$(pz)_4]_2$, $Co[H_2B(pz)_2]_2$, and $Co[HB(pz)_3]_2$. The rotating platinum electrode *vs.* sce was used for $Fe[HB(pz)_3]_2$ and $Fe[B(pz)_4]_2$.

Both $Cu[H_2B(pz)_2]_2$ and $Cu[B(pz)_4]_2$ were found to undergo reversible one-electron reduction at about $\epsilon_{1/2} = 0.29$ v. The cobalt compounds, $Co[H_2B(pz)_2]_2$ and $Co[HB(pz)_3]_2$, were oxidized (one electron) at +0.2 and −0.09 v, respectively. $Co[HB(pz)_3]_2$ underwent a two-electron reduction at −2.13 v, while its Fe(II) counterpart could not be reduced in the +0.34- to −2.75-v range. $Fe[HB(pz)_3]_2$ and $Fe[B(pz)_4]_2$ underwent one-electron oxidation at +0.27 and 0.37 v, respectively.

Acknowledgment. The author wishes to thank Miss Lucille E. Williams who carried out the polarographic studies.

Cyanonitrene. Reaction with Saturated Hydrocarbons[1]

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Abstract: Cyanonitrene was generated thermally from cyanogen azide, and its intermediacy in reactions with saturated hydrocarbons was established by means of isotopic labeling. The nitrene exhibits pronounced selectivity in insertions into C–H bonds, which in the absence of a solvent occur in a stereospecific manner. Mechanisms are discussed.

In contrast to the well-documented chemistry of carbenes,[3] their nitrogen counterparts (nitrenes)[4] have received serious attention by organic chemists only recently.[5] In 1962, Barton and Morgan[6] reported the first examples of intramolecular C–H insertions[7] of alkylnitrenes to afford either five- or three-membered rings, and Lwowski and Mattingly[8] presented the first case of an intermolecular insertion[7] in the reaction of carbethoxynitrene with cyclohexane.

The recent synthesis of cyanogen azide (N_3CN)[9] has provided a direct route for the generation of the highly symmetrical molecule NCN, "cyanonitrene." In the present paper we report on the thermal generation of NCN and on the mechanism of its reactions with saturated hydrocarbons.

Results and Discussion

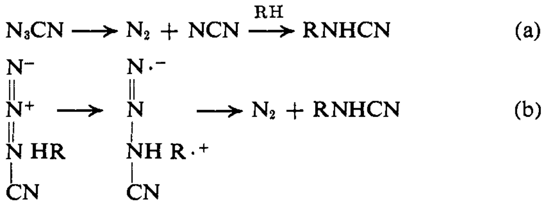
Unlike most organic azides which require temperatures in excess of 100° for fragmentation to the corresponding nitrenes,[4] cyanogen azide smoothly evolves nitrogen when heated to 40–50°. Kinetics have not been studied in detail but the rate of nitrogen evolution appears to be first order in dilute solutions. In addition the rate of nitrogen evolution depends on the polarity of the solvent employed, being more rapid in nonpolar media (hydrocarbons) than in polar media (ethyl acetate, acetonitrile). These facts are consistent with unimolecular fragmentation of the highly polar azide to two nonpolar species. When the decomposition of the azide is conducted in a paraffinic hydrocarbon, alkylcyanamides **1** are formed in yields of 55–70%.

$$N_3CN + RH \xrightarrow[40\text{–}50^\circ]{} N_2 + \underset{\mathbf{1}}{RNHCN}$$

For example, thermolysis of a 1% solution of N_3CN[10] in cyclohexane at 50° afforded cyclohexylcyanamide (**1**, R = C_6H_{11}) in 57% yield. The product showed strong infrared absorption at 3200 (NH) and 2210 (C≡N) and nmr signals at τ 4.3 (doublet, 1 H), 7.0 (multiplet, 1 H), and 7.9–9.0 (multiplet, 10 H); cyclohexylcyanamide was characterized by hydrolysis to cyclohexylurea on boiling with 10% sulfuric acid.

Isotopic Labeling Experiments. In photolytic or thermolytic reactions of azides with saturated hydrocarbons to yield insertion products, a likely mechanism involves unimolecular fragmentation of the azide to the corresponding nitrene and nitrogen followed by insertion[7] of the nitrene into C–H bonds. Although this is the most reasonable sequence of events, there usually is no unequivocal experimental evidence excluding an alternative mechanism in which the azide itself reacts with the hydrocarbon. The two possible mechanisms are depicted in Scheme I.[11]

Scheme I



$$N_3CN \longrightarrow N_2 + NCN \xrightarrow{RH} RNHCN \qquad (a)$$

$$\begin{array}{l} N^- \\ \| \\ N^+ \\ \| \\ N\ HR \\ | \\ CN \end{array} \longrightarrow \begin{array}{l} N\cdot^- \\ \| \\ N \\ | \\ NH\ R\cdot^+ \\ | \\ CN \end{array} \longrightarrow N_2 + RNHCN \qquad (b)$$

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[1] This work was described in preliminary form: A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *J. Am. Chem. Soc.*, **87**, 2296 (1965).

[2] To whom inquiries may be addressed at the Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210.

[3] For an excellent account see W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

[4] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[5] The term nitrene is used here to indicate a monovalent nitrogen species which adds to double bonds and inserts into C–H bonds.

[6] D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962). See, however, D. H. R. Barton and A. N. Starratt, *J. Chem. Soc.*, 2444 (1965).

[7] The term insertion is used here to indicate end result rather than mechanistic detail.

[8] W. Lwowski and T. W. Mattingly, Jr., *Tetrahedron Letters*, 277 (1962).

[9] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

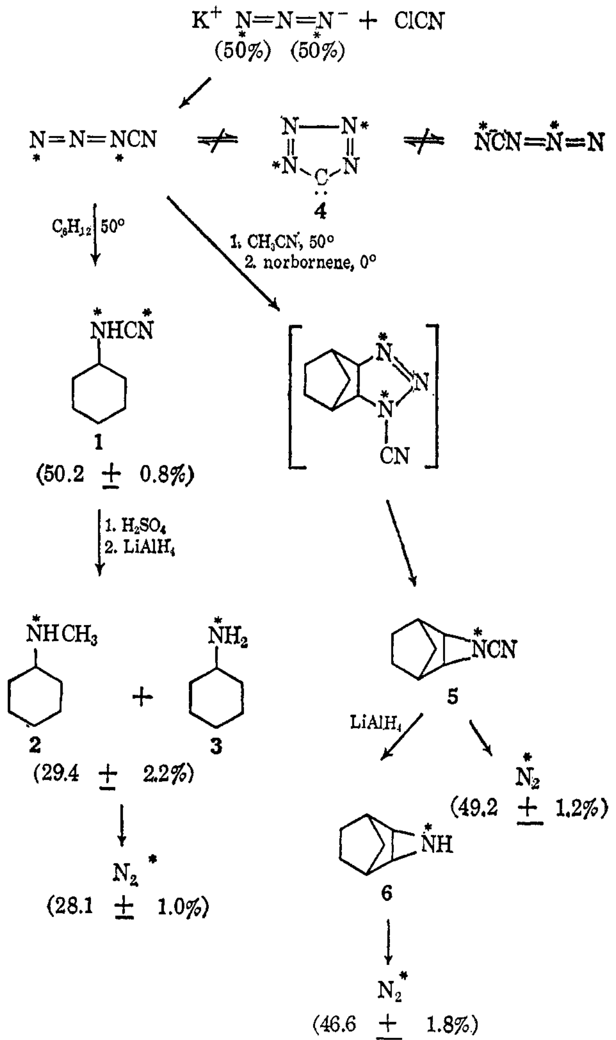
[10] This experiment was first carried out by Dr. F. D. Marsh.

[11] In Scheme Ib the dipolar intermediate is supposed to be associated with singlet N_3CN and the diradical species with triplet N_3CN. Thus, abstraction of hydrogen might occur as either hydride ion or as a hydrogen atom.

An umambiguous distinction between paths a and b should be possible in principle by isotopic labeling experiments. Theory suggests that the lowest singlet and triplet states of NCN are linear. Symmetry demands that the two nitrogen atoms of NCN are equivalent, whereas no such equivalence can be achieved in path b. To elucidate this point we studied the insertion reaction employing appropriately labeled N_3CN.

The procedure used is shown in Scheme II. The degree of isotopic enrichment at the various stages was determined mass spectrometrically employing the natural abundances of the same materials prepared in parallel experiments but starting with unenriched potassium azide. The results of these experiments are clearly consistent with the intermediacy of *free* cyanonitrene in which the two nitrogen atoms are chemically indistinguishable.[12] The possibility that scrambling of the label occurs prior to decomposition of the azide, perhaps through a rapid prereaction equilibrium between a cyclic form **4** and two equivalent but differently tagged linear forms of N_3CN, was tested by allowing the azide to decompose partially in acetonitrile and then adding norbornene.[9] The virtual identity of the amount of label in **5** and its subsequent hydrolysis product **6** precludes the occurrence of any significant prereaction scrambling.

Scheme II



Electronic Structure of NCN. Cyanonitrene has ten bonding electrons. Simple valence theory predicts the lowest energy electronic configuration for cylindrically symmetrical NCN to be $\ldots 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 1\pi_g^2$, where π_g^2 could be $\pi_g^2(x)$, $\pi_g^2(y)$, or $\pi_g^1(x)\pi_g^1(y)$. Therefore, we have a situation where two electrons have to be distributed among two degenerate molecular orbitals. According to multiplet theory such an arrangement should give rise to one triplet and three singlet states: ${}^3\Sigma_g^-$, ${}^1\Sigma_g^+[\ldots \pi_g^1(x)\pi_g^1(y)]$; and two ${}^1\Delta_g[\ldots \pi_g^2(x)$ and $\ldots \pi_g^2(y)]$. Electron repulsion considerations suggest that the triplet should be lowest in energy and hence represent the ground state.

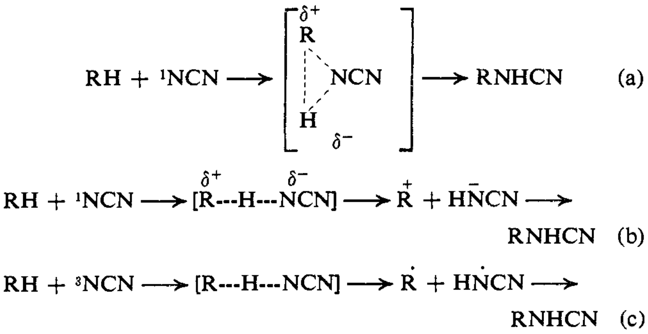
Theory was verified by a number of recent spectroscopic studies involving flash photolysis,[13,14] electron paramagnetic resonance,[15] and matrix isolation[16] experiments. The results of all these investigations point strongly to ${}^3\Sigma_g^-$ as the ground state. Support for this conclusion was also provided recently by flash photolysis experiments in which N_3CN was photolyzed in the absence of an inert gas diluent.[17] Under these conditions the originally observed species was the ${}^1\Delta_g$ singlet which decayed to ${}^3\Sigma_g^-$ at a measurable rate. Further information concerning the structure of NCN derives from a vibrational analysis[13] of its ultraviolet spectrum which afforded a carbon–nitrogen distance very close to that of a C=N bond, suggesting structure **7** as a good representation for the ground state.

$$\cdot N{=}C{=}N\cdot$$

7

Selectivity of the Insertion Reaction. The mild conditions employed in the present work for the generation of NCN suggest that it is produced in a low-energy electronic state. It is reasonable to assume that reacting NCN would be in the lowest electronic state of a given multiplicity, since radiationless decay is usually extremely rapid compared to diffusion. Hence, only the ${}^3\Sigma_g^-$, ${}^1\Sigma_g^+$, and ${}^1\Delta_g$ states need concern us here. For these low-lying states the three distinct modes of reaction shown in Scheme III are formally possible.[18]

Scheme III



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[12] The small excess label in amines **2** and **3** (28.7% ^{15}N instead of the theoretical value of 25.0%) is probably at least partly due to an isotopic bias of the insertion, *i.e.*, a slight preference of the ^{15}N site over the ^{14}N site of NCN to undergo reaction.

(13) G. Herzberg and D. N. Travis, *Can. J. Phys.*, **42**, 1658 (1964).

(14) G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, **42**, 3735 (1965).

(15) E. Wasserman, L. Barash, and W. A. Yager, *J. Am. Chem. Soc.*, **87**, 2075 (1965).

(16) D. E. Milligan, M. E. Jacox, and A. M. Bass, *J. Chem. Phys.*, **43**, 3149 (1965).

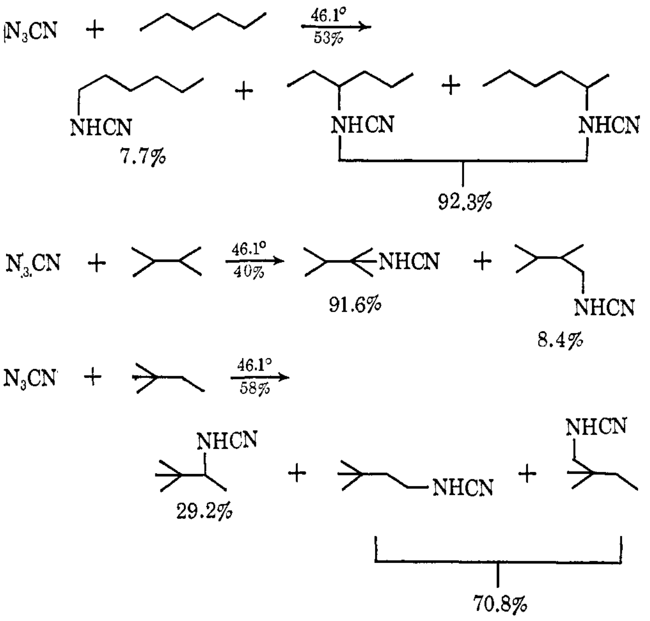
(17) H. W. Kroto, *ibid.*, **44**, 831 (1966).

(18) This is correct only for the low-energy states considered here in which the reactive electrons are roughly isoenergetic. In higher excited electronic states the distinction between singlets and triplets in

Of these, (a) and (c) represent the commonly considered one-step and two-step mechanisms for singlet and triplet species, respectively. Path b becomes a distinct possibility only with highly electrophilic species such as NCN which possess a vacant low-energy bonding MO, *e.g.*, π_g, of $^1\Delta_g$.

To obtain information about the mechanism of the insertion, we determined the selectivity of the reaction with various types of C–H links both in intramolecular and intermolecular competition experiments. In the intramolecular competition experiments, N_3CN was thermolyzed at 46.1° in *neat* *n*-hexane, 2,3-dimethylbutane, and 2,2-dimethylbutane to afford the corresponding alkylcyanamides in the yields and relative amounts indicated in Scheme IV. The proportions of the various products were determined from the nmr spectra of the crude mixtures (see Product Analysis).

Scheme IV



The product distributions in Scheme IV are given as relative rates in Table I (A). The pronounced selectivity of NCN indicated by these results suggests that appreciable C–H bond rupture occurs in the transition state, but does not provide any relevant information concerning the details of the bond-breaking process which could enable us to decide among the possible reaction paths. Of the three rate-limiting transition states shown in brackets in Scheme III, only (b) closely resembles that of an SN1 process with hydride ion partly bound to NCN acting as the leaving group. At first glance it appears that the discrimination of NCN for the various types of hydrogen is far too low for such a process.[19] However, this comparison is not strictly correct, since we may be witnessing a duality of mechanism akin to that observed in solvolytic displacements. For example, singlet NCN could be reacting by path a with primary C–H bonds, by path b with tertiary C–H bonds, and by a combination of paths a and b with secondary C–H bonds. Therefore, in order to distinguish among the three possible alternatives, it was necessary to devise additional experiments. It is known that in saturated carbocycles the rate of formation of an incipient carbonium ion is a sensitive function of ring size. For example, cyclooctyl tosylate and cycloheptyl tosylate solvolyze, respectively, >286 and 31 times as rapidly as cyclohexyl tosylate, which in turn is roughly as reactive as isopropyl tosylate.[20] These rate differences are commonly attributed[20] to the required hybridization changes involved in the incipient formation of carbonium ions, which occur more readily in the cyclooctyl and cycloheptyl systems than in the cyclohexyl system. This information coupled with the fact that of the three mechanisms in Scheme III only (b) requires any drastic hybridization changes[21] suggested that a determination of the relative ease with which NCN reacts with the C–H bonds of various cycloalkanes may provide significant information concerning the occurrence or absence of mechanism b. Furthermore, the comparison of the results ought to be free of the ambiguity introduced by a possible duality of mechanism since the C–H bonds involved are all of the same type.

Table I.[a] Reactivity of Cyanonitrene with C–H Bonds of Saturated Hydrocarbons at 46.1 ± 0.1°

A			B		
HC	H	Affinity	HC	H	Affinity
2,3-Dimethylbutane	Prim	1.0	*n*-Hexane	Sec (α)	1.62
	Tert	67.0		Sec (β)	1.30
n-Hexane	Prim	1.0	Cyclohexane	Sec	1.00
	Sec	9.0			
			Cycloheptane	Sec	1.21
2,2-Dimethylbutane	Prim	1.0	Cyclooctane	Sec	1.2 ± 0.1
	Sec	14.8			

[a] Values are corrected for statistical factors.

We have carried out intermolecular competition experiments and have found virtually no difference in reactivity among the methylene hydrogens of *n*-hexane, cyclohexane, cycloheptane, and cyclooctane. The results are collected in Table I (B). We interpret the observed lack of discrimination of NCN for the methylene groups of the three monocycles to mean that, at least in the absence of a solvent, secondary and certainly the less reactive primary C–H bonds do not react by a hydride-abstraction process such as that indicated in Scheme IIIb. These experiments do not, of course, provide any information concerning the mode of reaction of tertiary C–H bonds. Hydride abstraction here should be more favorable than with the other types of C–H bonds because of the production of a more stable tertiary cation.

Additional support for the nonoccurrence of mechanism b was obtained in the following manner. If an ion pair is produced, the carbonium ion might be amenable to skeletal rearrangement if it is of appropriate structure. Carbonium ion **8** is particularly susceptible to skeletal reorganization to ion **9**, *e.g.*, both

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reactions does not appear to be as well defined. For a discussion of this point see A. G. Anastassiou, *J. Am. Chem. Soc.*, **89**, 3184 (1967).

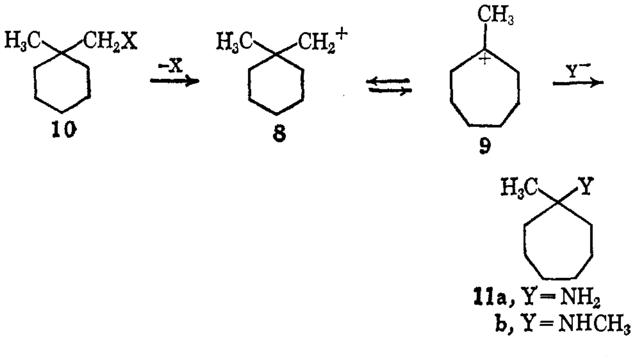
(19) Larger rate differences are usually observed in SN1 processes. For example, *t*-butyl bromide solvolyses *ca.* 10^7 times as fast as isopropyl bromide: L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 945 (1940).

(20) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 95.

(21) This statement rests on the assumption that (1) little rehybridization is necessary in the three-center process a, and (2) the commonly accepted view that alkyl radicals are not subject to any stringent hybridization requirements.

oxidative decarboxylation[22] of acid **10** (X = COOH) and nitrous acid deamination of the corresponding amine **10**, (X = NH_2)[23] yield **11** as the major product and material with intact skeleton is not produced (Scheme V). In the present work, cyanogen azide was thermolyzed in 1,1-dimethylcyclohexane and the crude cyanamide mixture was converted to the corresponding amino and methylamino compounds with excess lithium hydride. Gas-liquid partition chromatographic (glpc) analysis established the absence (<2%) of the amines **11** (Y = NH_2, $NHCN_3$).[24,25]

Scheme V



Stereochemistry of the Insertion Reaction. In principle, the direct insertion mechanism (a) and that involving hydrogen abstraction–recombination (b) ought to be distinguishable stereochemically. Path a is expected to be stereospecific leading to over-all retention of configuration, whereas path b should generate the products in a stereochemically random fashion under some conditions. In order to distinguish between these two mechanisms, we examined the stereochemical course of the insertion reaction. We employed the stereoisomeric 1,2-dimethylcyclohexanes as paraffinic substrates because of their ready availability in high purity and because the key products, 1-amino- and 1-methylamino-1,2-dimethylcyclohexane, are known in both stereoisomeric (but unassigned) forms. The results of these experiments are depicted in Scheme VI and tabulated in Table II.

Scheme VI

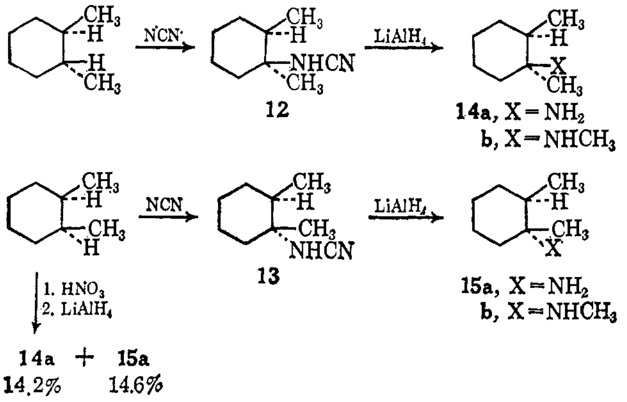


Table II. Stereochemistry of the Insertion Reaction of Cyanonitrene into the Tertiary C–H Bonds of *cis*- and *trans*-1,2-Dimethylcyclohexane

Hydrocarbon	Temp, °C	Products, %: *trans*-RNHCN (**12**)	Products, %: *cis*-RNHCN (**13**)
trans	46.1	>98	<2
cis	46.1	<2	>98

It is seen that the reaction is highly stereospecific, each isomeric substrate producing a single (>98%) stereoisomeric cyanamide which was identified in each case by analysis of the configurationally homogeneous mixture of 1-amino- and 1-methylamino-1,2-dimethylcyclohexane (**14a,b** and **15a,b**). These products were assigned the indicated stereochemistry on mechanistic grounds, since the absolute stereochemistry of the known isomers has not yet been determined. It should be noted that a reversal of these assignments would imply that stereospecific insertion occurs with net inversion of configuration, which we consider unlikely. The assignments are also consistent with the glpc data which show that the more sterically hindered *cis* isomers have higher retention times. Irrespective of the specific assignments, the observed stereospecificity is consistent with a one-step insertion process and militates against any two-step processes such as those depicted in (b) and (c), which could lead to stereospecific product formation only in the unlikely event that recombination of the intermediate ion or radical pair occurs prior to inversion of the asymmetric center.

To obtain some information concerning this latter point, we have examined the stereochemical fate of the tertiary 1,2-dimethylcyclohexane radical generated in the liquid-phase, free-radical nitration[26] of *cis*-1,2-dimethylcyclohexane with 50% nitric acid. The amine mixture obtained by reduction of the originally produced nitro compounds consisted of 28% of a 1:1 *cis–trans* mixture of 1-amino-1,2-dimethylcyclohexane. This is in keeping with the anticipated configurational instability of the hydrocarbon radical.

Product Analysis. In the intramolecular competition experiments, cyanogen azide was thermolyzed in the various hydrocarbon substrates to yield mixtures of cyanamides. The constitutions of the *crude* mixtures were determined from the nmr spectra (neat). Under these conditions the N–H proton appears at $\tau \sim 4.2$ and is quite sharp, exhibiting splitting consistent with the number of hydrogen atoms at the α-carbon.[27] The protons bound to the α-carbon appear at $\tau \sim 7$. Both these signals are well separated from the remaining absorptions which appear in the usual aliphatic region. All attempts to separate the various isomeric products in mixtures by gas-liquid partition chromatography were unsuccessful because of their extremely low volatility. Satisfactory product identification rests on correct elemental analyses of the high-vacuum distillation product mixtures and nmr and infrared spectra. The absence of any significant amount of impurity in the crude mixtures is indicated by the iden-

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[22] C. Walling, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 421.

[23] R. Kotani, *J. Org. Chem.*, 30, 350 (1965).

[24] Authentic materials were synthesized according to R. Jacquier and H. Christol, *Bull. Soc. Chim. France*, 596 (1957).

[25] The selectivity values shown in Table I suggest that *ca.* 6% of the product should arise from attack on primary C–H which, in the event that a carbonium ion is an intermediate, should mostly afford **11** (Y = $NHCH_3$). The amount of **11** expected is well above the detection limits of our glpc analysis.

[26] H. Shechter and D. K. Brain, *J. Am. Chem. Soc.*, **85**, 1806 (1963).

[27] For example, the N–H proton of *neat* cyclohexylcyanamide appears as a doublet ($J \sim 5$ cps) at τ 4.3 and that of *neat* *t*-butylcyanamide as a sharp singlet at τ 4.2.

tity of their spectral characteristics (nmr, infrared) compared with those of the analytically pure mixtures.

In the intermolecular competition runs, N_3CN was thermolyzed in the appropriate hydrocarbon pair, the composition of which was determined previously by glpc. The mixtures of cyanamides produced were converted to the corresponding amino and methylamino derivatives by treatment with excess lithium aluminum hydride in boiling tetrahydrofuran; the relative amounts of the amines were then determined by glpc. The various amines were characterized by direct comparison of their retention times and mass spectrometric cracking patterns with those of authentic samples. Similarly, in the reaction of NCN with the 1,2-dimethylcyclohexanes, the mixture of amines after reduction was analyzed by glpc, and the key isomers were characterized by direct comparison of glpc retention times and mass spectrometric cracking patterns with those of authentic samples.[28] Similar methods of conversion to amines and of analysis were employed in the reaction of 1,1-dimethylcyclohexane with NCN and *cis*-1,2-dimethylcyclohexane with nitric acid.

Conclusions

Thermolysis of cyanogen azide at 40–50° affords free cyanonitrene which, in the absence of an inert diluent, reacts with tertiary C–H bonds stereospecifically. Information about the insertion process into the less reactive secondary and primary C–H bonds is not as easily accessible experimentally. Here the mechanism may depend on the relative rates for direct insertion (path a) and intersystem crossing of singlet NCN to its triplet ground state (${}^1NCN \rightarrow {}^3NCN$); *i.e.*, if direct insertion is more rapid than intersystem crossing, singlet NCN will insert in a one-step process, whereas if the reverse is true, the reaction will occur by a hydrogen atom abstraction–recombination process by triplet NCN. Evidence will be presented in a subsequent paper that at least in the case of tertiary C–H bonds the direct insertion mechanism prevails. A hydride-abstraction–recombination process by singlet NCN does not in all probability occur with either type of C–H bond.

Experimental Section[29]

Extreme caution should be exercised in handling cyanogen azide. When neat it detonates with great violence and it should be prepared and used only in solvents. Solutions of cyanogen azide in paraffinic hydrocarbons can be handled safely, but should nevertheless be viewed as potentially explosive because of its poor solubility in nonpolar solvents. The concentration of such solutions should not exceed 5%.

Materials. Activated sodium azide[30] was used throughout. Of the hydrocarbons, 2,3-dimethylbutane, 2,2-dimethylbutane, and *cis*- and *trans*-1,2-dimethylcyclohexane were "Phillips Research Grade" and were used without further purification. Cyclohexane, cycloheptane, cyclooctane, 3-methylpentane, 1,1-dimethylcyclohexane, and *n*-hexane were treated with concentrated sulfuric acid and carefully fractionated before use. The materials thus obtained were >99.6% pure by glpc (conditions D). Labeled potassium azide (*ca.* 95 atoms % ${}^{15}N$ at positions 1 and 3) was purchased from Merck Sharp and Dohme of Canada.

Thermolysis of Cyanogen Azide in *n*-Hexane. Cyanogen chloride (50 ml) was allowed to evaporate into a stirred suspension of sodium azide (6.0 g) in *n*-hexane (30 ml) maintained under nitrogen and contained in a three-necked flask fitted with thermometer, inlet tube, and condenser held at −5 to 0° by a circulation coolant. The addition was made over a 2.5-hr period, while the temperature of the mixture was maintained at −4 to 0°. The suspension was then stirred at room temperature overnight, *n*-hexane (70 ml) was added, and the excess cyanogen chloride was removed at room temperature[31] at 100–200-mm pressure. The suspension was subsequently filtered under nitrogen pressure into a graduated cylinder. To the clear filtrate was then added more *n*-hexane to a total volume of 295 ml. A 2-ml sample of this solution gave 7 ml of gas when treated with trimethyl phosphite in an azotometer at 0–2° (46% yield).

The solution was subsequently transferred into a 500-ml, three-necked, round-bottomed flask fitted with thermometer and condenser. A water test meter was connected through a Dry Ice trap to the top of the condenser. When the solution was heated at 48–52° with stirring for 18 hr, 900 ml (∼90%) of gas was evolved. The yellow hexane solution was subsequently filtered free of any residue, and the volatile constituents of the filtrate were evaporated at 40° under water-aspirator pressure to yield a residual orange oil. This was distilled in a molecular still at ∼0.05 μ and a maximum bath temperature of 90°. The colorless distillate amounted to 2.76 g (53% yield based on N_3CN) and the residual resin to 0.5 g. The infrared spectrum of the distillate exhibits characteristic strong bands at 3180 (N–H) and 2200 ($C \equiv N$) cm^{-1}. The nmr spectrum is equally consistent with signals at τ 4.2 (doublet), 7.0 (multiplet), and 8.3–9.2 (multiplet).

Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.48; H, 11.12; N, 22.87.

Thermolysis of Cyanogen Azide in 2,3-Dimethylbutane, 3-Methylpentane, and 2,2-Dimethylbutane. A procedure similar to that described for *n*-hexane was employed. The results are given in Table III.

Intramolecular Competition Runs. The following general procedure was employed. Cyanogen azide was prepared by stirring overnight under reflux (∼15°)[32] a mixture of 2.0 g of sodium azide and *ca.* 40 ml of cyanogen chloride under nitrogen. The appropriate hydrocarbon was then added, and the excess cyanogen chloride removed at room temperature[31] (100–200 mm). The suspension was subsequently filtered under nitrogen pressure and the clear filtrate made up to *ca.* 200 ml by further addition of hydrocarbon. The solution was transferred into a one-necked, round-bottomed flask fitted with a condenser, and the flask was placed in a constant-temperature water bath maintained at 46.1 ± 0.1°. The solution was held at this temperature for *ca.* 21 hr; the theoretical amount of nitrogen had then been evolved. The mixture was then filtered free from any traces of precipitate that might be present, and the filtrate was concentrated to a tan oil under water-aspirator pressure and below 40°. A 250-cps nmr spectrum of the residual oil was determined immediately, and the areas of interest were carefully cut and weighed. The results of duplicate runs are shown in Table IV. In each case the nmr and infrared spectra of these mixtures were the same as those of their analytically pure counterparts described above.

The figures in Table IV were corrected for statistical factors and translated into the relative rates shown in Table I (A) by the following relations: a, for products derived from 2,3-dimethylbutane, tertiary product/primary product = $(A_1 - A_2/2)/(A_2/2)$; b, for products derived from *n*-hexane and 2,2-dimethylbutane, secondary product/primary product = $[A_1 - (A_2 - A_1)]/(A_2 - A_1)$.

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[28] K. E. Hamlin and M. Freifelder, *J. Am. Chem. Soc.*, 75, 369 (1953).

[29] All melting points and boiling points are uncorrected. Nmr spectra were measured with a Varian A-60 spectrometer and infrared spectra with a Perkin-Elmer 21 spectrometer. The glpc results were obtained under the following conditions: A, 2 m × 0.24 in. stainless steel column packed with 20% tetrakis(hydroxyethyl)ethylenediamine (THEED) on 60–80 mesh Chromosorb W (*not* acid washed) at 101° with the vaporizer at 155°, helium was used as the carrier gas at a flow rate of 60 cc/min; B, same as in A except column and vaporizer temperatures were 102 and 165°, respectively; C, 2 m × 0.25 in. stainless steel column packed as in A and B at 119° and the vaporizer at 175°, carrier gas and flow rate were as in A and B; D, 2 m × 0.25 in. copper column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEG) on 60–80 mesh Gas Chromosorb R at 52° with the vaporizer at 120°; E, 12 ft × 0.75 in. stainless steel column of 20% THEED on Chromosorb W (*not* acid washed) at 110°, and a helium flow rate of 810 cc/min.

[30] P. A. S. Smith, *Org. Reactions*, 3, 382 (1946).

[31] It is essential that the temperature be kept above +10° to avoid separation of a highly explosive layer of neat cyanogen azide.

[32] It is essential to keep the temperature of the condenser at *ca.* −5 to 0° to contain the cyanogen chloride (bp 12°). In the course of one run, failure of the cooling system led to a violent explosion.

Table III. Thermolyses of Cyanogen Azide in C_6H_{14} Hydrocarbons

Hydrocarbon	Yield of N_3CN, %	Yield of cyanamide, %[a]	Spectral data: Infrared (neat), cm^{-1} N–H	C≡N	Nmr (neat), τ N–H	α(C–H)	Other	Elemental composition,[b] %
2,3-Dimethylbutane	85	40	3205	2217	4.3	7.0	8.1–9.1	C, 66.82 H, 11.13 N, 22.46
2,2-Dimethylbutane	58	42	3210	2200	4.3	7.2	8.8–9.3	C, 66.57 H, 10.94 N, 22.19
3-Methylpentane	88	41	3200	2210	4.2	6.9	8.2–9.3	C, 66.42 H, 11.05 N, 22.05

[a] Based on N_3CN. [b] Found.

Table IV. Nmr Data of Intermolecular Competition Experiments

Hydrocarbon	Area A_1 Wt, g	Chem shift, τ	Area A_2 Wt, g	Chem shift, τ
n-Hexane	0.1750	4.2	0.1890	7.0
	0.2459		0.2640	
2,3-Dimethylbutane	0.0912	4.3	0.0152	7.0
	0.0868		0.0145	
2,2-Dimethylbutane	0.2080	4.2	0.2701	7.2
	0.2095		0.2695	

Table V. Quantitative Data from Intermolecular Competition Runs

Hydrocarbon mixture	Composition[a]	Reaction	Composition of amine mixtures[d] A	B	C	D	E	F	G	H	I	J
Cyclohexane	37.0	1[b]	8.5	24.3	9.2	21.1	9.4	14.2	...	...	...	...
n-Hexane	63.0											
Cyclohexane	67.6	2[c,e]	16.2	39.2	...	...	...	...	11.3	30.9	...	...
Cycloheptane	32.4											
Cyclohexane	75.6	3[c,e]	20.0	43.1	...	...	...	...	...	...	7.5	25.1
Cyclooctane	24.4											

[a] Mole %, determined by glpc under conditions D. [b] Average of four glpc determinations under conditions A. [c] Average of three glpc determinations under conditions C. [d] Weight %, A = cyclohexylamine, B = N-methylcyclohexylamine, C = 2-aminohexane, D = 2-methylaminohexane, E = 3-aminohexane, F = 3-methylaminohexane, G = cycloheptylamine, H = N-methylcycloheptylamine, I = cyclooctylamine, and J = N-methylcyclooctylamine. [e] In these runs, known mixtures of the amines were used for quantitative glpc calibrations.

Intermolecular Competition Runs. The procedure was essentially the same as that described for the intramolecular competition runs. The appropriate hydrocarbon mixture was added, the cyanogen chloride removed, the suspension filtered, and the filtrate made up to 200-ml volume. The exact composition of the mixture was determined by glpc. The reaction mixture was then heated at 46.1 ± 0.1° in a constant-temperature water bath for 20 hr. The crude cyanamides were isolated in the usual way and were treated with lithium aluminum hydride according to the following procedure.

A solution of the crude cyanamide mixture (3.0 g) in tetrahydrofuran (50 ml) was added with stirring to a boiling suspension of lithium aluminum hydride (5.0 g) in tetrahydrofuran (150 ml) over a period of 1.5 hr. The mixture was stirred under reflux for an additional 15 hr. It was cooled in an ice bath and treated carefully with a saturated aqueous solution of sodium sulfate until the slurry turned white. The mixture was filtered and the filter cake washed with tetrahydrofuran. The filtrate was made strongly acid with 25 ml of concentrated hydrochloric acid and evaporated to dryness to afford a hygroscopic, crystalline, tan solid. This product was dissolved in 15 ml of distilled water, and the resulting solution transferred into a 50-ml separatory funnel. The funnel was placed in an ice bath, and the solution was made strongly basic by the addition of sodium hydroxide pellets. The mixture was shaken vigorously; the layers were allowed to separate, and the dark upper layer was collected and dried over sodium hydroxide pellets under nitrogen and analyzed by glpc. The results are shown in Table V. All amines except 2- and 3-methylaminohexane were identified by direct comparison of their glpc retention times and mass spectrometric cracking patterns with those of authentic samples. The structural assignments of 2- and 3-methylaminohexane derive from the mass spectrometric cracking patterns which are fully consistent with these structures. The relevant data employed in the identification of the amines are compiled in Table VI.

Table VI. Identifying Features of the Amines

Compd[a]	Retention time, min	Molecular ion, *m/e*	100% ion, *m/e*
A	5.6[b]	99	56
A	32.8[c]	99	56
B	4.1[b]	113	70
B	24.2[c]	113	70
C	10.6[c]	101	44
D	8.0[c]	115	58
E	8.8[c]	101	58
F	5.8[c]	115	72
G	11.4[b]	113	56
H	7.7[b]	127	70
I	21.4[b]	127	56
J	14.1[b]	141	70

[a] See Table V. [b] Retention times under glpc conditions C. [c] Retention times under glpc conditions A.

Preparation of 1-Amino- and 1-Methylamino-1-methylcycloheptane. 1-Amino-1-methylcycloheptane was prepared as described in the literature.[24] To a solution of this material (1.75 g) in chloroform (15 ml) was added with stirring freshly distilled chloral (2.6 g) at such a rate as to maintain the temperature at 0–2°. The mixture was then stirred at room temperature overnight. Removal of the volatile constituents at water aspirator pressure gave an oil, bp 85–86° (1 mm). The colorless distillate amounted to 2.4 g, $n^{24}D$ 1.4991. A solution of this material (2.4 g) in ether (8 ml) was added with stirring to a suspension of lithium aluminum hydride (2.1 g) in ether (30 ml) maintained at ice-bath temperature. The resulting mixture was stirred under reflux for 2 hr. The mixture was cooled in an ice–salt bath and treated with 10% aqueous sodium hydroxide until the solid turned completely white. The suspension

Table VII

Temp, °C (mm)	Amount, g	$n^{24}D$	Composition[a]
100–106 (38)	0.4	1.4639	**11a**, 35.7%; **11b**, 17.0%
108–113 (39–42)	0.78	1.4654	**11a**, 8.0%; **11b**, 14.8%

[a] Amounts were determined by glpc under conditions C. Structural assignments were made on the basis of mass spectrometric cracking patterns. Compound **11a**: molecular ion at *m/e* 127, 100% ion at *m/e* 70; compound **11b**: molecular ion at *m/e* 141, 100% ion at *m/e* 84.

was filtered; the filter cake was washed with ether, and the combined extracts were dried over sodium hydroxide pellets. The ether was then removed and the residual liquid distilled (see Table VII).

Thermolysis of Cyanogen Azide in 1,1-Dimethylcyclohexane. Cyanogen azide, prepared from 2.0 g of sodium azide and 40 ml of cyanogen chloride, was thermolyzed at 46.25 ± 0.05° in 110 ml of 1,1-dimethylcyclohexane. The cyanamide mixture (2.5 g) was isolated as described previously. This product was subsequently reduced with lithium aluminum hydride in tetrahydrofuran in the usual manner. The amine mixture amounted to 2.0 g. Glpc analysis of the mixture under conditions C indicated the absence of **11a** and **11b**.

Preparation of 1-Amino-1,2-dimethylcyclohexane. This compound was prepared as described in the literature.[28] Nitration (aluminum nitrate nonahydrate) of a 2:1 mixture of *cis*- and *trans*-1,2-dimethylcyclohexane and subsequent catalytic hydrogenation (Raney nickel) of the resulting nitro compounds gave a stereoisomeric mixture of *cis*- and *trans*-1,2-dimethylcyclohexane. The component with the higher retention time (30.9 min, conditions A) constituted 51% of the mixture and the one with the lower retention time (20.3 min, conditions A), 42.4% of the mixture. The components with the higher and lower retention times are assigned the *cis* and the *trans* configurations, respectively. The two isomers were separated by preparative glpc under conditions E. Stereoisomers **14a** and **15a** exhibit identical mass spectrometric cracking patterns (100% ion at *m/e* 70; molecular ion at *m/e* 127). Their infrared spectra are identical except for minor differences in the fingerprint region.

1-Methylamino-*trans*-1,2-dimethylcyclohexane and 1-Methylamino-*cis*-1,2-dimethylcyclohexane. Stereopure **14a** and **15a** were converted to the monomethyl derivatives by the procedure described for the conversion of **11a** to **11b**.

1. ***cis* Isomer 15b.** A 2.5-g sample of the *cis*-amino compound **15a** gave 0.77 g of colorless amine, bp 81–82° (33 mm). Glpc analysis under conditions A showed 54.8% **15a** (*RT* (retention time) = 30.9 min) and 32.7% **15b** (*RT* = 23.6 min). The mass spectrum of **15b** shows 100% ion at *m/e* 84 and molecular ion at *m/e* 141.

2. ***trans* Isomer 14b.** A 2.5-g sample of **14a** gave 0.57 g of amine. Glpc analysis under conditions A indicated 66.9% **14a** (*RT* = 20.3 min) and 29.0% **14b** (*RT* = 13.0 min). The mass spectrum of **14b** shows 100% ion at *m/e* 84 and molecular ion at *m/e* 141 and is qualitatively identical with the spectrum of its stereoisomer **15b**.

Thermolysis of Cyanogen Azide in *cis*-1,2-Dimethylcyclohexane. Cyanogen azide, prepared from 2 g of sodium azide and 40 ml of cyanogen chloride, was heated at 46.05 ± 0.05° in 200 ml of *cis*-1,2-dimethylcyclohexane. The resulting mixture of cyanamides was isolated and converted to the corresponding amines (2.2 g) in the usual way (lithium aluminum hydride in tetrahydrofuran). The mixture was analyzed by glpc (conditions A) and consisted of 0.5% **14b** (*RT* = 12.8 min), <0.3% **14a**, 28.9% **15b** (*RT* = 23.7 min), and 15.4% **15a** (*RT* = 30.4 min). Compounds **14b**, **15b**, and **15a** were identified mass spectrometrically.

Thermolysis of Cyanogen Azide in *trans*-1,2-Dimethylcyclohexane. The mixture of amines (2.0 g) was obtained by a procedure analogous to that described for the *cis* hydrocarbon. Glpc analysis under conditions A gave 25.3% **14b** (*RT* = 12.8 min), 14.7% **14a** (*RT* = 19.7 min), and <0.3% **15a**. Compounds **14b** and **14a** were identified by their mass spectrometric cracking patterns.

Nitration of *cis*-1,2-Dimethylcyclohexane. A mixture of *cis*-1,2-dimethylcyclohexane (50 g) and 50% nitric acid (350 g) was stirred at the boiling temperature (oil bath at 140°) for 3 hr. The mixture was allowed to cool to room temperature; the layers were separated, and the aqueous layer was cooled in ice and extracted with two 50-ml portions of ether. The ether extracts were combined with the organic layer and washed first with four 50-ml portions of 20% aqueous sodium hydroxide, then with water, and finally dried over Drierite. Removal of the ether and the excess hydrocarbon at 50° (10 mm) and distillation of the residue gave a pale yellow liquid (3.23 g, 4.6%), bp 82–87° (3–5 mm); $n^{25}D$ 1.4667. This product was treated with lithium aluminum hydride in the usual way and glpc analysis of the crude amine mixture under conditions A indicated the presence of 14.2% **14a** (*RT* = 19.5 min) and 14.6% **15a** (*RT* = 30.0 min). The two materials exhibit essentially identical mass spectrometric cracking patterns with a molecular ion at *m/e* 127 and a 100% ion at *m/e* 70.

Thermolysis of ^{15}N-Labeled Cyanogen Azide in Cyclohexane. Cyanogen azide in cyclohexane (290 ml) was prepared from isotopically labeled potassium azide (2.1 g) according to the procedure already described. This solution was heated at 49–50° overnight, and the crude cyclohexylcyanamide (2.27 g, 57%) was isolated in the usual way and distilled at *ca.* 0.003 μ to afford 1.54 g of pure **1**. The purified cyanamide was suspended in 10 ml of distilled water, 20 drops of concentrated sulfuric acid was added, and the mixture was stirred under reflux for 0.5 hr. The precipitated white solid was isolated by filtration, washed with water, and dried in a drying pistol, yielding 1.1 g (63%) of cyclohexylurea, mp 186–186.7°. A suspension of this material (1.1 g) in tetrahydrofuran (30 ml) was added with stirring to a boiling mixture of lithium aluminum hydride (2.0 g) in tetrahydrofuran (130 ml) under nitrogen. The addition was made over 1 hr, and the mixture was stirred under reflux for an additional 24 hr. The usual work-up afforded a yellow liquid which was dried over sodium hydroxide pellets and distilled (10–20 mm). The colorless distillate (**2** + **3**) amounted to 0.25 g. The corresponding unenriched materials were prepared analogously.

Analysis. Starting potassium azide was burned to nitrogen and the isotopic enrichment of this species determined mass spectrometrically: atom % of ^{15}N in nitrogen = 3.26, total ^{15}N in potassium azide = 3.26 × 3 = 9.78%, atom % of ^{15}N in the terminal position of azide less the ^{15}N natural abundance (net enrichment): $[(9.78 - 0.36)/2] - 0.36 = 4.35$.

The amount of ^{15}N in **1** and **2** was determined mass spectrometrically employing the ratio of intensities of molecular ion + 1 to molecular ion. The results are shown in Table VIII.

Table VIII. Ratio of Intensities of Molecular Ion + 1 to Molecular Ion at 70 ev

	1 (^{14}N), %	**1** (^{15}N), %	**2** (^{14}N), %	**2** (^{15}N), %
	8.92	13.29	8.17	10.66
	8.86	13.31	8.18	10.71
	8.89	13.31	8.16	10.74
	8.87	13.22	8.12	10.56
	8.85	13.20	8.00	10.72
			8.12	10.74
			8.17	10.64
			8.20	10.74
Av	8.86	13.26	8.14	10.69

Total ^{15}N enrichment in **1** = 4.40%
Total ^{15}N enrichment in **2** = 2.55%

Compound **2** was burned to nitrogen and the isotopic enrichment was determined mass spectrometrically (in duplicate); total enrichment in **2** = 2.35%, 2.55%.

Reaction of Norbornene with ^{15}N-Labeled Cyanogen Azide. Enriched cyanogen azide was prepared from 2 g of isotopically labeled potassium azide and 35 ml of cyanogen chloride. To the cyanogen chloride suspension was added 55 ml of water-free acetonitrile; the excess cyanogen chloride was removed at 100–200 mm, and the residual suspension was pressure filtered under nitrogen. The clear acetonitrile solution amounted to 55 ml and liberated 7.5 cc of gas (N_2) per 1 ml of sample when treated with trimethyl phosphite. The solution was subsequently maintained at 49° for 2.5 hr. At the conclusion a 1-ml sample of the solution liberated 6.5 cc of gas. The mixture was cooled in an ice bath, and a solution of freshly distilled norbornene (6 g) in acetonitrile (30 ml) was added over 1.5 hr, while the temperature was maintained at −2 to 4°. After the addition was complete (theoretical amount of gas had been evolved), the reaction mixture was held at room temperature for an additional 16 hr. Removal of the volatile constituents under water-aspirator pressure and at 55° gave 2.4 g of an orange oil. This product was dissolved in benzene (10 ml) and passed through a chromatographic column containing 100 g of grade IV

'Woelm" neutral alumina. Evaporation of the eluents (400 ml) afforded a slightly tan oil, which exhibited a strong infrared band at 2200 ($C\equiv N$) and 1730 ($C=O$) cm^{-1}. Distillation of this material through a micro-Vigreux column gave pure cyanoaziridine as a colorless liquid (1.53 g, 41%), bp 97° (0.35 mm), the infrared spectrum of which showed a strong band at 2200 cm^{-1} and no absorption at 1730 cm^{-1}.

Removal of the nitrile group from **6** was accomplished as follows. A solution of the cyanoaziridine (1.53 g) in ether (15 ml) was added to a stirred suspension of lithium aluminum hydride (0.24 g) in ether (25 ml) over 20 min. The temperature of the mixture was maintained below 25° throughout the addition by an ice bath. The suspension was then stirred at reflux for 3 hr. The suspension was subsequently cooled with an ice-salt bath and treated with a saturated aqueous solution of sodium sulfate. The white suspension was filtered; the colorless filtrate was dried over anhydrous sodium sulfate and the ether removed. Distillation of the residual oil through a short path head at 0.2–0.5 mm with a bath temperature of 150° afforded a colorless semisolid (0.80 g, 67%) which solidified immediately when placed on a porous plate. The infrared spectrum of this material was identical in all respects with that of an authentic sample.[33]

Analysis. Starting potassium aizide was burned to nitrogen and the isotopic enrichment of this species determined mass spectrometrically: atom % of ^{15}N in nitrogen = 3.25, total ^{15}N in potassium azide = $3.25 \times 3 = 9.75\%$, atom % of ^{15}N in terminal position of azide less the ^{15}N natural abundance (net enrichment): $[(9.75 - 0.36)/2] - 0.36 = 4.33$.

Compounds **5** and **6** were converted to nitrogen, and the isotopic enrichment was determined mass spectrometrically (in duplicate): total enrichment in **5** = 4.18%, 4.38%; total enrichmenti n **6** = 3.90%, 4.19%.

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The Electronic Multiplicity of Thermally Generated Cyanonitrene[1]

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Abstract: The stereochemistry of the insertion of cyanonitrene, generated thermally from cyanogen azide, into the tertiary C–H bonds of *cis*- and *trans*-1,2-dimethylcyclohexane was studied in a variety of solvents. The stereospecificity observed when the reaction was conducted in the absence of a solvent was completely preserved in acetonitrile and fully destroyed in methylene bromide. In methylene chloride and ethyl acetate, the reaction is stereoselective. Triplet cyanonitrene displays a slightly more pronounced discrimination in selecting between secondary and tertiary C–H bonds than does singlet cyanonitrene. Mechanisms are discussed.

Recent years have witnessed a number of elegant and fruitful investigations concerning the electronic states of neutral electron-deficient fragments (carbenes,[3] nitrenes, etc.). In most cases, information about ground electronic states is readily available through a variety of spectroscopic methods such as electron paramagnetic resonance (epr) and flash photolysis. In contrast, information concerning electronic configurations of such species during the course of chemical reactions is not easily accessible and can only be adduced by an interplay of intuitive reasoning and experiment, the former being very often controversial. In chemical reactions, three situations arise: (1) the reacting species is in the ground electronic state, (2) the reacting species is in the first excited electronic state (usually of different multiplicity than the ground state), and (3) the reacting species is a composite of both ground electronic state and first excited electronic state. The great majority of reactions involving neutral electron-deficient intermediates is complicated by situation 3. The most widely employed criterion for arriving at the electronic multiplicity of a reacting carbene was advanced 11 years ago by Skell and Woodworth[4] and concerns the stereochemistry of addition of such a fragment to olefinic bonds. It states that singlet carbenes should add in one step to yield cyclopropanes in a stereospecific fashion, whereas the triplet counterparts ought to react by means of a diradical intermediate which, being essentially a free rotator, leads to stereorandom ring closure. Skell's postulate has received ample experimental support over the years and constitutes a reliable working hypothesis. Care must be exercised in its use, however, since, as has been repeatedly pointed out, it cannot be justified theoretically.[3,5] Three recent reports lend particularly strong support to the postulate. These deal with the effect of dilution by a nonolefinic substrate on the stereochemistry of addition of fluorenylidene[6] and dicyanocarbene,[7] both of which have triplet ground states,[8,9] to the isomeric 2-butenes and of carbethoxynitrene[10] to *cis*- and *trans*-4-methyl-2-pentene. In each case, the stereoselectivity

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