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Free-Radical Cyanation. Novel Free-Radical Reaction of Methyl Cyanofornate or Cyanogen with 2,4-Dimethylpentane

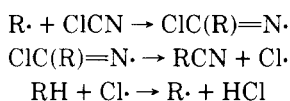
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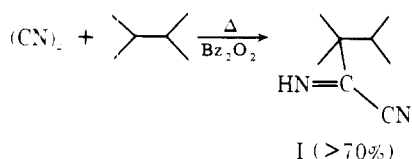
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The peroxide-initiated free-radical chain cyanation of several hydrocarbons with methyl cyanofornate has been observed. The reaction is proposed to proceed through the intermediacy of an iminyl radical formed from the addition of an alkyl radical to the carbon-nitrogen triple bond. The resulting iminyl radical undergoes β -scission to form the alkyl cyanide (>70%), carbon dioxide, and a methyl radical which subsequently carries the chain. Only traces of products possibly arising from carbonyl addition were observed. The peroxide promoted reaction of the reagent with 2,4-dimethylpentane yielded only minor amounts of the three possible cyanides (20%), but gave as the major product in 55% yield the difunctionalized cyclic hydrocarbon, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene. The reaction pathway for the formation of the cyclized product proceeds by addition of the first formed tertiary alkyl radical to the cyano triple bond to form the iminyl radical, the same radical used to rationalize the chain cyanation; internal hydrogen abstraction by the iminyl radical formed from this addition (six-membered ring transition state), followed by addition of the new tertiary radical to the nitrogen of the imine double bond (five-membered ring transition state) and disproportionation of the new radical to yield the difunctionalized cyclic product in a nonchain process. Consistent with this mechanism was the observation that a modest yield (22%) of difunctionalized cyclic product, 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene, was formed by the nonchain reaction of cyanogen with 2,4-dimethylpentane.

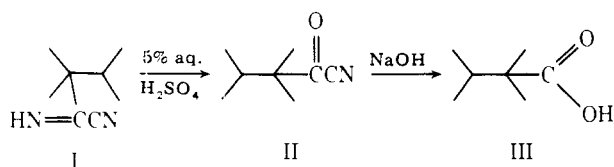
Cyanogen chloride was shown to undergo an initiated free-radical chain cyanation reaction with a variety of hydrocarbon substrates.¹



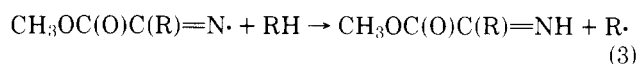
In the course of this investigation we reported that cyanogen underwent an initiated chain reaction with 2,3-dimethylbutane to give an exceptionally high yield of a single substitution product, I. The iminocyanide (I) could be quantitatively



converted by hydrolysis to its acyl cyanide (II) or its carboxylic acid (III).

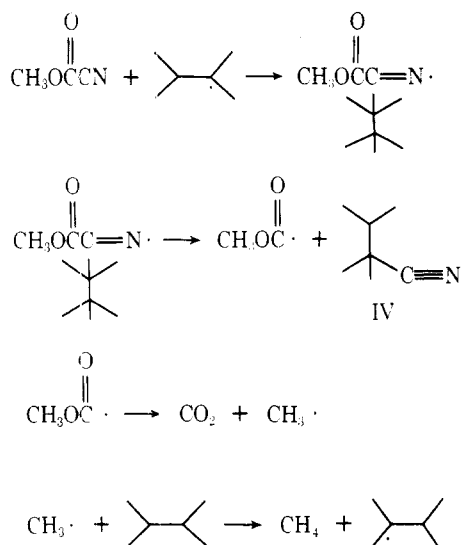


The selective homologation of a hydrocarbon by one or two functionalized carbon atoms has some potential synthetic utility. The cyanation reaction with cyanogen chloride was successful, but unfortunately the reaction with cyanogen failed when tried with a large number of other substrates.² In an attempt to find yet another cyanating reagent (sequence 1, 2, 4) or to find a general method to synthesize the intermediate acyl cyanide (via carbonyl addition- β -scission) or its hydrolytate, the keto acid, in mechanistically analogous manners (sequence 1-3 followed by hydrolysis) the reactions of a number of hydrocarbons with methyl cyanofornate were attempted.



Results and Discussion

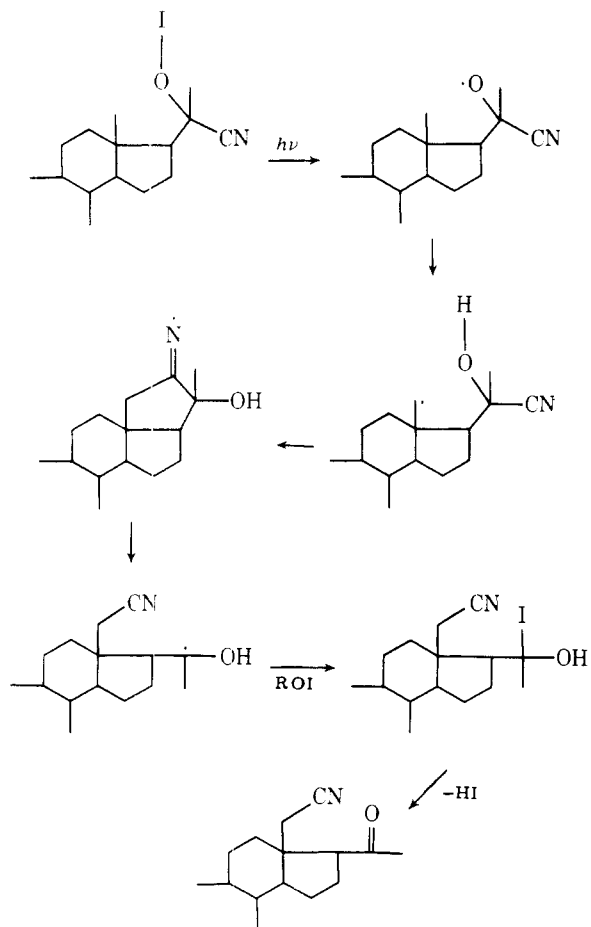
Solutions of methyl cyanofornate (0.235 M) and benzoyl peroxide (10-24 mol %) in 2,3-dimethylbutane were heated in sealed degassed reaction tubes at 99 °C for 5.5 h. One major product was detected (GLC) which resulted from the reaction of methyl cyanofornate and 2,3-dimethylbutane, α,α,β -trimethylbutyronitrile (IV). The product appears to be formed by a short chain process, since an optimum yield (77%) was



obtained, at 89% conversion, when 24 mol % of benzoyl peroxide was used. Accompanying the cyanide a 35–40% yield of methane could be isolated. GLC-mass spectrometry of the reaction mixture showed the presence of a number of higher boiling minor products, two of which (3.7%) could be rationalized as having a molecular formula of $\text{C}_9\text{H}_{15}\text{O}_2\text{N}$, a 1:1 addition product of 2,3-dimethylbutane and methyl cyanofornate.

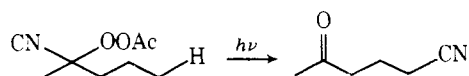
In the same manner cyclohexane yielded cyclohexyl cyanide (72%) and 37–40% of methane when 24 mol % of benzoyl peroxide was used. A 35% yield of cyclohexyl cyanide was likewise obtained using 10 mol % of benzoyl peroxide.

Reactions involving free-radical addition to the cyanide triple bond have been demonstrated in a number of cases involving both intramolecular and intermolecular reactions. The



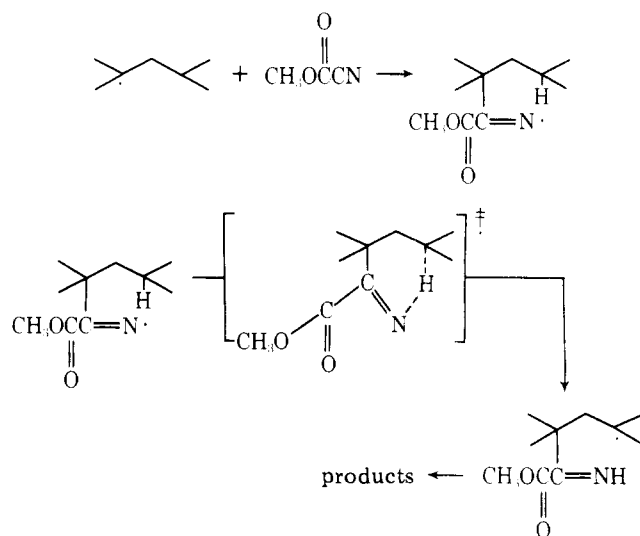
cyanation reactions of cyanogen chloride¹ and bromide³ are examples of intermolecular addition- β -scission reactions, while the chain propagation steps proposed for the reactions of alkyl radicals with cyanogen are a sequence involving addition followed by hydrogen abstraction.¹

Intramolecular rearrangements occurring via an iminyl radical intermediate generated from the addition of an alkyl radical to an adjacent cyanide group have been reported by Heusler and Kalvoda.^{4,5} The mechanism proposed to explain the products formed suggested that an alkoxy radical, generated photochemically from the hypiodite, abstracted an adjacent hydrogen in a six-membered ring transition state and that the intermediate iminyl radical was formed via the formation of a five-membered ring transition state. A similar reaction has recently been observed during the photolytic rearrangement of a number of α -peracetoxy nitriles to ketonitriles.^{6,7}



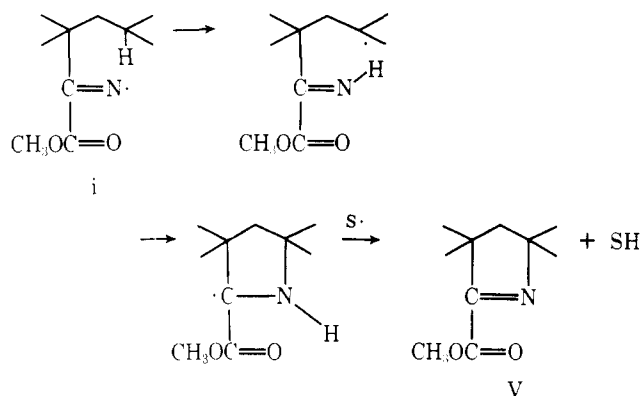
The reactions of the two substrates, cyclohexane and 2,3-dimethylbutane, with methyl cyanofornate yielded products which could be rationalized by the addition of the radical to the cyanide triple bond, followed by β -scission; no products derived from carbonyl addition were isolated, although in the case of the reaction of 2,3-dimethylbutane two minor products, $\text{C}_9\text{H}_{15}\text{O}_2\text{N}$ (3.7%), were detected (GLC-MS) which could conceivably be rationalized as carbonyl addition products.

The cyanation reactions of the cyanogen halides and methyl cyanofornate and the reaction of 2,3-dimethylbutane with cyanogen¹ have all been proposed to proceed via radical addition to cyanide; in the latter reaction the iminyl radical formed, instead of undergoing a β -scission, abstracted a tertiary hydrogen to continue the chain. In an attempt to observe the combination of both addition and abstraction by the intermediate proposed for the cyanation reactions of methyl cyanofornate, the reaction of the reagent with 2,4-dimethylpentane was carried out. Since the reaction of the alkane, 2,3-dimethylbutane, with the reagent leads to addition, followed by β -scission, it was hoped that if the tertiary hydrogen



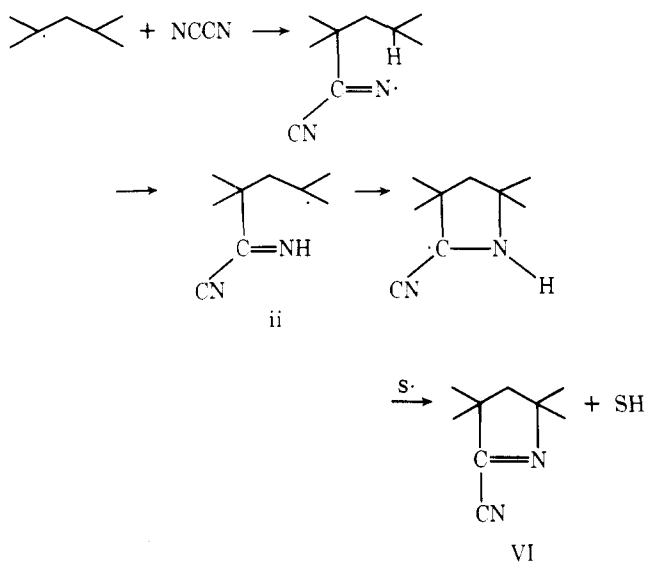
was made more favorably disposed toward abstraction (internal abstraction) that this pathway could be observed. In accord with this prediction the reaction yielded 2,4-difunctionalized products. The reaction of (0.9 M) methyl cyanofornate and benzoyl peroxide (48 mol %) in 2,4-dimethylpentane yielded, in addition to small amounts of primary (6%), secondary (12%), and tertiary (2%) cyanides, a heterocyclic ester, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene

(V, 55%). The formation of the heterocyclic ester can be rationalized by a mechanism utilizing a unique but simple sequence of reactions which occur subsequent to the formation of the iminyl radical (i).



Internal abstraction of the iminyl radical forms a new tertiary radical which is in position to add to the nitrogen of the imine double bond in a five-membered ring transition state. The new carbon-centered radical would be relatively stable, being adjacent to both the nitrogen and the ester carbonyl, and would eventually disproportionate to form the heterocycle V.

Since a cyanide addition-abstraction sequence has been shown to proceed in the reactions of cyanogen with 2,3-dimethylbutane¹ and since the reaction of 2,4-dimethylpentane and methyl cyanoformate is now proposed to proceed through a cyanide addition-internal abstraction reaction followed by another internal addition, the reaction of cyanogen with 2,4-dimethylpentane might be expected to produce a 2,4-difunctionalized cyclic product in the same manner. The intermediate radical (ii) would then be in a favorable steric ar-



angement to add internally to the adjacent imine in a five-membered ring transition state to form, as previously proposed, a carbon-centered radical which is stabilized by its adjacent groups, in this instance nitrogen and cyano groups. The stabilized radical upon disproportionation would yield the cyclized product. As predicted, when a mixture of 2,4-dimethylpentane (2 mL) and cyanogen (6.1×10^{-4} mol, 0.30 M) were allowed to react with benzoyl peroxide (105 mol %) a 22% yield of 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene (VI) was obtained. Since the disproportionation reaction is a chain-termination step it is not surprising that a chain sequence was not observed and that only this modest yield was obtained.

Experimental Section

Materials. The hydrocarbons 2,3-dimethylbutane (>99.88%), 2,4-dimethylpentane (>99.72%), and cyclohexane (>99.5%, Phillips research grade) were used without further purification.

Methyl cyanoformate was prepared according to the method of Childs and Weber:⁸ bp 92–94 °C (690 mm) [lit.⁸ bp 95–96 °C (760 mm)]; n_{25}^{D} 1.3712. The IR and NMR spectra were identical with those reported.

Cyanogen (Matheson Co., Inc.) was distilled before use.

Reaction of Methyl Cyanoformate with 2,3-Dimethylbutane.

A mixture of methyl cyanoformate (200 mg, 2.35 mmol) and benzoyl peroxide (137 mg, 0.566 mmol) in 2,3-dimethylbutane (10 mL, 77 mmol) was placed in a Pyrex ampule, degassed, and thermostated at 99 °C for 5.5 h. The reaction mixture was subjected to GLC analysis (8 ft \times $\frac{1}{8}$ in., 5% UCON polar, 50 HB, 2000 on Chromosorb W, 45–200 °C). The analysis showed three major fractions: a low-boiling fraction containing 2,3-dimethylbutane, benzene, and unreacted methyl cyanoformate (11%); a middle fraction containing a single compound, and a high boiling fraction containing a large number of compounds which were not identified. The middle fraction was isolated by preparative GLC and shown to be α,α,β -trimethylbutyronitrile (77%). The structure of the nitrile was assigned by a comparison of its IR and NMR spectrum with those of an authentic sample.¹

Methane was fractionated, measured using a Toepler pump by conventional vacuum line techniques, and was identified and its purity checked by comparing its GLC retention time and mass spectrum with those of an authentic sample.

Reaction of Methyl Cyanoformate with Cyclohexane. A mixture of methyl cyanoformate (200 mg, 2.35 mmol) and benzoyl peroxide (137 mg, 0.57 mmol) in cyclohexane (10 mL, 93 mmol) was placed in a Pyrex ampule and the reaction was carried out and analyzed as was the reaction using 2,3-dimethylbutane. GLC analysis showed 7% of unreacted methyl cyanoformate. The middle fraction from this reaction was a single component, cyclohexyl cyanide (72%). The structure of this nitrile was assigned by a comparison of its IR and NMR spectrum with those of an authentic sample.

Reaction of Methyl Cyanoformate with 2,4-Dimethylpentane.

A mixture of methyl cyanoformate (114 mg, 1.34 mmol) and benzoyl peroxide (654 mg, 2.70 mmol) in 2,4-dimethylpentane (2 mL, 13.4 mmol) was placed in a Pyrex ampule, degassed, and sealed. The ampule was thermostated at 99 °C for 9 h and opened and the reaction mixture was analyzed by GLC (8 ft \times $\frac{1}{8}$ in., 7% SE-30 on Chromosorb W, 110 °C). The analysis showed three major fractions. A low-boiling fraction contained unreacted 2,4-dimethylpentane, benzene, and three other compounds identified as 2,2,4-trimethylpentanonitrile (2%), 2-isopropylisopentanitrile (12%), and 3,5-dimethylhexanonitrile (6%) (in order of their elution). The middle fraction was composed of a single compound, 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene (55%). The high boiling fraction contained a large number of compounds which were not identified.

The three cyanides (primary/secondary/tertiary) were collected as a mixture by preparative GLC (10 ft \times $\frac{1}{4}$ in., 10% SE-30 on Chromosorb W). An elemental analysis of this sample showed it to be a pure mixture of the three nitriles. Anal. Calcd for $C_6H_{15}N$: C, 76.45; H, 12.07; N, 11.18. Found: C, 76.75; H, 12.23; N, 10.94. The mixture could be separated and collected individually by preparative GLC and their structures were assigned on the basis of their IR and NMR spectra.

2,2,4-Trimethylpentanonitrile: NMR ($CDCl_3$) δ 1.02 (d, J = 6 Hz, 6 H), 1.36 (s, 6 H), 1.42 (d, J = 6 Hz, 2 H), 1.82 (m, J = 6 Hz, 7 H); IR (CH_2Cl_2) ν 2230 cm^{-1} ($C\equiv N$).

2-Isopropylisopentanitrile: NMR ($CDCl_3$) δ 1.0 (d, J = 6 Hz, 6 H), 1.06 (d, J = 6 Hz, 6 H), 1.92 (m, J = 6 Hz, 3 H); IR ($CHCl_3$) ν 2220 cm^{-1} ($C\equiv N$).

3,5-Dimethylhexanonitrile: IR ($CHCl_3$) ν 2225 cm^{-1} . The NMR sample appeared to be admixed with the other isomers and the spectrum could not be analyzed, although it was consistent with the assigned structure. However, the microanalysis of the mixture and the identification of the other two possible isomers allowed its assignment.

The structure of 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene, collected by preparative GLC (SE-30 column), was assigned on the basis of its microanalysis, its mass spectrum, and its IR and NMR (^{13}C and 1H) spectrum: IR (CH_2Cl_2) ν 1735 ($-CO_2CH_3$), 1622 cm^{-1} ($-C=N-$); mass spectrum m/e 183 (M^+ , 11.9%), 168 ($M^+ - 15$, 63.5%), 127 ($M^+ - 56$, 24%), 124 ($M^+ - 59$, 19.1%), 42 ($M^+ - 141$, 100%); NMR ($CDCl_3$) chemical shifts, multiplicity, and assignments are given in Figure 1 for both the 1H and ^{13}C spectrum. Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.28. Found: C, 65.46; H, 9.20.

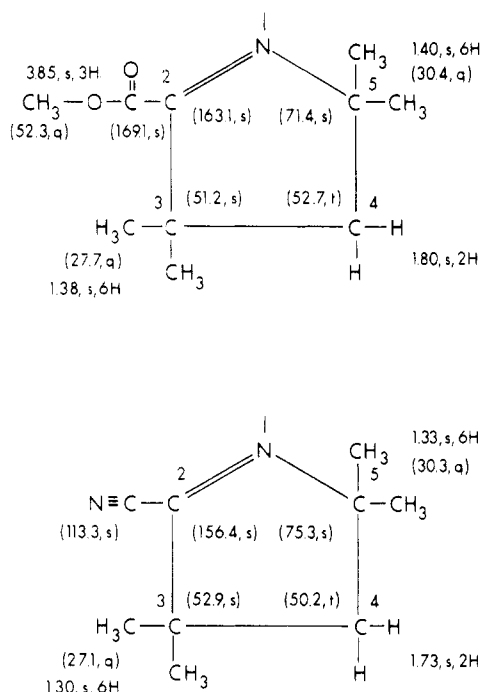


Figure 1. NMR spectral assignments for compounds V and VI. Chemical shifts and multiplicities for ^1H spectra δ downfield from Me_4Si , ^{13}C spectral assignments (parenthesis) ppm downfield from Me_4Si .

The mass spectrum and elemental analysis of V clearly established its molecular formula to be $\text{C}_{10}\text{H}_{17}\text{NO}_2$. The ^1H NMR showed two sets of chemically nonequivalent methyl groups, one pair of methylene protons, and one set of protons assignable to the absorption for a methyl ester. The ^{13}C NMR and IR spectra allow the assignment of the structure given in Figure 1. The chemical shift of the ester carbonyl (169.1 ppm) agrees with its IR absorption (1735 cm^{-1}), while the C-2 absorption can only be a doubly bonded carbon and is in agreement with its assignment as an iminyl carbon whose IR absorption appears at 1622 cm^{-1} . The C-4 ^{13}C chemical shift is that of a methylene group flanked by two tertiary carbon atoms, and its absorption was inconsistent with any other structural arrangement that could be drawn. With these partial structural features the only structure that can be assigned for V was 2-carbomethoxy-3,3,5,5-tetramethylazacyclopent-1-ene.

Reactions run using various amounts (50–200 mol %) of benzoyl peroxide gave the optimum yields of the above four products under the above conditions.

The Reaction of 2,4-Dimethylpentane with Cyanogen. A mixture of cyanogen (0.61 mmol, 0.305 M) and benzoyl peroxide (155 mg, 0.64 mmol, 0.32 M) in 2,4-dimethylpentane (2 mL, 13.4 mmol) was placed in a Pyrex ampule, degassed, sealed, and heated at 98°C for 3 h. After heating the reaction ampule contained a light brown supernatant solution and a dark brown polymeric material (presumably polymeric cyanogen⁹).

Analysis of the supernatant liquid by GLC showed three major fractions: a low boiling fraction containing unreacted 2,4-dimethylpentane and benzene (identical GLC retention times with those of the authentic materials), a middle fraction containing a single compound, and a high boiling fraction containing a large number of compounds which were not identified. The middle fraction was isolated by preparative GLC and shown to be 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene (22%). The structure of this compound was

assigned on the basis of its IR, NMR (^1H and ^{13}C) and mass spectrum and its elemental analysis: IR (CH_2Cl_2) ν 2240 (CN, very weak), 1620 cm^{-1} ($-\text{C}=\text{N}-$). NMR (CDCl_3), see Figure 1 for ^1H and ^{13}C spectral assignments. The mass spectrum of VI showed M^+ , $\text{M}^+ - 1$, $\text{M}^+ - 15$ peaks: m/e 150.1152 (8.4%), calcd for $\text{C}_9\text{H}_{14}\text{N}_2^+$, 150.1157; 149.1075 (5.5%), calcd for $\text{C}_9\text{H}_{13}\text{N}_2^+$, 149.1079; 135.0923 (100%), calcd for $\text{C}_8\text{H}_{11}\text{N}_2^+$, 135.0922. Anal. Calcd for $\text{C}_9\text{H}_{14}\text{N}_2$: C, 71.95; H, 9.39. Found: C, 71.72; H, 9.30.

The mass spectrum and elemental analysis of VI clearly established its molecular formula to be $\text{C}_9\text{H}_{14}\text{N}_2$. The ^1H NMR shows that there are two sets of chemically nonequivalent methyl groups and one pair of methylene protons. The ^{13}C NMR and IR spectra along with the above information allows the assignment of the structure given in Figure 1. The chemical shift of the nitrile carbon (113.3 ppm) agrees with its IR absorption (2240 cm^{-1}), while the remaining nitrogen double bonded to carbon C-2 influences the chemical shift of that carbon to appear at 156.4 ppm. The IR absorption of the iminyl group at 1620 cm^{-1} supports this structural assignment. The C-4 ^{13}C chemical shift is that of a methylene group flanked by two tertiary carbon atoms and its absorption was inconsistent with any other structural arrangement that could be drawn. With these partial structural features the only structure that can be assigned for VI was 2-cyano-3,3,5,5-tetramethylazacyclopent-1-ene.

Reactions run using varying amounts (30–155 mol %) of benzoyl peroxide gave the optimum yield of dinitrile under the above conditions.

Nuclear Magnetic Resonance Spectra. The ^1H NMR spectra were determined on a Varian HA-100 spectrometer fitted with a Digilab FTS/NMR-3 data system.

The ^{13}C NMR spectra were determined on natural abundance samples at 22.628 MHz (Bruker HFX-90) or at 15.08 MHz (Bruker WP-60) in 10-mm sample tubes. $\text{Cr}(\text{acac})_3$ was added to reduce the relatively long relaxation time of the $-\text{C}\equiv\text{N}$ carbon.

Mass Spectra. Mass spectra were determined using an AEI MS-12 mass spectrometer attached to a gas chromatograph (Varian 1400), and coupled to a computer data system (Nova-3) with program DS-50. The high-resolution mass spectra were obtained using an AEI MS-50 mass spectrograph (70 eV), which was likewise coupled to the Nova-3 data handling computer.

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Registry No.—IV, 26154-43-8; V, 69462-08-4; VI, 69462-09-5; methyl cyanofornate, 17640-15-2; 2,3-dimethylbutane, 79-29-8; cyclohexane, 110-82-7; cyclohexyl cyanide, 766-05-2; 2,4-dimethylpentane, 108-08-7; 2,2,4-trimethylpentanonitrile, 69462-10-8; 2-isopropylisopentanonitrile, 62391-96-2; 3,5-dimethylhexanonitrile, 69462-11-9; cyanogen, 460-19-5.

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