be seen that with increasing ROH concentration the exchange proceeds increasingly through $CH_3SOCH_2^-K^+$. Because we are unable to measure the relative concentrations of $CH_3SOCH_2^-K^+$ and $RO^-K^+$, we cannot assign rate constants for these reactions. The evidence is clear, however, that some $CH_3SOCH_2^-K^+$ must be present and reacting. This is also consistent with our observation that alkylations with $CH_3SOCH_2^-$ can be carried out almost instantaneously even in the presence of large amounts of alcohol.[4]

The results reported here are surprising in view of what has been assumed regarding the composition of solutions of DMSO–ROH–$RO^-K^+$.[5] It is possible that DMSO, behaving as a protic solvent, exerts a leveling effect similar to that of other solvents and that the apparent basicity of the solvent medium relative to "typical" carbon acids is a thermodynamic effect which involves ROH and $CH_3SOCH_2^-K^+$. Until now there has been no unambiguous way of determining the composition of the basic species undergoing reaction. It is clear, from our work as well as that of Ritchie,[6] that the properties of DMSO as a solvent for base-catalyzed reactions are significantly different from those expected of an "inert" solvent. As we have pointed out previously,[3] DMSO should not be characterized as aprotic, in spite of a continuing tendency for some workers to designate it in this way.[7] We emphasize that analyses of kinetic and thermodynamic basicities in DMSO must be approached with caution.

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[5] See ref 1 for literature references.

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[8] Stauffer Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1967.

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## The Electronic Multiplicity of Photolytically Generated Cyanonitrene

*Sir:*

We recently reported[1] that thermal fragmentation of cyanogen azide ($N_3CN$) in solution occurs with over-all conservation of spin to produce electronically excited singlet cyanonitrene (${}^1NCN$) which inserts stereospecifically into tertiary C–H bonds. In addition, we indicated[2] that initially produced singlet NCN will, under certain conditions, undergo efficient spin-forbidden decay to its triplet (${}^3\Sigma_g{}^-$) ground state[3–5] which reacts in a totally stereorandom fashion with tertiary C–H links. Similar conclusions concerning the electronic multiplicity of initially formed NCN and its spin-forbidden crossing to the ground state were also arrived at from experiments involving flash photolysis of $N_3CN$ in the gas phase.[6] Recent work,[7] however, on the flash photolysis ot $N_3CN$ in a solid nitrogen matrix appears to indicate that the photofragmentation of this molecule is not a simple process, as the multiplicity of initially produced NCN was found to be a function of the energy of the light employed. For example, it was observed that irradiation of $N_3CN$ through quartz produces singlet (${}^1\Delta_g$) NCN, whereas illumination through a Pyrex filter generates NCN exclusively in its ${}^3\Sigma_g{}^-$ ground state. To reconcile these results with the known ultraviolet spectrum of $N_3CN$[8] ($\lambda_{max}$ 2750 ($\epsilon$ 103) and 2200 Å ($\epsilon$ 2157)) it was suggested[7] that, whereas decomposition of this molecule from the 2200-Å excited state occurs with conservation of spin, fragmentation from the lower energy state (2750 Å) violates the requirement of quantization of spin. Alternatively, the direct formation of ${}^3\Sigma_g{}^-$ NCN was viewed to occur with over-all conservation of spin on the condition that the 2750-Å band in the spectrum of $N_3CN$ represents a singlet-to-triplet transition.[9]

Though both suggestions account for the facts, it is not clear why spin is not conserved in the fragmentation of the azide from a low-energy excited state or, if the 2750-Å band is indeed due to a spin-forbidden transition, why it should be as intense as it is. In an attempt to answer these questions satisfactorily we carried out the photolysis of $N_3CN$ at a variety of wavelengths and determined the electronic multiplicity of the generated NCN by examining the stereochemical course of its insertion into the tertiary C–H bonds of 1,2-dimethylcyclohexane. Irradiations of solutions of $N_3CN$ in the hydrocarbon were carried out at ~15° with a 450-w "Hanovia" high-pressure lamp employing Vycor (absolute cutoff point at ~2120 Å), Corex (absolute cutoff point at ~2580 Å), and Pyrex (absolute cutoff point at ~2800 Å) filters. As anticipated on the basis of the ultraviolet spectrum of $N_3CN$, nitrogen evolution was considerably slower on illumination through Pyrex than through Vycor or Corex.[10] Reduction of the resulting cyanamides to the corresponding amino and methylamino substrates and gas chromatographic analysis of these was accomplished in the manner described in earlier reports.[1,2] The results are collected in Table I.

The data collected in Table I clearly establish that photolytically generated NCN inserts into tertiary C–H

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[1] A. G. Anastassiou and H. E. Simmons, *J. Am. Chem. Soc.*, **89**, 3177 (1967).

[2] A. G. Anastassiou, *ibid.*, **89**, 3184 (1967).

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[7] L. J. Schoen, *ibid.*, 45, 2773 (1966).

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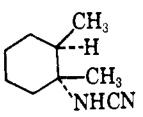
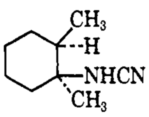
[10] Nitrogen evolution on irradiation of $N_3CN$ through either Vycor or Corex occurred *ca.* six times faster than when the irradiation was carried out through Pyrex. This rate difference strongly suggests that fragmentation of $N_3CN$ occurs from an electronically excited state rather than from a vibrationally excited ground state.

bonds stereospecifically, irrespective of light wavelength employed in its generation. In addition the gas chromatographs displayed by the three photolysis mixtures (reactions 1–3) were found to be virtually superimposable on one another and also qualitatively identical with that afforded by the mixture of amines formed from thermolysis of $N_3CN$ in the same hydrocarbon (reaction 4). This suggests a close similarity between NCN





produced thermally and that generated photolytically. It is also interesting to note that the proportion of products from insertion of NCN into tertiary C–H bonds appears to be consistently greater in the thermal than in the photochemical reaction. This is not unexpected, since input energy considerations require that photolysis produce a "hotter" NCN than thermolysis.

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

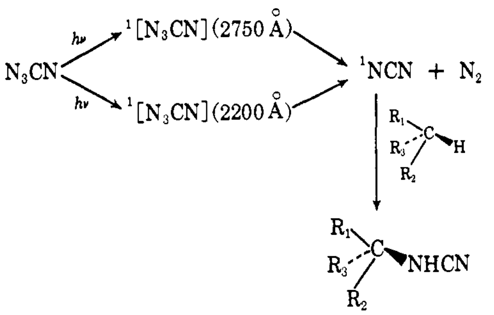
| Reaction | Conditions for decomposition of $N_3CN^a$ | Hydrocarbon | % *cis*-RNHCN (1)[b] | % *trans*-RNHCN (2)[b] |
|---|---|---|---|---|
| 1 | $h\nu$, $\lambda$ >2120 Å | *cis* | 41 | <0.5 |
| 2 | $h\nu$, $\lambda$ >2580 Å | *cis* | 39 | <0.5 |
| 3 | $h\nu$, $\lambda$ >2800 Å | *cis* | 34 | <0.5 |
| 4 | $\Delta$, 50° | *cis* | 44 | <0.5 |
| 5 | $h\nu$, $\lambda$ >2800 Å | 74% *cis*<br>26% *trans* | 29 | 7 |
| 6[2] | $\Delta$, 43.5° | 74% *cis*<br>26% *trans* | 52 | 10 |

[a] Photolyses were carried out at ~15°. [b] Proportion in total product mixture.

Translating the stereochemical results in terms of electronic multiplicity of generated NCN we conclude that *photolysis of cyanogen azide with light ranging from 2100 to ~3000 Å produces exclusively singlet NCN, and consequently that both the 2200- and the 2750-Å bands in the spectrum of $N_3CN$ arise from singlet–singlet transitions.* Our conclusions, though in contradiction with previous suggestions[7,9] based on spectroscopic work, are clearly in keeping with theory. Insofar as the photolysis of $N_3CN$ described here can be compared to that carried out in a solid nitrogen matrix, we offer the following tentative explanation to account for the discrepancy between the two sets of results. Irradiation through quartz very probably generates highly vibrationally excited singlet NCN. In a rigid matrix vibrational relaxation of this species to a level from which isoenergetic crossing to the $^3\Sigma_g^-$ potential surface could occur is undoubtedly a relatively slow process. Therefore the employed[7] delay times of 30–200 $\mu$sec between flash and analysis lamp are adequate for observation of the initially formed $^1\Delta_g$ state.[11] On the other hand photolysis of $N_3CN$ through Pyrex would probably produce $^1\Delta_g$ NCN in a low vibrational level from which isoenergetic crossing to the $^3\Sigma_g^-$ state ought to occur rapidly. Hence, it is not inconceivable that under these latter conditions the lifetime of the $^1\Delta_g$ state will be reduced to a value below the minimum delay time employed (30 $\mu$sec) so that singlet NCN may escape detection altogether and its decay product $^3\Sigma_g^-$ NCN may erroneously be characterized as a primary fragment. The situation in our chemical experiments is quite different in that here insertion of initially produced singlet NCN into tertiary C–H bonds occurs more rapidly than decay to the $^3\Sigma_g^-$ ground state.[2]

Our findings are summarized in Scheme I.

**Scheme I**



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[11] A lifetime of ~500 $\mu$sec has been estimated for $^1\Delta_g$ NCN, generated by irradiation of $N_3CN$ through quartz.[7]

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## Linkage Isomerism in Phenylmercuric Benzenesulfinate

*Sir:*

Recently there has been considerable interest in complexes of metals with sulfinate ions,[1–10] and especially in the structures of sulfinato complexes formed by sulfur dioxide insertion into metal–carbon bonds.[1,3,4,7,8]

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