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<thead>
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<th>Title</th>
<th>STUDIES ON PHOTOCHEMICAL REACTIONS OF AROMATIC NITRILES</th>
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<td>Mizuno, Kazuhiko</td>
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STUDIES ON PHOTOCHEMICAL REACTIONS
OF AROMATIC NITRILES

KAZUHIKO MIZUNO

OSAKA UNIVERSITY
OSAKA, JAPAN
JANUARY, 1976
STUDIES ON PHOTOCHEMICAL REACTIONS OF AROMATIC NITRILES

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Preface

This thesis deals with the studies accomplished by the author under the guidance by Professor Hiroshi Sakurai at the Institute of Scientific and Industrial Research, Osaka University.

The author would like to express his sincere thanks to Professor Hiroshi Sakurai for his invaluable guidance and constant encouragement throughout this investigation since 1971.

The author is also deeply grateful to Dr. Chyongjin Pac and Assistant Professor Setsuo Takamuku for their helpful suggestion and discussions. Grateful acknowledgements are also made to Dr. Susumu Toki and Dr. Yoshiki Okamoto for their helpful suggestions through stimulating discussions with the author.

Much thanks is given to Professor Nobutami Kasai and his co-workers for their X-ray analyses. The author is also very grateful to Assistant Professor Shinji Murai for his valuable suggestions about the silyl enol ethers in chapter 5.

The author expresses his gratitude to Mr. Hisanori Okamoto for his collaboration in the course of experiment. The author's grateful thanks is also due to all the members in the Institute of Scientific and Industrial Research and in the Faculty of Engineering, who have made spectroscopic measurements and elemental analyses. The author wishes to thank all the members of Sakurai Laboratory for their friendship.

Finally the author would like to thank his father Toshihiko Mizuno for his continuous encouragement and his wife Mari Mizuno for her warm-hearted encouragement.

Suita, Osaka
January, 1976

Kazuhiko Mizuno
List of Papers

The contents of this thesis are composed of the following papers.

(1) Photochemical Reactions of Aromatic Compounds. XI. The Photochemical Cycloaddition of Vinyl Ethers to α-Naphthonitrile
C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai

(2) The photocycloaddition of 9-Cyanophenanthrene and 9-Cyanoanthracene with Vinyl Ethers and Furan
K. Mizuno, C. Pac, and H. Sakurai

(3) The stereoselective Photocycloaddition of Indene and Phenyl Vinyl Ether to α-Naphthonitrile
C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai

(4) Photoreaction of 2-Naphthonitrile and Vinyl Ethers; a Novel Photorearrangement of the Primary Cycloadduct
K. Mizuno, C. Pac, and H. Sakurai

(5) Photochemical Reactions of Aromatic Compounds. XVII. The Photocyclization of N-(o-Chlorobenzyl)aniline
K. Mizuno, C. Pac, and H. Sakurai

(6) Photochemical Reactions of Aromatic Compounds. XVIII. Photoaddition of Benzophenone to Aromatic Amines
C. Pac, K. Mizuno, T. Tosa, and H. Sakurai

(7) Photocycloaddition of Olefins to 9-Cyanophenanthrene. Singlet Exciplex or Triplet Mechanism Depending on Olefins
K. Mizuno, C. Pac, and H. Sakurai

(8) Photochemical Reactions of Aromatic Compounds. XX. Photocycloaddition of 9-Cyanoanthracene to Furan and Mono- and Dimethyl-furans
K. Mizuno, C. Pac, and H. Sakurai
(9) Stereospecific Photocycloaddition of 1-Naphthonitrile with cis- and trans-1-Phenoxypropenes
K. Mizuno, C. Pac, and H. Sakurai

(10) Photoreactions of Silyl Enol Ethers of α-Tetralone and α-Indanone with Electron Deficient Olefins, The Photo-Michael Reaction
K. Mizuno, H. Okamoto, C. Pac, H. Sakurai, S. Murai, and N. Sonoda

(11) Photochemical Reactions of Aromatic Compounds. XXIII. Photochemical Reactions of Alkyl Vinyl Ethers with 2-Naphthonitrile
K. Mizuno, C. Pac, and H. Sakurai

(12) Photochemical Cyanation of Aromatic Hydrocarbons with Cyanide Anion
K. Mizuno, C. Pac, and H. Sakurai

(13) Photo-Birch Reduction of Aromatic Hydrocarbons Using Sodium Borohydride and 1,4-Dicyanobenzene
K. Mizuno, H. Okamoto, C. Pac, and H. Sakurai
# Contents

Preface .................................................................................................................. ii  
List of Papers .......................................................................................................... iii  

Introduction ............................................................................................................. 1  

<table>
<thead>
<tr>
<th>Chapter 1</th>
<th>Photocycloaddition of 9-Cyanoanthracene to Furan and Mono- and Dimethyl-furans</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Introduction</td>
</tr>
<tr>
<td>1-2</td>
<td>Results</td>
</tr>
<tr>
<td>1-3</td>
<td>Discussion</td>
</tr>
<tr>
<td>1-4</td>
<td>Experimental</td>
</tr>
<tr>
<td>1-5</td>
<td>References and Footnotes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 2</th>
<th>Photoreaction of Electron Rich Olefins to 9-Cyanophenanthrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Introduction</td>
</tr>
<tr>
<td>2-2</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>2-3</td>
<td>References and Footnotes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 3</th>
<th>Photochemical Reactions of Alkyl Vinyl Ethers with 2-Naphthonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Introduction</td>
</tr>
<tr>
<td>3-2</td>
<td>Results</td>
</tr>
<tr>
<td>3-3</td>
<td>Discussion</td>
</tr>
<tr>
<td>3-4</td>
<td>Experimental</td>
</tr>
<tr>
<td>3-5</td>
<td>References and Footnotes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 4</th>
<th>Stereochemistry on Photocycloaddition to Aromatic Rings</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>Introduction</td>
</tr>
<tr>
<td>4-2</td>
<td>Substrate Selectivity of 9-Cyanoanthracene and 9-Cyanophenanthrene</td>
</tr>
<tr>
<td>4-3</td>
<td>Stereoselective Photocycloaddition of Indene and Phenyl Vinyl Ether to 1-Naphthonitrile</td>
</tr>
<tr>
<td>4-4</td>
<td>Stereospecific Photocycloaddition of 1-NN with cis- and trans-Phenoxypropene and Methoxypropene</td>
</tr>
<tr>
<td>4-5</td>
<td>References and Footnotes</td>
</tr>
<tr>
<td>Chapter 5</td>
<td>The Photo-Michael Reactions. Photoreaction of 1-Naphthonitrile with Silyl Enol Ethers</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5-1</td>
<td>Introduction</td>
</tr>
<tr>
<td>5-2</td>
<td>Results and Discussion</td>
</tr>
<tr>
<td>5-3</td>
<td>References and Footnotes</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>The Photo-Birch Reduction and Photo-cyanation of Aromatic Hydrocarbons in the Presence of 1,4-Dicyanobenzene</td>
</tr>
<tr>
<td>6-1</td>
<td>The Photo-Birch Reduction</td>
</tr>
<tr>
<td>6-2</td>
<td>Photochemical Cyanation</td>
</tr>
<tr>
<td>6-3</td>
<td>References and Footnotes</td>
</tr>
<tr>
<td>Conclusion</td>
<td></td>
</tr>
</tbody>
</table>
**Introduction**

In the last decade, much attention has been paid to the interaction of aromatic compounds in the excited state with dienes, olefins, and amines in the ground state. A photoexcited molecule may be deactivated by another ground state molecule even if the energy transfer from the excited molecule to the other molecule is energetically unfavourable. In these deactivation, exciplexes have been suggested as the intermediates.\(^1\) The term, 'exciplex', which was derived from 'excited complex' by analogy to 'excimer' (= 'excited dimer') is a stoichiometric molecular complex which is formed only in an electronically excited state and is dissociative in the ground state.\(^1\) The initial work of the chemistry of exciplex has been spectroscopically investigated by Weller,\(^2\) Mataga,\(^3\) and Hammond\(^4\), who have provided a lot of information about the formation and decay processes of emissive or non-emissive exciplexes. On the basis of these information, possible mechanistic pathways from exciplex and exciplex dynamics are shown as following scheme:

Possible Pathways from Exciplex and Exciplex Dynamics

\[
\begin{align*}
A + D & \overset{k_r}{\underset{k_d}{\rightleftharpoons}} [\text{Exciplex}] \overset{k_c}{\rightarrow} \text{Cycloaddition etc.} \\
A & \overset{hv}{\rightarrow} A + D + (hv) \overset{k_d}{\rightarrow} A + D \\
A & \overset{k_i}{\rightarrow} A^- + D^+ (\text{ionic reaction}) \\
A & \overset{k_{is}}{\rightarrow} \text{Singlet energy transfer}
\end{align*}
\]

\[
\frac{\phi_F}{\phi_F^0} = 1 + k_q \tau [D] \\
k_q = \left( \frac{k_d^c + k_c^d + k_i}{k_r + k_r^d + k_c^d + k_i} \right) k_r
\]

A: electron acceptor, D: electron donor

In organic photochemistry,\(^9\) the following evidences are required for exciplex intermediacy: as basic requirements; 1) electronically excited nature, 2) finite life-time, and as experimental evidence; 3) endothermic fluorescence quenching, 4) appearance of new emission accompanied by 3), 5) linear relationship between \(\log k_q\) and ionisation potentials or reduction potentials of A \((E_{A^-}/A)\) of quencher, 6) apparent negative temperature de-
pendency of $k_{q}$, 7) selective quenching of exciplex. Based on these evidences, exciplex intermediacy has been suggested in 1) photocycloaddition reaction, 2) photo-electron transfer reaction, 3) singlet energy transfer reaction, 4) other photoreactions such as proton transfer reaction or proton addition reaction etc., although direct and confirmative evidences are almost lacking. Among these photoreactions, photocycloadditions of unsaturated compounds to aromatic rings, which are inert in the ground state, have been investigated as synthetic routes for novel cyclic compounds and recently the stereochemistry, implying synthetically important means, of photocycloaddition to aromatic rings has been discussed in terms of exciplexes. However, a clear elucidation for the relationship between the stereochemistry of the photocycloadducts and the role of exciplexes has not been afforded in the present stage.

The main purpose of this thesis is to investigate the photochemical reactions of aromatic nitriles as electron acceptor with some electron donating molecules with the view to developing a new synthetic route utilizing the advantages of the photochemical reactions and obtaining the fundamental information about the relationship between the stereochemistry in the photocycloaddition to aromatic rings and the role of exciplexes. Moreover, the reaction of cation radicals of aromatic hydrocarbons formed in polar solvents with nucleophiles are also investigated.

In chapter 1, the photochemical (4 + 4) cycloadditions of 9-cyanoanthracene with furan and methylated furans have been described. The mechanism has been discussed on the basis of kinetic results and fluorescence measurements. Chapter 2 deals with the photoreaction of 9-cyanophenanthrene with electron rich olefins. Excited species of these photoreactions have been discussed on the basis of Michler's ketone sensitisation, isoprene quenching experiments, kinetic studies, fluorescence measurements and solvent effects. In chapter 3, a novel photoreaction of 2-naphthonitrile and alkyl vinyl ethers have been described. In order to elucidate the mechanistic pathways affording products, photochemical and thermal interconversions have been investigated. In chapter 4, the stereochemistry on photocycloaddition to aromatic rings have been described. Stereoselective and/or stereospecific photocycloadditions to aromatic nitriles have been discussed in terms of exciplexes. Chapter 5 deals with the photo-Michael reaction of silyl enol ethers with 1-naphthonitrile. Reductive alkylation of aromatic nitriles has been described. Chapter 6 deals with the efficient photo-Birch reduction and photo-cyanation of aro-
matic hydrocarbons by sodium borohydride and sodium cyanide in the presence of 1,4-dicyanobenzene in polar solvents have been described.

References


Chapter 1 Photocycloaddition of 9-Cyanoanthracene to Furan and Mono- and Dimethyl-furan

1-1 Introduction

Photocycloadditions of unsaturated compounds to aromatic rings have been investigated as synthetic routes for novel cyclic compounds and have been discussed in relation to exciplexes. Recent papers have described several new examples of photocycloaddition to anthracene, viz. (4 + 2n) photocycloaddition of conjugated dienes and cycloheptatriene to anthracene, intramolecular photocycloaddition of 1-(9-anthryl)-3-(1-naphthyl)-propane, and photochemical crossdimerisations between two different anthracenes and between anthracenes and tetracene. It has been suggested that these photoreactions involve exciplexes, but evidence is lacking.

However, photocycloaddition of heteroaromatic compounds to anthracene has not been reported. In this chapter, the author describes the photoreactions of 9-cyanoanthracene (9-CA) with furan (1a), the methylated furans (1b-d), 1-methylpyrrole (5) and thiophene (6) and provides evidence for the formation of exciplexes between the excited singlet 9-CA and the heterocyclic compounds.

1-2 Results

Irradiation of a benzene solution of 9-CA containing a large excess of 1a gave a 1:1-cycloaduct (2a) in 50% isolated yield, accompanied by 20% of 9-CA photodimer (4). The product (2a) was isolated by chromato-

<table>
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<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>mp(°C)</th>
<th>yield(%)</th>
<th>mp(°C)</th>
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</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>144-145</td>
<td>50</td>
</tr>
<tr>
<td>b</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>decomp.</td>
<td>( &gt; 90)</td>
</tr>
<tr>
<td>c</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>165</td>
<td>93</td>
</tr>
<tr>
<td>d</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
<td>decomp.</td>
<td>( &gt; 90)</td>
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graphy on silica gel and characterised by spectroscopic methods. The mass spectrum of 2a showed no molecular ion but intense fragment peaks at m/e 203 and 68, while the dihydro-isomer (3a) exhibited a molecular ion at m/e 273. The u.v. spectrum of 2a showed similar absorption maxima to that of 9,10-dimethyl-9,10-dihydroanthracene, indicating the presence of the 9, 10-dihydroanthracene chromophor. The i.r. spectrum showed absorptions at 2240(-CN), 1628(C=C), and 1052 cm\(^{-1}\)(C-O-C).

N.m.r. spectra\(^{10}\) were recorded at 60 and 100 MHz. In the 60 MHz spectra the signals of H-14 and -15 appeared as a broad singlet (\(\delta 5.92\)) at a similar chemical shift to the olefinic protons of 2,5-dihydrofuran [\(\delta 5.78\) br (s)],\(^{11}\) indicating the nearly symmetrical nature of the double bond.

Photochemical (4 + 4) addition of the methyl-substituted furans (1b-d) to 9-CA to give the adducts (2b-d) occurred similarly. 3-Methylfuran (1c) gave a quantitative yield of the adduct (2c). The location of the methyl group in 2c at C-15 was assigned from the n.m.r. data; the signal of H-13 is broadened by a small coupling (J 1.0 Hz) with H-14 whereas the signal of H-11 appears as a sharp doublet.

2-Methylfuran (1b) and 2,5-dimethylfuran (1d) at 0-5 °C gave the (4 + 4) cycloadducts (2b) and (2d) in quantitative yields, respectively. The

![Figure 1 N.m.r. spectrum of 2a in CDCl\(_3\) (100 MHz)](image-url)
adducts (2b) and especially (2d) were thermally unstable and rapidly decomposed into 9-CA at room temperature, so that they could not be isolated in pure form. Irradiation at ambient temperature did not lead to accumulation of the adducts, but only resulted in the gradual formation of 4, so procedures involving these adducts were carried out at < 0 °C. For example, after irradiation of 9-CA and 1b at 0-5 °C, evaporation of volatile materials below 0 °C under high vacuum left solid 2b exclusively, whose structure was determined from the n.m.r. spectrum of a mixture containing a small amount of 9-CA (Table 1). Since 2d immediately decomposed at > 5 °C, the n.m.r. spectrum was not recorded.

After irradiation at 0-5 °C, however, hydrogenation of the solutions over palladium-charcoal gave the dihydrocompounds (3b) and (3d) (Table 1) were in accord with the structures assigned.

In contrast to the photoreactions with furan, irradiation of 9-CA with 1-methylpyrrole (5) or thiophene (6) gave no crossadduct and resulted in quantitative formation of the dimer (4).

1-3 Discussion

A singlet mechanism for the photocycloaddition with 1a was established by quantum yield measurements and fluorescence quenching studies. The quantum yield measurements are shown in Figure 2. From the slope (44 mol dm⁻¹) and the intercept (5.0), the k_qT value was calculated as 0.11 dm³ mol⁻¹, which was in excellent agreement with the value (0.1 ± 0.03 dm³ mol⁻¹) obtained from fluorescence quenching studies. In the case of 1b-d, quantum yield measurements were not carried out, because of difficulties owing to rapid decomposition of the adducts (2b) and (2d). However,

### Table 1

<table>
<thead>
<tr>
<th>Product</th>
<th>Spectral data of products</th>
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<tbody>
<tr>
<td>N.m.r. [8(CDC1₃) (J in Hz)]</td>
<td>ν_max [KBr] cm⁻¹</td>
</tr>
<tr>
<td>2a</td>
<td>4.07 (1H, d, J₁₈,₁₁ 6.8), 4.71 (1H, dd, J₁₈,₁₁ 1.1), 4.98 (1H, d, J₁₈,₁₁ 1.6), 5.65 (1H, d, J₁₈,₁₁ 1.6), 7.35 (8H, m)</td>
</tr>
<tr>
<td>2b</td>
<td>1.64 (3H, s), 4.03 (1H, d, J₁₈,₁₁ 7.7), 4.88 (1H, dd, J₁₈,₁₁ 1.1), 5.82 (1H, d, J₁₈,₁₁ 6.6), 7.35 (8H, m)</td>
</tr>
<tr>
<td>2c</td>
<td>1.66 (3H, s), 4.06 (1H, d, J₁₈,₁₁ 6.6), 4.40 (1H, d, J₁₈,₁₁ 1.6), 5.42br (1H, s), 7.35 (8H, m)</td>
</tr>
<tr>
<td>3a</td>
<td>1.69 (2H, m), 1.90 (2H, m), 4.09 (1H, d, J₁₈,₁₁ 7.7), 4.42 (1H, t, J₁₈,₁₁ 7.7), 4.57 (1H, d, J₁₈,₁₁ 7.7), 7.35 (8H, m)</td>
</tr>
<tr>
<td>3b</td>
<td>1.59 (3H, s), 1.60 (4H, m), 4.07 (1H, d, J₁₈,₁₁ 7.7), 4.40 (1H, t, J₁₈,₁₁ 7.7), 7.35 (8H, m)</td>
</tr>
<tr>
<td>3d</td>
<td>1.40 (3H, s), 1.60 (3H, s), 1.70br (4H, s), 3.84 (1H, s), 7.35 (8H, m)</td>
</tr>
</tbody>
</table>

*100 MHz. | *ν_max(CH₃CN) 262 (ε 720), 289 (1130), and 277 nm (1640). | *λ_max CH₃CN 267 (ε 487), 271 (403), and 275 nm (768). | *Contaminated with a small amount of 9-CA.
it is reasonable to propose a common singlet mechanism for the photocycloaddition with \textit{la–d}, since fluorescence quenching was more efficient with \textit{lb} and \textit{ld} than with \textit{la}. Since the photocycloaddition with furan occurs from a singlet exciplex,\textit{lb} an exciplex mechanism can also be expected to operate in the photocycloaddition of 9-CA with \textit{la–d}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{Plots of $\Phi_{\text{A}}^{-1}$ vs. [\textit{la}]$^{-1}$ for degassed cyclohexane solutions, where [9-CA] = 1.3 x 10$^{-4}$ mol dm$^{-3}$}
\end{figure}

In this regard, it is interesting that $k_{qT}$ values obtained from fluorescence quenching increase as the ionisation potentials of the quenchers decrease, indicating the charge-transfer nature of the fluorescence.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{Fluorescence spectra of 9-CA solutions [9-CA] = 5 x 10$^{-4}$ mol dm$^{-3}$: I, in cyclohexane in the absence of quencher; II, in cyclohexane in the presence of 1.0 mol dm$^{-3}$ (\textit{ld}); and III, in cyclohexane in the presence of 1.0 mol dm$^{-3}$ (5)}
\end{figure}
quenching. Moreover, fluorescence quenching by \(1d\) and \(5\) was accompanied by enhancement of the longer wavelength (Figure 3). This observation cannot be ascribed to a solvent effect of the added quenchers on the fluorescence of 9-CA, since the fluorescence spectrum of a tetrahydrofuran solution of 9-CA exhibited a simple bathochromic shift accompanied by some broadening but no new emission. Appearance of a new emission provides direct evidence for the formation of exciplexes.\(^{12}\) Thus, these observations appear to support an exciplex mechanism for both the fluorescence quenching and the photocycloaddition.

\[
\begin{align*}
9\text{-CA}(S_1) + Q & \xrightarrow{k_r} \text{Exciplex} \xrightarrow{k_c} \text{Product} \\
\text{hv} \downarrow \frac{1}{\tau} & \quad k_n \quad A; \quad 9\text{-CA} \quad Q; \quad 1a-d
\end{align*}
\]

As simplified exciplex mechanism is shown in the Scheme from which rate equations (i) and (ii) are derived. The decay pathways of 9-CA (\(S_1\)) and exciplex involve all the unimolecular processes except the product forming path. The reversible dissociation of exciplex should be taken into account, since exciplex formation of 1-naphthonitrile-furan is known to be reversible.\(^{1b}\)

Table 2

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Ionisation potential (eV)</th>
<th>(k_q\tau/\text{dm}^3\text{ mol}^{-1}) (^a)</th>
<th>(10^{-9}k_q/\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>9.04(^c)</td>
<td>0.1 (\pm) 0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>1b</td>
<td>8.31(^c)</td>
<td>2.7 (\pm) 0.03</td>
<td>0.9</td>
</tr>
<tr>
<td>1d</td>
<td>8.01(^c,d)</td>
<td>22.0</td>
<td>7.3</td>
</tr>
<tr>
<td>5</td>
<td>7.95(^e)</td>
<td>30.6</td>
<td>10.2</td>
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\(^a\) Air-saturated cyclohexane solution; \([9\text{-CA}] = 5 \times 10^{-4} \text{ mol dm}^{-3}\). \(b\) The value of \(k_q\) is calculated by estimating the life-time of the excited singlet 9-CA as 3 ns; see ref. 13. \(^c\) D. W. Turner, Adv. Phys. Org. Chem., 4, 31(1966). \(^d\) Estimated value from the ionisation potential of 2,3-dimethylfuran. \(^e\) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, Analyt. Chem., 42, 1064 (1970).
The value of $k_q$ with each quencher can be calculated by estimating the life-time of excited singlet 9-CA as 3-4 ns, from the oxygen quenching method. On the basis of the assumption proposed by Hammond et al., a linear relationship between ionisation potentials and logarithmic $k_q$ values is obtained (Table 2 and Figure 4), again probably supporting the exciplex mechanism. A relatively high value of the limited quantum yield for disappearance of 9-CA ($\phi_A = 0.2$) would eliminate a triplet mechanism, since the fluorescence efficiency of 9-CA is reported to be higher than 0.8.

![Figure 4](image)

**Figure 4** Correlation of quencher rate constants ($k_q$) for 9-CA with the vertical ionisation potentials of the quencher

The stereochemistry of this photocycloaddition can be discussed in terms of the intermediates. Only (4 + 4) addition took place, unlike the photoaddition of 9-CA with acyclic 1,3-dienes and of anthracene with cyclopentadiene and cycloheptatriene, which were interpreted by the sequence exciplex $\rightarrow$ biradical $\rightarrow$ cycloadduct. Moreover, the photocycloadditions with 1b and 1c were regiospecific. Although it is uncertain whether the photoaddition of 9-CA with 1a-d is stepwise or concerted, these observations would appear to suggest a different mechanism from the biradical mechanism and to imply important effects of the exciplex-configuration on both the addition mode and orientation, such that the exciplexes of 9-CA-1a-d possess a finite sandwich type configuration favourable to (4 + 4) addition. Finally, it should be noted that 1-methylpyrrole quenched fluorescence of 9-CA in an diffusion-controlled rate via exciplex formation but gave no adduct. Since the pyrrole ring is well known to be more aromatic than furan, cycloaddition to pyrrole would require a higher activation energy, and this would disfavour this reaction. Thus, ionisation potentials of quenchers are important in exciplex formation, but the exciplex $\rightarrow$ product pathway appears to depend on the chemical nature of quencher.
1-4 Experimental

**General.** U.v. spectra were measured with a Hitachi 124 and i.r. spectra with a Hitachi EPI-S2 spectrophotometer. N.m.r. spectra were obtained with a Hitachi-Perkin-Elmer R-24 spectrophotometer (60 MHz) and a JEOL JNM JS-100 instrument (100 MHz) for solutions in deuteriochloroform containing tetramethylsilane as internal standard. Mass spectra were recorded with a Hitachi MPF-2A spectrofluorometer. Analytical g.l.c. was carried out with a Shimadzu GC-2C machine equipped with a flame-ionisation detector using a column of SE-30 (5% on Shimalite W, 0.75 m) at 200 °C. M.p.s. were measured for samples in capillaries.

Irradiation in preparative experiments was carried out with an Eikosha PIH 300 W high-pressure mercury arc for benzene solutions (30 ml) containing 9-CA (0.3 g) and la-d (5 ml) in test-tube. Column chromatography was carried out on silica gel (Merck kieselgel 60). Elemental analyses and spectral data are listed in Table 1 and 3.

**Materials.** 9-Cyanoanthracene (9-CA) was prepared from anthracene-9-carbaldehyde according to the reported method and was recrystallised three times from glacial acetic acid (80% yield, m.p. 179 °C) and lc was prepared according to the method described in the literature. Commercial la, lb, ld, lc, and le (Tokyo Kasei) were refluxed and distilled over calcium chloride under a nitrogen stream prior to use. Benzene was purified as described previously and spectrograde cyclohexane (Nakara Chemicals) was used without further purification.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Elemental analyses of products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Found (%)</td>
</tr>
<tr>
<td>2a</td>
<td>84.1 4.85 5.15</td>
</tr>
<tr>
<td>2c</td>
<td>84.2 5.3 4.9</td>
</tr>
<tr>
<td>3a</td>
<td>83.5 5.55 5.15</td>
</tr>
<tr>
<td>3b</td>
<td>83.6 5.95 4.9</td>
</tr>
<tr>
<td>3d</td>
<td>83.7 6.35 4.64</td>
</tr>
</tbody>
</table>

a From methanol. b From methanol-benzene.
Quantum Yields. — Cyclohexane was used as solvent and the concentration of 9-CA was $1.28 \times 10^{-4}$ mol dm$^{-3}$. Monochromatic light at 365 nm was isolated from a high-pressure mercury arc (450 W) by using a combined glass filter of Toshiba UV-35 and UV-DIB and the light intensity ($I_0$) was determined with a potassium ferrioxalate actinometer to be $3.014 \times 10^{-7}$ einstein cm$^{-2}$ min$^{-1}$. Samples placed in an optical cell (10 x 10 x 45 mm) were thoroughly degassed by four freeze-thaw cycles under a high vacuum ($< 10^{-3}$ mmHg) and then irradiated by 365 nm light. Decrease of the absorbance at 362 nm ($E_{cd}$) during the irradiation was monitored at appropriate time intervals (t/min). Plots of natural logarithmus of $(e^{E_{cd}} - 1) \text{ vs. } t$ were linear. Quantum yields $[\Phi_A]$ for the disappearance of 9-CA were obtained from the slopes or the lines by applying the equation $\ln(e^{E_{cd}} - 1) = -1000\epsilon\Phi_A I_0 t + C$, where $\epsilon$ is the molar absorption coefficient of 9-CA at 362 nm ($6.73 \times 10^4$ dm$^2$ mol$^{-1}$) and $C$ is a constant.

Photoreaction with Furan. —— After irradiation for 60 h at ambient temperature, a precipitate was filtered off to yield the photodimer 4 (10 mg, 3.3%). Column chromatography with benzene-hexane (3 : 1) as eluent gave 9-CA (70 mg, 23.3% recovered) and then 9-cyano-9,10,11,13-tetrahydro-9,10[2',5']-furanoanthracene (2a) (195 mg, 50%) which was recrystallised from methanol, m.p. 144.5 °C (decomp.). Further elution with benzene gave the dimer (4) (50 mg, 16.7%). Hydrogenation of a methanolic solution of 2a (50 mg) over Pd-charcoal gave 9-cyano-9,10,11,13,14,15-hexahydro-9,10[2',5']-furanoanthracene (3a), in quantitative yield.

Photoreaction with 2-Methylfuran. —— Irradiation for 40 h at 0-5 °C resulted in complete disappearance of the yellow colour of 9-CA, and t.l.c. of the solution on silica gel show the formation of a product. Removal of solvent and 1b in vacuo at 0 °C left a white solid, which contained exclusively 2b (t.l.c. and n.m.r.). The solid gradually turned yellow, owing to formation of 9-CA. Pd-charcoal (ca. 10 mg) was added to the irradiated solution and then the solution was stirred under hydrogen at 0-5 °C for 24 h. Filtration of the catalyst and evaporation of the solvent and 1b left a solid which was recrystallised from methanol to yield pure 9-cyano-9,10,11,13,14,15-hexahydro-13-methyl-9,10[2',5']-furanoanthracene (3b).

Photoreaction with 3-Methylfuran. —— After irradiation at ambient temperature (37 h), removal of solvent and unchanged 1c in vacuo left a solid, which was fairly pure 2c. (n.m.r.). The solid was recrystallised from methanol to yield pure 9-cyano-9,10,11,13-tetrahydro-15-methyl-9,10[2', 5']-furanoanthracene (2c) (390 mg, 93%).
Photoreaction with 2,5-Dimethylfuran. —— After irradiation for 20 h at 0-5 °C, the irradiated solution was hydrogenated over Pd-charcoal (10 mg) at 0-5 °C for 24 h. Filtration of Pd-charcoal and evaporation of solvent and left a white solid which was recrystallised from methanol-benzene to yield pure 9-cyano-9,10,11,13,14,15-hexahydro-11,13-dimethyl-9,10[2',5']-furanoanthracene (3d).

Photoreaction of 1-Methylpyrrole and Thiophene. —— Irradiation of a benzene solution containing 9-CA and 1-methylpyrrole (5) gave the dimer (4) (270 mg, 90%). Similarly, photoreaction with thiophene (6) afforded 4 (280 mg, 93%). In both cases, t.l.c. analyses of the irradiated solutions showed only starting materials and 4 and no crossadducts.

1-5 References and Footnotes


10 The n.m.r. spectrum of 2,5-dihydrofuran ring in 2a is similar to that of the cycloadduct of 1-cyanonaphthalene with furan; see ref. 1b.
12 A charge-transfer complex is not formed in the ground state, since the u.v. spectrum of 9-CA in the presence of 1a–d or 5 is identical with that in the absence of quencher.
16 The (4 + 4) photoaddition of anthracene with acyclic dienes was suggested to be concerted; see ref. 4a.
Chapter 2  Photoreactions of Electron Rich Olefins to 9-
Cyanophenanthrene

2-1 Introduction

Photocycloaddition to various aromatic nitriles, occurring across aromatic rings,\(^1\text{-}^5\) usually proceed via excited singlet nitriles, and the mechanism are discussed in relation with exciplexes.\(^1\text{-}^3\) However, it has been reported that benzonitrile undergoes photocycloaddition to tetra-substituted, very electron-rich ethylenes at the nitrile function in an excited singlet state, whereas that occurs to less electron-rich olefins across the benzene ring from \(\pi,\pi^*\)-triplet state.\(^5\text{a}\) This divergency in mechanism depending on olefins is interesting, since exciplexes would appear to play important roles. In this chapter, the author describes the photoreaction of 9-cyanophenanthrene (9-CP) with methyl vinyl ether (1a), ethyl vinyl ether (1b), 2-methyl-2-butene (1c), 2,3-dimethyl-2-butene (1d), and 2,5-dimethyl-2,4-hexadiene (1e) to yield common cyclobutane compounds in a stereoselective manner and show that photoreactions with the former three olefins occur from triplet 9-CP, whereas in the latter two cases singlet exciplexes play important roles.

2-2 Results and Discussion

Irradiation of a benzene solution of 9-CP in the presence of 1a-e\(^6\) gave a 1:1-cycloadduct (2a-e) (Scheme); in each case, only a single isomer was isolated. Analytical and spectral data were in accord with the

<table>
<thead>
<tr>
<th></th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>R(^3)</th>
<th>R(^4)</th>
<th>mp (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>141</td>
<td>80 (60)</td>
</tr>
<tr>
<td>b</td>
<td>OEt</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>117-118</td>
<td>80 (60)</td>
</tr>
<tr>
<td>c</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
<td>Me</td>
<td>212-213</td>
<td>100 (&gt;90)</td>
</tr>
<tr>
<td>d</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>185-188</td>
<td>100 (&gt;90)</td>
</tr>
<tr>
<td>e</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
<td>-CH=CM(_2)</td>
<td>97.5-98.5</td>
<td>100 (&gt;65)</td>
</tr>
</tbody>
</table>
assigned structures, and the assignment were based mainly on n.m.r. spectra (Table 3 and 4). V.p.c. and n.m.r. analyses of photolysates or crude products showed that the stereoisomer of 2a, 2b, 2c, or 2e could not be detected to any appreciable extent (<1-5%),
showing the stereoselective nature of the photocycloadditions.

The formation of compounds 2a, 2b, and 2c was not only sensitised by Michler's ketone but also quenched by isoprene, apparently indicating the intermediacy of triplet 9-CP. In contrast, the photoreaction with 2d could not be sensitised but was remarkably quenched by Michler's ketone. Moreover, quenching by isoprene was not significant up to 1.0 mol dm\(^{-3}\) in the diene. Thus, these results suggest a singlet mechanism. For the photocycloaddition of le to 9-CP, a singlet mechanism was established by fluorescence quenching studies and quantum yield measurements, which gave identical \(k_T\) values, 162 and 168 mol\(^{-1}\) dm\(^{3}\), respectively (Figure 1).

From a mechanistic point of view, it is noteworthy that the fluorescence quenching by le was accompanied with enhancement of longer wavelength emission and appearance of an isoemissive point at 427 nm (Figure 2). Further increase in concentration of le up to ca. 0.3 mol dm\(^{-3}\) resulted in appearance of a new weak, broad emission at \(\lambda_{\text{max}}\) 410-420 nm, demonstrating the formation of a singlet exciplex. The exciplex of 9-CP and le can be considered to be a charge-transfer complex in nature from the solvent dependent shift of the exciplex emission (Table 1). This would therefore suggest that the photocycloaddition of le to 9-CP proceeds
Figure 2  Fluorescence spectra of 9-CP solutions [9-CP] = 1 x 10^{-4} mol dm^{-3}: I, in cyclohexane in the absence of quencher; II, in cyclohexane in the presence of 0.3 mol dm^{-3} le; III, in cyclohexane in the presence of 0.01 mol dm^{-3} le. 

via a singlet exciplex. Moreover, the k_T values obtained from fluorescence quenching increase as the ionisation potentials of the quenchers including furans and other electron rich olefins decrease, indicating the charge-transfer nature of the fluorescence quenching (Table 2). A linear relationship between ionisation potentials and logarithmic k_T values is obtained (Figure 3), again probably supporting the exciplex mechanism.

Table 1  The bathochromic shift of the exciplex emission

<table>
<thead>
<tr>
<th>Solv.</th>
<th>C_6H_{12}</th>
<th>n-Bu_2O</th>
<th>Et_2O</th>
<th>CH_3COCH_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε</td>
<td>2.02</td>
<td>3.06</td>
<td>4.34</td>
<td>20.7</td>
</tr>
<tr>
<td>λ_{max} (ex)</td>
<td>415</td>
<td>425</td>
<td>435</td>
<td>483</td>
</tr>
</tbody>
</table>

a [9-CP] = 1.0 x 10^{-4} mol dm^{-3} and [le] = 0.3 mol dm^{-3} in air-saturated solutions.

This exciplex mechanism would be supported by the observation that the photoreaction of 9-CP with le in methanol gave 9,10-dihydro-9-cyanophenanthrene (4) and a solvent-incorporated product (5) in 90% yields which apparently arise from ion radicals. This type of solvent effect could also
Table 2

Values of $k_T$ from fluorescence quenching $^a$

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Ionisation potential (eV)</th>
<th>$k_T/Q$ dm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>la</td>
<td>8.93</td>
<td>0.10 (0.10)</td>
</tr>
<tr>
<td>lb</td>
<td>8.89</td>
<td>0.16</td>
</tr>
<tr>
<td>lc</td>
<td>8.53</td>
<td>0.42 (19.8)</td>
</tr>
<tr>
<td>ld</td>
<td>7.84</td>
<td>96.5 (130)</td>
</tr>
<tr>
<td>le</td>
<td>9.19 (130)</td>
<td>&lt; 0.01 (&lt; 0.03)</td>
</tr>
<tr>
<td>vinyl acetate</td>
<td>9.19</td>
<td>0.17 (37.8)</td>
</tr>
<tr>
<td>dihydropyrane</td>
<td>8.34</td>
<td>0.06</td>
</tr>
<tr>
<td>furan</td>
<td>9.04</td>
<td>0.80 (6.18)</td>
</tr>
<tr>
<td>2-methylfuran</td>
<td>8.31</td>
<td>5.40</td>
</tr>
<tr>
<td>2,5-dimethylfuran</td>
<td>8.01</td>
<td>5.55</td>
</tr>
<tr>
<td>1-methylpyrrole</td>
<td>7.95</td>
<td>1.47 (50.0)</td>
</tr>
<tr>
<td>1-ethoxypropene</td>
<td>8.04</td>
<td>3.32 (15.3)</td>
</tr>
<tr>
<td>indene</td>
<td>8.81</td>
<td>74.7 (94.9)</td>
</tr>
<tr>
<td>benzofuran</td>
<td>8.36</td>
<td>15.1 (100.7)</td>
</tr>
<tr>
<td>1-methoxy-2-methylpropene</td>
<td>7.65</td>
<td>&lt; 0.01 (&lt; 0.01)</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>8.72</td>
<td>&lt; 0.01 (&lt; 0.01)</td>
</tr>
</tbody>
</table>

$^a$ Quenching of 9-CP fluorescence by olefins; aerated cyclohexane solution; [9-CP] = 5 x 10$^{-5}$ mol dm$^{-3}$; excitation at 310 nm. Numerals in parentheses are the values of $k_T$ in aerated methanolic solutions.

Figure 3  
Correlation of quenching constants $\log k_T$ for 9-CP with the IP of the quencher.
be observed in the photoreaction with Id; irradiation of a methanolic solution of 9-CP in the presence of Id gave 50% of 4 and 20-30% of solvent-incorporated products 6 (cis and trans isomers) accompanied with ca. 10% of 2d. Accordingly, a singlet exciplex mechanism would be favourable for the photoreaction with Id, though direct evidence is lacking. In contrast, any solvent-incorporated product was not formed by irradiation of a methanolic solution of 9-CP in the presence of la, lb, or lc, suggesting again a different mechanism from that of the photoreactions with Id and le.

Thus the mechanism of these photocycloadditions depends on electron densities of olefins, i.e., ionisation potentials. This divergency in mechanism would be interpreted in terms of competition between the exciplex formation and intersystem crossing as well as efficiencies to final products from exciplexes, the higher the ionisation potential of olefin, the slower the exciplex formation and the lower the efficiency will become.
### Table 3

**Elemental analyses of products**

<table>
<thead>
<tr>
<th>Product</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Formula</th>
<th>Found(%)</th>
<th>Required(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>82.5</td>
<td>5.9</td>
<td>5.1</td>
<td>C_{19}H_{15}NO</td>
<td>82.75</td>
<td>5.8</td>
</tr>
<tr>
<td>2b</td>
<td>82.95</td>
<td>5.95</td>
<td>4.85</td>
<td>C_{19}H_{17}NO</td>
<td>82.9</td>
<td>6.2</td>
</tr>
<tr>
<td>2c</td>
<td>87.7</td>
<td>6.85</td>
<td>5.2</td>
<td>C_{20}H_{19}N</td>
<td>87.85</td>
<td>7.0</td>
</tr>
<tr>
<td>2d</td>
<td>87.5</td>
<td>7.55</td>
<td>4.6</td>
<td>C_{21}H_{21}N</td>
<td>87.75</td>
<td>7.35</td>
</tr>
<tr>
<td>2e</td>
<td>88.0</td>
<td>7.15</td>
<td>4.55</td>
<td>C_{23}H_{23}N</td>
<td>88.15</td>
<td>7.4</td>
</tr>
<tr>
<td>4</td>
<td>87.55</td>
<td>5.25</td>
<td>6.75</td>
<td>C_{19}H_{11}N</td>
<td>87.75</td>
<td>5.4</td>
</tr>
</tbody>
</table>

### Table 4

**Spectral data of products**

<table>
<thead>
<tr>
<th>Products</th>
<th>N.m.r. (^a) [(\delta (J \text{ in Hz})]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2a(^b)</td>
<td>2.08(1H, dt, J 11), 2.59(1H, dt, J 8), 3.51(3H, s), 3.6(1H, dd), 4.48(1H, dd), 7.3(6H, m), 8.0(2H, m)</td>
<td></td>
</tr>
<tr>
<td>2b(^b,d)</td>
<td>1.24(3H, t, J 8), 2.08(1H, dt, J 11), 2.57(1H, dt, J 10), 3.56(1H, dd), 3.7(2H, q), 4.61(1H, dd), 7.3(6H, m), 8.0(2H, m)</td>
<td></td>
</tr>
<tr>
<td>2c(^b)</td>
<td>0.84(3H, s), 0.98(3H, d), 1.54(3H, s), 2.0(1H, dq, J 10 and 7), 3.52(1H, d), 7.3(6H, m), 7.95(2H, m)</td>
<td></td>
</tr>
<tr>
<td>2d(^b)</td>
<td>0.54(3H, s), 0.86(3H, s), 1.18(3H, s), 1.63(3H, s), 3.89(1H, s), 6.95(1H, m), 7.25(5H, m), 7.9(2H, m)</td>
<td></td>
</tr>
<tr>
<td>2e(^b)</td>
<td>0.64(3H, s), 1.48(3H, s), 1.62(3H, s), 1.68(3H, s), 3.72(1H, t, J 10), 4.29(1H, d), 4.81br(1H, d), 6.9(1H, m), 7.3(5H), 7.95(2H)</td>
<td></td>
</tr>
<tr>
<td>4(^c,e)</td>
<td>3.13(2H, d, J 7.8), 3.96(1H, t), 7.5(8H, m)</td>
<td></td>
</tr>
<tr>
<td>5(^c,f)</td>
<td>0.97(12H, s), 1.18(12H, s), 3.03(6H, s), 5.22(2H, d, J 15), 5.65(2H, d)</td>
<td></td>
</tr>
<tr>
<td>6(^c,g)</td>
<td>cis; 0.42(3H, s), 0.69(3H, s), 1.12(3H, s), 124(3H, s), 3.27(3H, s), 3.72(1H, d, J 4.5), 4.24(1H, d), 7.1-7.9(8H, m)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>trans; 0.26(3H, s), 1.02(3H, s), 1.05(3H, s), 1.47(3H, s), 3.18(3H, s), 3.29(1H, d, J 15), 3.86(1H, d), 7.1-7.9(8H, m)</td>
<td></td>
</tr>
</tbody>
</table>

---

\(^a\) 100 MHz. \(^b\) \(\delta (CDCl_3)\). \(^c\) \(\delta (CCl_4)\). \(^d\) \(\gamma\) cyclohexane. \(^e\) \(\delta\) max (KBr) 2230 (C=O), 1130 cm\(^{-1}\) (C-O-C); m/e 275 (M\(^\dagger\)), 203, 72. \(^f\) \(\nu\) max (KBr) 2240 cm\(^{-1}\) (C=O); m/e 205 (M\(^\dagger\)). \(^g\) \(\nu\) max (film) 1650 (C=C), 1076 cm\(^{-1}\) (C-O-C); m/e 141 (M\(^\dagger\)/2) and observed MW 284 (calcd. for C_{28}H_{34}O_{2} 282) by vapor pressure osmometry. \(^h\) \(\nu\) max (film) 2250 (C=C), 1070 cm\(^{-1}\) (C-O-C); m/e 319 (M\(^\dagger\)), 203, 115.
In line with this, Ib and lc, possessing higher ionisation potential, are very poor quenchers for fluorescence of 9-CP. Finally it should be noted that the photocycloaddition of la, Ib, and lc to 9-CP is commonly stereoselective, in sharp contrast to that of electron deficient olefins to phenanthrene which occurs from triplet phenanthrene or triplet exciplexes to yield mixtures of cyclobutane compounds. Although reasonable discussion of this stereoselectivity requires concrete determination of structures of the cycloadducts, a triplet exciplex mechanism would render an attractive speculation; for example, triplet exciplexes of 9-CP and la-c might be expected to be more strongly bonded than those of phenanthrene and electron deficient olefins.

2-3 References and Footnotes

1 (a) C. Pac, T. Sugioka, and H. Sakurai, Chem. Lett., 39(1972); (b) T. Sugioka, C. Pac, and H. Sakurai, ibid., 667(1972); (c) C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, ibid., 187(1973); (d) K. Mizuno, C. Pac, and H. Sakurai, ibid., 309(1973); (e) C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, Bull. Chem. Soc. Japan, 46, 238(1973); (f) K. Mizuno, C. Pac, and H. Sakurai, J. C. S. Perkin I, 2360(1974); (g) ibid., in the press.


6 A benzene solution (50 ml) containing 0.3 g of 9-CP and 5-10 ml of an olefin, placed in a test tube, was irradiated under nitrogen atmosphere at ambient temperature by a high-pressure mercury arc. In the case
of le, over irradiation led to accumulation of secondary products.

Endo or exo configuration of C7-substituents of 2c and 2e has not been determined yet. Endo-location of alkoxy group of 2a and 2b was tentatively assigned from comparison of n.m.r. spectra with those of similar compounds; see ref. le and chapter 3 and 4.

In n.m.r. analyses of reaction mixtures obtained by irradiation of 9-CP and 1b or le, difficulties were encountered, since some oligomeric and/or polymeric materials of the olefin were formed. However, there was observed no signal of epimers in n.m.r. spectra of crude products, after such oligomeric materials had been removed by column chromatography on a short column of silica gel.

The photocycloaddition of benzene solutions 1.5-2.0 mol dm\(^{-3}\) in la-c and 1.0 mol dm\(^{-3}\) in isoprene occurs at a rate only one-fourth that was very inert to quenching of fluorescence of 9-CP (k\(_q\) \(<\) 0.1 mol\(^{-1}\) dm\(^3\)) and photoreaction with 9-CP.

Quantum yield for disappearance of 9-CP was determined for degassed cyclohexane solution containing various amounts of le (1.0-0.0042 mol dm\(^{-3}\)) at 313 nm, using a potassium ferrioxalate actinometer.

Ionic nature for the formation of 4 was confirmed by irradiation of a methanol-O-d solution containing 9-CP and 1d or le which gave 9,10-dideuterio-9-cyanophenanthrene in place of 4.


The exciplex to cycloadduct probabilities are very low for reactions of phenanthrene singlet with electron poor olefins; R. A. Caldwell, private communication.


Alternatively, this stereoselectivity could be simply interpreted by steric factors. However, the exclusive formation of the sterically unfavourable endo adducts $2a$ and $2b$ cannot be reasonably interpreted. In this regard, it is noteworthy that photocycloaddition of 9-CP to trimethyl silyl vinyl ether, containing more bulky group than $1a$ and $1b$, gave both endo and exo cycloadducts in a ratio of 3:2; K. Mizuno, H. Okamoto, C. Pac, and H. Sakurai, unpublished results, see chapter 5.
Chapter 3  Photochemical Reactions of Alkyl Vinyl Ethers with 2-Naphthonitrile

3-1 Introduction

Photocycloaddition of unsaturated compounds to naphthalenes exhibits interesting stereochemical aspects and solvent effects which have been discussed in terms of exciplexes.\textsuperscript{1-7} This chapter describes the photocycloadditions of alkyl vinyl ethers to 2-naphthonitrile (2-NN), including product distribution under various conditions and a discussion of mechanism.

3-2 Results

The product distributions in photoreactions of the nitrile (2-NN) with the ethers (1) depend on the filters used, the concentrations of ethers, and the reaction temperature, but not on solvent. Irradiation of 2-NN containing an excess of 1a-b at 313 nm afforded a single (2 + 2) cycloadduct (2a-b) in 80-90% yield.\textsuperscript{8} When Pyrex was used as filter (transmission $> 280$ nm), the adduct (2a-b) was initially produced, and further irradiation led to gradual accumulation of compounds (3a-b), (5a-b), (6a-b), and (7a-b), with concomitant consumption of 2a-b. Ultimately, when 90-
95% of the nitrile (2-NN) had been consumed, the adduct (2a-b) had almost disappeared, and 3a-b was obtained in 70% yield. When a large excess of 1a-b was used, the formation of 2a-b was efficient and accumulation of the other products was slow. The dihydrobenzocyclo-octene (4a-b) was obtained only in a small amount at low conversion by irradiation through an

<table>
<thead>
<tr>
<th>Temp. Conv.</th>
<th>Yields(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter b</td>
<td></td>
</tr>
<tr>
<td>(°C)</td>
<td>(%)</td>
</tr>
<tr>
<td>(A) 20 ± 5</td>
<td>70</td>
</tr>
<tr>
<td>(B) 20 ± 5</td>
<td>95</td>
</tr>
<tr>
<td>(B) 20 ± 5</td>
<td>50d</td>
</tr>
<tr>
<td>(C) 0 ± 3</td>
<td>80</td>
</tr>
<tr>
<td>(C) 20 ± 5</td>
<td>40</td>
</tr>
</tbody>
</table>

a A solution in benzene (4 ml) containing 0.05 g of 2-NN and 1 ml of 1b. Product distribution was determined by g.l.c. analyses and in parentheses are shown the isolated yields based on 2-NN consumed in the photoreaction of 2-NN and 1a on a preparative scale. b See text. c Less than ca. 5% of combined yield; see text. d A neat solution of 1b (4 ml) containing 0.05 g of 2-NN.

aqueous solution of potassium hydrogen phthalate (transmission > 300 nm) at 20 ± 5 °C. On the other hand, irradiation of a methanolic solution at 0 ± 3 °C through this filter solution gave a 2:2-adduct (8a-b), formed in lesser amounts at 20 ± 5 °C. Thus, all the products were isolated by careful column chromatography on silica gel; the product distribution is summarised in Table 1. However, yields of minor products (4-8) were poorly reproducible.

The structure of products isolated were determined from their spectral properties (Table 2) and analytical data (Table 4) and in some cases by chemical transformation. The skeletal arrangement of the adducts 2a was readily determined by the n.m.r. spectrum, which shows the olefinic resonances as an AB quartet at δ5.65 and 6.67 (J 10 Hz) and aliphatic ABCX signals at δ2.35 (2H, m), 3.4 (1H, dd), and 4.36(1H, dd). The endo-
structure was assigned from the chemical shift of H-2 (δ4.34), which is similar to that of H-1 (δ4.40) of the endo-adduct rather than that of the exo-adduct (δ4.09) in the photoreaction of 1-naphthonitrile (1-NN) and methyl vinyl ether (1a).4 The 1,2-dihydonaphthalene structure was supported by the u.v. spectrum [λmax 270(ε6510) and 262 nm(6480) in cyclohexane].9

The mass spectrum of the cyclobutene (3a) showed the parent peak at m/e 211 but different fragment peaks from those of 2a. The u.v. spectrum [λmax 280(ε380), 268(510), and 260 nm(435)] did not correspond to a 1,2-dihydonaphthalene chromophore nor to an anisole chromophore, but was similar to that of benzonitrile. Moreover, 3a exhibits i.r. absorption at 1565 cm⁻¹, which is assignable to the stretching vibration of a cyclobutene double bond.10 In the n.m.r. spectrum (Figure 1) the aromatic resonances appear as simple ABX signals at δ 7.10 (d, J 8 Hz), 7.26 (dd, J 8 and 1 Hz), and 7.65 (d, J 1Hz) and the coupling constants between the olefinic protons (J 3 Hz) and between each olefinic proton and the adjacent methine proton (J 1 Hz) are consistent with a fused
cyclobutene structure as shown by molecular models. Extensive double irradiation experiments established that coupling of H-3 with H-4 (J 11.2 Hz) and H-2a (J 5.6 Hz) are very similar to those of axial-axial and axial-equatorial vicinal couplings respectively of cyclohexane derivatives, whereas those of H-3 with H-4 (J 4.5 Hz) and H-2a (J 3 Hz) are very similar to values for equatorial-axial and equatorial-equatorial vicinal couplings, thus confirming the trans-relationship between H-4 and H-2a.

Addition of the shift reagent Eu(fod)₃ caused the signal of only one of the aromatic protons to move rapidly downfield (Figure 2). Since coordination involving both the cyano- and methoxy-groups is expected this signal must be assigned to H-5, demonstrating the presence of the cyano-group at C-6. This structural assignment for 3a-b was further supported both by thermal rearrangement of 3a-b to 5a-b and by photochemical formation of 3b from 4b. The product (3a) could be that assigned a benzonorbornene structure by McCullough.

The u.v. [λ<sub>max</sub> cyclohexane 280(ε2520) and 261 nm(2320)] and i.r. spectra (ν<sub>max</sub> (KBr) 2250 and 1635 cm<sup>-1</sup>) of compound (5a) showed that it is a nitrile possessing a conjugate diene chromophore. The n.m.r. spectra showed that 5a and 5b each had three aromatic protons (ABX spin system), three olefinic protons, and four aliphatic protons. The structures assigned are in good accord with the n.m.r. data. Moreover, irradiation of 5a-b gave the cyclobutenes (6a-b) and acidic hydrolysis of 5b occurred ef-

Figure 3 Stern-Volmer plots of fluorescence quenching by 1b: (A) in methanol, (B) in acetonitrile, (C) in benzene, (D) in benzene ([2-NN] = 1.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> for (A)-(C) and [2-NN] = 0.1 mol dm<sup>-3</sup> for (D)).
### Table 2
Spectral data of products

<table>
<thead>
<tr>
<th>Product</th>
<th>N.m.r.[^{a}] [δ(J in Hz)]</th>
<th>m/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a[^{b,d}]</td>
<td>2.35(2H, m), 3.4(1H), 3.43(3H, s), 4.34(1H, dd, J(<em>{1,2}) 7.5 and 9), 5.65(1H, dd, J(</em>{3,8b}) 1, J(_{3,4}) 10), 6.65(1H, d), 7.1(4H, m)</td>
<td>211(M(^{+})), 153, 58</td>
</tr>
<tr>
<td>2b</td>
<td>1.23(3H, t, J 7), 2.2(1H, m), 2.6(1H, m), 3.39br(1H, dd, J(<em>{1,8b}) 7.5 and 11), 3.61(2H, qd, J 2.5), 4.42(1H, dd, J(</em>{1,2}) 7.5 and 9), 5.63(1H, dd, J(<em>{3,8b}) 1, J(</em>{3,4}) 10), 6.65(1H, d), 7.1(4H, m)</td>
<td>225(M(^{+})), 153, 72</td>
</tr>
<tr>
<td>3a[^{b,e}]</td>
<td>1.32(1H, ddd, J(<em>{3,4}) 11.2, J(</em>{3,3}) 12.8, J(<em>{2a,3}) 5.6), 2.37(1H, ddd, J(</em>{3,4}) 4.5, J(<em>{2a,3}) 3), 3.45br(1H, s), 3.50(3H, s), 3.98br(1H, d, J(</em>{2a,8b}) 4), 4.30(1H, dd), 5.87(1H, d, J(<em>{1,2}) 3), 6.17(1H, dd, J(</em>{2,2a}) 1), 7.10(1H, d, J(<em>{7,8}) 8), 7.26(1H, dd, J(</em>{5,7}) 1), 7.65(1H, d)</td>
<td>211(M(^{+}))</td>
</tr>
<tr>
<td>3b</td>
<td>1.3(1H, m), 1.32(3H, t, J 7), 2.37(1H, ddd, J(<em>{3,4}) 4.5, J(</em>{3,3}) 12.8, J(<em>{2a,3}) 3), 3.44br(1H, s), 3.66(2H, q), 3.96(1H, d, J(</em>{2a,8b}) 4), 4.26(1H, dd, J(<em>{3,4}) 11), 5.80(1H, d, J(</em>{1,2}) 3), 6.17(1H, d), 7.12(1H, d, J(<em>{7,8}) 8), 7.30(1H, dd, J(</em>{5,7}) 1), 7.68(1H, d)</td>
<td>225(M(^{+}))</td>
</tr>
<tr>
<td>4a[^{b,f}]</td>
<td>2.40br(1H, dd, J(<em>{9,10}) 11, J(</em>{9,9}) 17), 2.90br(1H, d), 3.11(3H, s), 4.96(1H, dd, J(<em>{9,10}) 4), 5.52br(2H, d), 6.10br(1H, d, J(</em>{5,6}) 12), 6.39(1H, d), 7.12(1H, d, J(<em>{3,4}) 8), 7.45(1H, d, J(</em>{1,3}) 2), 7.68(1H, d)</td>
<td>211(M(^{+}))</td>
</tr>
<tr>
<td>4b</td>
<td>1.16(3H, t, J 7), 2.45br(1H, ddd, J(<em>{9,10}) 11, J(</em>{9,9}) 17, J(<em>{8,9}) 3), 2.93br(1H, dd, J(</em>{9,10}) 4), 3.23(2H, q), 5.14(1H, dd), 5.56br(2H, d), 6.15br(2H, d), 6.15br(1H, d, J(<em>{5,6}) 12), 7.16(1H, d, J(</em>{3,4}) 8), 7.47(1H, dd, J(_{1,3}) 2), 7.75(1H, d)</td>
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Table 2 (Continued)

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<th>Compound</th>
<th>Chemical Shifts</th>
<th>Mass Spectral Data</th>
</tr>
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<tbody>
<tr>
<td>5a&lt;sup&gt;c,g&lt;/sup&gt;</td>
<td>2.50 (2H, m), 3.08 (2H, t, J&lt;sub&gt;5,6&lt;/sub&gt; 7), 3.73 (3H, s), 5.11br (1H, d, J&lt;sub&gt;8,9&lt;/sub&gt; 6), 5.44 (1H, dt, J&lt;sub&gt;7,8&lt;/sub&gt; 13, J&lt;sub&gt;6&lt;/sub&gt; 3.5), 5.59 (1H, ddt, J&lt;sub&gt;6,8&lt;/sub&gt; 1.5), 7.29 (1H, d, J&lt;sub&gt;3,4&lt;/sub&gt; 8.2), 7.60 (1H, dd, J&lt;sub&gt;1,3&lt;/sub&gt; 1.8), 7.71 (1H, d)</td>
<td>211 (M&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>5b&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.39 (3H, t, J 7), 2.52 (2H, m), 3.07 (2H, t, J&lt;sub&gt;5,6&lt;/sub&gt; 7), 3.85 (2H, q), 5.07br (1H, d, J&lt;sub&gt;8,9&lt;/sub&gt; 5.5), 5.24 (1H, dt, J&lt;sub&gt;8,9&lt;/sub&gt; 13, J&lt;sub&gt;6&lt;/sub&gt; 3.5), 5.52 (1H, ddt, J&lt;sub&gt;6,8&lt;/sub&gt; 1.5), 7.10 (1H, d, J&lt;sub&gt;3,4&lt;/sub&gt; 8), 7.39 (1H, dd, J&lt;sub&gt;1,3&lt;/sub&gt; 1.8), 7.44 (1H, d)</td>
<td>225 (M&lt;sup&gt;+&lt;/sup&gt;)</td>
</tr>
<tr>
<td>6a&lt;sup&gt;b,h&lt;/sup&gt;</td>
<td>1.46 (1H, tt, J&lt;sub&gt;2a&lt;/sub&gt; 4.5, J&lt;sub&gt;3&lt;/sub&gt; 3, J&lt;sub&gt;3,4&lt;/sub&gt; 4.5 and 13.5), 2.01br (1H, d), 2.51 (1H, dt, J&lt;sub&gt;4,4&lt;/sub&gt; 15), 2.80br (1H, d), 3.25 (3H, s), 3.33 (1H, m), 5.85 (1H, dd, J&lt;sub&gt;2,2a&lt;/sub&gt; 1, J&lt;sub&gt;1,2&lt;/sub&gt; 3), 6.30 (1H, d), 7.18 (1H, d, J&lt;sub&gt;5,6&lt;/sub&gt; 7.5), 7.38 (1H, dd, J&lt;sub&gt;6,8&lt;/sub&gt; 2), 7.86 (1H, d)</td>
<td>211 (M&lt;sup&gt;+&lt;/sup&gt;), 197</td>
</tr>
<tr>
<td>6b&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.26 (3H, t, J 7), 1.46 (1H, tt, J&lt;sub&gt;2a&lt;/sub&gt; 4.5, J&lt;sub&gt;3&lt;/sub&gt; 3, J&lt;sub&gt;3,4&lt;/sub&gt; 4.5 and 13.5), 2.00br (1H, d), 2.60 (2H, m), 3.30 (1H, m), 3.48 (2H, q), 5.87 (1H, d, J&lt;sub&gt;1,2&lt;/sub&gt; 3), 6.31 (1H, d), 7.18 (1H, d, J&lt;sub&gt;5,6&lt;/sub&gt; 8), 7.46 (1H, dd, J&lt;sub&gt;6,8&lt;/sub&gt; 2), 7.86 (1H, d)</td>
<td>225 (M&lt;sup&gt;+&lt;/sup&gt;), 197</td>
</tr>
<tr>
<td>7a&lt;sup&gt;b,i&lt;/sup&gt;</td>
<td>2.28br (1H, d, J 18), 2.6-3.4 (3H, m), 3.15 (1H, m), 4.02 (3H, s), 4.34 (1H, d, J 7) 7.10 (3H, m), 7.38 (1H, m)</td>
<td>211 (M&lt;sup&gt;+&lt;/sup&gt;), 196, 115</td>
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<tr>
<td>7b&lt;sup&gt;j&lt;/sup&gt;</td>
<td>1.30 (3H, t, J 7), 2.27br (1H, d, J 18), 2.6-3.4 (3H, m), 3.15 (1H, m), 4.25 (1H), 4.28 (2H, dq, J 2), 7.10 (3H, m), 7.35 (1H, m)</td>
<td>225 (M&lt;sup&gt;+&lt;/sup&gt;), 196, 115</td>
</tr>
<tr>
<td>8a&lt;sup&gt;c,k&lt;/sup&gt;</td>
<td>1.7 (6H, m), 2.3 (2H, m), 3.14 (6H, s), 4.40 (2H, dd, J&lt;sub&gt;9,10&lt;/sub&gt; 5 and 10), 5.97 (2H, d, J&lt;sub&gt;5,6&lt;/sub&gt; 12), 6.34 (2H, d), 7.19 (2H, d, J&lt;sub&gt;3,4&lt;/sub&gt; 8), 7.48 (2H, dd, J&lt;sub&gt;1,3&lt;/sub&gt; 1.6), 7.72 (2H, d)</td>
<td>4.22 (M&lt;sup&gt;+&lt;/sup&gt;), 358, 198</td>
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Table 2 (Continued)

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<th>Additional Information</th>
</tr>
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<td>8b</td>
<td>1.12 (6H, t, J 7), 1.7 (6H, m), 2.3 (2H, m), 3.23 (4H, q), 4.49 (2H, dd, J 9, 10 5.5 and 10), 5.97 (2H, d, J 5, 6 12), 6.34 (2H, d), 7.16 (2H, d, J 3, 4 8), 7.46 (2H, dd, J 1, 3 1.8), 7.75 (2H, d)</td>
<td>450 (M+)</td>
</tr>
<tr>
<td>g_c,1</td>
<td>2.6 (2H, m), 3.22 (2H, t, J 5, 6 7), 3.62 (1H, d, J 8, 9 6.5), 3.64 (1H, d, J 3, 4 8.2) 5.55 (2H, m), 7.26 (1H, d, J 3, 4 8.2), 7.65 (1H, dd, J 1, 3 2), 7.95 (1H, d)</td>
<td>197 (M+)</td>
</tr>
</tbody>
</table>

a 100 MHz. b δ (CCl₄). c δ (CDCl₃). d λ cyclohexane (ε) 270 (6510s), and 262 nm (6840); ν max. (film) 2250, 1635, and 1130 cm⁻¹. e λ cyclohexane (ε) 280 (380), 268 (510), and 260 nm (s); ν max. (film) 2250, 1565, and 1095 cm⁻¹. f λ acetonitrile (ε) 278 nm (4850). g λ cyclohexane (ε) 280 (2520) and 261 nm (2320); ν max. (KBr) 2250, 1635, and 1095 cm⁻¹. h λ cyclohexane (ε) 282 (415), 272 (720), and 265 nm (625); ν max. (film) 2240, 1570, and 1100 cm⁻¹. i λ cyclohexane (ε) 271 (1060) and 263 nm (960). j ν max. (film) 2200 cm⁻¹. k λ acetonitrile (ε) 265 nm (12100). l λ cyclohexane (ε) 325 (245), 295 (s), and 288 nm (840); ν max. (KBr) 2220 and 1673 cm⁻¹.
ficiently to give the enone (9) in good yield, again supporting the dienol ether structure. The ketone (9) shows an i.r. band at 1673 cm\(^{-1}\) and \(n-\pi^*\) u.v. band at 325 nm (ε245 in cyclohexane), both characteristic of an aromatic ketone. The structure of 9 was established by analysis of its n.m.r. spectrum; the chemical shifts of the two olefinic protons are almost identical (δ5.55 (2H, m)) and very similar to that of the olefinic protons of cyclo-octene (δ 5.54), indicating non-conjugation of the double bond with the carbonyl group. Double-irradiation experiments supported this assignment. The cyano-group was thus considered to be on the aromatic ring, and the position was readily determined to be C-3 by the chemical shift of the X-proton in the ABX system of 9, which is considerably greater (δ 7.95) than that of 5a (δ 7.71) unlike those of the A and B protons. This can be attributed to the deshielding effect of the carbonyl group in 9 on the peri-proton (X = H-4).

Spectral data and m.p.s. of compounds (4a), (7a), and (8a) were essentially identical with those reported by McCullough et al. \(^7\) The author accepts the structures assigned by them, which are in good accordance with the spectral properties.

3.3 Discussion

The adduct (2b) comprises nearly 90% of the primary products. Its formation was neither quenched by isoprene and oxygen nor sensitised by benzophenone and Michler’s ketone, thus it probably occurs via the excited singlet of 2-NN. The singlet mechanism was unambiguously confirmed by

![Figure 4](image)

*Figure 4* Plots of $\bar{\phi}_{-A}^{-1}$ vs. $[lb]^{-1}$ for air-saturated benzene solutions in the presence of isoprene, where $[2-\text{NN}] = 1.13 \times 10^{-3}$ mol dm\(^{-3}\) and [isoprene] = 0.03 mol dm\(^{-3}\)
Figure 5 Plots of $\varphi_{2b}^{-1}$ vs. $[lb]^{-1}$ for air-saturated benzene solutions in the presence of isoprene, where $[2\text{-NN}] = 0.1 \text{ mol dm}^{-3}$ and $[\text{Isoprene}] = 0.5 \text{ mol dm}^{-3}$.

kinetic results. Fluorescence of 2-NN was inefficiently but significantly quenched by $lb$, the $k_T$ values for air-saturated benzene solutions being $0.46 \text{ mol}^{-1} \text{ dm}^3$ ($[2\text{-NN}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$) and $0.24 \text{ mol}^{-1} \text{ dm}^3$ ($[2\text{-NN}] = 0.1 \text{ mol dm}^{-3}$) (Figure 3). The difference between the $k_T$ values for dilute and concentrated solutions can be attributed to different lifetimes of 2-NN at different concentrations, since excimer formation must be taken into account in the case of a concentrated solution. In fact the fluorescence spectrum of a concentrated solution was markedly different from that of a dilute solution.

The quantum yields of disappearance of 2-NN $[\varphi_{-A}]$ and formation of $2b$
for solutions in benzene in the presence of isoprene at 313 nm were determined with varying concentrations of \( \text{lb} \). Thus, linear plots of \( 1/\phi_2 \) vs. \( 1/(\text{lb}) \) were obtained, from which the slopes and the intercepts were determined respectively as 8.7 mol dm\(^{-3}\) and 3.5 for \( \phi_2 \) runs (\([2-\text{NN}] = 1.13 \times 10^{-3} \text{ mol dm}^{-3}\) ) and 23.7 mol dm\(^{-3}\) and 4.6 for \( \phi_2 \) runs (\([2-\text{NN}] = 0.1 \text{ mol dm}^{-3}\) ) (Figure 4 and 5).

When these values and the

Table 3

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Adiabatic ionisation potential</th>
<th>Solvent(^a)</th>
<th>( k_{rT}/(\text{dm}^3\text{mol}^{-1}) )</th>
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<tbody>
<tr>
<td>( \text{lb} )</td>
<td>8.49(^b)</td>
<td>benzene</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>benzene(^c)</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>methanol</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetonitrile</td>
<td>2.98</td>
</tr>
<tr>
<td>2,3-Dimethylbut-2-ene</td>
<td>8.05(^d)</td>
<td>benzene</td>
<td>1.15(^e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>methanol</td>
<td>148(^f)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acetonitrile</td>
<td>167(^f)</td>
</tr>
</tbody>
</table>

\(^a\) Air-saturated solution; \([2-\text{NN}] = 1.1 \times 10^{-3} \text{ mol dm}^{-3}\). \(^b\) M. P. Niemczyk, N. E. Schore, and N. J. Turro, Mol. Photochem., 5, 69(1973). \(^c\) \([2-\text{NN}] = 0.1 \text{ mol dm}^{-3}\). \(^d\) G. N. Taylor, Chem. Phys. Lett., 10, 355(1971). \(^e\) Measured in this work. \(^f\) See ref. 17a.

Quenching constants of isoprene (\( k_{rT(I)} \)) were applied to equation (ii), the \( k_{rT} \) values were calculated as 0.44 mol\(^{-1}\) dm\(^3\) for \( \phi_2 \) and 0.23 mol\(^{-1}\) dm\(^3\) for \( \phi_2 \), in excellent agreement with the values obtained from the fluorescence quenching studies on the corresponding solutions.

Fluorescence quenching in polar solvents is much more effective than for a solution in benzene (Table 3), showing that \( k_r \) is greater in polar solvents, since life-times of 2-NN in methanol and cyclohexane are known to be almost identical.\(^{14}\)

This solvent effect can be reasonably interpreted by assuming the intervention of an intermediate possessing charge-transfer character as suggested in a previous paper.\(^4\) Since such an intermediate (probably an exciplex)\(^{15}\) is expected to be more stabi-
lised in polar solvents than in less polar solvents, it would be predicted that values of $k$ would increase of solvent polarity. The exciplex intermediacy is further supported by the greater effectiveness of fluorescence quenching with 2,3-dimethylbut-2-ene, which possesses a lower ionisation potential (Table 3). Moreover, we observed that the fluorescence quenching by 2,3-dimethylbut-2-ene in a dilute solution in benzene was accompanied by enhancement of longer wavelength emission, due to the appearance of a new weak emission (exciplex emission) at longer wavelength (390-440 nm).

In relation to solvent effects on mechanistic pathways from exciplexes, however, it is of interest that the systems 2-NN-la-b and 2-NN-2,3-dimethylbut-2-ene reveal different solvent effects. In the latter case, the photoreaction of a methanolic solution gives solvent-incorporated adducts, and moreover the fluorescence quenching in methanol is one hundred times more effective than that in benzene, suggesting occurrence of a rapid electron-transfer reaction as established for some exciplex-forming systems. In contrast, the former system does not show such drastic solvent effects on both product distribution and fluorescence quenching rate, implying negligible importance of electron-transfer reactions, even in polar media. The solvent effects can rather be interpreted in terms of solvation of a 2-NN-la-b exciplex depending on solvent polarity. In this regard, it is notable that the quantum yield (0.046) for disappearance of 2-NN in a dilute methanolic solution in the presence of

![Scheme 2]

**Scheme 2**

\[ a; R = \text{Me} \quad b; R = \text{Et} \]
of 2.0 mol dm$^{-3}$ of $1b$ was significantly lower than that in a benzene solution (0.123), probably owing to solvation of the exciplex by methanol which leads to faster decay (greater $k_n$) in comparison with the decay in benzene. Alternatively, the lower quantum yield in methanol could be interpreted in terms of hydrogen bonding of a 1,4-diradical intermediate as has been discussed for Norrish type II photoelimination of ketones.$^{18}$ However, the intermediacy of a diradical is not consistent with the selective formation of the thermodynamically less stable $2b$ in both methanol and benzene.

The change of the product distribution in irradiation through Pyrex is of mechanistic interest. This is shown dramatically by the u.v. spectra (Figure 6; irradiation at 313 nm of a dilute solution of 2-NN in cyclohexane containing $1b$ resulted in a spectrum essentially identical with that of $2b$, which rapidly collapsed to a spectrum similar to that of $3b$ on further irradiation of the solution through Pyrex. The author previously ascribed this change to the photorearrangement of $2a-b$; this has been now found to be erroneous, since $2a-b$ are quantitatively decomposed into 2-NN.

![Figure 6](image)

**Figure 6** Spectral Change of a cyclohexane solution containing 2-NN ($4.0 \times 10^{-4}$ mol dm$^{-3}$) and $1b$ (2.0 mol dm$^{-3}$); solid line spectra: 313 nm irradiation for 0 (I), 20 (II), and 80 min (III); dotted line spectra: irradiation of mixture (III) through Pyrex for 50 (IV), 110 (V), and 180 min (VI)
and 1a-b by either direct irradiation through Pyrex or sensitisation with benzophenone, Michler’s ketone, and 2-NN, but do not give compounds 3a-b and the other products at all, even at -60 °C.

The change in product distribution is now thought to be due to continuous accumulation of the minor products during irradiation through Pyrex, as 2a-b is decomposed in competition with its formation by light of longer wavelength than 280 nm. This interpretation is in good accord with the observations that irradiation at 313 nm or in the presence of a large excess of 1a-b through Pyrex resulted in no appreciable or only a small change in product distribution, since 2a-b is not appreciably photolysed at 313 nm or accumulates faster than it decomposes in the presence of a large excess of 1a-b even during irradiation through Pyrex.

In order to elucidate the mechanistic pathways affording the minor products (ca. 5% of the primary products), photochemical and thermal interconversions were investigated; the results are shown in Scheme 2. Details of these reactions will be published elsewhere, but some significant points will be discussed in relation to the mechanism of formation of these products.

None of the products 4, 5, and 7 is formed by secondary photoreactions of the other products. Compound 6 is evidently an artefact formed by photocyclisation of 5 since irradiation of the latter gave 6 in quantitative yield. Likewise, 3 and 8 are formed by photochemical ring closure and dimerisation of 4; this was confirmed by irradiation of 4 in solution through Pyrex, giving 3 and 8 in good yield. Moreover, there is a remarkable temperature dependence of the ratio of the product 3 and 8: 0.5: 1 at 0 ± 3 °C, 1.0:1 at 20 ± 5 °C, and 2.0:1 at 70 ± 5 °C, in good accord with the observation that the yield of 8 is higher at 0 ± 3 °C than at 20 ± 5 °C. However, it is doubtful that all the product 3 formed from the photoreaction of 2-NN with 1 is obtained by photocyclisation of 4, since the expected yield of 3 based on the 3:8 ratio never exceeds 50% at best (at 20 ± 5 °C)\(^19\) and the observed yield is 70%. Therefore, 3 appears to be formed by another route as well. Since the products 3-5 have similar skeletons, their formation could be interpreted in terms of a common transient compound 10, which is formed by the photoaddition of 1 to the C(8)-C(8a) bond of 2-NN; the intervention of vibrationally excited 4 arising from cleavage of the remaining single bond at this position in 10 provides a reasonable route to 4 and 5, since 4 thermally rearranged to 5 and/or the cis, trans-diene 11 generated by the bond cleavage would be a
possible precursor of 3 and 8 by analogy with the thermal cyclisation and dimerisation of cis,trans-cyclo-octa-1,3-diene. Alternatively, formation of 3 could be explained in terms of a [1,3] sigmatropic shift of the naphthalene 8,8a-bond in 10. The mechanism for formation of 7 cannot be reasonably discussed at present. However, formation of compounds 3, 4, 5, and 7 is not sensitised by benzophenone and Michler’s ketone, suggesting the intermediacy of the excited singlet state of 2-NN, though it is not clear whether or not these products are formed via an exciplex.

In summary, the (2 + 2) photocycloaddition of 1 to 2-NN occurs in a stereoselective manner unlike that to 1-NN, but both the systems 2-NN-1 and 1-NN-1 reveal similar solvent-dependent behaviour of quantum yields and fluorescence quenching rates, implying the intervention of exciplexes which have a similar charge-transfer nature but different configurational stabilities. Moreover, the photoreactions of 2-NN with 1 could be of use for the preparation of various cyclic compounds, by suitable choice of filters and thermal or photochemical rearrangement of the photoproducts.
3-4 Experimental

Materials. —— Commercial thiophene-free benzene was washed with sulphuric acid until no further colouration of the acid layer took place, then with water, and distilled from sodium. Reagent grade methanol was distilled from calcium hydride. Ethyl vinyl ether (Nakarai Chemicals) was distilled over calcium chloride under nitrogen before use. Methyl vinyl ether (Tokyo Kasei) was distilled from a gas cylinder before use. 2-Naphthonitrile (Tokyo Kasei) was purified by vacuum distillation and subsequent recrystallisation from hexane (m.p. 66-67 °C).

General. —— N.m.r. spectra were obtained with a Hitachi-Perkin-Elmer R24 spectrophotometer (60 MHz) and a JEOL JNM JS-100 instrument (100 MHz) for solutions in carbon tetrachloride or dueteriochloroform containing tetramethylsilane as internal standard, i.r. spectra with a Hitachi EPI-S2 spectrophotometer, u.v. spectra with a Hitachi 124 spectrophotometer, and fluorescence spectra with a Hitachi MPF-2A spectrofluorimeter. Yields and product ratios were determined by g.l.c. with a Shimadzu GC-2C machine equipped with a flame-ionisation detector (column of 5% Ucon Oil LB-550X on Celite 545; 0.75 or 1.5 m; 160 °C). M.p.s. were measured for samples in capillaries.

Quantum Yields. —— (a) The solutions were prepared by dissolving the nitrile (2-NN) \((1.13 \times 10^{-3} \text{ mol dm}^{-3})\), the ether \((\text{lb}) (0.8-4.0 \text{ mol dm}^{-3})\), and isoprene \((0.03 \text{ mol dm}^{-3})\) in benzene or methanol. Monochromatic light at 313 nm was obtained from a high-pressure mercury arc (450 W) by passage through a Toshiba UV-D25 glass filter and aqueous potassium chromate \((0.2 \text{ g dm}^{-3}; 10 \text{ mm path length})\). The light intensity \((I_0)\) was determined by potassium ferrioxalate actinometry to be \(2.01 \times 10^{-7} \text{ einstein cm}^{-3} \text{ min}^{-1}\). Sample solutions placed in an optical cell \((10 \times 10 \times 45 \text{ mm})\) were irradiated and the decrease of absorbance at 316 nm \((A)\) was monitored. Plots of \(\ln (e^A - 1)\) vs. irradiation time \((t/\text{min})\) were linear. Quantum yields for the disappearance of 2-NN \(\left[ \Phi_A \right]\) were obtained from the slopes of the lines by applying the equation \(\ln (e^A - 1) = -1000\varepsilon_\text{A} I_0 t + C\), where \(\varepsilon\) is the molar absorption coefficient of 2-NN at 316 nm \((8.9 \times 10^2 \text{ dm}^2 \text{ mol}^{-1})\) and \(C\) is a constant. In all the runs, conversions were less than 10%.

(b) The quantum yields for formation of 2b \(\left[ \Phi_{2b} \right]\) were determined for solutions in benzene \(0.1 \text{ mol dm}^{-3}\) in 2-NN, \(0.05 \text{ mol dm}^{-3}\) in isoprene and \(0.5-4.0 \text{ mol dm}^{-3}\) in lb. Relative quantum yields were obtained by using a 'merry-go-round' apparatus immersed in water at 20 ± 2 °C. Light
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<th>Required (%)</th>
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<td>79.8 6.05 6.55</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;NO</td>
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<tr>
<td>3a</td>
<td>50-51&lt;sup&gt;a&lt;/sup&gt;,&lt;sup&gt;f&lt;/sup&gt;</td>
<td>79.35 5.95 6.5</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;NO</td>
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<td>108-110&lt;sup&gt;a&lt;/sup&gt;,&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>C&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;NO</td>
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<sup>a</sup> From hexane.  <sup>b</sup> From methanol.  <sup>c</sup> From benzene.  <sup>d</sup> From ethanol.  <sup>e</sup> Decom.  <sup>f</sup> Lit.  

mp (°C); 2a [73-74], 3a [50-51], 4a [111-112], 7a [94-95] and 8a [270-280]. See ref. 7.
filtered through the filter (A) (see later) was used to irradiate samples (4 ml) in matched Pyrex tubes. After irradiation, p-methoxybenzophenone (internal standard) was added to each irradiated solution and the amounts of 2b formed were determined by g.l.c. analysis. The absolute quantum yield in the presence of 4.0 mol dm\(^{-3}\) of 1b was 0.097. In all the runs, conversions were less than 5%.

Photoreactions of 2-Naphthonitrile with Alkyl Vinyl Ethers. ——

General procedures. Irradiation was carried out with an Eikosha PH3 300 W high-pressure mercury arc at room temperature. The following filters were employed: (A) 5.0 x 10\(^{-4}\) mol dm\(^{-3}\) aqueous potassium chromate in a Pyrex vessel (10 mm path length; 313 nm), (B) Pyrex (>280 nm), and (C) 2.4 x 10\(^{-2}\) mol dm\(^{-3}\) aqueous potassium hydrogen phthalate in a Pyrex vessel (10 mm path length; >300 nm). In control runs, a solution in benzene (4 ml) containing the nitrile 2-NN (0.05 g) and the ether 1b (1 ml) or a solution of 2-NN (0.05 g) in 1b (4 ml) was irradiated and the photolysate was analysed by g.l.c. Oxygen-free nitrogen was bubbled through the solutions for 30 min before irradiation. In preparative experiments, a solution in benzene or methanol (200 ml) containing 2-NN and 1a-b was irradiated for 20-50 h. The solvent and the excess of 1a-b were removed, and the residue was subjected to column chromatography over silica gel (Merck Kieselgel 60) with benzene–hexane as eluant. After elution of unchanged 2-NN with benzene–hexane (1:3), compounds 7a-b, 4a-b, 2a-b, 5a-b, and 6a-b were isolated in sequence by elution with 1:2, 1:1.8, 1:1, 3:2, and 4:1 solvent mixtures, respectively. Since the procedures for the photoreactions of 2-NN with 1a and with 1b were almost identical, only the former reaction is described.

(a) With filter (A). A solution in benzene containing 2-NN (1.0 g) and 1a (30 g) was irradiated at 20 ± 5 °C for 40 h. Column chromatography afforded starting materials 2-NN (0.3 g), endo-2-methoxy-1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-2a-carbonitrile 2a (0.73 g, 76%), m.p. 71.5–72.5 °C (from hexane), and small amounts of other products (ca. 0.1 g).

(b) With filter (B). A solution in benzene containing 2-NN (2.0 g) and 1a (30 g) was irradiated at ambient temperature for 50 h. Column chromatography afforded the nitrile 2-NN (0.1 g), 3,3a,4,8b-tetrahydro-2-methoxycyclopent[a]indene-2-carbonitrile 7a (0.2 g, 8%), m.p. 89.5–92 °C (from hexane), 2a,3,4,8b-tetrahydro-4-methoxycyclobuta[a]naphthalene-6-carbonitrile 3a (1.2 g, 46%), m.p. 50–51 °C (from hexane), 5,6-dihydro-10-methoxybenzocyclo-octene-2-carbonitrile 5a (ca. 0.02 g), m.p. 106.5–108 °C (from methanol), 2a,3,4,8b-tetrahydro-8b-methoxycyclobuta[a]naphtha-
lene-7-carbonitrile 6a (0.1 g, 4%), m.p. 92–93 °C (from hexane), and a mixture of adducts.

(c) With filter (C). A methanolic solution containing 2-NN (2.0 g) and 1a (30 g) was irradiated at ambient temperature for 20 h. During irradiation a solid was precipitated, and was filtered off to yield the cyclobutabis(benzocyclo-octene) 8a (0.05 g, 4%), m.p. 290–300 °C (decomp.) (from benzene). After evaporation of methanol and the excess of 1a, column chromatography gave the nitrile 2-NN (1.1 g), compound 7a (ca.0.1 g), 9,10-dihydro-10-methoxybenzocyclo-octene-2-carbonitrile 4a (0.1 g, 8%), m.p. 108–110 °C (from hexane), and compounds 3 (ca. 0.25 g) and 2a (ca. 0.4 g).

Photolyses and Pyrolyses of the Adducts (2a and b). — A solution in methanol or benzene solution of 2a-b (0.1 g in 4 ml) in a Pyrex tube was irradiated with a high-pressure mercury arc (300 W). During the irradiation, g.l.c. analyses of the photolysate were carried out 1 h intervals for the initial 5 h; it was found that the amount of nitrile 2-NN increased linearly with disappearance of 2a-b and no other compounds were formed at 100% conversion.

Irradiation of a solution in benzene of 2a-b (0.01 g) in the presence of 2-NN (0.03 g), benzophenone (0.03 g), or Michler's ketone (0.03 g) for less than 2 h also resulted in complete decomposition to 2-NN. Pyrolyses of 2a-b at 230–250 °C again gave 2-NN.

Pyrolyses of the Adducts (3a and b). — On heating crystalline 3a-b (0.1 g) at 200–210 °C for 1 h under nitrogen, a brownish materials was obtained, which was chromatographed on silica gel. Elution with benzene–hexane (1:2; 500 ml) gave the benzocyclo-octene 5a-b (ca. 70 mg, 70%), and further elution afforded brownish glassy materials which were not identified.

Pyrolyses of the Adducts (4a and b). — Crystalline 4a-b (0.01 g) in a Pyrex tube was degassed and heated at 280 ± 5 °C for 15 min; the n.m.r. spectrum of the resultant mixture showed formation of 5a-b in ca. 70% yield.

Irradiation of the Adduct (4b). — A solution in benzene of 4b (0.01 g in 5 ml) in a Pyrex tube at 0 ± 3 °C for 6 h, at 20 ± 5 °C for 3 h, or at 70 ± 5 °C for 30 min was irradiated with a high-pressure mercury arc. During the irradiation, g.l.c. analyses of the photolysate were carried out at 20 min intervals; it was found that compound 3b was formed linearly with disappearance of 4b but the total yields were decreased. After irradiation, removal of solvent left a solid which was
shown to consist of 3b and 8b by the n.m.r. spectra ca. (ratios 1:2, 1:1, and 2:1 respectively).

Irradiation of the Benzocyclo-octenes (5a and b). —— An ethereal solution of 5a (0.2 g in 100 ml) in a Pyrex vessel was irradiated with a high-pressure mercury arc for 5 h. After irradiation, removal of solvent left an oil containing 6a and a small amount of 5a; subsequent chromatography afforded pure 6a (0.18 g). Similarly, irradiation of 5b afforded 6b quantitatively, but the product did not solidify, even on storage in a refrigerator for 2 months.

Acid-catalysed Hydrolyses of the Benzocyclo-octene (5b). —— To ethanolic hydrochloric acid (0.1 N; 100 ml) was added an ethanolic solution of 5b (0.2 g) and the solution was left for a week at an ambient temperature. After removal of two-thirds of the solvent, the solution was extracted with ether. The extract was washed with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride, dried (MgSO₄), and evaporated. The brownish residue was chromatographed on silica gel to afford 3-cyano-9,10-dihydrobenzocyclo-octene-5(6 H)-one 9 (0.12 g), m.p. 106.5–107.5 °C (from methanol).

3-5 References and Footnotes


\[
\begin{align*}
\text{Benzene} & \quad 1 : 1 \\
\text{Methanol} & \quad 1 : 2
\end{align*}
\]


G.l.c. of the photolysate showed the presence of traces of other products, in amounts too small for unambiguous identification.


In the absence of isoprene, curved Stern-Volmer plots were obtained, owing to sensitised decomposition of 2b by 2-NN.


A charge-transfer complex is not formed in the ground state, since the u.v. spectrum of 2-NN in the presence of 1b is identical with that in the absence of 1b.


Irradiation of 4 in the presence of 2-NN at 20 ± 5 °C did not give 3 in appreciable amount, showing the absence of the sensitisation by 2-NN.

Chapter 4 Stereochemistry on Photocycloaddition to Aromatic Rings

4-1 Introduction

Recently, the stereochemistry of the photocycloaddition to aromatic rings has been discussed in terms of exciplexes. The configuration of exciplex can be expected to reflect the stereoselectivity of the cycloaddition and addition modes, i.e., \((2 + 2)\), \((2 + 4)\), \((4 + 4)\) additions and so on, if it is an intermediate which has some rigid configuration. In this chapter, the stereochemistry on photocycloaddition to aromatic rings via exciplexes is described.

4-2 Substrate Selectivity of 9-Cyanoanthracene and 9-Cyano­phenanthrene

4-2-1 Introduction

Previously, Sakurai et al. have reported that the photoreaction of 1-naphthonitrile (1-NN) with alkyl vinyl ethers (la-b) affords only \((2 + 2)\) adducts (2) and (3), whereas that with furan (4) gives only \((4 + 4)\) adducts (5). If 9-cyanoanthracene (9-CA) and 9-cyanophenanthrene (9-CP) having the reactive sites fixed on the \(C_9\) and \(C_{10}\) positions are used instead of 1-NN though the photocycloaddition of 9-CA with 4 and 9-CP with la-b were described in chapter 1 and 2, the possible photocycloaddition will be expected to occur in \((4 + 4)\) and \((4 + 2)\) types for 9-CA and in \((2 + 2)\) and \((2 + 4)\) types for 9-CP. In order to investigate the addition modes, the author carried out, in this section, the photoreaction of 9-CA with la-b and 9-CP with 4.

4-2-2 Results and Discussion

Irradiation of a benzene solution of 9-CA containing a large excess of la-b through a glass filter ( >300 nm) with a high-pressure mercury
arc gave no cross adduct, but only resulted in the quantitative formation of the dimer of 9-CA under the same conditions in the photoreactions of 9-CA with 4 in chapter 1. The photoreaction of 9-CP with 4 also resulted in the formation of the dimer of 9-CP (20%) and the recovery of 9-CP (70-80%).

The present results are in sharp contrast to those of the photoreaction of 1-NN with la-b and 4. Since the fluorescence of 9-CP and 9-CA was quenched by both 1b and 4, it is surprising that 9-CP and 9-CA have the distinct and reverse substrate selectivity in the photoreactions with la-b and 4. At the present stage, therefore, the substrate-selectivity may be possibly interpreted as being caused by the lifetimes and/or the configuration of exciplexes; in the case of the exciplex between 9-CP and 4 or 9-CA and la-b, the life time is too short for the reaction to occur and/or the configuration is unfavourable for the cycloaddition.

4-3 Stereoselective Photocycloaddition of Indene and Phenyl Vinyl Ether to 1-Naphthonitrile

4-3-1 Introduction

The photoreaction of 1-naphthonitrile (1-NN) with la-b affords both the endo-cycloadduct (2a-b) and exo-isomer (3a-b), whereas the (4 + 4) photocycloaddition of 4 to 1-NN is highly stereoselective and remarkably dependent on solvent used. The difference between the above two photoreactions may be interpreted by the stability and/or the configuration of exciplexes, since such planar molecule as 4 can be expected to form more stable and rigid exciplexes than linear la-b. If this is the case, more conjugated olefins will undergo the photocycloaddition to 1-NN with...
an enhanced stereoselectivity.

4-3-2 Results and Discussion

Irradiation of l-NN in the presence of an excess of indene (6) gave a single product (7) at an initial stage. The structure of 7 was determined by the following data: \( \nu_{\text{max}} \) (nujol) 2240 (C=O) and 1640 cm\(^{-1}\) (C=C); \( \lambda_{\text{max}} \) (acetone) 302 (sh), 273 (7690), and 265 nm (7690); m/e 269 (M\(^+\), very weak), 153, and 116; \( \delta \) (CC\(_4\)) (60 MHz) 2.75 (endo H-3, dd), 3.18 (exo H-3, dd), 3.85 (H-2, dddd), 4.1 (H-7, ddd), 4.36 (endo H-6, dd), 5.38 (H-8, dd), 6.0 (H-9, d), and 6.6-7.3 (aromatic protons, 8H, m); \( J \) 3.3 19, \( J \) 2.3 3.2, \( J \) 2.3 = \( J \) 2.6 = \( J \) 6.7 8, \( J \) 7.8 4.5, \( J \) 8.9 10 and \( J \) 2.7 1.5 Hz (Figure 1).

Figure 1  N.m.r. spectrum of the photoadduct (7) in CC\(_4\)

The complex n.m.r. signals at \( \delta \) 3.7-4.6 consist of a downfield triplet and two triplets with further splittings. Upon irradiation at \( \delta \) 2.95 (or 5.38), the triplet at \( \delta \) 3.85 (or 4.10) collapses into a doublet with splittings. This spin decoupling results and the first order analysis in comparison with 100 MHz data establish the vicinal couplings of H-2 with H-6, H-3, and H-3' and of H-7 with H-6 and H-8 and a long range coupling between H-2 and H-7. Thus, all the spectral data support the skeletal arrangement for 7 figured in Chart. It is interesting to note that 7 is not an expected product derived from a stable 1,4-biradical.
The fact that H-8 and H-9 exhibit the signals at unusually high field than the corresponding protons in any similar compounds can be reasonably interpreted in terms of anisotropic effect of the endo-located benzene ring of the indane part as being observed in a benzotricyclic compound. In fact, molecular models of 7 with the endo-configuration show that the benzene ring is just located over the C₈-C₉ bond.

![Diagram of molecular structure and reactions](image)

Irradiation of 1-NN in the presence of phenyl vinyl ether (8) gave a sole (2 + 2) cycloadduct (9) in 70-80% yields along with the formation of 2:2-adducts. The spectral data for 9: \( \nu_{\text{max}} \) (KBr) 2220 (C=N), 1630 (C=C), and 1240 cm\(^{-1}\) (Ar-O-C); \( \lambda_{\text{max}} \) (acetoniitrile) (c) 300(560), 273(7800), and

![N.m.r. spectra of 2b, 3b, and 9](image)
265 nm (8900); m/e 273 (M⁺, very weak), 153, and 120; δ°CDCl₃ (60 MHz) 2.27 (H-7, ddd), 2.7 (H-7, ddd), 3.2 (H-6, ddd), 5.22 (H-8, dd), 5.72 (H-5, dd), 6.36 (H-4, d), and 6.75-7.5 (aromatic protons, 9H, m); J₄,5 10, J₅,6 6, J₆,7 = J₇,8 = 8, J₆,7 = J₇,7 = 10.5 and J₇,8 8.5 Hz. N.m.r. spectra of 2b, 3b, and 9 were shown in Figure 2.

Figure 3  A stereoscopic view of 9

The spectral data support the skeletal arrangement for 9 figured in Chart. For structural elucidation, it is notable that the n.m.r. spectrum of 9 (Figure 2) is very similar to that of 2b rather than that of 3b except the signals of ethoxyl group and aromatic protons and downfield shifts in the signals of 9. The spectral similarity may suggest the endo-configuration for 9. Moreover, the structure of 9 was decided on the endo-configuration by the X-ray analysis. Figure 3 shows a stereoscopic view of 9 and a view of the packing arrangement along 010 is shown in Figure 4. At any rate, 6 and 8, more conjugated olefins than la-b, undergo the photocycloaddition to 1-NN in a stereoselective manner.

Figure 4  A view of the packing arrangement along 010
In contrast to the photoreactions of benzene solutions, irradiation of methanolic and acetonitrile solutions of 1-NN containing 6 or 8 gave complex mixtures. The fluorescence from cyclohexane solutions of 1-NN was quenched by indene (6) with a diffusion controlled rate. The results obtained may suggest exciplex intermediacy and may support the author's prediction.

4-4 Stereospecific Photocycloaddition of 1-NN with cis- and trans-Phenoxypropenes and Methoxypropenes

4-4-1 Introduction

In the preceding section, the author described the stereoselective (2 + 2) photocycloaddition of 1-NN with phenyl vinyl ether (8) which gave exclusively an endo-adduct, unlike that with alkyl vinyl ethers (1a-b). This endo-selective orientation would imply a stereospecific nature of the photocycloaddition. The author describes in this section the stereospecific photocycloaddition of cis- and trans-1-phenoxypromenes [(10c) and (10t)] and cis- and trans-1-methoxypropenes [(11c) and (11t)] to 1-NN.

4-4-2 Results and Discussion

Irradiation of a benzene solution containing 1-NN and an excess of 10c through Pyrex by a high-pressure mercury arc gave 12c (80%), mp 138.5-139.5 °C and 13c (10%), mp 101-102 °C. Similarly, irradiation of 1-NN and 10t gave 12t (85%), mp 97.5-98.5 °C and 13t (5%) an oil. Products were

\[
\begin{align*}
\text{10t} & \quad + \quad \text{PhO} \quad \text{H} \\
& \quad \xrightarrow{\text{hv}} \\
& \quad \text{12c (80%)} \\
& \quad \text{mp 138.5-139.5 °C} \\
& \quad \text{13c (<10%)} \\
& \quad \text{mp 101-102 °C}
\end{align*}
\]

\[
\begin{align*}
\text{10t} & \quad + \quad \text{PhO} \quad \text{H} \\
& \quad \xrightarrow{\text{hv}} \\
& \quad \text{12t (~85%)} \\
& \quad \text{mp 97.5-98.5 °C} \\
& \quad \text{13t (~5%)}
\end{align*}
\]
isolated by column chromatography on silica gel.

Analytical and spectral data were in accord with the assigned structures, and the assignments were based mainly on n.m.r. spectra (Figure 5 and Table 1); close analyses of chemical shifts of the aliphatic and olefinic protons of the four adducts allowed to determine endo or exo configuration of the phenoxy and methyl groups of each adducts by considering anisotropic effects of dihydronaphthalene ring and the substituents. These structural assignments were also supported by retro-grade thermolyses and photolyses of the adducts. Thermolyses of 12c and 13c to 10c at 300-350 °C took place in 90 ± 5% specificity, whereas 12t and 13t were decomposed into 10t in 70 ± 5% specificity. Among these adducts, 12c was least stable. On the

<table>
<thead>
<tr>
<th>Compd.</th>
<th>H-4</th>
<th>H-5</th>
<th>H-6</th>
<th>H-7</th>
<th>H-8</th>
<th>Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>12t</td>
<td>6.37</td>
<td>5.90</td>
<td>2.75</td>
<td>2.75</td>
<td>4.73</td>
<td>1.21</td>
</tr>
<tr>
<td>13t</td>
<td>6.45</td>
<td>5.75</td>
<td>3.45</td>
<td>3.45</td>
<td>4.55</td>
<td>1.21</td>
</tr>
<tr>
<td>12c</td>
<td>6.48</td>
<td>5.57</td>
<td>3.60</td>
<td>3.06</td>
<td>5.32</td>
<td>0.95</td>
</tr>
<tr>
<td>13c</td>
<td>6.35</td>
<td>5.75</td>
<td>3.05</td>
<td>2.75</td>
<td>4.80</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Table 1  N.m.r. data of photoadducts (δ ppm in CDCl₃)
other hand, irradiation of acetonitrile solutions of the cis- and trans-adducts in the presence of ferrocene resulted in complete stereospecific formation of 10c and 10t respectively.

In a similar manner, photoreaction of 1-NN and 1lc afforded the stereospecific (2 + 2) cycloadducts (14c) and (15c), and irradiation of 1-NN and 1lt also gave the stereospecific cycloadducts (14t) and (15t). These adducts were isolated by column chromatography on silica gel and these structures were assigned by spectral properties.

It is noteworthy that 12c and 12t possessing the endo-located phenoxy group are much more favourably formed than 13c and 13t respectively, though this endo orientation is sterically unfavourable. The endo-selective orientation of the phenoxy group can be interpreted by assuming the intervention of exciplexes possessing fairly rigid configuration between excited 1-NN and the phenoxy ring of the olefins, as previously speculated. The formation of the exo-adducts 13c and 13t apparently arises from the exo approach of olefins which can intervene in competition with the endo one.
even in minor importance, by added steric effects of the methyl group to 
the exciplex formation and the subsequent process. Thus, the ori-
entational selectivity in the photocycloaddition of l-NN with vinyl ethers 
appears to be affected by both electronic and steric factors of the sub-
stituents of vinyl ethers, though the former would be important with 
olefins containing a phenoxy group. In this regard, it is of interest 
to note that the photocycloaddition of l-NN with cis- and trans-1-tri-
methylsiloxybut-1-enes, having no planar \( \pi \)-electron system conjugated with 
double bond as well as \( 1lc \) and \( 1lt \), occurs stereospecifically but leads to 
the complete loss of such orientational selectivity, such that two stereo-
specific cycloadducts are formed in equal amounts with each olefin. \(^{14,15}\) 
The stereospecificity would therefore be maintained independently of the 
nature of the substituents.

4-5 References and Footnotes

   46, 238(1973).
   R. A. Caldwell and L. Smith, ibid., p. 2994; J. Cornelisse, V. Y. Merritt, 
   and R. Srinivasan, ibid., 95, 6197(1973); K. E. Wilzbach and L. Kaplan, 
   ibid., 93, 2073(1971); N. C. Yang, J. Libman, L. Barret, jun., M. H. Hui, 
4. a) C. Pac, T. Sugioka, and H. Sakurai, Chem. Lett., 39(1972); b) T. 
   Sugioka, C. Pac, and H. Sakurai, ibid., 667(1972).
6. For instance, in the case of 9-CA, the slopes of the Stern-Volmer plots 
   were found to be 0.25 (a) and 0.19 mol dm\(^{-3}\) (b) for the benzene solutions.
7. Irradiation was carried out through a glass filter (> 300 nm) with a high 
   pressure mercury arc. Over-irradiation led to the formation of un-
   tractable materials in substantial amounts.
8. The normal chemical shifts of the protons corresponding to the \( C_8 \)- and 
   \( C_9 \)-protons of 7 are in the range of \( \delta \) 5.7-6.32 and 6.2-6.63 respective-
   ly. For example, see ref. 2; "VARIAN NMR spectra Catalog" compiled by 
   N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Varian Associates(1962),


10 The 2:2-adduct melts at 268-269 °C. Although the structure has not been firmly established yet, it appears to be a dimer of 9 as judged from the spectral data.

11 N. Kasai et al., unpublished results.

12 In the absence of ferrocene or 1,3-dienes, irradiation of 12c and 12t gave 10c and 10t in 95 + 1% and 98 + 1% specificity at zero time irradiation, respectively.

13 Similar stereospecific photocycloadditions were also observed in the photoreactions of 2-naphthonitrile (2-NN) and 11c and 11t and 9-CP and 11c and 11t; K. Mizuno, C. Pac, and H. Sakurai, unpublished results.

14 See chapter 5; K. Mizuno, H. Okamoto, C. Pac, and H. Sakurai, unpublished results.

15 Speculated exciplex configuration of 1-NN = 8 and 9-CP = 2,5-dimethyl-2,4-hexadiene (chapter 2).
Chapter 5 The Photo-Michael Reactions. Photoreactions of 1-Naphthonitrile with Silyl Enol Ethers

5-1 Introduction

In previous chapters, it is shown that the photoreactions of aromatic nitriles with alkyl vinyl ethers give the regioselective (2 + 2) cycloadducts in excellent yields. These regioselective photocycloadditions are appreciable to the photo-Michael reactions using silyl enol ethers in the place of alkyl vinyl ethers, since silyl enol ethers as both electronic equivalent of alkyl vinyl ethers and synthetic equivalent of enols are used as the excellent addend in some Michael-type reactions. In this chapter, the author describes the photo-Michael reactions of silyl enol ethers with 1-naphthonitrile (1-NN).

Michael reactions

\[ \text{A} + \text{B} \rightarrow \text{C} \]

photo-Michael reaction

\[ \text{OSiMe}_3 + \text{X} \rightarrow \text{OSiMe}_3 \]

5-2 Results and Discussion

The trimethyl silyl enol ethers (1a-c) were prepared from the corresponding ketone and aldehydes. The typical procedure is described for

\[ \text{CH}_3\text{OR} + \text{Me}_3\text{SiCl} + \text{DBU} + \text{ZnCl}_2 \xrightarrow{0 \, ^\circ \text{C, 4 h}} \text{in n-Octane} \]

\[ \text{CH}_3\text{CH}_2\text{CHO} + \text{Me}_3\text{SiCl} + \text{NET}_3 \xrightarrow{60-80 \, ^\circ \text{C, 4 h}} \text{in DMF} \]

cis- and trans-mixture(1c)
the photoreaction of l-naphthonitrile (1-NN) with the silyl enol ethers. Irradiation of a benzene solution of 1-NN and the trimethyl silyl enol ether of acetone (1b) through Pyrex by a high-pressure mercury arc gave 1:1-cycloadduct (2b) in 90% yield. 6 2b is a mixture of two isomers. One of them was isolated by column chromatography on silica gel and the structure is confirmed by i.r., u.v., mass, and n.m.r. spectra (Table 1). 2b was readily hydrolyzed by a methanolic solution containing 5% acetic acid at

\[
\text{CN} \quad \text{R}^1 \quad \text{R}^2 \quad \text{OSiMe}_3 \\
\text{hv} \quad 280\text{nm} \\
\text{2a-c} \\
\text{3a-c} \\
\text{4b} \\
\text{5b}
\]

50 ± 5 °C to give Michael product (3b) in 94%. 3b is a mixture of two isomers and chromatography afforded each isomer. More conveniently, 3b was obtained in similar net yield even by direct hydrolysis of the reaction mixtures without isolating 2b.

Similarly, irradiation of 1-NN and the silyl enol ethers (1a) and (1c) and subsequent hydrolyses gave again the Michael product (3a) and (3c) in good yield; yields are listed in Chart.

These photoproducts (2a-c) and the Michael products (3a-c) were decomposed to 1-NN in the case of the hydrolysles by strong acids or bases. The hydrogenation of 2b and subsequent hydrolysis by 0.1 N hydrochloric acid afforded 5b in good yield.

Synthetic advantages of this method would be provided by (1) neutral conditions of the photoreaction, (2) efficient hydrolysis of the photoproduct by either acids or bases even under mild conditions and (3) selective alkylation. 2 It is well-known that the Michael reaction is a synthetic method for bond formation between activated carbons and Michael acceptors under basic conditions. 9 However, there has been no report, to the author's knowledge, using aromatic rings as the Michael acceptors. The present results suggest that the aromatic nitriles are good Michael acceptor in some Michael-type reactions.
Table 1

Spectral data of products

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
<th>m/e</th>
<th>ν&lt;sub&gt;max&lt;/sub&gt; (film)</th>
<th>ν&lt;sub&gt;max&lt;/sub&gt; (KBr)</th>
<th>δ(CCl&lt;sub&gt;4&lt;/sub&gt;)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (EtOH)</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (CCl&lt;sub&gt;4&lt;/sub&gt;)</th>
<th>Found: C, H, N</th>
<th>Calc. for C&lt;sub&gt;17&lt;/sub&gt;H&lt;sub&gt;21&lt;/sub&gt;NOSi: C, H, N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>74-75</td>
<td>283</td>
<td>153</td>
<td>2240 (C=N), 1240, 840, 750 cm&lt;sup&gt;-1&lt;/sup&gt; (C-O-Si), 265 nm (ε 5930)</td>
<td>-0.16 (3H, s), 1.72 (3H, s), 2.13 (1H, dd, J 8 and 11), 2.32 (1H, dd, J 9.5), 3.02 (1H, ddd, J 6), 5.81 (1H, dd, J 10) 6.32 (1H, d), 7.4 (4H, m), C, 71.95; H, 7.55, N, 4.95.</td>
<td>265nm (ε 5930)</td>
<td>265 nm (ε 5930)</td>
<td>C, 71.95; H, 7.55; N, 4.95.</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>78-79</td>
<td>197</td>
<td>153</td>
<td>2240 (C=N), 1745 cm&lt;sup&gt;-1&lt;/sup&gt; (C=O)</td>
<td>2.62 (1H, dd, J 8 and 18 Hz), 2.83 (1H, dd, J 6 Hz), 3.2br (1H, m), 3.93 (1H, d, J 8.5 Hz), 5.90 (1H, dd, J 4 and 9.5 Hz), 6.56 (1H, d), 9.76 (1H, s), C, 79.45; H, 5.35; N, 7.1.</td>
<td>260nm (ε 7760)</td>
<td>2240 (C=N), 1745 cm&lt;sup&gt;-1&lt;/sup&gt; (C=O)</td>
<td>C, 79.45; H, 5.35; N, 7.1.</td>
<td></td>
</tr>
<tr>
<td>3a'</td>
<td></td>
<td>211</td>
<td>153</td>
<td>2240 (C=N), 1710 cm&lt;sup&gt;-1&lt;/sup&gt; (C=O)</td>
<td>2.56 (1H, dd, J 6 and 18), 2.88 (1H, dd, J 6), 3.4 (1H, m), 4.1 (1H, d, J 6), 5.91 (1H, dd, J 4 and 9.8), 6.46 (1H, d), 7.3 (4H, m), 9.62 (1H, s)</td>
<td>260nm (ε 7230)</td>
<td>2240 (C=N), 1710 cm&lt;sup&gt;-1&lt;/sup&gt; (C=O)</td>
<td>C, 79.6; H, 6.2; N, 6.65.</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>79-80</td>
<td>213</td>
<td>153</td>
<td>2240 (C=N), 1710 cm&lt;sup&gt;-1&lt;/sup&gt; (C=O)</td>
<td>2.13 (3H, s), 3.2 (1H, m), 4.14 (1H, d, J 5.5), 6.00 (1H, dd, J 4.5 and 10), 6.55 (1H, d), 7.3 (4H, m), C, 79.85; H, 6.05; N, 6.7.</td>
<td>263nm (ε 295)</td>
<td>2240 (C=N), 1710 cm&lt;sup&gt;-1&lt;/sup&gt; (C=O)</td>
<td>C, 79.85; H, 6.05; N, 6.7.</td>
<td></td>
</tr>
</tbody>
</table>

-55-
It should be noted that an important point of this method is regioselectivity of the photoreaction of l-NN and enol ethers and that silyl enol ethers can be used as both the electronic equivalent of alkyl vinyl ethers and the synthetic equivalent of enols.\textsuperscript{10}

5-3 References and Footnotes


\[
\begin{align*}
\text{OSi(CH}_3\text{)}_3 & \quad \text{R} \quad \text{hv} \quad \text{(CH}_3\text{)}_3\text{SiO} \quad \text{R} \quad \text{H}^+ \\
\text{(I) } n=2 & \quad \text{(IIIa) } R=\text{CO}_2\text{CH}_3 & \quad \text{(IV) } n=2 & \quad \text{(VI) } a; \text{79} \\
\text{(II) } n=1 & \quad \text{(IIIb) } R=\text{CH}_2 & \quad \text{(V) } n=1 & \quad \text{b; } \text{86} \\
& \quad \text{(IIIc) } R=\text{COCH}_3 & & \quad \text{c; } \text{51}\text{**} \\
& & \quad \text{(VII) } a; \text{72} & \quad \text{n=1} & \text{b; } \text{40}\text{**} \\
& & & \quad \text{c; } \text{30}\text{**} \\
\end{align*}
\]

* Based on unrecovered (I) or (II).
** The formation of polymeric materials is remarkable.


6 A benzene solution(150 ml) containing l-NN(2 g) and a silyl enol ether (15-20 ml) was irradiated for 20-30 h under a nitrogen atmosphere through Pyrex by a high-pressure mercury arc.
Similar photocycloadducts were obtained in the photoreaction of 9-cyano-phenanthrene with $\text{la}$ and spectral properties of cyclobutane compounds were obtained as follows:

<table>
<thead>
<tr>
<th>IR $\nu$</th>
<th>2250(-CN), 1260,1155,840 cm$^{-1}$</th>
<th>2210(-CN),1250,1150,840 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass</td>
<td>254(-Me),153,116,101</td>
<td>304(-Me),203,116,101</td>
</tr>
</tbody>
</table>

![Spectral Data]

Irradiation of 1-NN with cis-1c and trans-1c afforded the stereospecific photocycloadducts respectively; cf. K. Mizuno, C. Pac, and H. Sakurai, J. C. S. Chem. Comm., 648(1974) and see chapter 4. N.m.r. spectra of 2c were shown in next page.

Similarly, irradiation of 9-cyanophenanthrene with cis-1c and trans-1t afforded stereospecific photocycloadducts respectively.

The photoaddition of enolized acetylacetone to an alkene was reported; P. de Mayo and H. Takeshita, Canad. J. Chem., 41, 440 (1963).

N.m.r. spectra of 2c.
Chapter 6  The Photo-Birch Reduction and the Photo-cyanation of Aromatic Hydrocarbons in the Presence of 1,4-Dicyanobenzene

6-1 The Photo-Birch Reduction

6-1-1 Introduction

The Birch reduction is a well-known synthetic method for the reduction of aromatic rings via anion radicals and dianion of aromatic compounds. Such anionic species can also be generated by photoreactions of some donor-acceptor pairs in polar solvents, thus leading to a Birch-type of photoreduction.

\[ A + D \xrightarrow{hv} A^- + D^+ \] in polar solvents

A; Electron acceptor, D; Electron donor

Similar photoreductions of aromatic compounds have been accomplished in low yields by other reductants such as sodium borohydride and sodium sulphite. In the case of sodium borohydride, the direct attack of hydride or electron transfer from the borohydride to excited aromatic rings has been suggested as the mechanism. In this section, the author describes an efficient photo-Birch reduction of phenanthrene, anthracene, and naphthalene by sodium borohydride in the presence of 1,4-dicyanobenzene, possibly via the cation radicals of the aromatic hydrocarbons, which is different from the previous borohydride reduction.

6-1-2 Results and Discussion

Irradiation of a 10% aqueous acetonitrile solution (200 ml) containing phenanthrene (1) (2.77 g), sodium borohydride (2.7 g) and 1,4-dicyanobenzene (DCB) (1.92 g) through Pyrex by a high-pressure mercury arc for 8 h gave 9,10-dihydrophenanthrene (4) (1.7 g, 71%), 1 (0.3 g), and DCB (0.3 g).

\[ \text{DCB} + \text{CN} \xrightarrow{hv} \text{CH}_3\text{CN} - \text{CN}_2 \xrightarrow{\text{H}_2\text{O}} \]

\[ X = \text{H or } ^2\text{H} \]

70%
In a similar way, the photoreaction of anthracene (2) and naphthalene (3a) gave 9,10-dihydroanthracene (5) mp. 104-106 °C (70%) and 1,4-dihydronaphthalene (6) (30%) respectively. In the case of 2-methyl, 2,3-dimethyl-, and 2,6-dimethyl-naphthalenes (3b-d), the photoreductions gave a mixture of dihydronaphthalenes.

\[
\begin{align*}
\text{CN} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{CN} & \quad \text{CN} \\
\text{H} & \quad \text{X} \\
\text{CH}_3\text{CN-} & \quad \text{H}_2\text{O/NaBH}_4 & \quad \text{hv} & \quad \text{H}_2 & \quad \text{CN} \\
\end{align*}
\]

\[
\begin{align*}
\text{CN} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{CN} & \quad \text{CN} \\
\text{H} & \quad \text{X} \\
\text{CH}_3\text{CN-} & \quad \text{H}_2\text{O/H} & \quad \text{hv} & \quad \text{H}_2 & \quad \text{CN} \\
\end{align*}
\]

The photoreduction requires the co-existence of sodium borohydride, water, and DCB, the absence of each leading to only low yield or lack of reduction. In place of DCB, 1,2- and 1,3-dicyanobenzenes can also be effectively used this photoreduction.

When the photoreduction of 1 or 2 was carried out in the presence of deuterium oxide instead of water, a monodeuteriated compound was produced predominantly, ([\(^2\text{H}_2\]) 0%, [\(^2\text{H}_1\]) 70-80% and [\(^2\text{H}_0\]) 20-30%) demonstrating the involvement of one proton from the water in the reduction pathway.

\[
\begin{align*}
\text{A} + \text{D} & \quad \text{hv} & \quad \text{A}^- + \text{D}^+ & \quad \text{H}^- & \quad \text{A}^- + \cdot \text{DH} & \quad \text{A} + \cdot \text{DH} & \quad \text{X}_2\text{O} & \quad \text{A} + \text{DHX} \\
\end{align*}
\]

Since the photoreaction in the absence of DCB is very slow, direct attack of hydride on the excited hydrocarbons is very unlikely. Since formation of 3a-DCB exciplex is known \(^9\) and moreover some exciplexes dissociate into ion radicals in polar media, \(^10\) initiation by electron-transfer from the excited hydrocarbons (D) to DCB would give a possible mechanism pathway; \(^11\) nucleophilic attack of hydride on the cation radicals.
(D⁺) generates the radicals (·DH) which are either reduced by electron re-
versal from DCB anion radicals (DCB⁻) and subsequent protonation, or under-
go bimolecular disproportionation to give the reduced compound DH₂ to a
minor extent (equation).¹²

6-2 Photochemical Cyanation
6-2-1 Introduction

The photochemical nucleophilic substitution of aromatic compounds, es-
pecially nitro-compounds, has been extensively investigated¹³ and can be
used for the preparations of aromatic compounds. However, photoaddition
of nucleophiles to aromatic hydrocarbons is not so well known.¹⁴ This
section shows the efficient photo-cyanation of phenanthrene (1) and naphtha-
lene (3a) with cyanide anion in the presence of 1,4-dicyanobenzene (DCB).

6-2-2 Results and Discussion

Irradiation of an NN-dimethylformamide (DMF)-water (3:1) solution con-
taining 1 (600 mg) and NaCN (3 g) in the presence of DCB (120 mg) through
Pyrex by a high-pressure mercury arc gave 9-cyanophenanthrene (9-CP), mp
107-108 °C (40 mg, 6%), 9-cyano-9,10-dihydrophenanthrene (7), mp 82-83 °C

(315 mg, 49%), and a mixture of the dimer of 9-CP and dicyanated compounds
(150 mg).¹⁵ The presence of both water and DCB is essential for the
photo-cyanation as in the photo-Birch reduction of aromatic hydrocarbons
with sodium borohydride in the presence of DCB; in the absence of DCB, the

ArH + + ArCN + ArH₂(CN)

ArH = Naphthalene, Phenanthrene, Anthracene
photo-cyanation occurs only with < 1/15th efficiency in comparison to that in the presence of DCB, and 7 is not formed in the absence of water though a small amount of 9-CP was produced. In the absence of NaCN, moreover, irradiation gave no products, and 1 and DCB were completely recovered.

Similarly, irradiation of a DMF-water (3:1) solution of naphthalene and NaCN in the presence of DCB afforded mono-cyanated compounds (30%) and dicyanotetrahydronaphthalene (15%). Aromatisation of the mono-cyanated compounds with Pd-charcoal gave 1-naphthonitrile (1-NN) in excellent yield, while 2-naphthonitrile was not detected. Photo-cyanation of anthracene (2) also occurs to give 9-cyanoanthracene (9-CA), mp 179 °C. 

\[
\begin{align*}
\text{ArH}^+ + \text{CN}^- & \rightarrow \cdot \text{ArH-CN} \\
\text{H-ArH-CN} & \rightarrow \text{ArH-OR}
\end{align*}
\]

ArH: Aromatic Hydrocarbons, A; DCB

The essential role of DCB in the photo-cyanation suggests that nucleophilic attack of cyanide anion on the excited hydrocarbons is unfavourable; the photocyanation could reasonably be interpreted in terms of nucleophilic attack of cyanide anion on cation radicals of the aromatic hydrocarbons which are generated by electron transfer from excited hydrocarbons to DCB.11

6-3 References and Footnotes

3 J. A. Barltrop, Pure Appl. Chem., 33, 179.

Percentage yields are based on unrecovered hydrocarbons. As the conversion increased, DCB was consumed and benzonitrile was formed to some extent.

H. Beens and A. Weller, Acta Phys. Polon., 34, 593(1968); the author also observed the exciplex emission of 1 and DCB in benzene solutions.


U.v. spectral measurements showed no indication of the formation of charge-transfer complexes in the ground state.

A referee of J. C. S. Chem. Comm. pointed out alternative mechanistic pathways, i.e. electron transfer from borohydride to the exciplex or direct attack of borohydride to the exciplex, which cannot be ruled out.


Percentage yields are based on unrecovered hydrocarbons. DCB was also consumed as the conversion increased.

Composed of 1-cyanodihydronaphthalene isomers, 1-naphthonitrile and other compounds.
Conclusion

The results obtained from the present investigation may summarised as follows;

(1) In the photoreactions of 9-cyanoanthracene (9-CA) with furan, 2-methyl-, 3-methyl-, and 2,5-dimethyl-furan, the (4 + 4) cycloadducts, 9-cyano-9,10,11,13-tetrahydro-9,10[2',5']-furanoanthracene and its methyl substituted derivatives, have been obtained in good yields. Irradiation of 9-CA in the presence of thiophene or 1-methylpyrrole gives no cycloadducts. An exciplex mechanism was suggested for these reactions on the basis of fluorescence measurements and kinetics.

(2) In the photoreactions of methyl vinyl ether, ethyl vinyl ether, 2-methyl-2-butene, 2,3-dimethyl-2-butene or 2,5-dimethyl-2,4-hexadiene to 9-cyanophenanthrene (9-CP), only one (2 + 2) cycloadduct have been obtained in good yields. The photoreactions with the former three olefins were established to occur from the triplet nitrile by the Michler's ketone-sensitisation and isoprene quenching experiments. In the latter two cases, however, singlet exciplexes were suggested to be the intermediates from the observation that an exciplex emission appeared in the fluorescence spectra of 9-CP in the presence of 2,5-dimethyl-2,4-hexadiene and the photoreactions of methanolic solutions gave solvent-incorporated products, apparently arising from ion radicals.

(3) Irradiation of 2-naphthonitrile (2-NN) and an alkyl vinyl ether at 313 nm gave only a single (2 + 2) cycloadduct, endo-2-alkoxy-1,2,2a,8b-tetrahydrocyclobuta[a]naphthalene-2a-carbonitrile (2) in 80-90% yield. On the other hand, irradiation through Pyrex (> 280 nm) ultimately afforded a cyclobutene, 4-alkoxy-2a,3,4,8b-tetrahydrocyclobuta[a]naphthalene-6-carbonitrile (3) (70%), as a main product, accompanied by various 1:1 adducts (4)-(7). Pyrolyses of the products (3) and (4) afforded 10-alkoxy-5,6-dihydrobenzocyclo-octene-2-carbonitrile (5) in good yields; irradiation of 5 gave 8b-alkoxy-2a,3,4,8b-tetrahydrocyclobuta[a]naphthalene-7-carbonitrile (6) in quantitative yield. From a kinetic study, the formation of the adduct (2) is established as occurring from the lowest excited singlet state of 2-NN.

(4) In the photocycloaddition of 1-naphthonitrile (1-NN) with indene, phenyl vinyl ether, and cis-, and trans-1-phenoxypropenes, endo-selective (2 + 2) cycloadducts have been predominantly obtained in good yields. Moreover, stereospecific photocycloadditions have been observed in the photoreactions of 1-NN and the latter two olefins or cis-, and trans-1-
methoxypropenes. It was suggested that the configuration of exciplexes might play important roles in these endo-selectivity and stereospecificity.

(5) In chapter 5, the photo-Michael reactions via cyclobutane compounds obtained from the photoreactions of 1-naphthonitrile and silyl enol ethers have been described with the view to developing a new synthetic reaction.

(6) In chapter 6, the efficient photoreduction and photocyanation of aromatic hydrocarbons such as phenanthrene, naphthalene, and anthracene by sodium borohydride and sodium cyanide in the presence of 1,4-dicyanobenzene in polar solvents have been described.