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).

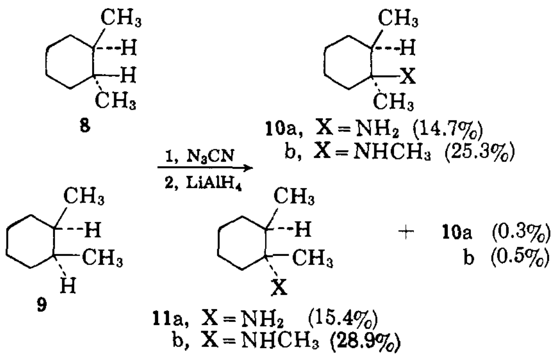
$$\mathrm{RH} + {}^{1}\mathrm{NCN} \longrightarrow \mathrm{TS} \longrightarrow \text{products} \qquad (1)$$

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

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

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]


8

9

10a, X = NH_2 (14.7%)
b, X = $NHCH_3$ (25.3%)

11a, X = NH_2 (15.4%)
b, X = $NHCH_3$ (28.9%)

+ **10a** (0.3%)
b (0.5%)

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)).

[7] Structural assignments were based on direct comparison of the mass spectral patterns and g.c. retention times with those of authentic materials.

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

[9] G. J. Pontrelli and A. G. Anastassiou, *J. Chem. Phys.*, in press.

[10] Irradiated with a low-pressure mercury arc at *ca.* 20°.

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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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[2] P. Borrell, *ibid.*, **86**, 3156 (1964).

[3] P. Ausloos and R. E. Rebbert, *ibid.*, **86**, 4512 (1964).

[4] J. N. Butler and G. B. Kistiakowsky, *ibid.*, **82**, 759 (1960).

[5] T. Terao and S. Shida, *Bull. Chem. Soc. Japan*, **37**, 687 (1964).

[6] F. A. L. Anet, R. F. W. Bader, and A. Van der Awera, *J. Am. Chem. Soc.*, **82**, 3217 (1960).

[7] B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *ibid.*, **81**, 1081 (1959).

[8] H. M. Frey, *ibid.*, **82**, 5947 (1960).

[9] G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

[10] J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).

enes are present when ketene is irradiated at an average wave length of about 3200 Å. Dissociation of an excited ketene molecule would be expected to give singlet methylenes if the state is singlet and to give triplet methylenes if the state is triplet. It has been suggested[11] that some of the anomalies in methylene behavior may be due to varying ratios of singlet to triplet radicals. We wish to report data which bear on this point.

Earlier work[12] has indicated a marked difference in photochemical behavior of ketene at wave lengths around 2700 Å. from that at wave lengths around 3700 Å. The behavior at 3200 Å. is intermediate between the two cases. At 2700 Å. the quantum yield of carbon monoxide formation is 2 within experimental error. At 3700 Å. it is both pressure and temperature dependent. Also oxygen reduces the ethylene yield at 2700 Å. from about 0.91 to about 0.64. This yield, however, is not dependent on oxygen pressure. At 3650 Å. the ethylene yield is strongly dependent on oxygen pressure and is reduced to less than one-third of its oxygen-free value. Yields at 3700 Å. are temperature dependent and the apparent activation energy for dissociation of excited ketene is roughly 4 kcal.

Frey[8] and Simons and Rabinovitch[10] have used *cis*-butene-2 to distinguish between singlet and triplet methylenes, and this device has been used in the present work. Let α be the fraction of methylenes in the singlet state and $1 - \alpha$ the fraction in the triplet state. Then the ratio of "singlet type" products to "triplet type" products will be

$$R = \frac{\alpha + {}^1/_2(1 - \alpha)}{{}^1/_2(1 - \alpha)} = \frac{1 + \alpha}{1 - \alpha}$$

This equation assumes that $CH_2(T)$ gives only *cis*- and *trans*-dimethylcyclopropane and that these do not isomerize. Thus the value of α calculated in this way may be slightly low. In the present instance this ratio will be equal to (*cis*-1,2-dimethylcyclopropane + *cis*-pentene-2 + 2methylbutene-2)/*trans*-1,2-dimethylcyclopropane = R.

The products were analyzed by gas chromatography. The light source was an Osram 500-w. lamp. Emission from this lamp is nearly a continuum. By color filters one region extending from 2650 to 2950 Å. (A) was isolated and another from 3460 to 3820 Å. (B) was also used. The following average results in the absence of foreign gas were obtained: region A, $R = 14 \pm 3$; region B, $R = 4 \pm 1$. Hence $\alpha = \sim 0.88 \pm 0.04$ for region A and 0.6 ± 0.1 for region B if the data are taken at face value. However "hot" molecules are formed by reaction of methylenes with the butene,[13,14] and these may isomerize before they lose vibration energy. In the limit this phenomenon would give an apparent value of 0.5 for α. The effect can be minimized by adding an inert gas such as nitrogen and at moderate pressures the complication of inducing the singlet to triplet transition of methylenes will be unimportant. If nitrogen is added, the data indicate that in the region from 2650 to 2950 Å. the fraction of singlet methylenes is over 0.98. In the longer wave region the true value of α is undoubtedly well below 0.5. It is interesting to note that the fraction of triplet methylenes in the long wave region agrees well with that found by Simons and Rabinovitch.[10]

Tentatively one can suggest that triplet methylenes react more rapidly with oxygen than do the singlet methylenes. This will explain at least partially the effect of oxygen on ethylene yields.[121,5]

It is suggested, therefore, that at short wave lengths the primary photochemical process in ketene is

$$CH_2{=}C{=}O + h\nu = CH_2\,(S) + CO \tag{1}$$

The data do not show whether or not (1) occurs immediately or after a time lag, but since there is no effect of pressure at 2700 Å. presumably dissociation at this wave length is very rapid.

At the longer wave lengths the primary process should be

$$\begin{aligned}
CH_2{=}C{=}O + h\nu &= CH_2{=}C{=}O\,(S) && (2)\\
CH_2{=}C{=}O\,(S)\,(+M) &= CH_2\,(S) + CO\,(+M) && (3)\\
&= CH_2{=}C{=}O\,(T)\,(+M) && (4)\\
CH_2{=}C{=}O\,(T)\,(+M) &= CH_2\,(T) + CO\,(+M) && (5)\\
&= CH_2{=}C{=}O\,(+M) && (6)
\end{aligned}$$

where (S) denotes a singlet state and (T) triplet state.[12,16]

The data do not permit conclusions to be drawn about the role of collisions in (3)-(6) inclusive. The data of Simons and Rabinovitch[10] require (4) to be bimolecular. Possibly (4) is a quasi-unimolecular reaction.[11] For the time being we prefer to reserve judgment on this point. Further details will be published later.

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2-Decaprenylphenol, Biosynthetic Precursor of Ubiquinone-10[1a]

Sir:

A biosynthetic precursor of ubiquinone has now been isolated in pure form, and its structure has been established as 2-decaprenylphenol[1b] or 2-[3′-methyl-2-butenylenakis(3′-methyl-2′-butenylene)]phenol (I), a new substance. It is very likely that 2-decaprenylphenol is a member of a new group of 2-multiprenylphenols (II) which are in the biosynthetic pathways of the corresponding members of the ubiquinone[1] group (III). Also, it is plausible that such 2-multiprenylphenols, including lower (*i.e.*, n = 3, 4, and 9) homologs and 2-phytylphenol (IV), are precursors by other path-

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[1] (a) Coenzyme Q. LXV. (b) Nomenclature is based on a recommendation of an IUPAC–IUB Commission of Biochemical Nomenclature.