'Woelm" neutral alumina. Evaporation of the eluents (400 ml) afforded a slightly tan oil, which exhibited a strong infrared band at 2200 (C≡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 × 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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(33) F. D. Marsh, M. E. Hermes, and H. E. Simmons, to be published.

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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(1) Communicated in preliminary form: A. G. Anastassiou, *J. Am. Chem. Soc.*, **88**, 2322 (1966).

(2) Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210.

(3) For a critical and thorough account see: P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, Chapter 12.

(4) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(5) Hoffmann has recently advanced the notion that symmetry rather than multiplicity of an electronic state is the deciding factor in the stereochemical course of addition: R. Hoffmann, Abstracts of Papers, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 109K.

(6) M. Jones, Jr., and K. R. Rettig, *J. Am. Chem. Soc.*, **87**, 4013 (1965).

(7) E. Ciganek, *ibid.*, **88**, 1979 (1966).

(8) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

(9) E. Wasserman, L. Barash, and W. A. Yager, *ibid.*, **87**, 2075 (1965).

(10) W. Lwowski and J. S. McConaghy, Jr., *ibid.*, **87**, 5490 (1965).

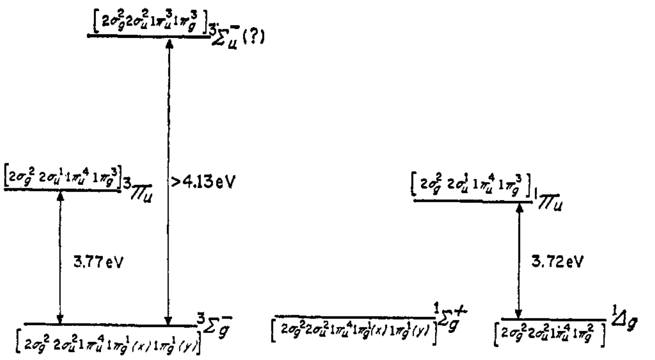

Figure 1. Observed spectroscopic states of cyanonitrene.

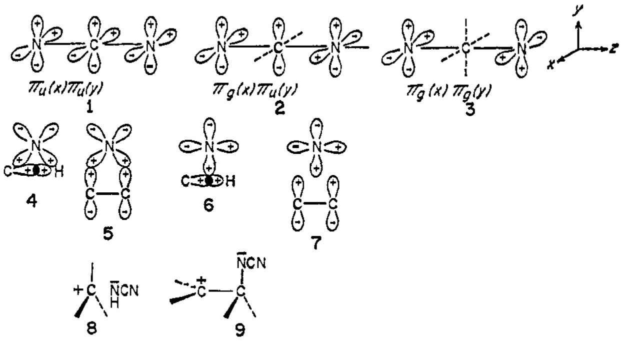

Figure 2. Symmetry requirements of cyanonitrene in addition and insertion reactions.

of the addition decreases drastically with increasing amount of diluent, a condition which favors situation 1 indicated above. Furthermore, in the case of dicyanocarbene[7] at high dilution, the same relative amounts of stereoisomeric cyclopropanes are formed starting from either olefinic isomer, in full agreement with Skell's free rotator model of the intermediate diradical.

Results and Discussion

In the present paper, we present a full account of our work dealing with the electronic multiplicity of reacting cyanonitrene (NCN) generated thermally from cyanogen azide (N_3CN). We chose not to study the stereochemical course of the addition of NCN to olefins because of a major experimental difficulty. Cyanogen azide itself reacts readily with olefinic functions[11] at room temperature, with over-all loss of molecular nitrogen, to yield products which, in the absence of appropriate isotopic labeling, are indistinguishable from those expected to form from NCN. Hence, we employed the stereochemistry of the insertion reaction into the C–H bonds of paraffinic hydrocarbons as a criterion of electronic multiplicity.

Electronic Structure of NCN. In the preceding paper[12] we mentioned that NCN has been studied by a variety of spectroscopic methods and the configuration of the ground electronic state and a few excited states determined. The information derived from these studies is compiled in Figure 1. It is interesting to consider the various configurations in connection with their ability to undergo stereospecific reactions with C–H bonds and olefinic functions. In so doing, we will not discuss the triplet states since here the stereochemistry of the reaction is independent of symmetry and configuration and depends only on factors succeeding the homolytic bond-breaking step, such as the magnitude of the rate of radical recombination *vs.* that of loss of configurational integrity, both of which are sensitive functions of environment.

The *donor* molecular orbitals (highest occupied MO's) of C–H and C=C bonds are of symmetry[13] σ_g and π_u, respectively. In the transition state, these could interact in either a bonding or antibonding fashion depending on the symmetry of the *acceptor* MO (lowest unoccupied) of the electron-deficient species. In the present case, since the transition state almost certainly involves interaction of a single nitrogen atom of NCN with the C–H or the C=C bond, the symmetry of the *acceptor* MO as a whole is of no consequence and what is important is the local symmetry of that MO on the interacting nitrogen atom. This, coupled with the cylindrical symmetry of linear NCN, suggests that the nature of the interaction ought to be independent of the π symmetry of NCN, *i.e.*, both the π_g and π_u MO's of NCN can interact with C–H and C=C bonds in a bonding fashion. This is shown diagrammatically (molecular axis of NCN (z) perpendicular to the plane of the paper) in **4** and **5** of Figure 2. In Figure 2 are also shown the various π-orbital combinations of linear NCN. The two low-lying singlets of NCN, $^1\Sigma_g^+$ and $^1\Delta_g$, are similar with respect to symmetry of the *acceptor* MO(s), which in both cases is π_g, but differ in the way this degenerate MO is occupied. In $^1\Sigma_g^+$, each π_g is occupied singly whereas in $^1\Delta_g$, one is filled and the other empty (Figure 1). This difference in the occupancy of the π_g MO will in all probability determine the nature of overlap in the transition state. Thus the $^1\Sigma_g^+$ state having evenly occupied *acceptor* MO's will probably overlap with the *donor* MO's of C–H and C=C in the fashion shown in **4** and **5**, whereas electron repulsion considerations would suggest that the $^1\Delta_g$ state ought to interact as shown in **6** and **7**, with maximum overlap occurring between the *donor* MO and the empty π_g MO of the acceptor. Translating this crude picture into stereochemistry, we conclude that of the two low-lying singlet states, $^1\Sigma_g^+$ should react stereospecifically in a one-step, three-center process whereas the $^1\Delta_g$ state could probably react by way of the dipolar intermediates shown in **8** and **9** for C–H insertion and C=C addition, respectively. This latter process could lead to nonstereospecific results.

The higher energy singlet $^1\Pi_u$ poses an interesting problem in connection with insertion and addition reactions. Here, one π_g and one σ_u MO are singly occupied, and we have a situation where two paired electrons differ widely in energy. This energy difference will weaken the pairing between the two electrons, and it is not inconceivable, especially since the two electrons are in MO's of different spatial symmetry, that enough weakening could occur so as to allow the two electrons to behave independently. If this occurs, it would be possible for the $^1\Pi_u$ state to react with C–H and C=C bonds by a radical process commonly reserved for triplet species. It should be noted, however, that reaction of NCN in its $^1\Pi_u$ state is very unlikely irrespective of the substrate employed since its deactiva-

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

(12) A. G. Anastassiou and H. E. Simmons, *ibid.*, **89**, 3177 (1967).

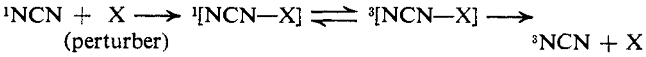
(13) This is strictly the symmetry of the bare bond.

tion to either the $^1\Sigma_g^+$ or $^1\Delta_g$ state ought to occur very rapidly compared to chemical reaction.

Controlled Generation and Reaction of Singlet and Triplet NCN. In previous work,[12] we studied the stereochemical course of the insertion reaction of thermally generated NCN into the tertiary C–H bonds of the two stereoisomeric 1,2-dimethylcyclohexanes and found it to occur with virtually complete stereospecificity. This result is best rationalized by assuming that the reaction occurs in one step by way of singlet NCN. The singlet nature of the reacting NCN is also suggested from considerations of spin conservation in the thermal fragmentation of N_3CN as well as the experimental conditions employed. Thus the low decomposition temperature strongly suggests that singlet N_3CN fragments to singlet molecular nitrogen[14] and, by the principle of conservation of spin, to singlet NCN which in the absence of a solvent would probably undergo reaction prior to collisional deactivation to the lower energy $^3\Sigma_g^-$ state. Nevertheless, the stereochemical results can also be accommodated by a hydrogen abstraction by triplet NCN followed by spin inversion and recombination of the resulting radical pair, provided these latter processes are rapid compared to configurational inversion of the hydrocarbon radical.[15] To obtain definitive information concerning the nature of reacting NCN, it was therefore necessary to design experiments which would unambiguously distinguish between the two mechanisms. One simple way of achieving this is by inducing NCN to insert nonstereospecifically under conditions strongly favoring the presence of triplet NCN. We have examined this possibility by conducting the insertion reaction in the presence of various inert diluents. Under these conditions, collisional deactivation of the originally formed NCN to its $^3\Sigma_g^-$ ground state should compete favorably with reaction. In the course of these experiments, we have also uncovered a thermochemical heavy atom effect. Since this effect provided most of the rationale in designing our experiments, it appears appropriate at this point to briefly summarize its mechanism.

The ability of heavy atoms to promote spin-forbidden electronic transitions is a well-recognized phenomenon and has been the subject of extensive spectroscopic and theoretical studies.[16] Both intramolecular (heavy atom incorporated in the substrate) and intermolecular (heavy atom incorporated in the solvent) "heavy-atom" effects have been observed spectroscopically. For example, the ultraviolet spectrum of 9,10-dibromoanthracene in a light solvent exhibits a fairly intense singlet to triplet ($S_0 \rightarrow T_1$) absorption, whereas that of the parent hydrocarbon, determined under the same conditions, does not. Also the spectrum of neat 1-chloronaphthalene does not possess an $S_0 \rightarrow T_1$ band, whereas the spectrum of the same molecule determined in ethyl iodide does possess one. There exists a formal similarity between the deactivating processes available to the photoexcited states of a stable molecule and those open to carbenes and nitrenes. In both cases, conservation of spin requires the originally produced state to be a singlet which given an appropriate environment and enough time could decay to a lower energy triplet. However, the similarity ends here since the $S_1 \rightarrow T_1$ intersystem crossing in the photoexcited substrate has to compete with the far more efficient spin-allowed $S_1 \rightarrow S_0$ process, whereas in the case of an electron-deficient fragment with a triplet ground state intersystem crossing $S_1 \rightarrow T_0$ is the only path available for deactivation. This lack of spin-allowed deactivation in most nitrenes and carbenes makes the use of external perturbations to the quantization of spin, such as the "heavy-atom" effect, exceedingly valuable in determining and controlling electronic multiplicity chemically. Two distinct processes are necessary for efficient collisional intersystem crossing which in the present case involves an $S_1 \rightarrow T_0$ transition: (1) vibrational deactivation of the vibronically excited molecule to low vibrational levels of the first excited electronic state, from which energy transfer to high vibrational levels of the ground state can occur; and (2) removal of spin forbiddenness through coupling of spin and orbital angular momenta. The first process is strictly collisional and should depend on the number of degrees of freedom available to the perturbing molecule, as well as the number of perturbing molecules,[17] whereas the second is a function of the amount of spin–orbit coupling introduced by the perturber molecule which in turn depends on the spin–orbit coupling constant (ζ) of the atom responsible for the perturbation. Some relevant ζ values are:[18] C, 28; N, 70; O, 152; Cl, 587; Br, 2460; and I, 5060 cm^{-1}. For the case of NCN, the over-all mechanism for collisional deactivation is depicted in Scheme I.

Scheme I



$$\underset{}{^1\text{NCN}} + \underset{\text{(perturber)}}{\text{X}} \longrightarrow {}^1[\text{NCN—X}] \rightleftharpoons {}^3[\text{NCN—X}] \longrightarrow {}^3\text{NCN} + \text{X}$$

It is clear, therefore, from these considerations that an inert solvent containing one or more heavy atoms or other perturbing functionalities should fulfill the various requirements for efficient relaxation to the ground electronic state. With this in mind and because in the absence of a solvent insertion of NCN into the C–H bonds of *cis*- and *trans*-1,2-dimethylcyclohexane occurs stereospecifically, we studied this reaction employing CH_2Cl_2, CH_2Br_2, CH_3CN, and $CH_3COOC_2H_5$ as solvents. The results are compiled in Table I.

It is amply clear from the data in Table I that the insertion reaction can be induced to occur nonstereospecifically by the use of appropriate solvents. The results obtained with the methylene halide solvents (reactions 4–12) are especially interesting. Both CH_2Cl_2 and CH_2Br_2 contain the same number and type of atoms and hence should be equally effective in deacti-

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(14) The alternate process, *i.e.*, $N_3CN \overset{\Delta}{\rightarrow} {}^3N_2 + {}^3NCN$, is undoubtedly unfavorable energetically since the $^1N_2 \rightarrow {}^3N_2$ energy separation is in all probability much larger than the $^3NCN \rightarrow {}^1NCN$ energy gap.

(15) Inversion of the asymmetric center with respect to NHCN can occur either by rotation of the hydrocarbon radical by 180° prior to recombination with the counterradical or by migration of $\dot{N}HCN$ to a site at which recombination would invert the configuration of the original hydrocarbon.

(16) Heavy atoms are known to enhance the probability of spin-forbidden transitions through coupling of spin and orbital angular momenta. See, for example, C. D. Dijkgraaf and G. J. Hoitjink, "Quantum Chemistry Symposium," *Tetrahedron Suppl.*, 2, 179 (1963); and J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 294–300.

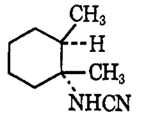
(17) For a striking example of the effect of the number of degrees of freedom available to an inert diluent on the rate of intersystem crossing of methylene, see R. F. Bader and J. I. Generosa, *Can. J. Chem.*, 43, 1631 (1965).

(18) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 29.

Table I. Stereochemistry of the Insertion of Cyanonitrene into the Tertiary C–H Bonds of *cis*- and *trans*-1,2-Dimethylcyclohexane as a Function of Solvent

Reaction	Solvent	Concn,[a] %	Hydrocarbon	Temp,[b] °C	% *cis*-RNHCH (**10**)[d]	% *trans*-RNHCN (**11**)[d]	Over-all yield,[c] %
1	None	100	*cis*	43.5	>98	<2	44
2	None	100	*trans*	43.5	<2	>98	46
3	None	100	74% *cis* 26% *trans*	43.5	83	17	45
4	CH_2Cl_2	10	*cis*	41.0	75	25	26
5	CH_2Cl_2	10	*trans*	41.0	36	64	32
6	CH_2Cl_2	10	74% *cis* 26% *trans*	41.0	70	30	27
7	CH_2Cl_2	2	*cis*	41.0	62	38	34
8	CH_2Cl_2	2	*trans*	41.0	39	61	23
9	CH_2Br_2	10	*cis*	43.5	52	48	28
10	CH_2Br_2	10	*trans*	43.5	52	48	26
11	CH_2Br_2	10	74% *cis* 26% *trans*	43.5	54	46	20
12	CH_2Br_2	10	*trans*	53.0	50	50	24
13	CH_3CN	10	*cis*	53.0	>98	<2	19
14	CH_3CN	10	*trans*	53.0	<2	>98	19
15	$CH_3COOC_2H_5$	10	*cis*	53.0	53	47	21
16	$CH_3COOC_2H_5$	10	*trans*	53.0	44	56	23
17	$CH_3COOC_2H_5$	2	*cis*	53.0	52	48	11
18	$CH_3COOC_2H_5$	2	*trans*	53.0	50	50	13

[a] Volume per cent of hydrocarbon in solvent. [b] Maintained to within ±0.1. [c] Yield of a 1:1 mixture of amino- and methylamino-1,2-dimethylcyclohexanes, based on sodium azide. [d] Compounds **10** and **11** are



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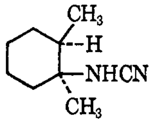

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vating NCN by a strictly collisional process. In actual fact, however, the heavier of the two solvents appears to be more efficient in the over-all deactivation of NCN. This is most readily seen from the results of reactions 4, 5, 9, and 10. In CH_2Cl_2 the reaction loses its stereospecificity in part but still exhibits considerable stereochemical bias toward retention of the original configuration,[19] whereas in CH_2Br_2, the reaction is stereochemically random, yielding the same mixture of stereoisomers irrespective of the stereochemical identity of the pure hydrocarbon substrate (reactions 9 and 10) or the hydrocarbon mixture (reaction 11). The greater efficacy of CH_2Br_2 in destroying the stereospecificity of the reaction is indicated even more strikingly from the results of reactions 7 and 8. Here it is seen that in CH_2Cl_2 the insertion is still strongly stereoselective even when the ratio of solvent to hydrocarbon is increased by a factor of 5 over that of reactions 4, 5, 9, and 10. We interpret these results to mean that NCN reacts partly as a triplet in CH_2Cl_2 and exclusively as a triplet in CH_2Br_2, and we conclude that the hydrogen-abstraction–recombination process by which in all certainty this species reacts with C–H bonds occurs in a completely nonstereospecific fashion. This is in full agreement with the notion that triplet NCN is produced from decay of singlet NCN since CH_2Br_2, possessing a heavier halogen, is required by theory to be the more effective of the two solvents in bringing about singlet–triplet interconversions. The widely different effectiveness of the two halocarbon solvents in destroying the stereospecificity of the reaction clearly eliminates the possibility that we are witnessing deactivation of an originally produced stereospecifically inserting singlet, say ${}^1\Sigma_g{}^+$, to a lower energy, nonstereospecifically inserting singlet, say ${}^1\Delta_g$. Deactivation within such a spin-allowed process should be strictly collisional and should be independent of the nature of the halogen in the inert diluent. In this context, it should be noted that the results of reactions 4–12 can be rationalized without invoking a difference in the effectiveness between CH_2Cl_2 and CH_2Br_2 in deactivating NCN. For example, it could be argued that the same relative amounts of singlet and triplet NCN are produced in both solvents but that in CH_2Cl_2, unlike CH_2Br_2, the hydrocarbon fragment has a good memory of its origin, and recombination leads to product in a stereoselective fashion. In view of the similarity of the two halocarbons, we consider such a process to be a very poor alternative to the operation of a "heavy-atom" effect. Alternatively it could be rationalized that the different results in the two halocarbons are due to partial reaction of NCN with solvent. At first glance, this explanation is especially appealing because of the lower yields observed in the halocarbons, However, to explain the results on this basis, one has to assume that CH_2Br_2 scavenges singlet NCN exclusively whereas CH_2Cl_2 reacts with both spin variants of NCN. Again the structural similarity of the two solvents makes this situation very unlikely. In connection with the poorer yields observed when the reaction was carried out in the halocarbons, it should be noted that these do not detract in any way from the significance of the stereochemical results. For example, even on the extreme assumption that the difference in yields between the reactions carried out in CH_2Cl_2 and CH_2Br_2 (20–34%) and those conducted in the absence of a solvent (44–46%) is due exclusively to

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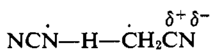
(19) The configurational assignment rests on rational assumptions rather than experimental fact (see ref 12).

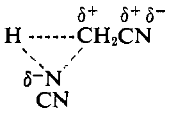
reaction of singlet NCN with solvent, one can readily estimate a minimum stereochemical crossover of 17% in CH_2Cl_2 and 22% in CH_2Br_2, as compared to <2% in the neat hydrocarbon.

Acetonitrile presents an interesting case. It is seen from the results of reactions 13 and 14 that this solvent is completely effective in preserving the stereospecificity of the reaction. Two possible explanations come to mind: (1) acetonitrile is totally ineffective in promoting singlet to triplet interconversions, and (2) triplet NCN is produced but is trapped effectively by CH_3CN. The low over-all yields of reactions 13 and 14 point strongly to the latter explanation as the correct one. In fact, it is reasonable to assume that an electron-deficient molecule such as CH_3CN would react preferentially with the less electrophilic triplet NCN. For example, for reaction of NCN with the C–H bonds of acetonitrile, there should be, for obvious reasons, a distinct preference for hydrogen abstraction by triplet NCN over direct insertion by singlet NCN. These two processes are depicted by **12** and **13**, respectively. In great contrast to acetonitrile, ethyl acetate is almost as ineffective as CH_2Br_2 in preserving stereospecificity, as is seen from the results of reactions 15 to 18. We can conceive of a number of reasons as to why this should be so. (1) Ethyl acetate, containing a greater number of atoms than the other inert diluents studied here, ought to be the most effective in the purely collisional part of the deactivation process. In addition, the carbonyl functionality in all probability introduces some triplet character to the ground state[20] of ethyl acetate, a property that should make this solvent effective in promoting intersystem crossing in NCN by the mechanism in Scheme I. (2) Triplet NCN could form from singlet NCN by a process involving spin exchange with the solvent, *i.e.*, $^1NCN + {}^1[CH_3COOC_2H_5] \rightarrow {}^3NCN + {}^3[CH_3COOC_2H_5]$. (3) The loss of stereospecificity may be due to reaction of singlet NCN by a hydride-abstraction–recombination process ($RH + {}^1NCN \rightarrow R^+N^-HCN \rightarrow RNHCN$) which ought to be more favorable in ethyl acetate than in the less polar halocarbon solvents. (4) The presence of relatively large amounts of triplet NCN could be a consequence of preferential scavenging of singlet NCN by solvent. Of these four, possibilities 2 and 3 can be eliminated fairly readily. In (2), the occurrence of a spin-transfer process between NCN and solvent requires that the $S_0 \rightarrow T_1$ energy separation in ethyl acetate be smaller than or equal to the $T_0 \rightarrow S_1$ energy gap in NCN. This is not the case; T_1 in ethyl acetate is probably in the vicinity of 130 kcal/mole above the ground state[21] whereas, as one can readily see from Figure 1, the maximum possible $T_0 \rightarrow S_1$ separation in the NCN system has to be less than 3.72 ev or 87 kcal/mole.[22] Possibility 3 can be reasonably dismissed on the argument that if hydride abstraction occurs in ethyl acetate, it should occur in acetonitrile as well, since both solvents ought to provide equally favorable polar environments. The complete stereospecificity of the reaction in acetonitrile attests to the absence of such a two-step process. The two remaining possibilities (1 and 4) are both attractive, but a distinction between them is not possible on the available information. It is quite possible that ethyl acetate derives its efficacy for destroying the stereospecificity of the reaction from both processes.



$\dot{N}C\dot{N}\text{—H—}\overset{\delta^+\delta^-}{CH_2CN}$

12



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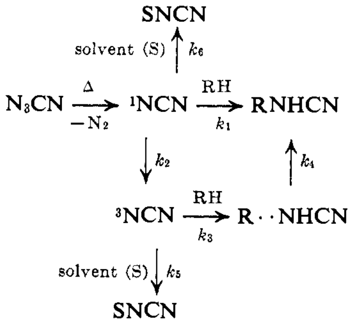
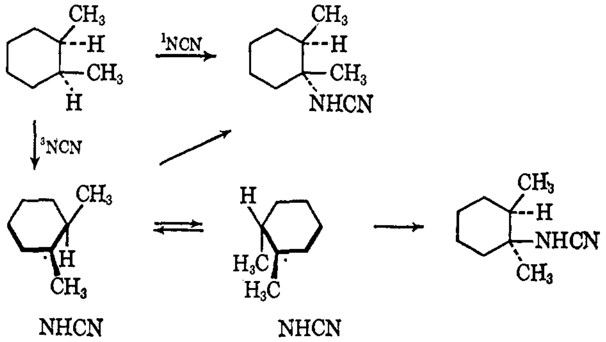
The results collected in Table I are best rationalized by the set of reactions shown in Scheme II. Within this mechanism, k_1 is much larger than k_2 in the absence of a solvent, comparable to k_2 in CH_2Cl_2 and much smaller than k_2 in CH_2Br_2 and possibly $CH_3COOC_2H_5$. In CH_3CN, k_5 is probably large compared to k_3, leading to results identical with those obtained in the case where $k_1 >> k_2$. In $CH_3COOC_2H_5$, a large k_6 may be partly responsible for the similarity of the results to those obtained when $k_2 >> k_1$. It should be noted that any radical processes involving attack by substrate or solvent radicals on N_3CN can be reasonably dismissed since under these conditions stereoisomerization of the hydrocarbon by way of its radical should set in. In all cases, the recovered hydrocarbon was uncontaminated with its isomer. The stereochemical details of the reaction (employing the *cis* hydrocarbon as reference) are depicted in Scheme III. Here equilibration between the stereoisomeric radicals should be a rapid process compared with over-all recombination.

Scheme II



Scheme III



The ready and efficient environmental control of the electronic multiplicity of NCN described here provides a convenient means for studying reactions of the two spin variants separately. In order to determine the elec-

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(20) This is a consequence of the small singlet to triplet energy gap which characterizes n–π* states.

(21) This value represents the energy of the first excited n–π* singlet in ethyl acetate (J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 429). Experience suggests that the energy of the first excited triplet should be close to this value.

(22) The assumption here is that the usual energy alternation of singlets and triplets holds for the low-energy states of NCN, *i.e.*, $E(^1\Delta_g) < E(^3\Pi_u) < E(^1\Pi_u)$.

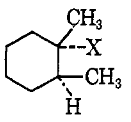
tronic multiplicity of NCN in a certain reaction, one needs to know the rate of that reaction relative to the rate of insertion into the tertiary C–H bonds of 1,2-dimethylcyclohexane. Reactions that involve a lower energy path than insertion into the tertiary C–H bonds should occur by way of singlet NCN when conducted in the absence of a solvent. Conversely under the same conditions, NCN could enter reactions that are slower than the reference reactions as either a singlet or a triplet. Furthermore, these latter reactions should occur exclusively through triplet NCN when conducted in CH_2Br_2. The complexity of the 1,2-dimethylcyclohexanes poses a serious problem in their use as reference compounds since they produce a large number of isomeric cyanamides, some of which may interfere in the observation and structural elucidation of the product(s) of interest. Hence, we examined the structurally simpler paraffinic substrates, cyclohexane and cyclopentane, as potential reference materials. The results are shown in Table II. It is clear from the data that the difference in reactivity betweeen the tertiary C–H bonds of the dimethylcyclohexanes and the methylene functions of the two cycloalkanes toward singlet NCN is quite small, indicating that the two cycloalkanes could conceivably be used as reference materials. These results also indicate a small difference between the reactivities of the tertiary C–H bonds of *cis*- and *trans*-1,2-dimethylcyclohexane. One can estimate a factor of 1.7 in favor of the *cis* isomer. Interestingly, the same factor can be derived from the results of reaction 3 and those of 4 and 5 (in conjunction with those of 9 and 10) shown in Table I. This small but reproducible difference in reactivity could be due to steric reasons since the tertiary hydrogens of the *trans* compound, being *cis* to the methyl groups, should be less accessible sterically. However, the difference is fairly small and could be the result of a recurring experimental error as well. Another interesting feature of the results of Table II is that triplet NCN discriminates slightly better (2.1 times) than singlet NCN between tertiary and secondary C–H bonds. This is consistent with the lower energy content of triplet NCN.

Table II. Relative Affinity of NCN for the Tertiary C–H Bonds of *cis*- and *trans*-1,2-Dimethylcyclohexane and the C–H Bonds of Cyclopentane and Cyclohexane at 43.5 ± 0.1°

Reaction	Solvent	Hydrocarbon[a]	C–H bond	Affinity[b,c]
19	None	A	3	4.2
		C	2	1.0
20	None	B	3	2.4
		C	2	1.0
21	None	B	3	3.5
		D	2	1.0
22	CH_2Br_2	B	3	5.0
		C	2	1.0

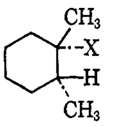
[a] A, *cis*-1,2-dimethylcyclohexane; B, *trans*-1,2-dimethylcyclohexane; C, cyclopentane; and D, cyclohexane. [b] In each reaction, the secondary C–H bonds are assigned the arbitrary value of 1.0. [c] Values are corrected for statistical factors.

Product Analysis. The information collected in Tables I and II was obtained as follows. Dilute solutions of N_3CN in the appropriate hydrocarbon(s) and solvent were thermolyzed at the temperatures indicated. Higher temperatures were necessary to effect thermolysis at reasonable rates in the more polar solvents CH_3CN and $CH_3COOC_2H_5$ in view of the greater stability of N_3CN in such media. A control experiment in CH_2Br_2 at the higher temperature (reaction 12) indicated that the results are not temperature dependent within the narrow temperature range employed here. The crude mixtures of cyanamides were converted to the corresponding amino and methylamino compounds by treatment with a large excess of lithium aluminum hydride in boiling tetrahydrofuran. The mixtures of amines were analyzed by gas–liquid partition chromatography (glpc), and the amines of interest, **14** to **17**, identified by direct comparison of their retention times and mass spectrometric cracking patterns with those of authentic materials.[23] The yields indicated are those of crude 1:1 mixtures of amino and methylamino compounds and are based on the amount of sodium azide employed in the preparation of cyanogen azide. The yields of all reactions conducted in the absence of a solvent were calculated from the weight of the crude amine mixture. The yields of the reactions which were carried out in a solvent were those calculated from the weight of the crude amines multiplied by a factor which was obtained by dividing the total glpc area of the amine mixture from that reaction by the total glpc area of the amine mixture obtained from the same hydrocarbon in the absence of a solvent. This method of calculation rests on the assumption that all volatile components in the product mixture of the reaction conducted in a solvent are amines derived from the hydrocarbon substrate(s). That this is a valid assumption is indicated from the virtual identity of the glpc patterns of mixtures from reactions in different solvents containing comparable amounts of the various stereoisomers. For example, the glpc patterns from reactions 13, 14, 15, and 16 are the same as those from 1, 2, 9, and 10, respectively. Only in one case (reaction 21) did the retention times of two amines of interest coincide. The amines were N-methylcyclohexylamine (**16b**) and 1-amino-*trans*-1,2-dimethylcyclohexane (**15a**). The relative amounts of these two components were estimated from the relatively constant ratio in which **15a** and **15b** are present in the various amine mixtures.



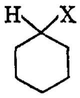
14

a, X=NH_2
b, X=$NHCH_3$



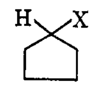
15

a, X=NH_2
b, X=$NHCH_3$



16

a, X=NH_2
b, X=$NHCH_3$



17

a, X=NH_2
b, X=$NHCH_3$

Conclusion

The results reported in this paper indicate that *thermolysis of cyanogen azide in the temperature range of 41–53° proceeds with conservation of spin to yield singlet NCN which inserts stereospecifically into tertiary C–H bonds. This species can be readily deactivated through collisions with a suitable inert diluent to triplet NCN which reacts with tertiary C–H bonds by a totally stereorandom hydrogen-abstraction–recombination process.* Triplet NCN is slightly more selec-

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[23] Authentic amines **14a**, **14b**, **15a**, and **15b** were prepared according to K. E. Hamlin and M. Freifelder, *J. Am. Chem. Soc.*, **75**, 369 (1953). See also ref 12.

Table III. Identifying Features of the Amines

Compd	Retention time, min	Molecular ion, *m/e*	100% Ion, *m/e*
14a	33.0	127	70
b	24.8	141	84
15a	21.2	127	70
b	13.5	141	84
16a	30.6	99	56
b	21.3	113	70
17a	16.0	85	56
b	12.4	99	70

Table IV. Quantitative Data of Reactions of the 1,2-Dimethylcyclohexanes with NCN in Various Solvents

Reaction[a]	Sodium azide, g	Cyanamide mixture, g	Amine mixture, g	Compn of amine mixtures,[b] %				Total glpc area, %	Over-all yield, %
				14a	**14b**	**15a**	**15b**		
1	2	2.6	1.8	20.0	30.5	...	~0.5	100	44
2	2	2.5	1.9	...	...	10.7	25.0	100	46
3	2	2.3	2.0	23.8	28.5	3.5	7.0	90	45
4	2	2.6	1.2	13.0	20.4	3.8	8.4	90	26
5	2	2.2	1.4	5.7	8.4	7.3	18.6	93	32
6	2	2.2	1.5	11.0	20.3	2.8	10.7	73	27
7	2	2.4	1.6	10.5	19.2	6.3	12.5	87	34
8	2	2.6	1.4	6.1	13.6	11.6	19.2	69	23
9	2	2.6	1.6	10.6	22.7	7.6	23.0	73	28
10	2	2.6	1.3	12.3	21.8	8.7	22.9	84	26
11	2	3.0	1.4	18.0	20.1	13.5	18.3	59	20
12	2	3.1	1.6	10.2	20.4	8.3	22.3	63	24
13	2	2.5	1.0	13.1	32.0	...	~0.5	77	19
14	2	2.1	1.0	...	...	8.9	24.6	78	19
15	2	2.5	1.4	9.7	18.1	9.0	14.7	61	21
16	2	2.6	1.3	7.9	12.9	9.0	18.5	72	23
17	2	1.5	0.8	13.0	20.6	11.5	19.1	55	11
18	2	1.3	0.6	7.8	15.7	7.8	16.4	90	13

[a] As per Table I. [b] By weight.

Table V. Quantitative Data of Reactions of NCN with the 1,2-Dimethylcyclohexanes, Cyclopentane, and Cyclohexane

Reaction[a]	Solvent	Hydrocarbon[b,c]	Amine mixture, g	Compn[d] of amine mixtures, %								Total glpc area, %	Over-all yield,[e] %
				14a	**14b**	**15a**	**15b**	**16a**	**16b**	**17a**	**17b**		
19	None	A = 46.4 C = 53.6	1.4	13.2	17.1	...	...	...	...	6.8	22.7	96	38
20	None	B = 37.0 C = 63.0	1.3	...	...	4.9	13.8	...	...	11.0	35.9	100	37
21	None	B = 39.6 D = 60.4	1.9	...	...	5.0	12.9	15.6	37.0	...	...	99	43
22	CH_2Br_2	B = 46.0 C = 54.0	1.5	9.5	11.6	6.1	14.8	...	...	8.4	26.7	79	27

[a] As per Table II. [b] A, *cis*-1,2-dimethylcyclohexane; B, *trans*-1,2-dimethylcyclohexane; C, cyclopentane; D, cyclohexane. [c] Mole per cent. [d] By weight. [e] Calculated on the assumption that the mixture consists of an equal amount of the components shown in columns 5–12.

tive in its reaction between tertiary and secondary C–H bonds than is singlet NCN, as is expected from its lower energy content. Overlap considerations suggest that, in the absence of perturbation in the transition state, the $^1\Sigma_g^+$ state is more likely to react stereospecifically with C–H and C=C bonds than is the $^1\Delta_g$ state.

Experimental Section[24]

Materials. Of the hydrocarbons employed, the 1,2-dimethylcyclohexane and cyclopentane were "Phillips Research Grade," and the cyclohexane was "Eastman Spectrograde." They all were better than 99.7% pure by glpc and were used without further purification. Of the solvents, ethyl acetate was "Fisher Reagent Grade," and acetonitrile (anhydrous) and dichloromethane were Eastman (White Label) and were used without further purification. Methylene bromide was purified by careful distillation immediately before use (better than 99.5% pure).

General Procedure of the Reaction. In the absence of a solvent, the reaction was carried out in the manner described in the preceding paper.[12] When a solvent was employed, the general procedure was as follows. Cyanogen azide was prepared in the usual manner[12] from sodium azide (2 g) and cyanogen chloride (*ca.* 50 ml). The appropriate solvent (*ca.* 100 ml) was added and the excess cyanogen chloride removed at 200–300 mm, through the condenser maintained at 5–10°, until the temperature of the suspension was 20–25°. The amount of time required for this operation varies with the solvent; polar media such as acetonitrile and ethyl acetate require longer periods. The suspension was filtered under nitrogen pressure and the filtrate made up to a total of 300 ml with solvent. To this was added the appropriate hydrocarbon or hydrocarbon mixture[25] (30 ml) and the well-mixed solution transferred into a one-necked, 500-ml flask fitted with a condenser and connected (through the top of the condenser) to a wet test meter by way of a trap maintained at Dry Ice–acetone temperatures.

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[24] Infrared spectra were obtained with a Perkin-Elmer 21 spectrometer, and mass spectra were determined with a Bendix time-of-flight mass spectrometer. The glpc results were obtained under the following conditions: A, 2 × 2 m × 0.25 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 165°; helium was used as the carrier gas at a flow rate of 74 cc/min; B, 2 m × 0.25 in., copper column packed with 20% 1,2,3-tris(2-cyanoethoxy)-propane (TCEGE) on 60–80 mesh Gas Chromosorb R at 52° with the vaporizer at 120°; helium was used as the carrier gas at a flow rate of 67 cc/min.

[25] The composition of this mixture was determined by glpc under conditions B.

The flask was immersed in a constant-temperature water bath and maintained to within 0.1° of the required temperature overnight, after which period the theoretical amount of nitrogen had evolved. The mixture was then filtered free of any traces of precipitate that might be present and a glpc sample (*ca.* 1 ml) taken from the filtrate and analyzed for type of hydrocarbon present, under conditions B. The remainder of the filtrate was then concentrated first under water-aspirator pressure at *ca.* 30–40° and then at 3–5 mm and room temperature to yield a light orange viscous oil (*ca.* 2 g), which exhibited strong characteristic –NHCN infrared absorption at 3200 (N–H) and 2200 cm^{-1} (C≡N). The cyanamide mixture was then converted to an amine mixture by treatment with a great excess of lithium aluminum hydride in boiling tetrahydrofuran as described in the preceding paper.[12] The mixture of amines was analyzed by gas–liquid partition chromatography under conditions A, and the amines of interest were identified by direct comparison of their glpc retention times and mass spectrometric cracking patterns with those of authentic samples. The relevant data employed in the identification are shown in Table III. The quantitative results are compiled in Tables IV and V. The yields tabulated were calculated from the weights of the crude amine mixtures in conjunction with the total glpc area observed in each case. For example, the yield of reaction 7 based on weight of amine mixture (assuming a 1:1 mixture of amino and methylamino compounds) is 39% which, after correction for total amount of volatile material, becomes 39 × 87/100 = 34%. The various reaction numbers correspond to those shown in Tables I and II.

Acknowledgment. The author is indebted to Miss Patricia Canfield for the glpc determinations.

The Preparation and Properties of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene and Its Derivatives

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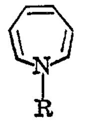
Received February 10, 1967

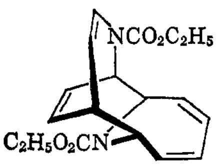
Abstract: The thermodynamically more stable dimers of 1-cyano-, 1-ethoxycarbonyl, 1-*t*-butoxycarbonyl, and 1-methylazepine are all representatives of the new 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene ring system. These compounds are formed from kinetically produced isomers which rearrange on further thermal treatment to the doubly bridged piperazine system. The chemistry of this system and the fully reduced 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane system is discussed in detail.

Recently, brief descriptions have appeared[1] of the dimers of 1-cyanoazepine (**1a**),[1a,b] 1-ethoxycarbonylazepine (**1b**),[1c] and 1-methylazepine (**1c**).[1d] Our more recent observation of the dimerization of 1-*t*-butoxycarbonylazepine (**1d**) suggests that this is a general property of the azepine nucleus. This paper is concerned with the thermally more stable dimers which belong to the new 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene ring system (**3**).



1a, R = CN
b, R = $CO_2C_2H_5$
c, R = CH_3
d, R = $CO_2C(CH_3)_3$
e, R = CON_3
f, R = CO_2CH_3

At relatively low temperatures, the parent azepines dimerize readily to kinetically controlled products which lack an element of symmetry. In particular, **1a** dimerizes at 25–60° to a white crystalline product, mp 220–221° dec,[1a,b] **1b** dimerizes at 130° to a white solid, mp 78°,[1c] and **1c** forms a colorless solid, mp 66°.[1d] The structure of the dimer of **1a** is different from that postulated for the dimers of **1b** (**2**)[1c] and **1c**[2] and it will be discussed elsewhere.[3] At higher temperatures, thermally more stable isomers are obtained which are 13,14-disubstituted 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraenes (**3**). Specifically, the dimer



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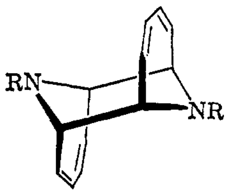

3a, R = CN
b, R = $CO_2C_2H_5$
c, R = CH_3
d, R = $CO_2C(CH_3)_3$
e, R = $CONH_2$
f, R = H
g, R = NO
h, R = C_2H_5
i, R = $CH_2CH{=}CH_2$
j, R = $CH_2CH_2CH{=}CH_2$
k, R = *trans*-$CH_2CH{=}CHC_6H_5$
l, R = CH_3CO
m, R = *cis*-$COCH{=}CHCO_2H$
n, R = C_6H_5CO
o, R = *p*-BrC_6H_4CO
p, R = C_6H_5NHCO
q, R = C_6H_5NHCS
r, R = $CO_2C_{10}H_{15}$
s, R = $COCH_2Cl$
t, R = $COCH_2N(C_2H_5)_2$
u, R = $CH_2CO_2C_2H_5$

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(1) (a) F. D. Marsh and H. E. Simmons, *J. Am. Chem. Soc.*, **87**, 3529 (1965); (b) A. L. Johnson and H. E. Simmons, *ibid.*, **88**, 2591 (1966); (c) L. A. Paquette and J. H. Barrett, *ibid.*, **88**, 2590 (1966); (d) K. Hafner and J. Mondt, *Angew. Chem.*, **78**, 822 (1966).

(2) K. Hafner, private communication.

(3) F. D. Marsh, A. L. Johnson, and H. E. Simmons, in preparation.