recently been recognized that some reactions in which orbital symmetry is not conserved may yet occur in a concerted manner.[4] These are, however, likely to be high-energy processes, requiring conditions of considerably greater severity than those used in the present work.

[4] J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, **5**, 402 (1972); J. A. Berson, *ibid.*, **5**, 406 (1972).

[5] G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Neff, *J. Amer. Chem. Soc.*, **81**, 4878 (1959).

[6] H. D. Waits and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 1911 (1964).

SCHEME I



the presence of small amounts of *tert*-octylaminomalononitrile (**1**) and of *tert*-octyliminomalononitrile (**9**)[7] is indicated by glpc.

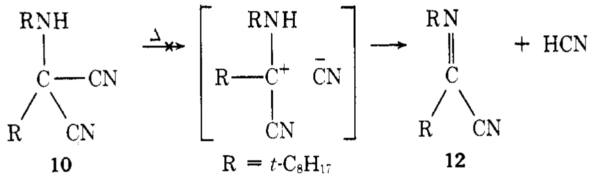
Moreover, hydrogen cyanide is evidently evolved as well, because among the above thermolysis products the diaminomaleonitrile **16** is the adduct of hydrogen cyanide to **3**,[8] while the iminoacetonitrile **12** is the (stoichiometric) product of elimination of hydrogen cyanide from **3**.

The restrictions imposed by the MO symmetry rules suggest that none of these products is formed by a concerted process. Specifically, the formation of the aminomalononitrile **10** by rearrangement of the aminocyanoketenimine **3** involves a 1,3 shift of a *tert*-octyl group from nitrogen to carbon. A concerted shift of this type is symmetry forbidden because it is equivalent to a suprafacial 1,3 shift in an allylic system with retention of configuration in the migrating group.[9] Steric considerations lead independently to the same conclusion: the linearity of the C–C–N system in both the initial ketenimine and the final nitrile makes it impossible for the migrating group to remain bonded to both ends of the unsaturated system throughout the rearrangement, as is required for a concerted process.

Concerted β-cis elimination is another symmetry-forbidden process. Concerted decomposition of the aminocyanoketenimine can, therefore, not account for the formation of the trimethylpentene **7** and the aminomalononitrile **1** (by way of its ketenimine tautomer **2**).

Similarly, the hydrogen cyanide that is formed in the thermolysis of **3** cannot originate by the forbidden β-cis-elimination route from the aminomalononitriles **1** or **10** (both of these are thermolysis products). For the case of **10**, this conclusion is experimentally verified. Upon β elimination of hydrogen cyanide **10** would give the iminoacetonitrile **12**. In the thermolysis of **3** in refluxing toluene for 18 hr **12** is a major product, but under identical conditions no **12**, and therefore no hydrogen cyanide, is produced from **10** which is quantitatively recovered.

In summary, a nonconcerted, rather than a concerted, mechanism is indicated for the thermolysis of **3**. That this process has homolytic features is suggested by the formation of thermolysis products such as 2,4,4-trimethylpentane (**8**) and the iminomalononitrile **9**, which is formally the product of dehydrogenation of **1**. On the other hand, the formation of hydrogen cyanide points to a heterolytic pathway, since the C≡N radical is a high-energy species.[10] The simplest nonconcerted heterolytic process leading to hydrogen cyanide and **12** is a β-trans elimination, involving initial ionization of aminomalononitrile **10** to give a cyanoimmonium cyanide and subsequent deprotonation of the immonium ion by the cyanide counterion to give **12**. This path is, however, *a priori* improbable for reasons mentioned above and is experimentally ruled out by the demonstrated thermal stability of **10** in refluxing toluene.



The formation of all isolated thermolysis products can be rationalized by a single mechanism with homolytic, as well as heterolytic, features if one assumes that the first intermediate is an intimate ion pair–radical pair hybrid in a solvent cage (**4**, Scheme I). This initial intermediate may directly proceed to products or, with increasing solvent separation, it may diverge into distinct ion pairs (**4b**) and radical pairs (**4a**). This seems a reasonable possibility, since both the radical and the anion derived from *tert*-octylamino-

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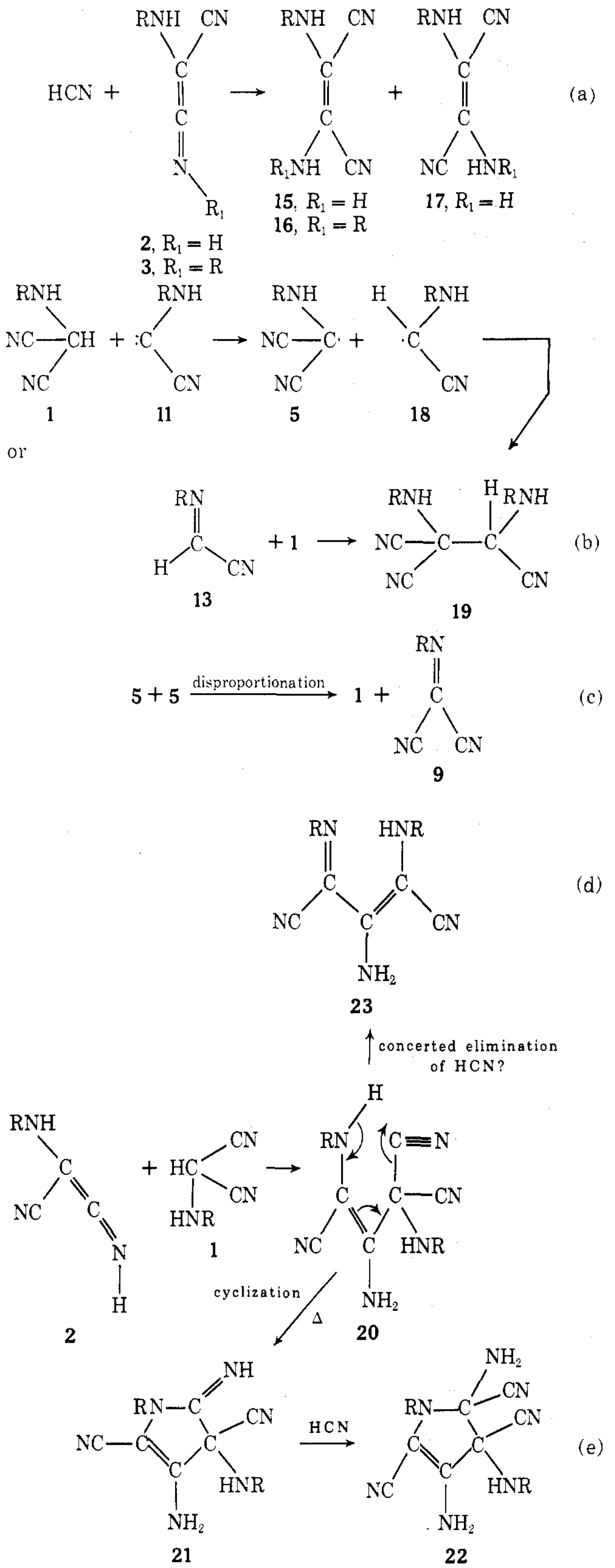
[7] Compound **9** is prepared in high yield by dehydrogenation of **1** with tetracyanoethylene or benzoyl peroxide.[1]

[8] L. deVries, *J. Org. Chem.*, **36**, 3442 (1971).

[9] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 114.

[10] J. C. Boden and B. A. Trush, *Proc. Roy. Soc., Ser. A*, **305**, 107 (1968).

SCHEME II



R = t-C_8H_{17}

malononitrile (**5** and **6**) are presumably resonance-stabilized species.[1]

Walling[11] has proposed a similar ion pair–radical pair hybrid—later diverging into distinct ion pairs and radical pairs—in order to account for the competing homolytic and heterolytic decomposition paths of acyl peroxides.

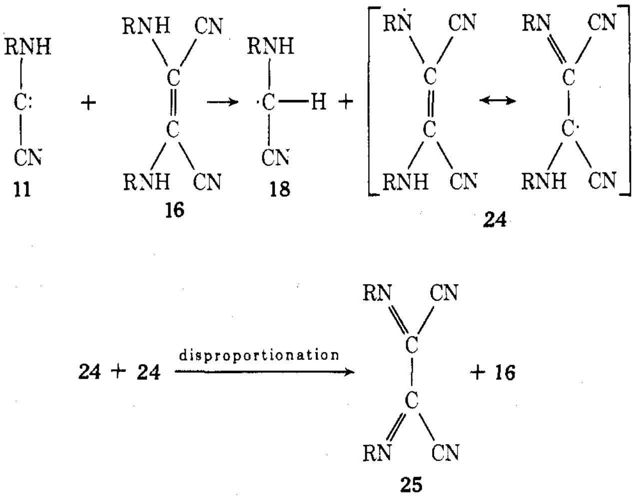
Recombination and disproportionation in **4**, **4a**, or **4b** can account for the formation of **7**, **8**, **9**, and **10**.

The ion pair **4b** also explains the formation of the iminoacetonitrile **12** and of hydrogen cyanide. Inside the solvent cage the aminomalononitrile anion **6** may expel a cyanide ion to give the aminocyanocarbene **11** (shown in the ylide form **11a**). Combination of **11** with R^+, followed by expulsion of a proton, results in formation of **12**. The hydrogen cyanide thus produced adds to **3** to give the isolated diaminomaleonitrile **16** (reaction a, Scheme II).

It may be significant that thermolysis of neat **3** (as opposed to **3** in refluxing toluene) gives no rearrangement product **10**. Under these conditions the main product is the iminoacetonitrile **12**.

Evidence presented earlier[1] suggests that the carbene **11** could be a fairly long-lived species, capable of diffusing out of the initial solvent cage to react with other molecules in the environment, primarily through hydrogen abstraction. The formation of the diiminosuccinonitrile **25** (Scheme III) can be rationalized in this manner, since under dehydrogenating conditions **25** is readily formed from the diaminomaleonitrile **16**. Esr shows that a stable radical is involved.[1]

SCHEME III



R = t-C_8H_{17}

It is proposed that abstraction of hydrogen from the diaminomaleonitrile **16** by the carbene **11** results in the initial formation of the radical **24**. Disproportionation of this radical then generates the diiminosuccinonitrile **25** and regenerates **16** (Scheme III). This mechanism is supported by the observation that the diiminosuccinonitrile **25** is also produced when the carbene **11** is generated (from the aminomalononitrile **1** and triethylamine) in the presence of an excess of the diaminomaleonitrile **16**.

Formation of the carbene **11** also suggests two routes —both discussed earlier[1]—to the diaminotricyanoethane **19** (reaction b, Scheme II).

(1) Hydrogen abstraction by the carbene **11** from the concomitantly formed aminomalononitrile **1** results in the formation of the glycinonitrile radical **18** and the

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[11] C. Walling, H. D. Waits, J. Milanovic, and C. G. Pappiaonnou, *J. Amer. Chem. Soc.*, **92**, 4927 (1970); see also J. E. Leffler and A. A. More, *ibid.*, **94**, 2483 (1972).

aminomalononitrile radical **5**. These radicals may combine to yield **19**.

(2) The carbene **11** first rearranges to the more stable iminoacetonitrile **13**, to which **1** adds to give **19**.

In summary, the mechanism shown in Scheme I could account for the formation of all products identified in the thermolysis of the aminocyanoketenimine **3**. Proof is however needed that the carbene **11** is not formed by an alternative route that does not involve the ion pair–radical pair intermediate **4**. Such a route could be thermal dissociation of the aminocyanoketenimine **3** to give **11** and *tert*-octylisonitrile (**14**, Scheme I). This would constitute a reversal of a reaction observed by Ciganek,[12] *i.e.*, the addition of a carbene to an isonitrile to give a ketenimine.

Such a direct formation of **11** is, however, very improbable. According to Hoffmann, Gleiter, and Mallory,[13] orbital symmetry rules demand that two dimerizing singlet carbenes approach each other in perpendicular planes to give an olefin. The principle of microscopic reversibility implies, therefore, that coplanar dissociation of an olefin to give two singlet carbenes (or other singlet species) is symmetry forbidden and that the π bond must first be broken in an initial 90° twist. Such a high-energy process would be required for thermal dissociation of **3** since the isonitrile **14** is a ground-state singlet as is assumedly the carbene **11**.[1] Glpc analysis confirms the nonoccurrence of this process, since *tert*-octylisonitrile was shown to be absent among the thermolysis products.

The thermolysis of ketene-*N*-*tert*-butylimines, which are structurally similar to **3**, has been reported to give isobutene and a nitrile.

$$R_1R_2C{=}C{=}NC(CH_3)_3 \xrightarrow{\Delta} R_1R_2CHCN + H_2C{=}C(CH_3)_2$$

Ciganek[14] found first-order kinetics for this reaction and proposed that it may be analogous to a reverse ene reaction. However, the required cyclic, six-membered transition state appears to be highly strained owing to the linearity of the ketenimine moiety. (See, however, ref 14.) Disproportionation of an ion pair–radical pair intermediate similar to **4** is an attractive alternative. Such a mechanism would be analogous to that proposed above for the thermolysis of **3**. Ciganek considered a radical mechanism but dismissed it because neither isobutane nor the dimers of the *tert*-butyl radical and of the radical $R_1R_2\dot{C}C{\equiv}N$ are found among the products. (In this system isobutane would originate from disproportionation of a pair of *tert*-butyl radicals.[14b]) Formation of these products is not expected, however, if an initial ion pair–radical pair proceeds directly to products within the solvent cage and does not dissociate to give individual radicals.

Thermolysis of the Aminomalononitrile 1.—Thermolysis of **1** in toluene gave a product mixture from which six products have been isolated and identified (Scheme II). For one of these the triaminotricyanopyroline structure **22** is proposed; the others are the two diaminodicyanoethylene isomers **15** and **17** (the maleonitrile and fumaronitrile structures are unassigned), the diaminotricyanoethane **19**, the enaminoimine **23**, and the iminomalononitrile **9**. Several additional products were separated by chromatography but were not identified, since they could not be purified by crystallization.

The initial step in the formation of triaminotricyanopyroline **22** may be Thorpe-type dimerization of **1** to give **20**. It is hypothesized that cyclization of this dimer gives **21**, to whose imino group hydrogen cyanide adds to give **22** (reaction e, Scheme II). A mechanistically similar cyclization of the trimer of malononitrile has been reported.[15] Other structures fit the formula of **22** ($C_{23}H_{39}N_7$), which was determined by elemental analysis and mass spectra, but only the triaminotricyanopyroline is consistent with the nmr evidence. (See Experimental Section.)

Formation of the remaining products in the thermolysis of **1** can be explained by a mechanism analogous to that proposed for the thermolysis of **3**. This implies a hybrid ion pair–radical pair intermediate which, among other products, gives rise to the carbene **11** and to hydrogen cyanide.

Addition of the hydrogen cyanide to **1** accounts for the formation of the two isomeric *N*-alkyldiaminodicyanoethylenes **15** and **17**[16] (reaction a, Scheme II).

The enaminoimine **23** may originate from insertion of the carbene **11** into the C–H bond of **1**, as proposed earlier[1] for the formation of **23** from **1** in triethylamine.

Under thermolytic conditions 1,4 elimination of hydrogen cyanide from the Thorpe dimer **20** must be considered a possible alternative route to **23** (reaction d, Scheme II). An uncatalyzed, concerted process of this type is MO symmetry allowed, but appears questionable in view of the mildness of the conditions. Not only does it require a hydrogen to leave from a relatively basic amino group but, additionally, the nitrile group is a very poor leaving group.

Conceivably, elimination of hydrogen cyanide from the Thorpe dimer **20** could also be bimolecular and autocatalyzed by one of the amino groups. However, this appears improbable as well, because the basicity of these amino groups is lowered owing to inductive or tautomeric electron withdrawal by the nitrile groups.

The iminomalononitrile **9** could originate from direct disproportionation of the radical pair–ion pair intermediate **4** with generation of molecular hydrogen (Scheme I, R_1 = H). Although this may occur, there is no experimental evidence to support the evolution of hydrogen.

It seems more likely that the aminocyanocarbene **11** is the hydrogen-abstracting species. According to a mechanism discussed earlier[1] (reaction b Scheme II), **11** initially abstracts a hydrogen atom from the aminomalononitrile **1**, to yield simultaneously the glycinonitrile radical **18** and the aminomalononitrile radical **5**. Combination of **5** and **18** gives the diaminotricyanoethane **19**. Disproportionation of **5** gives **9** and regenerates **1** (reaction c, Scheme II).

When *tert*-octylaminomalononitrile (**1**) is heated in the absence of solvent at 60°, a thermolysis mixture results which differs profoundly from that obtained in refluxing toluene. Under the solvent-free conditions, the enaminoimine **23** is still formed, but the diamino-

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[12] E. Ciganek, *J. Org. Chem.*, **35**, 862 (1970).

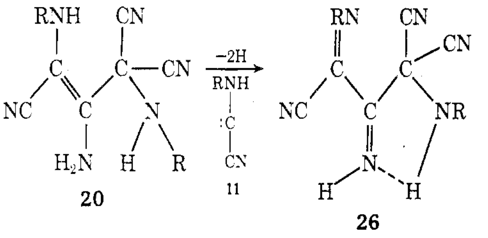
[13] R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, **92**, 1460 (1970).

[14] (a) E. Ciganek, *Tetrahedron Lett.*, **59**, 5179 (1969); (b) ref 14a, footnote 8.

[15] H. Junek and H. Sterk, *Z. Naturforsch.*, **22**, 732 (1967).

[16] The assignment of a 1-*tert*-octylamino-2-aminodicyanoethylene structure to **17** is based on elemental analysis, on mass spectrum, and on the striking similarity of its ir and nmr spectra to those of the configurationally isomeric **15**, which was isolated earlier.[1]

tricyanoethane **19** is not found, although it is a major component in refluxing toluene. Similarly, neat **1** gives very little of the triaminotricyanopyroline **22** and only a trace of *tert*-octyliminomalononitrile (**9**) is shown by glpc. On the other hand, relatively more of the diaminodicyanoethylene isomers **15** and **17** is found and additionally a new compound is isolated. According to elemental analysis and spectral evidence (see Experimental Section) this is 1-*tert*-octylimino-2-imino-3-*tert*-octylamino-1,3,3-tricyanopropane (**26**), which is formally the product of dehydrogenation of the Thorpe dimer **20**. The hydrogen abstraction which is implied in this formula is attributed to the aminocyanocarbene **11**.



Conclusion

It thus appears that the intermediates involved in the thermolyses of **1** and **3** are either identical with or are closely related to those postulated for the reactions of these same compounds in basic media. Under the latter conditions, most of the evidence for the intermediacy of *tert*-octylaminocyanocarbene was of an indirect nature. In the thermolysis reactions, however, this intermediate appears more directly implicated owing to the mechanistic restrictions imposed by the MO symmetry requirements.

Experimental Section

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

Materials.—*tert*-Octylaminomalononitrile (**1**)[1] and *tert*-octylaminocyanoketen-*N*-*tert*-octylimine (**3**)[8] were prepared as described in earlier papers.

***tert*-Octylamino-*tert*-octylmalononitrile (10) by Thermal Rearrangement of 3 in Toluene.**—An 11.4-g (0.037 mol) quantity of **3** 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 (36.0%) of pure **10** was recovered, mp 67.0–67.5°.

Anal. Calcd for $C_{19}H_{35}N_3$: C, 74.69; H, 11.54; N, 13.75. Found: C, 74.61; H, 11.63; N, 13.84.

Ir (CCl_4) 3405, 3360 (w, NH), 2235 cm^{-1} (vw, C≡N);[17] nmr (CCl_4) δ 0.97, 1.01 [18 H, 2 $C(CH_3)_3$], 1.26, 1.41 [each 6 H, $C(CH_3)_2$], 1.46, 1.54 ppm (each 2 H, CH_2); mass spectrum (70 eV) *m/e* 305 (M^+); mol wt 303 (Thermonam).

Formation of 1,2-Di-*tert*-octylamino-1,2,3-tricyanoethane (19) in Thermolysis of 3.—The pentane-insoluble part of the crystalline thermolysis residue of **3** was recrystallized from a benzene–hexane mixture. An 0.153-g amount (2.3%) of pure **19** was obtained, identified by ir spectrum and mixture melting point determination. Authentic **19**, prepared by thermolysis of **1** (see below), was used for comparison.

Glpc Analysis of Mother Liquors of 10. Identification of *tert*-Octylaminomalononitrile (1) and of *tert*-Octyliminomalononitrile (9).—The condensed mother liquors of **10** were analyzed by glpc. The support was 5% silicone SE-30 (General Electric Co.) on Chromosorb W (Johns-Manville). By means of the coinjection technique, three of the major components were identified as *tert*-octylimino-*tert*-octylacetonitrile (**12**), di-*tert*-octyliminosuccinonitrile (**26**), and di-*tert*-octylaminomaleonitrile (**16**). These substances were also isolated by column chromatography (see below).

Additionally, by means of the coinjection technique, two minor components were identified as *tert*-octylaminomalononitrile (**1**) and *tert*-octyliminomalononitrile[4] (**9**). Neither of these compounds could be isolated by column chromatography.

Chromatography of the Mother Liquors of 10.—The mother liquors of **10** were chromatographed through a silica column using mixed pentane–ether eluents of progressively increasing ether content.

***tert*-Octylimino-*tert*-octylacetonitrile (12) and Di-*tert*-octyliminosuccinonitrile (25) from Thermolysis of 3.**—Removal of the solvents from the pentane–ether (19:1) eluate left an oily residue. Distillation of this residue through a microstill yielded 1.1 g (10.7%) of **12** as a colorless oil, bp 82.0–82.5° (0.13 mm), $n^{20}{}_D$ 1.4582.

Anal. Calcd for $C_{18}H_{34}N_2$: C, 77.60; H, 12.33; N, 10.06. Found: C, 77.46; H, 12.31; N, 10.25.

Ir (neat) 1622 cm^{-1} (m, C=N); nmr (CCl_4) δ 0.93, 0.96 [18 H unresolved, 2 $C(CH_3)_3$], 1.18, 1.42 [each 6 H, 2 $C(CH_3)_2$], 3.36, 3.38 ppm (4 H, unresolved, 2 CH_2).

The residue remaining after distillation of **12** was dissolved in pentane, and the solution was treated with decolorizing carbon. After condensation and cooling to −40°, a crystalline precipitate was obtained. One additional crystallization gave 0.33 g (2.7%) of **25**, identified by ir spectrum and mixture melting point determination using authentic **25**.[8]

Di-*tert*-octylaminomaleonitrile (16) from Thermolysis of 3.—The pentane–ether (85:15) eluate yielded a crystalline residue which was recrystallized from hot hexane, yield 0.57 g (4.6%) of **16**, identified by ir spectrum and mixture melting point determination using authentic **16**.[8]

2,4,4-Trimethylpentene-1 and 2,4,4-Trimethylpentane from Thermolysis of 3.—The combined toluene solvent and volatile reaction products from the thermolysis of **3** were redistilled through a spinning band distillation column. The fraction with bp 94–104° (760 mm) weighed 0.8 g and consisted, according to the coinjection glpc method, of 2,4,4-trimethylpentene-1 (93%) and 2,4,4-trimethylpentane (7%). The corresponding yields in the thermolysis are 17.9 and 1.3%.

Thermal Stability of *tert*-Octylamino-*tert*-octylmalononitrile (10).—A 0.53-g quantity of **10** was dissolved in 10 ml of toluene. The solution was blanketed with nitrogen and heated at reflux for 19 hr. Removal of the toluene *in vacuo* left a residue that was recrystallized from pentane. After 2 hr at −15°, filtration yielded 0.50 g (94.3%) of a crystalline precipitate which was identical with the starting material according to ir spectra and mixture melting point determination.

Thermolysis of 3 in the Absence of Solvent. Isolation of Di-*tert*-octylaminomaleonitrile (16).—An 18.7-g quantity of **3** was blanketed with nitrogen and heated at 100–105° for 18 hr. At that time the characteristic ketenimine band at 2025 cm^{-1} was no longer present in the ir spectrum. The dark green liquid was dissolved in 50 ml of pentane and cooled to −10°. After 10 hr, filtration yielded 3.57 g (17.5%) of a colorless precipitate which was identified as **16** by ir spectrum and mixture melting point determination using authentic **16**.[8]

Isolation of *tert*-Octylimino-*tert*-octylacetonitrile (12) from Thermolysis of Neat 3.—The mother liquors of **16** were chromatographed through a silica column. From the 95:5 pentane–ether eluent, 1.72 g (10.1%) of an oil was obtained which, according to ir spectrum (see above) and glpc (coinjection), was almost pure **12**.

Formation of Di-*tert*-octyliminosuccinonitrile (25) from 16, 1, and Triethylamine.—A solution of 2 g (0.01 mol) of **1** and 3.3 g (0.01 mol) of **16** in triethylamine under a nitrogen atmosphere was stirred at room temperature for 14 hr. The triethylamine was removed *in vacuo*, and the partially crystalline residue was extracted with 50 ml of pentane. The pentane-insoluble part of the residue consisted of **16** according to ir spectrum and mixture melting point determination. Upon cooling to −15°, the pentane extract deposited additional **16** which was removed by filtration. The filtrate was chromatographed through a silica column. Pentane–ether (98:2) eluted a fraction which was further purified

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[17] Extremely weak C≡N bands are the rule in aminomalononitriles.[8]

by two crystallizations from pentane (3 ml) at −30° to yield 0.64 g (16.6%) of **25**, identified by ir spectrum and mixture melting point determination using an authentic sample.[8]

Thermolysis of 1 in Toluene. Isolation of 1-*tert*-Octyl-2,4-diamino-2,3,5-tricyano-3-*tert*-octylaminopyroline (22).—A 15-g quantity of **1** was dissolved in 100 ml of toluene, and the solution was kept at reflux for 15 hr in a nitrogen atmosphere. The toluene and the volatile products were removed by distillation *in vacuo*. The residue was diluted with 200 ml of pentane and allowed to stand for 15 hr in the refrigerator. Filtration gave a crystalline precipitate (A) and a filtrate (B). Extraction of the precipitate A with 200 ml of refluxing hexane gave an insoluble part (C) and a hexane solution (D). The hexane-insoluble part (C) was twice recrystallized from hot benzene to give 0.31 g (1.8%) of **22** as colorless crystals, mp 232–233°.

Anal. Calcd for $C_{23}H_{39}N_7$: C, 66.77; H, 9.52; N, 23.71. Found: C, 66.70; H, 9.61; N, 23.59.

Ir ($CHCl_3$) 3395, 3320 (m, NH_2, NH), 2172 (vs, $C\equiv N$), 1605, 1555, 1547, 1510 cm^{-1} (m, C=C and NH_2, NH deformation); nmr ($CDCl_3$) δ 0.792 [9 H, $C(CH_3)_3$], 1.016 [9 H, $C(CH_3)_3$], 1.592 [6 H, $C(CH_3)_2$], 1.97 [8 H, $C(CH_3)_2 + CH_2$], 2.218 [2 H, CH_2], 3.904 (4 H, 2 NH_2), 4.68 ppm (1 H, NHR); mass spectrum (70 eV) *m/e* 413 (M^+).

1,2-Di-*tert*-octylamino-1,2,3-tricyanoethane (19) from Thermolysis of 1 in Toluene.—The hexane solution D obtained in the thermolysis of **1** deposited a crystalline precipitate upon cooling to −10°. A second yield was obtained upon concentrating the mother liquors and cooling to −40°. Both precipitates were combined and after two recrystallizations from hot hexane, 1.14 g (18.2%) of **19** was obtained as colorless crystals, mp 116–116.5°.

Anal. Calcd for $C_{21}H_{37}N_5$: C, 70.13; H, 10.39; N, 19.48. Found: C, 70.47; H, 10.31; N, 19.32.

Ir (CCl_4) 3325 (mw with shoulders at 3365 and 3275, NH), 2245 and 2220 cm^{-1} (vw, $C\equiv N$); nmr ($CDCl_3$) δ 1.07 [18 H, 2 $C(CH_3)_3$], 1.28 and 1.32 [6 H, two heterosteric CH_3 in $C(CH_3)_2$], 1.50, 1.53, and 1.58 [10 H, unresolved multiplet, $C(CH_3)_2 +$ 2 CH_2], 1.85 and 2.05 (1 H, doublet, $J = 12.0$ Hz, NH, disappears on deuteration), 2.22 (1 H, singlet, NH, disappears on deuteration), 3.95 and 4.15 ppm (1 H doublet, $J = 12.0$ Hz, CH, replaced by singlet at 4.05 ppm on deuteration); partial mass spectrum above *m/e* 260 (70 eV) *m/e* (rel intensity) 359 (M^+, 0), 344 ($M^+ - CH_3$, 1.5), 332 ($M^+ - HCN$, 100), 317 ($M^+ - CH_3 -$ HCN, 3.1), 307 [$M^+ - (CN)_2$, 25.6], 288 ($M^+ - C_5H_{11}$, 11.8), 261 ($M^+ - C_5H_{11} - HCN$, 66.7).

1-*tert*-Octylamino-2-amino-3-*tert*-octylimino-1,3-dicyanopropene-1 (23) from Thermolysis of 1 in Toluene.—The orange-colored filtrate (B) obtained in the thermolysis of **1** was concentrated to a 75-ml volume and seeded with some crystals of **23** obtained in the decomposition of **1** in triethylamine.[1] After 10 hr in the refrigerator, filtration yielded a crystalline precipitate which was recrystallized from hexane (−10°), yield 1.08 g (5.9%) of yellow needles, identified as **23** by ir spectrum and mixture melting point determination using authentic **23**.[1]

Chromatography of the Mother Liquors of 23. Isolation of Additional Products of Thermolysis of 1 in Refluxing Toluene.—The mother liquors of **23** were chromatographed through a silica column using mixed pentane–ether eluents of progressively increasing ether content.

tert-Octyliminomalononitrile (9) from Thermolysis of 1.—From the pentane–ether (9:1) eluate 0.172 g (1.2%) of a brown oil was recovered which became almost colorless upon treatment with Norit. It was identified as slightly impure **9** by ir and nmr spectra[1] and by glpc (coinjection using authentic **9**).

Unchanged 1 and 1-*tert*-Octylamino-2-aminodicyanoethylenes (Cis or Trans) 17 and 15 from Pentane–Ether Eluate.—Pentane–ether (1:1) eluted two products. The brown residue from the initial fraction was extracted with pentane. Treatment of the pentane extract with Norit, followed by concentration and cooling to −78°, gave a crystalline precipitate. After two additional crystallizations from pentane (−78°) 0.237 g of unchanged **1** was recovered, melting at 35.0–35.5° and identified by ir spectrum and by the glpc coinjection technique using authentic **1**.

Similar treatment of the residue from a subsequent 1:1 pentane–ether fraction yielded 0.065 g (0.4%) of **17**, mp 83.7–84.2°.

Anal. Calcd for $C_{12}H_{20}N_4$: C, 65.45; H, 9.09; N, 25.46. Found: C, 65.46; H, 9.24; N, 25.57.

Ir (CCl_4) 3450 (m), 3360 and 3335 (doublet, ms), 3180 (w) (all NH_2 and NH), 2200 (ms), 2160 (sh, $C\equiv N$), 1615 (ms, C=C), 1580 cm^{-1} (sh, NH_2, NH deformation); nmr ($CDCl_3$) δ 1.05 [9 H, $C(CH_3)_3$], 1.33 [6 H, $C(CH_3)_2$], 1.58 (2 H, CH_2), 2.97 (1 H, NH), 3.90 ppm (2 H, NH_2); mass spectrum (70 eV) *m/e* 220 (parent).

Pentane–ether (1:3) eluted an additional product which was recrystallized from benzene, yield 0.18 g (1.1%) of **15**, identified by ir spectrum and by mixture melting point determination using a sample of authentic **15**.[1]

Thermolysis of Neat *tert*-Octylaminomalononitrile (1).—A 5.5-g quantity of **1** was blanketed with nitrogen and heated at 60° for 36 hr. The deep orange liquid was extracted by shaking with 50 ml of warm (50°) hexane to give a hexane extract (A) and a residue (B).

1-*tert*-Octylamino-2-amino-3-*tert*-octylimino-1,3-dicyanopropene-1 (23) from Thermolysis of Neat 1.—The hexane extract (A) was treated with Norit and condensed to a 10-ml volume. The solution was seeded with authentic **23** (see above). After 10 hr at −10°, the solution was filtered to give 0.21 g (3.1%) of **23** identified by ir spectrum and mixture melting point determination.

1-*tert*-Octylamino-2-amino-1,2-dicyanoethylene (17) from Thermolysis of Neat 1.—The mother liquors of **23** were chromatographed through a silica column. From the pentane–ether (1:3) eluent, 0.067 g (1.0%) of a crystalline product was obtained that was identified as **17** by ir spectrum and mixture melting point determination using a sample of authentic **17** (see above).

1-*tert*-Octyl-2,4-diamino-2,3,5-tricyano-3-*tert*-octylaminopyroline (22) from Thermolysis of Neat 1.—The hexane-insoluble residue B (see above) was dissolved in 25 ml of ether. Upon cooling to −10°, a crystalline precipitate formed, yield 0.072 g (1.2%) of **22**, identified by ir spectrum and mixture melting point determination.

1-*tert*-Octylamino-2-amino-1,2-dicyanoethylene (15) from Thermolysis of Neat 1.—The ether mother liquors of **22** were freed of solvent and the residue was dissolved in 10 ml of warm benzene. A 5-ml quantity of hexane was added, and the solution was cooled at −10° for 12 hr. Filtration yielded 0.53 g (8.5%) of **15**, identified by ir spectrum and mixture melting point determination using a sample of authentic **15**.[1]

1-*tert*-Octylimino-2-imino-3-*tert*-octylamino-1,3,3-tricyanopropane (26) from Thermolysis of Neat 1.—The mother liquors of **15** were freed of solvent *in vacuo*. The residue was extracted with 25 ml of refluxing hexane. The hexane extract was concentrated to a 5-ml volume and cooled to −10° for 12 hr. The crystalline precipitate was collected by filtration and once recrystallized from hot hexane (Norit treatment) to yield 0.093 g (1.7%) of **26** as yellow crystals, mp 131.5–132°.

Anal. Calcd for $C_{22}H_{36}N_6$: C, 68.70; H, 9.45; N, 21.85. Found: C, 68.76; H, 9.54; N, 22.07.

Ir ($CHCl_3$) 3475 (m), 3230 (w), and 3160 (w) (NH), 2215 (s, $C\equiv N$), 1610 (vs) and 1580 (s) (RN=CC=NH), 1515 cm^{-1} (NH deformation ?); nmr ($CDCl_3$) δ 0.90 [9 H, $C(CH_3)_3$], 0.97 [9 H, $C(CH_3)_3$], 1.56 [6 H, $C(CH_3)_2$], 1.93 [8 H, $CH_2 + C(CH_3)_2$], 2.06 (2 H, CH_2), 6.27 ppm (2 H, NH, disappears upon deuteration); mass spectrum (70 eV) *m/e* 384 (M^+).

Registry No.—**1**, 31819-52-0; **3**, 30768-56-0; **10**, 40127-69-3; **12**, 42271-33-0; **17**, 42271-34-1; **19**, 42271-35-2; **22**, 42447-97-2; **26**, 42447-98-3.