state for phenylacetylene as compared to the corresponding change from C_{sp}–C_{sp^3} to C_{sp^2}–C_{sp^3} for methylacetylene.[4]

The same type of bond hybridization change is incorporated in the model of Streitwieser, *et al.*,[5] for calculating secondary deuterium isotope effects. This model predicts that deuteriophenylacetylene should hydrate some 1.3 times faster than phenylacetylene. The observed reactivity shows that additional effects must be operating. Two may be suggested. Increased hyperconjugative stabilization may occur in III, R = H, where both carbon–hydrogen bonds are *ideally* situated for overlap with the empty p-orbital. The importance of such an effect in hyperconjugative enhancement of geminal coupling constants in allenic and ketenic structures has recently been discussed.[6] Alternatively, hydrogen bonding from the acetylenic hydrogen to solvent may provide more effective solvation in the transition state. Experimental work is in progress to clarify these points.

It is interesting to compare the relative ease of formation of vinylic and saturated carbonium ions from acetylenes and olefins, respectively. Rates of hydration of compounds reported here may be compared to those of cinnamic acids[7] and styrene.[1a]

Phenylpropiolic acid is hydrated 19 times more rapidly than *cis*-cinnamic acid; phenylacetylene is hydrated 2.3 times more rapidly than styrene under comparable conditions. Vinylic cations are thus seen to be more readily accessible in moderately acidic solutions than are ordinary carbonium ions.

A growing body of evidence has appeared recently implicating vinylic cations as intermediates in a variety of reactions. The protonation of acetylenes to vinylic cations has been invoked in discussions of the hydration of acetylenic ethers,[8–10] the hydration of 3-hexyne,[11] and the trifluoroacetic acid catalyzed reactions of 1- and 3-hexyne and 5-chloro-1-pentyne.[12] The acid-catalyzed cleavage of (phenylethynyl)triethylgermanes[13] has also been proposed to take place through these intermediates. Finally, studies of the solvolyses of α-bromostyrene[14] and α,β-unsaturated β-halocarboxylate ions[15] indicate that these, too, may proceed by way of vinylic cations. The present work constitutes one more piece of evidence to show that vinylic cations are relatively common reactive intermediates.

Acknowledgment. Supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the donors of these funds.

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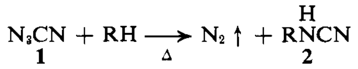
Received March 6, 1965

Cyanonitrene. Reaction with Saturated Hydrocarbons

Sir:

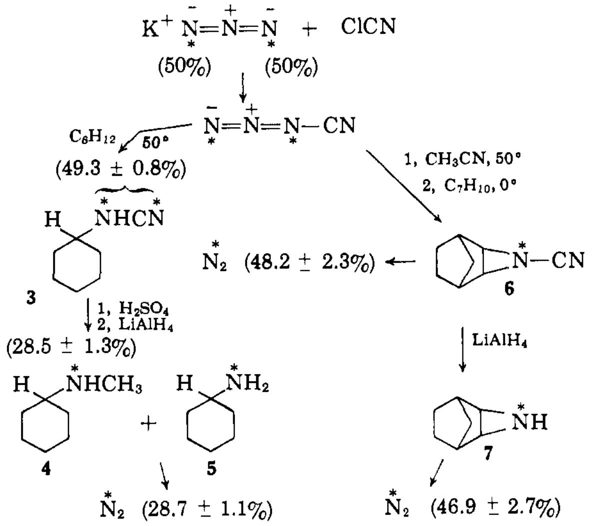
We wish to report on the thermally-induced reaction of cyanogen azide[1] with alkanes.

When solutions of cyanogen azide (**1**) in saturated hydrocarbons are heated at 40°, nitrogen is evolved and *primary* alkylcyanamides **2** are formed. A reasonable mechanism for this reaction involves decomposition of cyanogen azide to nitrogen and cyanonitrene followed by insertion[2] of the latter into a C–H bond.



$$\underset{\mathbf{1}}{N_3CN} + RH \xrightarrow[\Delta]{} N_2\uparrow + \underset{\mathbf{2}}{R\overset{H}{N}CN}$$

The transient existence of NCN was established by the use of isotopically labeled (^{15}N) cyanogen azide, which was prepared from KN*=N=N* and cyanogen chloride and was decomposed thermally in cyclohexane. The resulting cyclohexylcyanamide (**3**) was degraded as shown. Mass spectrometric analysis of **4** and of the nitrogen obtained from **4** and **5** on combustion afforded a value close to theory (25%) for complete scrambling, in keeping with the intermediacy of NCN. The possibility of prereaction scrambling was excluded by heating labeled cyanogen azide in acetonitrile, quenching with norbornene, and degrading the resulting cyanoaziridine **6** as shown.



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[2] The term insertion is used here in a general way to indicate end result rather than mechanistic detail.

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.

The relative affinity of NCN for insertion into C–H bonds was determined and is shown in Table I. The data compiled in A and B are the result of intramolecular[3,4] and intermolecular[5] competition, respectively.

The discrimination displayed in NCN insertions into different C–H bonds is consistent with schemes in which considerable C–H bond rupture has occurred in the transition state (TS).

$$\mathrm{RH} + {}^{1}\mathrm{NCN} \longrightarrow \mathrm{TS} \longrightarrow \text{products} \qquad (1)$$

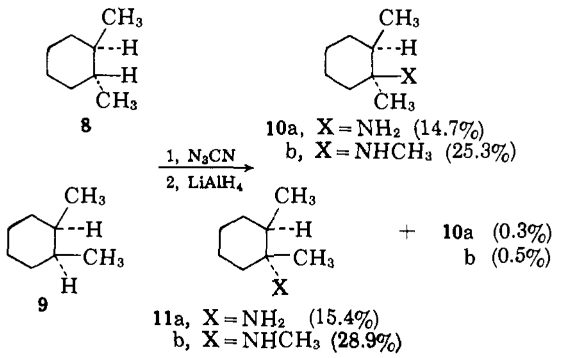
$$\mathrm{RH} + {}^{1}\mathrm{NCN} \longrightarrow \mathrm{TS} \longrightarrow \underset{+}{\mathrm{C}}\overset{\mathrm{H}}{\underset{-}{\mathrm{N}}}\mathrm{CN} \longrightarrow \text{products} \qquad (2)$$

$$\mathrm{RH} + {}^{3}\mathrm{NCN} \longrightarrow \mathrm{TS} \longrightarrow \underset{\cdot}{\mathrm{C}}\overset{\mathrm{H}}{\underset{\cdot}{\mathrm{N}}}\mathrm{CN} \longrightarrow \text{products} \qquad (3)$$

The virtually complete lack of discrimination of NCN in its reaction with the C_6, C_7, and C_8 monocycles tends to disfavor eq. 2.[6] Furthermore, thermolysis of cyanogen azide in 1,1-dimethylcyclohexane failed to yield any 1-cyanamido-1-methylcycloheptane which should have been an important product had a free carbonium ion intermediate been involved.

The stereochemistry of the reaction was examined with *cis*- and *trans*-1,2-dimethylcyclohexane. Cyanogen azide was thermolyzed in the presence of pure **8** and **9**, and the resulting cyanamide mixtures were converted with lithium aluminum hydride to the corresponding amino- and methylamino compounds in the proportions shown.[7]

The high stereoselectivity of this reaction is consistent with either reaction 1 or a special case of 2 or 3 in which the intermediate is a tight pair and recombination occurs prior to inversion, *i.e.*, the existence of a *free* intermediate is excluded by the present results.



Cyanonitrene was observed recently in the flash photolysis of diazomethane[8] and cyanogen azide,[9] and its ground state is ${}^{3}\Sigma_{g}^{-}$.

Preliminary work on the photolysis of cyanogen azide[10] indicates that in *n*-hexane cyanonitrene displays a sevenfold preference for insertion into a secondary C–H bond over insertion into a primary C–H bond.

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(3) The relative affinity of NCN for various C–H bonds is very similar to that displayed by carbethoxynitrene generated photolytically, by base-induced α-elimination (W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **86**, 3164 (1964)), or thermally (M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, No. **40**, 2945 (1964)).

(4) The crude mixtures of cyanamides were analyzed on the basis of their hydrogen n.m.r. spectra. The NH proton of the cyanamides appears at τ ~4.2 whereas the signals due to the C–H protons α to the NHCN function occur in the region τ 7.

(5) The values tabulated were obtained by gas chromatographic analysis of the mixtures of amino and methylamino compounds to which the corresponding cyanamides were converted with lithium aluminum hydride. The amines in the mixtures were identified by comparison of the g.c. retention times and mass spectrometric cracking patterns with those of authentic samples.

(6) In saturated carbocycles, reactivity is a more sensitive function of ring size during the production of an incipient carbonium ion, *e.g.*, solvolyses of tosylates (A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 95), than in the generation of the corresponding radical (G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958); E. S. Huyser, H. Schimke, and R. L. Burham, *J. Org. Chem.*, **28**, 2141 (1963)).

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Received March 11, 1965

The Photochemistry of Ketene. The Methylene Radical

Sir:

The relationship of excited state multiplicity to mode of dissociation is a matter of current interest.[1–3] Ketene is of interest because it has often been used as a source of methylene radicals.[4,5] Singlet methylene adds stereospecifically to double bonds[6,7] and inserts into carbon–hydrogen bonds.[8] Triplet methylene adds to double bonds nonstereospecifically and does not insert into carbon–hydrogen bonds. Herzberg has shown that the ground state of methylene is triplet[9] and that the lowest singlet state lies only a few tenths of an electron volt above the ground state.

Under ordinary experimental conditions, singlet methylenes do not cross over to triplet methylenes rapidly[6,10] and the reverse reaction would require an appreciable activation energy. Nevertheless, recent evidence[10] indicates that both singlet and triplet methyl-

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