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(10) The physical and chemical properties of **14** were identical with those reported by Eschenmoser.[9] We are most grateful to Professor Eschenmoser for providing us with additional detailed spectral data.

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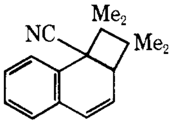
Exciplex and Electron-Transfer Chemistry.[1] Reactions of Naphthonitrile S_1 States with Tetramethylethylene

Sir:

There is much current interest in the photophysics[2-11] and photochemistry[1,10-18] of excimers and exciplexes, with particular regard to their role in cycloadditions and other photochemical processes. We have been active in this field for some time,[1,18] and have used nitriles in studying the photochemical effects of charge transfer. Aryl nitriles have recently attracted considerable attention because they can form fluorescent exciplexes with olefins.[7,11]

We now report recent work with 1- and 2-naphthonitrile (1-NN and 2-NN) and tetramethylethylene (TME), which indicates that (a) exciplexes of the nitriles and TME are intermediates in the cycloadditions which occur in benzene, (b) different factors seem to determine the formation of the exciplexes, and their collapse to products, and (c) in polar solvents, electron transfer dominates the chemistry. The results are as follows. Irradiation[19] of 1-NN and 2-NN with TME in benzene gives 1-cyano-7,7,8,8-tetramethyl-2,3-benzobicyclo[4.2.0]octa-2,4-diene (**1**), and the previously described[20] 6-cyano isomer (**2**), respectively.



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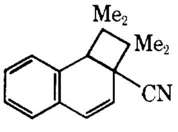

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The cycloadducts were isolated by chromatography. **1** had mp 60-61.5° and in the NMR spectrum (100 MHz, CCl_4 or $CDCl_3$) showed resonances at δ 1.40, 1.32, 1.00 and 0.81, singlets (area of each, 3), assigned to the methyl groups; a doublet of doublets at δ 3.20, J = 4.5 and 2.0 Hz (area 1), is assigned to the bridgehead methine proton; two doublets of doublets at δ 5.71, J = 10.0 and 4.5 Hz, and at δ 6.31, J = 10.0 and 2.0 Hz, are assigned to the vinylic protons, and multiplets at δ 7.1 (area 3) and at 6.9 (area 1) are assigned to the aromatic ring protons. **2** was obtained as an oil, and had NMR[20] and other spectra, in full agreement with the assigned structure.

Dilution plots for both of these addition reactions in benzene solvent are shown in Figure 1. The linear form of these plots is described by eq 1.

$$\Phi_a^{-1} = \Phi_{\rm lim}^{-1}(1 + K_{\rm sv}^{-1}[{\rm TME}]^{-1}) \qquad (1)$$

Φ_a is the quantum yield of addition, $\Phi_{\rm lim}$ is its value at infinite TME concentration, and $K_{\rm sv}$ is the slope of the Stern-Volmer plot for quenching of the naphthonitrile fluorescence by TME. Scheme I, which involves an exciplex intermediate,[11a] will be used to interpret the photochemistry in benzene. In this scheme,[11a]

$$K_{\rm sv} = \frac{k_q(k_p + k_d' + k_f')\tau}{k_{-q} + k_p + k_d' + k_f'}$$

where $\tau = (k_f + k_d)^{-1}$, and $\Phi_{\rm lim} = k_p/k_p + k_d' + k_f'$

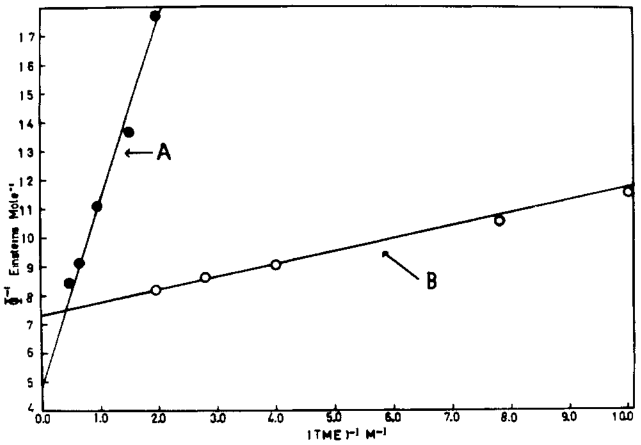


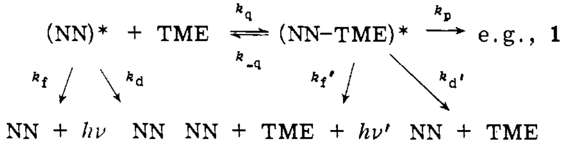
Figure 1. Dilution plots for cycloadduct formation in deoxygenated benzene: (A) 2-NN and TME giving **2**, (B) 1-NN and TME giving **1**. Values of slopes and intercepts are given in Table I.

Table I. Stern-Volmer Data and Limiting Quantum Yields for Naphthonitrile–TME Reactions[a] in Benzene

	1-Naphthonitrile	2-Naphthonitrile
$K_{\rm sv}$ (from fluorescence quenching), M^{-1}	41.7[b]	0.72
$K_{\rm sv}$ (from formation of adduct), M^{-1}	18.4, 22.8	0.68
$\Phi_{\rm lim}$	0.14	0.21

[a] All determinations were in deaerated benzene at 20°. [b] Value for hexane, taken from results of Taylor, ref 7, is 23.1.

Scheme I



Values for $\Phi_{\rm lim}$ and $K_{\rm sv}$ for 1-NN and 2-NN are given in Table I. $K_{\rm sv}$'s derived from fluorescence quenching, and from the plots in Figure 1, are in reasonable agreement. The additions clearly involve the naphthonitrile S_1 states.[21]

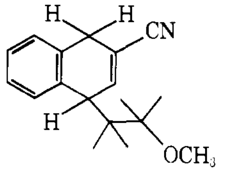
The simplest explanation for the different $K_{\rm sv}$'s but similar $\Phi_{\rm lim}$'s for the two naphthonitriles is that formation of the exciplex determines $K_{\rm sv}$, while its collapse to product determines $\Phi_{\rm lim}$.[1,22] A scheme involving separate, parallel processes for S_1 quenching and addition, respectively,[22,23] can also explain the results, but would require that the two processes vary in the same way with substitution of the naphthonitrile.

Calculation[24] of the enthalpies of exciplex formation using the reduction potentials and S_1 excitation energies of the naphthonitriles, and the oxidation potential of TME,[25] gives ΔH = −7.4 and −1.8 kcal/mol for 1-NN and 2-NN, respectively, with TME. The more negative ΔH for 1-NN and TME is consistent with the larger $K_{\rm sv}$ in that case.[26a] The difference in $K_{\rm sv}$ between 1-NN and 2-NN is not due to the difference in lifetimes of S_1.[27] Similar suggestions have been made[7,11a] concerning the relationship between ionization potentials of olefins and their behavior as quenchers of 1-NN fluorescence.

The similarity in $\Phi_{\rm lim}$ for the two reactions (Table I) shows that different factors control $\Phi_{\rm lim}$ ($=k_p/k_p + k_f' + k_d'$) and $K_{\rm sv}$. Thus, the exciplex which is the more stable (from 1-NN) collapses to product *less efficiently*. This could be consistent with a heteroexcimer bond which is longer in the more stable case (1-NN-TME) and shorter in the 2-NN-TME exciplex.[26b] Thus, radiationless processes

(k_d'), including chemical reaction (k_p), may be more rapid in the latter case, relative to k_f'. Interestingly, the exciplex from 2-NN and TME differs from 1-NN and TME[7,11a] in being nonfluorescent.

The remaining evidence derives from solvent effects. In benzene, the fluorescence of the 1-NN–TME exciplex[7] has $\Phi_{\mathrm{lim}} = 0.04$, and adduct **1** is formed. In acetonitrile, both exciplex fluorescence[7] and cycloaddition still occur, but with much lower efficiencies than in benzene. Similarly, with 2-NN and TME, formation of **2** is *totally quenched* in methanol; instead, products of photoreduction of 2-NN (e.g., **3** and **4**) are observed.[15e] Also, the fluorescence of 2-NN is quenched at the diffusion controlled rate (K_{sv} = 148 M^{-1}) in methanol. Thus, both quenching and reaction of 2-NN with TME apparently proceed by different mechanisms in methanol and benzene.



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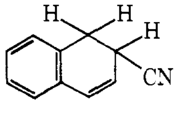

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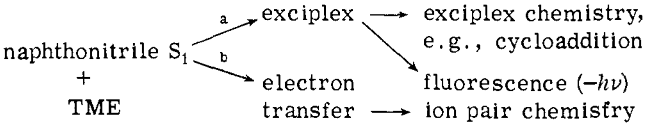
Each of the above pieces of data is an indication rather than a requirement of exciplex intermediacy in the cycloadditions. However, taken together the results make a strong case for Scheme II.[1,10,12,13,28-30] Path (a) is favored in benzene but (b) predominates in acetonitrile and methanol. In some solvents, both (a) and (b) pathways may be important.

Scheme II



Acknowledgments. We are grateful to Dr. O. E. Hileman, Jr., for help in determining the polarographic data and to Dr. G. N. Taylor for helpful discussions and for informing us of his results (ref 7) before publication. We also thank the National Research Council of Canada for awarding a Postgraduate Fellowship to Roderick C. Miller and for financial support through an operating grant.

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(26) (a) These calculations of ΔH in nonpolar media, using electrochemical data from polar media, can give erroneous estimates of the heats of formation of the exciplex. This is because the electrostatic attraction (stabilization) in the charge-transfer complex will be significant in the less polar media (−0.13 eV, ref 24b), and will be variable because the encounter distance will in general be different for different exciplexes. However, our point is simply that the K_{sv}'s in Table I are qualitatively in agreement with the above estimates of ΔH. (b) We thank Dr. G. N. Taylor for these suggestions.
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Reduction of New π-Bound Molybdenocene–Nitrile Complexes via Isolatable Iminium Intermediates

Sir:

In our continuing efforts to elucidate the possible role of electron deficient molybdenum species in nitrogenase, unique new molybdenocene complexes of organic nitriles have been prepared. Treatment of various nitriles with in situ generated molybdenocene[1,2] has resulted in the first synthesis of π-bound molybdenum–nitrile complexes (eq 1). Primary support for the suggested mode of coordination is the dramatic reduction in the infrared stretching frequency of the nitrile group. Acetonitrile, trifluoroacetonitrile, and benzonitrile complexes exhibit intense C≡N stretches at 494, 526, and 489 cm^{-1}, respectively, below that of the parent nitrile. These are the greatest reductions in C≡N stretching frequency ever observed upon coordination of these molecules. All of the molybdenum complexes are red, air-sensitive, sublimable solids. Mass spectra, ^1H and ^{19}F NMR data, and elemental analyses are consistent with the proposed structures.

Sterically induced η^2 coordination has been suggested