2-Acetoxy-2-methyl-3-hexanone (8c) and 4-Acetoxy-2-methyl-3-hexanone (9c):[16] NMR δ 0.83 (t),* 0.87 (t), 1.03 (dd),* 1.40 (s), 1.50 (m), 1.97 (s), 2.04 (s),* 2.35 (t), 2.75 (m),* 5.02 (dd);* mass spectrum, *m/e* 172 (2), 129 (9), 101 (15), 71 (32),* 59 (28), 43 (100). Peaks due to **9c** are marked by asterisks.

2-(Trimethylacetoxy)-2-methyl-3-hexanone (11c) and 4-(Trimethylacetoxy)-2-methyl-3-hexanone (12c):[16] NMR δ 0.87 (t), 0.98 (dd),* 1.17 (s), 1.38 (s), 1.50 (m), 1.75 (m),* 2.30 (t), 2.75 (m),* 4.96 (dd);* mass spectrum, *m/e* 214 (0.3), 143 (6), 85 (39), 71 (12),* 59 (22), 58 (5), 57 (100). Peaks attributable to **12c** are marked with an asterisk.

2-(Trimethylacetoxy)-2,5-dimethyl-3-hexanone (11d) and 4-(Trimethylacetoxy)-2,5-dimethyl-3-hexanone (12d):[16] NMR δ 0.88 (m), 1.17 (s), 1.40 (s), 2.22 (broad d), 2.75 (m),* 4.97 (d);* mass spectrum, *m/e* 228 (0.4), 170 (7), 143 (8), 85 (71), 59 (23), 57 (100). Peaks attributable to **12d** are marked with an asterisk.

2-Acetoxy-2,5,5-trimethyl-3-hexanone (8e)[15c] **and 4-Acetoxy-2,5,5-trimethyl-3-hexanone (9e):**[16] NMR δ 1.00 (s), 1.20 (d), 1.40 (s), 1.98 (s), 2.05 (s),* 2.30 (s), 4.83 (s);* mass spectrum, *m/e* 200 (2), 157 (71), 101 (24), 99 (45), 84 (s), 71 (12),* 69 (6), 59 (32), 57 (65), 43 (100). Peaks attributable to **9c** are marked with an asterisk.

2-(Trimethylacetoxy)-2,5,5-trimethyl-3-hexanone (11e) and 4-(Trimethylacetoxy)-2,5,5-trimethyl-3-hexanone (12e): NMR δ 1.00 (s), 1.18 (s), 1.40 (s), 2.27 (s), 4.78 (s);* mass spectrum, *m/e* 242 (0.2), 99 (15), 85 (32), 59 (15), 57 (100). Peaks in the spectra attributable only to **12e** are marked with an asterisk.

2-Acetoxy-2,6,6-trimethyl-3-heptanone (8f) and 4-Acetoxy-2,6,6-trimethyl-3-heptanone (9f):[16] NMR δ 0.87 (s), 0.97 (s),* 1.40 (s), 1.45 (m), 2.00 (s), 2.04 (s),* 2.30 (m), 2.75 (m),* 5.13 (t);* mass spectrum, *m/e* 214 (0.8), 171 (7), 139 (13), 113 (46), 101 (18), 85 (12), 71 (6),* 69 (12), 59 (27), 57 (36), 55 (7), 43 (100). Peaks in the spectra attributable only to **9f** are marked with an asterisk.

2-(Trimethylacetoxy)-2,6,6-trimethyl-3-heptanone (11f) and 4-(Trimethylacetoxy)-2,6,6-trimethyl-3-heptanone (12f):[16] NMR δ 0.07 (s), 0.95 (s),* 1.15 (d),* 1.20 (s), 1.40 (s), 1.45 (m), 2.30 (m), 2.66 (m),* 5.08 (t);* mass spectrum, *m/e* 256 (0.7), 198 (10), 143 (9), 139 (20), 113 (36), 85 (80), 71 (7),* 70 (6), 69 (9), 59 (26), 58 (7), 57 (100). Peaks attributable only to **12f** are marked with an asterisk.

2-(Trimethylacetoxy)-2,4-dimethyl-3-pentanone (15):[16] NMR δ 1.02 (d, 6 H), 1.16 (s, 9 H), 1.47 (s, 6 H), 2.80 (m, 1 H); mass spectrum, *m/e* 214 (0.8), 156 (27), 143 (32), 113 (8), 86 (10), 85 (20), 71 (38), 70 (15), 69 (11), 59 (100), 58 (24), 57 (93), 56 (9), 55 (8), 43 (100).

Acknowledgments. Financial support was provided by the National Science Foundation. Mr. Michael Lazarus carried out the reductions of 2,4-dibromo-2,6,6-trimethyl-3-heptanone.

Registry No.—**7a,** 1518-06-5; **7b,** 37010-00-7; **7c,** 69204-79-1; **7d,** 56829-66-4; **7e,** 69204-80-4; **7f,** 69204-81-5; **8a,** 10235-71-9; **8c,** 69204-82-6; **8e,** 21503-00-4; **8f,** 69204-83-7; **9a,** 36960-07-3; **9c,** 69204-84-8; **9e,** 69204-85-9; **9f,** 69204-86-0; **10a,** 563-80-4; **10b,** 565-69-5; **10c,** 7379-12-6; **10d,** 1888-57-9; **10e,** 40239-50-7; **10f,** 40238-56-0; **11a,** 69204-87-1; **11b,** 69204-88-2; **11c,** 69204-89-3; **11d,** 69204-90-6; **11e,** 69204-91-7; **11f,** 69204-92-8; **12a,** 69204-93-9; **12b,** 69204-94-0; **12c,** 69204-95-1; **12d,** 69204-96-2; **12e,** 69204-97-3; **12f,** 69204-98-4; **13,** 17346-16-6; **15,** 67889-09-2; 2,4-dimethyl-3-pentanone, 565-80-0; 2-acetoxy-2,4-dimethyl-3-pentanone, 21980-75-6.

References and Notes

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(14) We have since observed that material balances are improved by placing the entire reaction mixture, including mercury, in a separatory funnel for extraction by carbon tetrachloride. This appears to minimize losses by entrainment.
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Mechanistic Studies on the Photochemical Conversion of Enaminonitriles to Imidazoles

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Imidazoles are not formed by photolysis of the N,N-disubstituted enaminonitriles, 2-(dimethylamino)-1-cyclohexene-1-carbonitrile (**7**) and 3-(dimethylamino)acrylonitrile (**5**). These results show that the enaminonitrile must contain an NH group for the photochemical formation of the imidazole to proceed. *N*-Isopropyldiaminomaleonitrile (**11**) did not photodissociate to yield aminocyanocarbene (**4**) as shown by the absence of diaminomaleonitrile (DAMN) (**1**) as a photoproduct. Direct irradiation of *N*-isopropyliminoacetonitrile (**18A**) at −196 °C did not give the absorption spectrum attributed to aminocyanocarbene. Polymer formation was observed when the photolysis of **18A** was performed at room temperature. Benzophenone-sensitized photolysis of **18A** gave *N,N'*-diisopropyldiaminosuccinonitrile (**19A**). The reaction does not proceed by the dimerization of *N*-isopropylaminocyanocarbene to diisopropyldiaminomaleonitrile (**15**) followed by the reduction of **15,** since it was observed that **19A** is not formed by the benzophenone-sensitized photolysis of **15.** The significance of these results to the mechanism of the photochemical rearrangement of enaminonitriles to imidazoles and the postulated role of aminocyanocarbene as an intermediate in a number of thermal and photochemical reactions are discussed.

The photochemical conversion of the HCN oligomer, diaminomaleonitrile (DAMN) (**1**), to 4-aminoimidazole-5-carbonitrile (AICN) (**3**) is a key step in one of the pathways proposed for purine synthesis on the primitive earth (Scheme I).[1] This reaction has also been shown to be an efficient route for the synthesis of substituted imidazoles starting from the corresponding enaminonitrile.[2,3] The reaction is a monophotonic process in which the enaminonitrile with the cis orientation of the amino and cyano groups cyclizes to the imidazole.[3,4] The mechanism of the reaction has not been established with certainty. The route shown in path A of Scheme II finds support in the observation of IR bands at 2000 cm^{-1},

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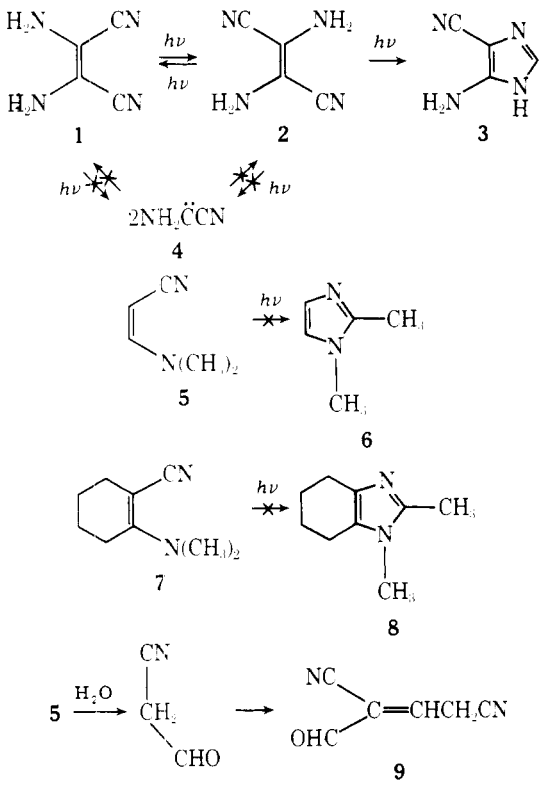
Scheme I

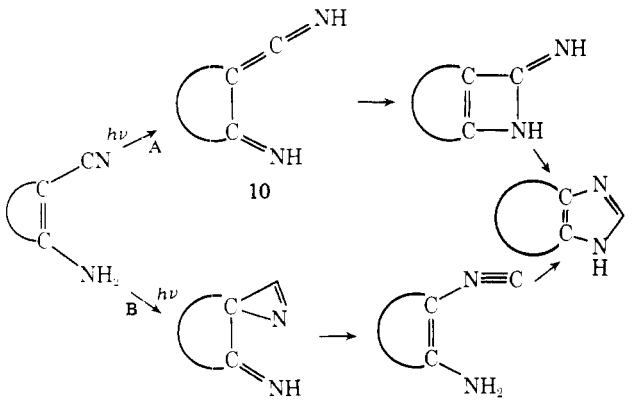


consistent with the ketenimine structure **10**, on irradiation of enaminonitriles at −77 and −196 °C.[3] Pathway B (Scheme II) is analogous to the mechanism established for the photochemical rearrangement of isoxazoles to oxazoles.[5]

Two observations which are not compatible with the mechanistic pathways proposed in Scheme II have been described. The first is the report that 3-(dimethylamino)acrylonitrile (**5**) cyclizes to the corresponding imidazole **6** with migration of one of the methyl groups (Scheme I).[6] Our previously reported studies demonstrated that this cyclization did not occur in a similar system.[3] The second is the formation of aminocyanocarbene (**4**) on irradiation of diaminomaleonitrile (**1**) (Scheme I).[7] This is an unlikely enaminonitrile photochemical reaction because it is not possible to form a similarly stabilized carbene by the photolysis of simple enaminonitriles (e.g., 3-aminoacrylonitrile), yet both **1** and 3-aminoacrylonitrile are photoisomerized to an imidazole.

In this report we present further data on the scope of the enaminonitrile photoisomerization to imidazoles. We also report mechanistic studies relevant to postulates of Becker and co-workers concerning the reaction pathway.[3,6] Finally, we discuss the evidence supporting the postulated role of aminocyanocarbene as an intermediate in a number of photochemical and thermal reactions.

Scheme II



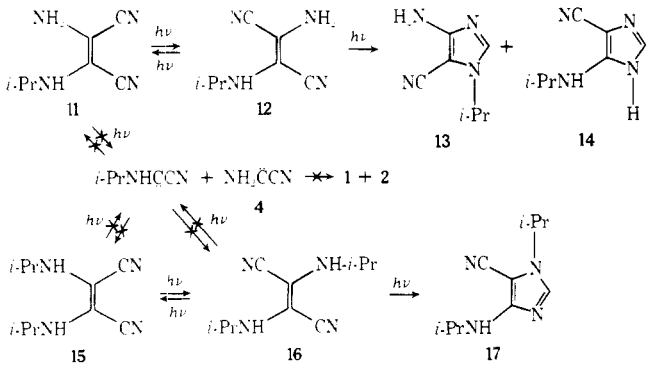
Cyclization of *N,N*-Dialkylenaminonitriles. The conflicting reports[3,6] concerning the photochemical cyclization of N,N-disubstituted enaminonitriles were reinvestigated by performing a careful search for the proposed imidazole reaction products in both of the previously reported systems. Photolysis of 2-(dimethylamino)-1-cyclohexene-1-carbonitrile (**7**) should yield 1,2-dimethyl-4,5,6,7-tetrahydrobenzimidazole (**8**) if cyclization to an imidazole occurs. If imidazole **8** were formed as a reaction product it would be expected to exhibit UV absorption at 226 nm as does 1-methyl-4,5,6,7-tetrahydrobenzimidazole.[3] Photolysis of **7** in methanol resulted in an 88% loss of starting material over a 2-h period with no increase in UV absorption near 226 nm. The photolysis of the monoalkyl derivative 2-(methylamino)-1-cyclohexene-1-carbonitrile proceeds in a markedly different way.[3] A well-defined absorption maximum develops at 226 nm within 15 min under comparable reaction conditions. It is apparent that the photochemistry of **7** involves processes other than imidazole formation.

Next we investigated the claim that photolysis of 3-(dimethylamino)acrylonitrile (**5**) yields 1,2-dimethylimidazole (**6**).[6] Photolysis of an aqueous solution of **5** under the published reaction conditions for 118 min resulted in an 87% loss of the starting material. However, no absorption maximum was detectable at 208 nm, the maximum for **6**. The limit of detection of **6** by UV in these experiments was 8.6×10^{-6} M. The reported[6] 38% conversion of **5** would have given a 3.2×10^{-5} M solution of imidazole **6**, an amount almost four times our limit of detection. In addition, imidazole **6** was not detectable by TLC analysis of the photolysate (a 6% yield represents the TLC limit of detection).

A competing thermal hydrolysis reaction of 3-(dimethylamino)acrylonitrile (**5**) to cyanoacetaldehyde which then condenses to the aldol dimer of cyanoacetaldehyde (**9**)[8] in aqueous solution may have led to misleading results in the previous photochemical experiments. We showed that **9** is formed when **5** is allowed to stand for extended periods in aqueous solution at room temperature. Our photolyses were completed in 118 min, before appreciable hydrolysis occurred, while 513 min was required in the previous study.[6] About 20% of the starting material would have undergone thermal hydrolysis during a 513 min time period. The photolysis of **5** was then investigated in methanol since we observed no thermal decomposition of **5** in this solvent. There was an initial rapid decrease and shift in the absorption maximum of **5** from 263 to 267 nm (probably a cis–trans isomerism) during the first 20 min of irradiation when the photolysis was performed in methanol. But then there was no measurable decrease in the 267 nm maximum over the next 98 min of irradiation. After a total irradiation time of 1546 min the absorbance at 267 nm decreased by only 19% with no corresponding increase in absorbance at 208 nm. In addition no 1,2-dimethylimidazole was detected in the photolysate by TLC. Control experiments demonstrated that 1,2-dimethylimidazole would be readily detectable if it were present in the yield reported.[6] Our results clearly demonstrate that 3-(dimethylamino)acrylonitrile is photochemically stable and that no 1,2-dimethylimidazole is obtained as a photoproduct.

These data demonstrate that *N,N*-dialkylenaminonitriles are not photochemically converted to the corresponding imidazoles. The requirement of an N–H grouping on the enaminonitrile for imidazole formation to take place is consistent with either of the two mechanistic pathways in Scheme II. The absence of IR absorption at 2000 cm^{-1} for the ketenimine function (**10**) on irradiation of the *N,N*-dimethyl derivative **7** at −196 °C and the absence of imidazole formation from **7** as well is consistent with, but does not establish, pathway A

Scheme III



as the route from enaminonitriles to imidazoles.

Aminocyanocarbene as an Intermediate in Thermal and Photochemical Reactions. It was postulated that aminocyanocarbene (4) was formed as an intermediate in the photolysis of diaminomaleonitrile.[7] This postulate was based on the yellow color (370–460 nm) observed on photolysis of DAMN (1) in a rigid matrix at −196 °C. This yellow color disappeared when the matrix melted and UV absorption associated with DAMN increased in intensity. The yellow color was assumed to be due to aminocyanocarbene (4) which dimerized to DAMN on warming. A similar yellow color (350–460 nm, maximum at 393 nm), ascribed to aminocyanocarbene, was observed on irradiating the lithium salt of 1-cyanoformamide *p*-toluenesulfonylhydrazone.[9] This yellow color also disappeared on warming and DAMN, HCN, N_2, and a substance with properties of the HCN oligomers were detected in the photolysate.[9]

The postulated photodissociation of DAMN to aminocyanocarbene (4) greatly increases the number of mechanistic pathways possible from enaminonitriles to imidazoles. As noted by Becker et al.[7] aminocyanocarbene could exist as a transient in fluid solution. An interest in the mechanism of the photorearrangement of enaminonitriles prompted our investigation of the formation of aminocyanocarbene in fluid solution.

The formation of aminocyanocarbene in solution was investigated by the photolysis of *N*-isopropyldiaminomaleonitrile (11). If the photochemical formation of aminocyanocarbene (4) and its thermal recombination are significant reaction pathways then diaminomaleonitrile (1) and diaminofumaronitrile (2) as well as the corresponding diisopropyl derivatives (15 and 16) should be observed as reaction products on photolysis of 11 (Scheme III). The photolysate of a 10^{-3} M solution of 11 was analyzed for DAMN (1) but none could be detected. A 0.5% yield of DAMN was the limit of detection of our TLC analysis. The possibility of the sensitized photodestruction of DAMN by energy transfer was investigated by the addition of 1% DAMN to *N*-isopropyldiaminomaleonitrile (11). Half of the DAMN remained after irradiating this mixture for 2 h, indicating that photosensitized destruction of DAMN is not a significant reaction pathway.

The photoproducts of 11 were found to be *N*-isopropyldiaminofumaronitrile (12) and the isomeric imidazoles 13 and 14. The formation of approximately equal amounts of 13 and 14 is noteworthy. The *N*-isopropyl group exerts little effect on the course of the rearrangement. Neither AICN (3) nor 1,4-diisopropyl-4-aminoimidazole-5-carbonitrile (17) was detected as photoproducts of 11. A 1% yield of AICN would have been detected by TLC. The absence of these imidazole products is consistent with our earlier conclusions that carbenes which dimerize to give diaminomaleonitrile or related structures are not formed during the irradiation. An authentic sample of 17 was prepared by the photolysis of 15.

The structures of 13 and 14 were differentiated on the basis of the NMR chemical shift of the methine proton of the isopropyl group which is at lower field in 13 (4.0 ppm) than 14 (4.3 ppm). It would be expected that the imidazole ring current would deshield the methine hydrogen of the alkyl group attached to the heterocyclic nitrogen of 13 more than it would the methine of the aminoalkyl group of 14.[11] The observation of the conversion of 12 to both 13 and 14 and of the facile photolysis of 15 to 17 provides a useful synthetic route to a variety of N-substituted imidazoles. The starting materials are readily prepared from the corresponding *N*-alkyliminoacetonitriles.[10,14]

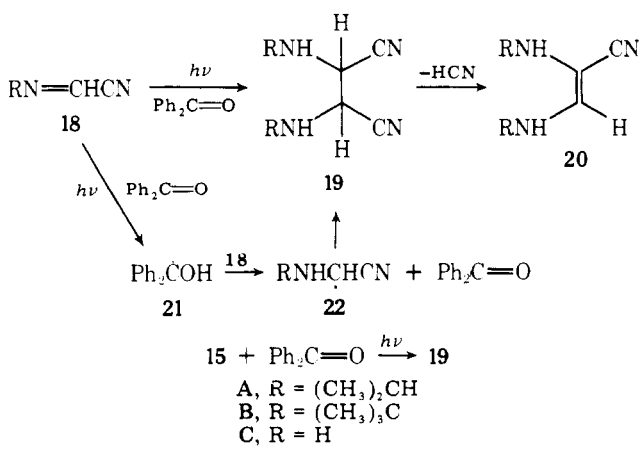
We attempted the synthesis of aminocyanocarbene derivatives by other routes so that we could investigate their possible role in the photorearrangement of enaminonitriles. The photolysis of *N*-alkyliminoacetonitriles (18) to the corresponding carbene was studied. Only polymer formation was observed on irradiation of 18A at 300 and 254 nm. Boyer et al.[15] independently observed similar results. Very little change was observed in the UV spectrum of 18A when it was irradiated at −196 °C and the spectrum was measured at that temperature. No UV absorption attributable to aminocyanocarbene (4) was detected.[7,9]

It is not clear from theoretical calculations whether the lowest energy form of aminocyanocarbene is the singlet or the triplet.[16] Consequently, we attempted the sensitized formation of the triplet carbene from *N*-alkyliminoacetonitriles. Small yields of the corresponding *N*-alkyldiaminosuccinonitriles 19A and 19B were obtained as reaction products in the benzophenone-sensitized photolysis of 18A and 18B. The structures of these unexpected photoproducts were established by spectral and analytical data. Further evidence for the assigned structures was the observation of the facile elimination of HCN when the compounds were dissolved in methanol as shown by the development of UV absorption in the vicinity of 265 nm characteristic of the enaminonitriles 20A and 20B.[3]

The formation of the diaminosuccinonitrile derivatives 19 was initially a surprising result since these compounds are formal reduction products of dimers from 18. This result may be understood if the first step in their formation is the abstraction of a hydrogen atom from the solvent[17] or the isopropyl methine or imidoyl group of 18A[18] by the benzophenone triplet with the formation of benzophenone ketyl radical (21) (Scheme IV). Radical 21 reacts with 18 to give a radical 22 which dimerizes to 19.[18] A similar dimerization of the dimethylaminocyanomethyl radical was recently reported.[19]

An alternative explanation for the formation of 19A is the photochemical reduction of diisopropyldiaminomaleonitrile (15) that was formed by the dimerization of isopropylaminocyanocarbene. This possibility was tested by the irradiation of benzophenone in the presence 15 (10^{-2} M) for 48 h. Virtu-

Scheme IV



15 + $Ph_2C{=}O$ $\xrightarrow{h\nu}$ 19

A, R = $(CH_3)_2CH$
B, R = $(CH_3)_3C$
C, R = H

ally quantitative recoveries of both benzophenone and **15** were obtained. If any of compound **19A** was formed it would have been in less than a 2% yield.

The products of the solution photochemistry of DAMN (**1**) or its alkyl derivatives **11** and **15** do not reflect the formation of aminocyanocarbene or its derivatives. There are three possible conclusions that may be drawn from these data:

(1) Aminocyanocarbene (**4**) is formed only at low temperatures in a rigid matrix but not in the solution phase at room temperature. This does not seem to be a reasonable postulate since photodissociation would be expected to proceed more efficiently at higher temperatures where there would be more thermal energy available for the postulated dissociation of the carbon–carbon double bond.

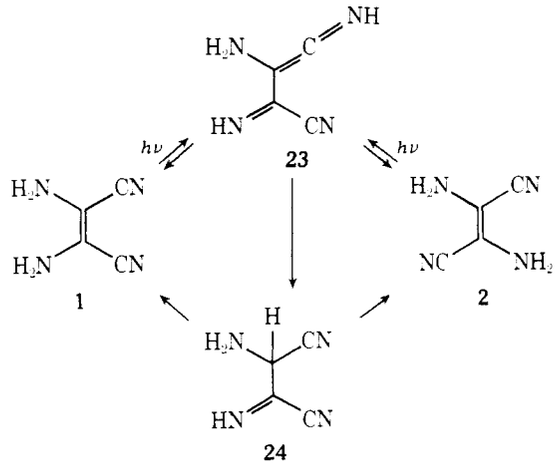
(2) Aminocyanocarbene (**4**) is formed at room temperature in the solution phase but it recombines so rapidly that it cannot be detected by the formation of "cross-over products" (e.g., the conversion of **11** to **1, 2, 15,** and **16**). This possibility was eliminated on the grounds that dimethylaminocyanocarbene does not undergo dimerization at all.[19] Consequently, a rapid dimerization of **4** would be very unlikely.

(3) Aminocyanocarbene (**4**) is not formed by the photolysis of DAMN (**1**) or its derivatives. We believe the experimental data support this view. The cornerstone of the identification of aminocyanocarbene as a DAMN photoproduct was its UV comparison with the photoproduct of the anion of 1-cyanoformamide tosylhydrazone, so this experiment must be considered first.[9] DAMN was isolated as a photoproduct of this anion and it was assumed that it was formed by the dimerization of aminocyanocarbene. After our experimental work was completed it was pointed out that dimerization of aminocyanocarbene is not a likely reaction pathway because of the coulombic repulsion resulting from the high electron density on the carbene carbon atom.[16,19] Since the photolysis of cyanoformamide tosylhydrazone anion probably generates a dimer of HCN, the more likely product is iminoacetonitrile (**18C**). Iminoacetonitrile has recently been identified as the product of the photolysis of azidoacetonitrile[15] in a reaction similar to the photolysis of 1-cyanoformamide anion in which aminocyanocarbene was claimed to be the photoproduct.[9] In addition, (a) iminoacetonitrile (**18C**) is calculated to be about 50 kcal more stable than the corresponding carbene (**4**), (b) structure **18C** would not give an ESR signal,[9] and (c) **18C** is known to react readily with HCN, another photoproduct of 1-cyanoformamide tosylhydrazone anion, to give DAMN and HCN oligomers.[10,20] The yellow coloration observed during the photolysis of the anion of cyanoformamide tosylhydrazone is more likely due to secondary processes unrelated to carbene formation.

Since it appears to be very unlikely that aminocyanocarbene is a photoproduct of the anion of 1-cyanoformamide tosylhydrazone, it follows that the identification of aminocyanocarbene as a photoproduct of DAMN, based on its synthesis from the tosyl anion, is incorrect. The only observation which remains to be explained is the initial decrease in UV absorption of DAMN on photolysis at −196 °C followed by an increase in its absorption on warming the matrix.[7] The decrease of DAMN was postulated to be due to its dissociation to aminocyanocarbene and its increase to the recombination of aminocyanocarbene moieties.[7] The latter is now considered to be an unlikely reaction pathway since this dimerization is not observed with (dimethylamino)cyanocarbene.[19] A more likely explanation of the photobleaching is the formation of ketenimine **23** or imino **24** tautomers of **1** and **2** (Scheme V) which would be stable at −196 °C but revert to DAMN on warming.[3] Ketenimine formation has been observed on the photolysis of other enaminonitriles at low temperatures.[3]

Aminocyanocarbene was initially proposed as an intermediate in the oligomerization of HCN.[9] However, this suggestion was negated by a large body of theoretical and experimental data which is consistent with *iminoacetonitrile* **18C** as the structure of the reactive intermediate.[10,16] The present work has shown that the two other reports of observation of this carbene are in error.[7,9] The only documented route to a carbene of this type is the formation of (dimethylamino)cyanocarbene by the thermolysis of (dimethylamino)maleonitrile.[19]

Scheme V



Experimental Section

Spectra were measured on the following instruments: UV, Unicam SP 800A; IR, Perkin-Elmer 137; NMR, Varian Model T-60; mass spectra, Hitachi Perkin-Elmer RMU6E. Photolyses were performed in a Rayonet Reactor fitted with lamps with their maximum output at 254, 300, or 350 nm. Thin-layer chromatography (TLC) was performed on silica gel using Eastman Chromagram sheets. The chromatograms were developed with benzene–CH_3OH (9:1), unless noted otherwise, and were visualized with UV light, I_2, or diazotized sulfanilic acid (DSA) reagent.[21] Column chromatography was performed on 40 g of silica gel in 24 in. × 1 in. glass columns. Solutions were degassed on a vacuum line by 3–6 freeze–pump–thaw cycles. DAMN was purchased from Terra-Marine Bioresearch and was purified either by sublimation or recrystallization from water. 3-(Dimethylamino)-*acrylonitrile* and 1,2-*dimethylimidazole* were used as received from Aldrich Chemical Co. Microanalyses were performed by Instranal Laboratory, Rensselaer, N.Y.

Photolysis of 2-(Dimethylamino)-1-cyclohexene-1-carbonitrile (7). A 3-mL 1.3×10^{-4} M solution of **7**[3] in methanol was irradiated with a 254-nm light source for 140 min at 5-min intervals. There was an 88% decrease in the absorption of **7** at 285 nm and a slight increase in the absorption below 210 nm, but the increase at 210 nm did not parallel the decrease at 285 nm.

Photolysis of 3-(Dimethylamino)acrylonitrile (5). An 8.32×10^{-5} M solution of **5** (3 mL) in doubly distilled water was irradiated with a 254-nm source for 118 min. There was no absorbance at 208 nm due to the formation of 1,2-dimethylimidazole (**6**). The limit of detection of **6** was determined by measuring its 208-nm absorbance in mixtures of **5** and **6** ranging from 0–17.8 mol % **6** when the concentration of **5** was 9.87×10^{-5} M and from 0–117.8 mol % **6** when the concentration of **5** was 1.47×10^{-5} M. In both series the limit of detection of **6** was 8.6×10^{-6} M. The photolyzed samples were concentrated, spotted on a TLC plate, and developed with $CHCl_3$–CH_3OH–NH_4OH 80:25:0.1.[6] No 1,2-dimethylimidazole was detectable under UV light or with I_2 vapor. A 6% yield of 1,2-dimethylimidazole could be detected by this procedure.

An 8.01×10^{-5} M solution (3 mL) of **5** in CH_3OH was irradiated with a 254-nm source. The absorbance decreased from 1.84 to 1.52 and shifted from 263 to 267 nm during the first 20 min. The absorbance remained unchanged during the next 98 min and decreased to 1.23 after 1546 min. There was no increase in absorption at 208 nm during the course of the photolysis. No 1,2-dimethylimidazole was detectable by TLC analysis using $CHCl_3$–CH_3OH–NH_4OH 80:25:0.1 as the developing solvent.[6] A 3-mL solution of a mixture 3-(dimethylamino)-acrylonitrile (**5**) and 1,2-dimethylimidazole in the same concentrations and proportions that were claimed to have formed as photoproducts[6] were chromatographed on the same TLC plate. Compound **5** was identified by its UV absorption while 1,2-dimethylimidazole gave a

readily detectable color with I_2 vapor.

Hydrolysis of 3-(Dimethylamino)acrylonitrile to 9. An 8.32×10^{-5} M aqueous solution of **5** was allowed to stand at room temperature for about 20 h. The maximum at 265 nm decreased from an absorbance of 1.76 to 1.12 (36%) with the development of a new absorption maximum at 311 nm. This new absorption maximum is similar to that reported for **9**.[8]

In a preparative experiment 250 mg of **5** was stirred in 7.5 mL of H_2O at 68 °C under an atmosphere of nitrogen for 3 days. The solution was cooled, diluted to 15 mL, acidified to pH 2.5, and extracted with ether. The brown ether layer was dried, boiled with charcoal for 1 min, and filtered. A solution of 0.5 M KOH in CH_3OH was added to the ether solution until no further precipitate formed and the solid was filtered and washed with ether. The solid was purified by dissolution in CH_3OH and reprecipitated by addition of ether. The light yellow solid was dried at 80 °C in vacuo for 5 min and identified as **9**: mp 260–262 °C (lit.[8] mp 259–261 °C); UV max (H_2O) 311 nm (lit.[8] 310 nm), (dilute HCl) 278 nm (lit.[8] 277 nm); the IR spectrum (KBr) was identical with those reported[8] for an authentic sample of **9** within ±10 cm^{-1}.

Photolysis of *N*-Isopropyldiaminomaleonitrile (11). (a) A 2×10^{-3} M solution of **11**[9] in 70 mL of CH_3OH was irradiated in a Pyrex vessel with a 300 nm-source for 26 h. The solution was concentrated to dryness and the residue washed with 5–30-mL portions of hexane. The starting material crystallized on concentrating the hexane and then the product (**12**) crystallized from the filtrate. This compound was further purified by three crystallizations from hexane; its structure was established as **12** by its UV max (CH_3OH) of 322 nm and a mass spectrum identical with that of **11**.[22] (b) A 3.33×10^{-3} M solution of **11** in 1 L of CH_3OH was photolyzed with a 350-nm light source for 63 h. The solvent was distilled and the residue chromatographed on silica gel. The starting material and **12** were eluted with benzene and benzene–$CHCl_3$ (1:3). Elution with $CHCl_3$–CH_3OH (99:1) yielded 30 mg of **13** as an oil: yellow color with DSA reagent; UV max (CH_3OH) 265, 227 (s), and 208 nm; ^1H NMR ($CDCl_3 + D_2O$) δ 1.5 (d, 6, 2 CH_3), 4.3 (p, 1, >CH), 7.2 (s, 1, =CH–). The tosylate salt was prepared by adding a solution of *p*-toluenesulfonic acid in ether dropwise to an ether solution of 15 mg of **13** until no further precipitate formed. The precipitate was filtered, washed with ether, and crystallized from $CHCl_3$ to give 24 mg of a white solid: mp 188–190 °C; IR(KBr) 3400, 3200, 2250, 1660 cm^{-1}; UV max (CH_3OH) 264 (ϵ 9.8×10^3), 223 nm (ϵ 1.56×10^4); ^1H NMR (D_2O) δ 1.5 (d, 6, CH_3), 2.4 (s, 3, CH_3), 7.6 (m, 4, phenyl), 8.4 (s, 1, =CH–) (the isopropyl methine proton was apparently masked by the HOD signal).

Anal. Calcd for $C_{14}H_{18}N_4SO_3$: C, 52.16; H, 5.63. Found: C, 52.25; H, 5.76.

Elution with $CHCl_3$–CH_3OH (96:4) yielded 25 mg of **14** as an oil which gave a red color with the DSA reagent: ^1H NMR ($CDCl_3$–D_2O) δ 1.35 (d, 6, 2 CH_3), 4.0 (p, 1, >CH), 7.4 (s, 1, =CH–). The tosylate salt was prepared as described for **13** and crystallized from CH_3OH–ether: mp 166–170 °C; UV max (CH_3OH) 255 (ϵ 1.04×10^4), 223 nm (ϵ 1.46×10^4); IR (KBr) 3500, 2232, 1637 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_4SO_3$: C, 52.16; H, 5.63. Found: C, 52.16; H, 5.99.

The original photolysate and the fractions obtained by column chromatography were carefully monitored by TLC using the DSA reagent to detect the presence of AICN (**3**). None could be detected when the photolyses were performed using 254-, 300-, and 350-nm light sources. A 5% yield would have been detected by the TLC procedures used.

Photolysis of *N*-Isopropyldiaminomaleonitrile (11) in the Presence of DAMN (1). A solution of 60 mg of **11** and 1 mg of **1** in 200 mL of CH_3OH was photolyzed with a 300-nm light source for 2 h. The solution was concentrated to 10 mL and 5 μL of this solution was applied to a TLC plate along with 5 μL of a solution of 1 mg of **1** in 10 mL of CH_3OH. The intensity of **1** in the photolysate was approximately half that of the standard.

Limit of Detection of DAMN (1). Varying amounts of stock solutions of **1** containing 0.055 and 0.0055 mg/mL were applied to TLC plates. The limit of detection using I_2 as the visualizing reagent was 10 μL of the 0.0055 mg/mL of solution. These data show that it would have been possible to detect a 0.15% yield of DAMN produced by the photolysis of *N*-isopropyldiaminomaleonitrile.

Photolysis of *N,N'*-Diisopropyldiaminomaleonitrile (15). A 2×10^{-3} M solution of **15** in 900 mL of CH_3OH was irradiated in a Pyrex vessel with a 350-nm light source for 43 h. The solution was concentrated to dryness and the residue chromatographed on silica gel. Elution with 1:1 benzene–petroleum ether gave 30 mg of *N,N*-diisopropyldiiminosuccinonitrile which was identified by direct comparison with an authentic sample (IR, ^1H NMR).[23] Elution with benzene gave starting material followed by 70 mg of **17**. Compound **17** was recrystallized from hexane: mp 90–92 °C; UV max (CH_3OH) 279 (ϵ 9.94×10^3), 230 (ϵ 4.92×10^3), 211 nm (ϵ 1.02×10^4); IR (KBr) 3325, 2200 cm^{-1}; ^1H NMR ($CDCl_3$–D_2O) δ 1.4 (d, 6, 2 CH_3), 1.6 (d, 6, 2 CH_3), 3.9 (p, 1, >CH), 4.3 (p, 1, >CH), 7.0 (s, 1, =CH–).

Photolyses of *N*-Isopropyliminoacetonitrile (18A). (a) A solution of 196 mg of **18A**[10] in 97 mL of hexane and 3 mL of CH_3OH in a Pyrex vessel was degassed and irradiated with a 300-nm light source for 4 h. Polymeric products were formed and no **15** was obtained. Similar results were obtained when a hexane solution of **18A** was irradiated with a 254-nm light source. (b) A 10^{-2} M solution of **18A** in 4:1 ethanol–methanol was cooled to a rigid glass at −196 °C and was irradiated for 30 min with a 300-nm light source. No change was observed when the UV was measured at −196 °C so the sample was irradiated with a 254-nm light for an additional 60 min. There was a slight increase in the UV absorption at 288 nm which may reflect syn/anti isomerism.[15] (c) A solution of 576 mg of **18A** and 910 mg of $Ph_2C{=}O$ in 120 mL of hexane was degassed and irradiated in Pyrex vessels with a 350-nm light source for 38 h. Benzpinacol started to precipitate from the reaction mixture after 24 h and 600 mg was filtered after 38 h. The filtrate was concentrated and chromatographed on silica gel. Elution with benzene–$CHCl_3$ gave 30 mg of **19A** after crystallization from hexane: mp 68–72 °C; UV max (CH_3CN) 204, (hexane) 202 nm (ϵ 835); IR (Nujol) 3400, 2257 (vw); ^1H NMR (CCl_4) δ 1.2 (overlapping doublets, 12, 4-CH_3), 1.8 (2, s, 2 NH, exchange with D_2O), 3.2 (m, 2, >CH–), 3.9 (s, 2, NCHCN).

Anal. Calcd for $C_{10}H_{18}N_4$: C, 61.82; H, 9.34; N, 28.84. Found: C, 61.92; H, 9.40; N, 28.71.

When the UV of **19A** was measured in CH_3OH an intense new band developed rapidly at 268 nm. The extinction coefficient of **20** was calculated as 1.8×10^4 on the basis of this absorption band. (d) When the photolysis described in (c) was repeated in benzene solution **19A** was obtained as a product but no benzpinacol was detected as a reaction product.

Photolysis of *N*-*tert*-Butyliminoacetonitrile (18B). A solution of 1100 mg of **18B**[14] and 960 mg of benzophenone in 200 mL of benzene was irradiated with a 350-nm light source in a Pyrex vessel for 36 h. The solution was concentrated and chromatographed on silica gel. Benzophenone was eluted with benzene–hexane mixtures and **19B** was eluted with benzene–$CHCl_3$ (3:1). Recrystallization of **19B** from hexane gave 25 mg of a white solid: mp 113–115 °C; UV max (hexane) 215 (ϵ 1061); ^1H NMR ($CDCl_3$) δ 1.2 (s, 18, $2(CH_3)_3C$), 1.6 (s, 2, NH), 3.7 (s, 2, NCHCN).[24]

Anal. Calcd for $C_{12}H_{22}N_4$: C, 64.86; H, 9.90; N, 25.20. Found: C, 64.93; H, 9.81; N, 24.91.

When the UV spectrum of this compound was measured in CH_3OH a new maximum formed at 263 nm which increased in intensity with time.

Attempted Benzophenone-Sensitized Photolysis of *N,N*-Diisopropyldiaminomaleonitrile (15). A solution of 192 mg of **15** (10^{-2} M) and 364 mg of benzophenone (1×10^{-2} M) was prepared in 100 mL of benzene and irradiated with a 350-nm source for 48 h. The photolysate was concentrated to 4 mL and chromatographed on a silica gel column. Elution with 120 mL of benzene gave a quantitative recovery of benzophenone. Elution with an additional 250 mL of benzene gave 180 mg of a material that was mainly **15**. That no **19A** was present in this fraction was established by dissolving 1 mg of this fraction in 10 mL of CH_3OH and measuring the UV spectrum immediately and after 24 h. If **19A** were present it would have been detected by the increasing UV absorption at 268 nm due to the formation of **20A**. No increase in absorption was observed at 268 nm due to the formation of **20A**. No increase in absorption was observed at 268 nm indicating the absence of **19A**. The limit of detection of **19A** is 7.8×10^{-6} M which is equivalent to a 2% yield in this reaction.

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Registry No.—**1**, 1187-42-4; **5**, 35520-40-2; **6**, 1739-84-0; **7**, 57090-87-6; **9**, 54585-04-5; **11**, 39148-03-3; **12**, 69177-92-0; **13**, 69177-93-1; **13** tosylate, 69177-94-2; **14**, 69177-95-3; **14** tosylate, 69177-96-4; **15**, 39480-13-2; **17**, 69177-97-5; **18A**, 39150-85-1; **18B**, 29553-20-6; **19A**, 69177-98-6; **19B**, 69177-99-7.

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Structures of Some Kepone Photoproducts and Related Chlorinated Pentacyclodecanes by Carbon-13 and Proton Nuclear Magnetic Resonance

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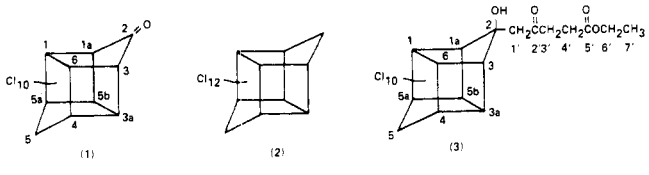
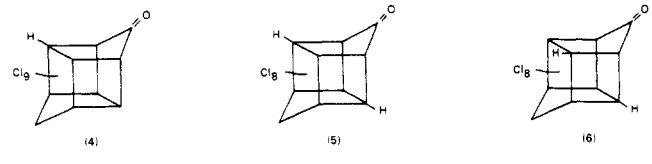
The pesticide Kepone, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one, the related compounds mirex, kelevan, a monohydro photoproduct of kelevan, kepone alcohol, kepone hydrate, and the mono- and dihydro photoproducts of Kepone hydrate in hydrocarbon solution were examined by ^{13}C and ^{1}H nuclear magnetic resonance (NMR). The Kepone photoproducts were isolated directly from the photolysis products for the first time. Their structures were determined unequivocally to be 1,1a,3,3a,4,5,5,5a,5b-nonachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one (monohydrokepone) and 1,1a,3,3a,4,5,5,5a-octachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one (dihydrokepone). The NMR data indicate that the major monohydro photoproduct of kelevan is that with the hydrogen substituent at the 3a or 5b position, anti to the OH substituent. In solution, Kepone can exist as a carbonyl form and as its hydrate, a *gem*-diol. These do not equilibrate at ambient temperatures on the NMR time scale. Without stringent drying, only the *gem*-diol forms of Kepone and its mono- and dihydro photoproducts are observed. Variable temperature ^{1}H NMR studies of monohydrokepone *gem*-diol indicated that it does not form intramolecular hydrogen bonds, but forms intermolecular hydrogen bonds to other monohydrokepone molecules and to water. This results in dimer formation, with a rapid monomer–dimer equilibrium and proton exchange between monomers, dimers, and water at ambient temperatures.

The severe environmental contamination by the pesticide Kepone, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one[16] (1), in late 1975 led to our intense involvement in studies of the chemistry of and analytical methods for this compound and its derivatives.





Kepone and the related pesticides mirex (2), dodecachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalene, and kelevan (3) have been the subject of several photochemical studies[1-6] performed to elucidate the mechanisms and products of the degradation of these compounds in the environment.[7]

Alley and his co-workers have photolyzed mirex, Kepone, and the dimethyl ketal of Kepone.[1,2] Using combined gas chromatography–mass spectrometry (GC–MS) and ^{1}H and ^{13}C nuclear magnetic resonance,[8] they characterized the photoproducts of mirex. Since they were unable to isolate the photoproducts of Kepone, the structures of these products were not fully determined. The GC–MS evidence did indicate only one possible structure for the monohydro photoproduct of Kepone (4), but two possible structures, 5 and 6, for the dihydro photoproduct.

To characterize the photolysis products of Kepone and to investigate means of synthesis of the photodegradation products for use in toxicological studies, we carried out a number of photolyses of pure Kepone, as its hydrate in hydrocarbon solution. The two major photoproducts, monohydrokepone and dihydrokepone, were isolated as their hydrates, and their structures were determined by GC–MS and ^{1}H and ^{13}C NMR.[9] Details of the isolation of the photoprod-