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PHOTOADDITION OF SOME 1,3-DIKETONATOBORON DIFLUORIDES TO AROMATIC COMPOUNDS

by

Xinxin Ouyang
B.Sc., Wuhan University, China, 1982
M.Sc., Wuhan University, China, 1985

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
Master of Science

in the Department
of
Chemistry

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October 1991

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PHOTOADDITION OF SOME 1,2-DIETONATO(TETRACHLORO)DIFLUORIDE

TO AROMATIC COMPOUNDS

Author: XINXIN OUYANG

(name)

Dec. 11, 1991
(date)
Abstract

The photochemistry of boron difluoride complexes of 2-acetylcyclohexanone (ACHBF₂), 2-acetylcyclopentanone (ACPBF₂), and acetylacetone (AABF₂) was investigated. Irradiation of these complexes in the presence of benzene gives 1:1 adducts as the primary photoproducts; in the case of ACHBF₂, toluene, chlorobenzene, benzonitrile, and methyl benzoate were also used as substrates. The 1,5-diketone photoadducts were assumed to be formed by a [2+2] photoaddition followed by cyclobutane ring opening and hydrolysis to give 1,2-addition products. These 1,5-diketone products undergo a variety of secondary thermal reactions, probably acid-catalyzed, to give enol ethers, enol acetates, acetophenones, and ketonylacetophenones. The efficiency of these secondary reactions determines the final products. Photoaddition to a monosubstituted benzene preferentially occurs at the 3,4-position. Photolysis of ACHBF₂ and benzene, under an oxygen atmosphere, gives an oxygenation product, a 10-membered lactone fused with a benzene ring derived from the enol ether, and an enol acetate from the oxidative-dehydrogenation of the primary photoadduct. The 10-membered lactone was shown by an X-ray crystallographic analysis to have the benzene ring and carbonyl group orthogonally oriented. The photoaddition of ACHBF₂ to benzene is neither sensitized by benzophenone nor quenched by 1,3-pentadiene or 1,3-cyclohexadiene, but it can be inhibited by using 1,2-dibromoethane through the heavy atom effect. All these suggest that singlet excited state of ACHBF₂ initiates the photoaddition. While the slopes \( k_{Q} \tau = 0.032 \) and 0.067 from the plots of \( 1/\Phi_{p} \) versus \([\text{benzene}]^{-1}\) are small for the photoaddition of ACHBF₂ to benzene, the
limiting quantum yields for the formation of enol ether are as high as 0.12 and 0.19 in acetonitrile and dioxane, respectively.

The photocycloaddition of AABF$_2$ to a polycyclic arene system was studied using a number of naphthalenes (naphthalene, 1-chloronaphthalene and methyl 2-naphthalenecarboxylate) and phenanthrenes (phenanthrene and 9-cyanophenanthrene). Primary 1,5-diketone adducts were isolated as stable products, and they are formed by a similar mechanism. It was found that the photoaddition is solvent-dependent; the reaction proceeds in ether but not in acetonitrile. No reaction was observed in either solvent for 1-methoxy- and 2-methoxynaphthalenes. In the case of phenanthrene to AABF$_2$, two stereoisomers were obtained with cis-addition product as the major one. It was suggested that the reaction involves an excited state phenanthrene.
Dedication

To my parents

To Jianxin and Yueyue
Acknowledgements

The author wishes to express her gratitude to:

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Phosphorescence spectrum of ACHBF₂ (0.03 M) in ether at 77 K.
CHAPTER 1 INTRODUCTION

1.1 1,3-Diketonatoboron Difluorides

1.1.1 1,3-Diketonatoboron Difluorides

Chelate compounds of 1,3-diketones with alkaline and transition metals are well investigated.\(^1,^2\) In general, the polarization of electron density in the chelate ring is assigned with the positive end at the metal and the negative end at the ligand\(^2,^3\) (Scheme 1-1).

Scheme 1-1

However, another group of chelate compounds, the complexes of 1,3-diketones with pseudo-metal elements, e.g., P\(^4,^5\), Si\(^6,^7\) and B\(^8,^9\), may bear an electron density distribution in the chelate ring opposite to that in the metal chelates. Of particular interest are 1,3-diketonatoboron difluorides because of their accessibility and thermolytic and hydrolytic stability,\(^10\) and unique properties as potential electron acceptor sensitizers.

The first report of the synthesis of 1,3-diketonatoboron difluorides was published in 1924.\(^11\) Since then, more than 20 analogs have been synthesized by reaction of 1,3-diketones with BF\(_3\).\(^12,^13\) The chelate structures of these difluorides (Scheme 1-2) are clearly
indicated by the spectroscopic data. Both $^1$H and $^{13}$C NMR spectra of acetylacetonatoboron difluoride (AABF$_2$) show an identical chemical shift for the two methyl groups in agreement with magnetic equivalency of the two methyl groups in the symmetric chelate structure. The UV/VIS absorption maximum showed similar absorbance energy but a great enhancement in the extinction coefficient when compared with those of the parent enols. IR spectra showed pronounced shifts to lower frequency in the absorption positions of carbon-carbon and carbon-oxygen double-bond frequencies. None of them gave any indication of free carbonyl groups. An X-ray crystallography study of benzoylacetonatoboron difluoride (BABF$_2$) demonstrated that the two B-O bonds (1.488 Å) have an identical bond length, and the same bond length (1.304 Å) is found for the two C-O bonds.

Scheme 1-2

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>$R^3$</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$</td>
<td>H</td>
<td>CH$_3$</td>
</tr>
<tr>
<td>2</td>
<td>$R_1R_2 = CH_2CH_2CH_2$</td>
<td>CH$_3$</td>
<td>ACHBF$_2$</td>
</tr>
<tr>
<td>3</td>
<td>C$_6$H$_5$</td>
<td>H</td>
<td>C$_6$H$_5$</td>
</tr>
<tr>
<td>4</td>
<td>$R_1R_2 = CH_2CH_2$</td>
<td>CH$_3$</td>
<td>ACPBF$_2$</td>
</tr>
</tbody>
</table>
Table 1-1  Some Properties of Selected 1,3-Diketonatoboron Difluorides.

<table>
<thead>
<tr>
<th>Compd.</th>
<th>m.p. (°C)</th>
<th>$-E_{1/2}^{\text{red}}$ (V)</th>
<th>IP (eV)</th>
<th>Dipole moment (D)</th>
<th>Δδ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AABF₂</td>
<td>43</td>
<td>2.08</td>
<td>9.05</td>
<td>7.6</td>
<td>0.65</td>
</tr>
<tr>
<td>BABF₂</td>
<td>157</td>
<td>1.71</td>
<td>8.81</td>
<td>-</td>
<td>0.42</td>
</tr>
<tr>
<td>DBMBF₂</td>
<td>197</td>
<td>1.60</td>
<td>-</td>
<td>6.7</td>
<td>0.42</td>
</tr>
</tbody>
</table>

a. Values taken from ref. 13 with reference to $10^{-3}$ M Ag⁺/Ag; b. Ref. 17; c. Difference of methine proton chemical shift (δ, ppm) between BF₂ compounds and the corresponding parent enols. See ref. 15 and 18.

The occurrence of the charge separation shown in Scheme 1-2 is based on the fact that these chelate compounds have large dipole moments (see Table 1-1) and that in $^1$H NMR studies the methine proton signals are shifted to lower field with respect to the corresponding parent enol forms of 1,3-diketones.¹⁵,¹⁸ These BF₂ complexes have been patented for use as electron acceptors in the fabrication of photoconducting materials.¹⁹

1.1.2 Photochemistry

From the photophysical and photochemical point of view, 1,3-diketonatoboron complexes have not received much attention.²⁰-²² One reported example is the photoinduced intramolecular alkyl migration reaction of dialkylboryl acetylacetone complexes²³,²⁴ to give compound 5 (Scheme 1-3), which upon acidic or oxidative hydrolysis gave substituted enone 6 and aldol 7, respectively.
Recently, the photocycloadditions of 1,3-diketonatoboron difluorides to olefins have been investigated in our group.\textsuperscript{25-27} Photoaddition of AABF\textsubscript{2} to cyclohexene gives product 8 (Scheme 1-4), which is identical to the product of the well known de Mayo reaction.\textsuperscript{28}

From the use of dibenzoylmethanatoboron difluoride (DBMBF\textsubscript{2}, 3) as a model compound, it has been demonstrated that the singlet excited state of DBMBF\textsubscript{2} undergoes photoaddition of the diketone moiety to simple olefins, and also sensitizes various electron rich olefins to undergo radical cation reactions. It has been suggested that the interaction of singlet excited DBMBF\textsubscript{2} with donor olefins involves some degree of electron transfer since there is a correlation between \( \log k_q \) (where \( k_q \) is the quenching rate constant of DBMBF\textsubscript{2} fluorescence by olefin) and the
ionization potentials of olefins. The photocycloaddition of DBMBF$_2$ to some olefins was shown to be regiospecific and highly stereoselective (Scheme 1-5). The mechanism was suggested to be unusual involving the excimer of DBMBF$_2$.

Scheme 1-5

\[
\begin{array}{c}
\text{R} = + \text{DBMBF}_2 \xrightarrow{\text{hv}, \text{CH}_3\text{CN}} \text{R} = \text{Ph} \text{Ph}
\end{array}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$(CH$_2$)$_3$</td>
<td>78%</td>
</tr>
<tr>
<td>CH$_2$=CH(CH$_2$)$_2$</td>
<td>92%</td>
</tr>
<tr>
<td>(CH$_3$)$_3$C</td>
<td>69%</td>
</tr>
</tbody>
</table>

1.2 Photocycloaddition of Aromatic Compounds

1.2.1 Benzene and Its Derivatives

Following the discovery in 1959 that maleic anhydride forms a remarkably stable 2:1 photoadduct with benzene, numerous other examples of photocycloaddition of ethylenic compounds to benzene rings have been reported. Benzene can add to alkenes to give three different products, the 1,2-, 1,3- and 1,4-adducts (route a, b, and c, respectively, in Scheme 1-6). The 1,2- and 1,3-addition modes are the most common, and the latter is currently receiving considerable attention.
The factors which influence the relative tendencies for 1,2- and 1,3-cycloaddition have been investigated by an orbital symmetry analysis. This studies concluded that 1,3-addition is symmetry allowed as a fully or partially concerted process from the excited singlet state ($S_1$) of benzene and the ground state ($S_0$) of the alkene. The same analysis suggested that 1,2-cycloaddition tends to be favored by charge transfer either to or from the aromatic ring, or by reaction of $S_0$ benzene to $S_1$ alkene. Benzene, toluene, and anisole react with acrylonitrile and $\alpha$-methylacrylonitrile to give the cyclobutanes, 9 and 10, as the only cycloadducts (Scheme 1-7). The photoaddition of benzene to simple olefins is usually from $S_1$ of benzene. Only acetylene appears to add to benzene via $S_1$ of acetylene, but the chemical and quantum yields are very low in comparison with those from the corresponding additions of alkene where the quantum yields can approach unity.
The formation of an exciplex intermediate between $S_1$ benzene and a ground state olefin has been proposed. Numerous investigations have provided results supporting this mechanism. Fluorescent exciplexes are formed from $S_1$ benzene (or toluene) and 1,3-dioxoles. The latter also add to arenes forming 1,2- and 1,3-addition products as shown in Scheme 1-8. Although both adducts are formed from $S_1$ benzene, it was shown that only the 1,3-adduct was formed via a quenchable exciplex, and the 1,2-addition proceeded directly from $S_1$ benzene.
Scheme 1-9 Correlation of reaction modes with free enthalpies of electron transfer in photoreactions of benzene with olefins
Scheme 1-9 shows a correlation between the mode selectivity (substitution, 1,2- and 1,3-cycloaddition) and the ΔG values for the electron transfer, as exemplified by the photoreaction of benzene and various alkenes.36

1.2.2 Naphthalene and Phenanthrene Derivatives

The current active interests in photocycloadditions of naphthalenes to olefins are focused on the mechanistic aspects.45-47 The actual distribution of products obtained varies and is dependent on the wavelength of irradiation, extent of conversion, solvent polarity, and structures of the reactants. For example, the addition of naphthalene (11) to acrylonitrile (Scheme 1-10) gives significant amounts of substituted naphthalenes (ranging from 1% in t-butyl alcohol to 95% in formic acid) in addition to the formation of cyclobutane adducts.48 The photoaddition of 2-cyanonaphthalene to methyl vinyl ether gives a complex mixture of products. Irradiation at 313 nm affords mainly cyclobutane adduct, but with a Pyrex-filtered mercury arc light source additional products are formed.49,50

Scheme 1-10
The photoaddition of naphthalenes to olefins conjugated to a carbonyl group is not common.\textsuperscript{51,52} One example is the intramolecular [2+2] photocycloaddition of 5-(arylmethyl)-3-phenylcyclopent-2-enones\textsuperscript{52} (Scheme 1-11), where the Ar groups are 1-naphthyl, 2-naphthyl and 9-phenanthryl. No photoadduct could be detected in the case of Ar = phenyl.

\textbf{Scheme 1-11}

\[
\text{Ph} \quad \text{Ar} \quad \text{hv} \quad \text{C}_6\text{H}_6 \\
\begin{array}{c}
\text{Ph} \\
\text{Ar}
\end{array} \\
\text{Ar} = 2\text{-naphthyl}
\]

The experiments carried out in our laboratory have shown that irradiation of a monosubstituted naphthalene derivative and enolized acetylacetone (AAH) gives 1,5-diketone product regiospecifically (Scheme 1-12) with a better yield in polar solvents, such as acetonitrile and methanol.\textsuperscript{53,54} The reaction involves the singlet excited state (S\textsubscript{1}) of naphthalene, but no exciplex fluorescence was observed.
It was found\textsuperscript{54,55} that trace amount of acids, such as $\text{H}_2\text{SO}_4$ or $\text{BF}_3\cdot\text{Et}_2\text{O}$ catalyzed the photoaddition of 2-NpCO$_2$CH$_3$ (12) to AAH and affected the regioselectivity of the reaction to give 13 as the major product (Scheme 1-13). The mechanism for this acid-catalyzed photoaddition was proposed to involve an intermediate derived from an emissive exciplex ($\lambda_{\text{max}} = 470 \text{ nm}$) of 2-NpCO$_2$CH$_3$ with sulfuric acid.\textsuperscript{55}
[2+2] photocycloaddition of phenanthrene to olefin derivatives always occurs at the 9,10-double bond of phenanthrene. Because of the nature of the substituents attached to phenanthrene and the olefinic bond, both singlet and triplet mechanisms have been proposed for the cycloaddition.\textsuperscript{56–58}

The photocycloaddition of 9-cyanophenanthrene (9-PN-CN, 15) to substituted \(\beta\)-methylstyrenes (Scheme 1-14) is noteworthy in that an emitting exciplex was shown to be the precursor of the cycloaddition product.\textsuperscript{56,59} The exciplex fluorescence (\(\lambda_{\text{max}} = 435\) nm) was quenched by dimethylacetylenedicarboxylate (DAD) with \(k_{q} = 64\) M\(^{-1}\). The formation of product 16 was similarly quenched by DAD with \(k_{q} = 62\) M\(^{-1}\) indicating that the exciplex proceeds the cycloaddition.

Scheme 1-13

\[
\begin{align*}
\text{12} & \quad \text{AAH} & \quad \text{13} & \quad \text{14} \\
\text{CN} & \quad \text{CO}_2\text{CH}_3 & \quad \text{H} & \quad \text{CO}_2\text{CH}_3 \\
\underbrace{\text{CH}_3\text{CN} \quad \text{CH}_3\text{CN}}_{\text{hv}} & \quad \text{CH}_3\text{CN} & \quad \text{CH}_3\text{CN} \\
\end{align*}
\]

Scheme 1-14

\[
\begin{align*}
\text{CN} & \quad \text{MeO} & \quad \text{H} & \quad \text{CH}_3 \\
\text{CN} & \quad \text{MeO} & \quad \text{H} & \quad \text{CH}_3 \\
\underbrace{\text{CN} \quad \text{MeO}}_{\text{hv}} & \quad \text{CN} & \quad \text{MeO} \\
\end{align*}
\]
1.3 Research Proposal

DBMBF$_2$ and AABF$_2$ have been studied in our lab as a new type of electron acceptors. Dibenzoylmethanatoboron difluoride (DBMBF$_2$, 3) was found to add to various types of olefins, but not to benzene$^{60}$ and other aromatic compounds. We decide to examine photophysical and photochemical behavior of some aliphatic 1,3-diketonatoboron difluorides (ACHBF$_2$, ACPBF$_2$, AABF$_2$). This decision was based on the following considerations:

(1) Chelation with a BF$_2$ group may modify 1,3-diketone reactivities with regard to their electron acceptability.

(2) The rigid structure of BF$_2$ complexes may give emission spectra, which can not be observed for the parent 1,3-diketones.

(3) The photochemistry of these types of BF$_2$ complexes is practically unknown.

(4) The BF$_2$ complexes possess extinction coefficients as high as 16,000, and therefore would absorb light very efficiently.

(5) The BF$_2$ complexes of interest are easily synthesized and purified.

The aims of this research project can be outlined as follows:

(1) To examine possible fluorescence and phosphorescence of the 1,3-diketonatoboron difluorides.

(2) To explore the photoreactivities of the BF$_2$ complexes towards aromatic systems, such as benzene, naphthalene and phenanthrene, and to compare these with those of the corresponding 1,3-diketones.

(3) To investigate the synthetic applications and mechanistic features of the reactions.
CHAPTER 2 RESULTS

2.1 Spectroscopic Studies of 1,3-Diketonatoboron Difluorides

2.1.1 Absorption Spectra

The UV-VIS spectra of ACHBF$_2$ (2) in various solvents were recorded, and the data are shown in Table 2-1. Figure 2-1 shows the absorption spectrum of ACHBF$_2$ in acetonitrile (a) and benzene (b). The absorption spectra of ACPBF$_2$ (4) in acetonitrile and AABF$_2$ (1) in ether are shown in Figure 2-1 (c) and (d).

The lowest singlet state energy ($E_s$) is estimated from the on-set of the absorption spectra using the wavelength ($\lambda$ in nm) at 1/3 absorption maximum$^6$ and found to be 89 kcal/mol for ACHBF$_2$ (at 322 nm), 88 kcal/mol for ACPBF$_2$ (at 323 nm) and 95 kcal/mol for AABF$_2$ (at 301 nm).

Attempts to detect a ground state complex between ACHBF$_2$ (0.030 M) and benzene (2.0 M) by absorption spectroscopy failed.

2.1.2 Emission Spectra of ACHBF$_2$

The phosphorescence spectra of the 1,3-diketonatoboron difluorides were measured in ether at 77 K. ACHBF$_2$ emitted phosphorescence (Figure 4-3) with a $\lambda_{\text{max}}$ at 426 nm while ACPBF$_2$ had $\lambda_{\text{max}}$ at 428 nm. The lowest excited triplet state energies ($E_T$) are estimated from the on-set of the
emission to be 67 kcal/mol and 66.5 kcal/mol, respectively. No phosphorescence was detected for AABF$_2$ under the same condition.

Both ACHBF$_2$ and ACPBF$_2$ emitted weak fluorescence near 345 nm. The fluorescence spectrum of ACHBF$_2$ in acetonitrile is shown in Figure 2-2. From the on-set of the emission spectrum, $E_s$ is estimated to be 90 kcal/mol, which is in agreement with the value obtained from the absorption spectrum.

Table 2-1 Absorption Spectroscopic Data for Some Boron Difluorides

<table>
<thead>
<tr>
<th>Compound $^a$</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$\log \varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACHBF$_2$</td>
<td>hexanes</td>
<td>304</td>
<td>13000</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>ether</td>
<td>304</td>
<td>13460</td>
<td>4.13</td>
</tr>
<tr>
<td></td>
<td>chloroform</td>
<td>305</td>
<td>13200</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>304</td>
<td>12860</td>
<td>4.11</td>
</tr>
<tr>
<td></td>
<td>benzene</td>
<td>306.5</td>
<td>12840</td>
<td>4.11</td>
</tr>
<tr>
<td>ACPBF$_2$</td>
<td>acetonitrile</td>
<td>305</td>
<td>13860</td>
<td>4.14</td>
</tr>
<tr>
<td>AABF$_2$</td>
<td>ether</td>
<td>286.5</td>
<td>16800</td>
<td>4.23</td>
</tr>
<tr>
<td>ACHH</td>
<td>acetonitrile</td>
<td>283.5</td>
<td>7980</td>
<td>3.90</td>
</tr>
<tr>
<td>ACPH</td>
<td>acetonitrile</td>
<td>283</td>
<td>4000</td>
<td>3.60</td>
</tr>
<tr>
<td>AAH</td>
<td>acetonitrile</td>
<td>271</td>
<td>6200</td>
<td>3.79</td>
</tr>
</tbody>
</table>

$^a$ The concentration of each compound is $1.0 \times 10^{-4}$ M except for ACHBF$_2$ in benzene ($0.95 \times 10^{-4}$ M). Cell length is 1.0 cm.
Figure 2-1 The absorption spectra of boron difluorides.

(a) ACHBF₂ in CH₃CN; (b) ACHBF₂ in benzene; (c) ACPBF₂ in CH₃CN; (d) AABF₂ in ether.
Figure 2-2  Fluorescence and excitation spectra of ACHBF$_2$ in acetonitrile (2.0 x 10^{-4} M). $S_{ex} = 6$ nm, $S_{em} = 3$ nm, $\lambda_{ex} = 280$ nm.
2.2 The [2+2] Photocycloadditions of 1,3-Diketonatoboron Difluorides to Aromatic Compounds

2.2.1 ACHBF₂ to Benzene and Its Derivatives

ACHBF₂ to Benzene

Photolysis of ACHBF₂ (2) in benzene under a nitrogen atmosphere with a 200 W Hanovia medium pressure lamp for 2.5 hours gave an enol ether product 17 (isolated yield 32%) and trace amount of acetophenone (18) as shown in Scheme 2-1.

Scheme 2-1

\[
\begin{align*}
\text{ACHBF}_2 & \quad \text{hv} \quad \text{Pyrex} \\
2 & \quad \text{chem} \\
& \quad 17 \\
& \quad 18
\end{align*}
\]

The structure of 17 was identified as 6-methyl-2,3,4,6-tetrahydro-1H-dibenzo[b,d]pyran based on its spectroscopic data (Table 4-1 to Table 4-4). The GC-MS (both EI and CI) showed its molecular weight to be 200 [EI, 200(M⁺, 21); CI, 201(M⁺+1, 100)], indicating that 17 is not a primary photoadduct (MW = 218) but a secondary product formed by the elimination of one molecule of water. Meanwhile, the lack of chemical shifts of olefinic proton in ¹H NMR spectrum and carbonyl carbon in ¹³C NMR spectrum imply that 17 is not derived from an aldol condensation
reaction of the primary product. The presence of a vinyl ether (C=O) group is supported by the occurrence of $^{13}$C NMR signals at chemical shifts of 150.57 ppm and 107.03 ppm in its $^{13}$C NMR spectrum (Table 4-4) and also by the strong C=O stretching band at 1658 cm$^{-1}$ in its IR spectrum (Table 4-2). The $^1$H NMR spectrum (Figure 2-3) gives a doublet at 1.61 ppm and a quartet at 5.08 ppm with a coupling constant of 6.4 Hz indicating the presence of a -CHCH$_3$ fragment. $^{13}$C NMR SEFT experiments revealed the presence of four CH$_2$ groups in compound 17.

![Figure 2-3](image)

Figure 2-3 $^1$H NMR spectrum of 17 in CDCl$_3$ (400 MHz).
Material balance of the above reaction (Scheme 2-1) was determined by GC analysis, and plotted in Figure 2-4. It clearly demonstrates that acetophenone is a secondary product. The sum of $[\text{ACHBF}_2] + [17] + [\text{CH}_3\text{COPh}]$ was always lower than the initial concentration of ACHBF$_2$ (0.030 M) indicating the presence of unisolated products. The amount of the unisolated products was increased rapidly upon longer irradiation.

![Figure 2-4](image)

**Figure 2-4** The material balance for the photoaddition of ACHBF$_2$ (0.030 M) to benzene (2.0 M) in 1,4-dioxane.
Photolysis of ACHBF$_2$ (2, 670 mg, 3.56 mmol) and benzene (43 mL) in acetonitrile (90 mL) in the presence of oxygen for 4 hours with a 200 W medium pressure mercury lamp afforded two products, 20 (yield 15%) and 19 (yield 1.6%) in addition to acetophenone (18).

The structure of 19 was assigned to be 1-methyl-3,4,5,6,7,8-hexahydro-1H-2-benzoicen-3,8-dione on the basis of its spectroscopic data (Tables 4-1 to 4-4). This identification was confirmed by X-ray crystallography (Figure 2-5). The GC-MS (EI and CI) gave its molecular weight as 232. The $^1$H NMR (in CDCl$_3$) shows a doublet of CH$_3$ at 1.57 ppm and a methine quartet at 6.05 ppm with a coupling constant of 6.6 Hz. The $^{13}$C NMR signals at 207.48 ppm and 170.09 ppm (in CDCl$_3$) and the IR stretching bands at 1709 (vs) and 1738 (vs) cm$^{-1}$ suggested the existence of a non-conjugated carbonyl group and an ester group. In addition, a distinct fluorescence peak at 330 nm, as shown in Figure 2-6, was observed in ether. This is not typical for compounds of this type. The crystal structure analysis (Figure 2-5) revealed that the carbonyl group is nearly perpendicular to the aromatic ring. The structure of the other product was identified to be 2-phenyl-1-cyclohexen-1-ol acetate (20). The $^1$H NMR spectrum of 20 in CDCl$_3$ revealed signals of five aromatic protons in the range of 7.20 to 7.30 ppm. This indicated a monosubstituted benzene ring. The strong IR absorption band at 1760 cm$^{-1}$ and the chemical shift at 169.31 ppm in $^{13}$C NMR confirm the ester group.
Figure 2-5  ORTEP drawing of the molecular structure of 19; important torsion angles (°) are C(2)-C(1)-C(13)-O(1), 101.0 (3); C(6)-C(1)-C(13)-O(1), 80.5 (3); C(1)-C(6)-C(7)-C(14), 93.4 (3).
Figure 2-6  Fluorescence (a) and excitation (b) spectra of 19 in ether (8.3 x 10^-4 M) at 25°C. $S_{\text{ex}} = 8$ nm, $S_{\text{em}} = 4$ nm, $\lambda_{\text{ex}} = 300$ nm.

The lactone 19 was also prepared by photooxygenation of 17. Photolysis of 17 in CH$_3$CN/CH$_3$OH (3:1 by volume) under an oxygen atmosphere for 75 min using methylene blue as a sensitizer and a 200 W medium pressure mercury lamp as the light source (GWV glass filter, cut off at 350 nm) resulted in the formation of 19 in 69% yield (isolated).
ACHBF$_2$ to Toluene

The irradiation of ACHBF$_2$ (2) in toluene with a 200 W Hanovia medium pressure mercury lamp for 7 hours led to the formation of two photoadducts, 21a and 21b (yield 24%), isolated as a mixture of ca. 1:1 ratio (determined by $^1$H NMR analysis) along with 3- and 4-methyl acetophenones (22b and 22a in a ratio of ca. 1:1 shown by $^1$H NMR spectroscopy, yield 6.3%.

The two regioisomers were identified as 6,9-dimethyl-2,3,4,6-tetrahydro-1H-dibenzo[b,d]pyran (21a) and 6,8-dimethyl-2,3,4,6-tetrahydro-1H-dibenzo[b,d]pyran (21b) on the basis of the two sets of signals which were similar to those of the enol ether 17 (Table 4-3) in the $^1$H NMR spectrum. 21a and 21b show very close chemical shifts in the $^1$H NMR spectrum except for the aromatic protons. The $^1$H NMR spectrum of the mixture gives two sets of three aromatic protons with one singlet (broad) and two doublet patterns, which clearly indicates 1,2,4-trisubstituted benzene ring. One compound has a singlet at 6.84 ppm and two doublets at 6.95 ppm and 7.06 ppm with coupling constant $\text{J} = 7.4$ Hz. When the signal at 7.06 ppm was decoupled, the doublet at 6.95 ppm became a singlet. The corresponding chemical shifts of the other isomer
are at 6.87 (s, broad), 6.91 (d, J = 7.3 Hz) and 6.96 (d, J = 7.3 Hz) ppm. The IR absorption at 1657 cm\(^{-1}\) is a strong evidence of C=C–O group, the presence of which is also supported by the chemical shifts of 150.58 ppm and 107.40 ppm in the \(^{13}\text{C}\) NMR spectrum. The structures of the two by-products 4-methylacetophenone (22a) and 3-methylacetophenone (22b) were identified by comparing their \(^1\text{H}\) NMR spectra with those documented in Sadtler Standard Spectra.\(^{64}\)

Photoxygenation of the mixture of 21a and 21b in CH\(_3\text{CN}/\text{CH}_3\text{OH}\) (3:1 by volume) was carried out using a 200 W medium pressure mercury lamp and a GWV glass filter (\(\lambda > 350\) nm) with methylene blue as the sensitizer. After irradiation for 1.5 hours, the isolated product (59% yield) was a mixture (ca. 1:1 ratio by \(^1\text{H}\) NMR) of 1,10-dimethyl-3,4,5,6,7,8-hexahydro-1H-2-benzoxecin-3,8-dione (23a) and 1,11-dimethyl-3,4,5,6,7,8-hexahydro-1H-2-benzoxecin-3,8-dione (23b); the structures are shown below.

![Structures](image)

The spectroscopic data for this mixture are given in Tables 4-1 to 4-4. The appearances of 1750 (vs) and 1720 (vs) cm\(^{-1}\) absorption bands in the IR spectrum and chemical shifts of 172.0 ppm and 208.0 ppm in the \(^{13}\text{C}\) NMR spectrum (in CDCl\(_3\)) are characteristics of an ester and non-conjugated carbonyl groups, respectively. The \(^1\text{H}\) NMR spectrum (CDCl\(_3\)) gives two sets of one singlet and two doublets for the aromatic protons.
as well as two sets of one doublet (CH$_3$) and one quartet (CH) with a coupling constant $J = 6.7$ Hz.

ACHBF$_2$ to Methyl Benzoate

Photolysis of a solution of methyl benzoate (24) and ACHBF$_2$ (2) in acetonitrile gave a yellow photolysate after 12.5 hours irradiation. GC analysis (200°C) showed an ACHBF$_2$ signal (Rt 1.43 min, 24%) and one product signal (Rt 1.18 min, 72%) (peak area ratio). Two acetylated compounds, as shown in Scheme 2-2, were isolated from the photolysate as a mixture of methyl 3-acetylbenzoate (25) and methyl 4-acetylbenzoate (26) in a ratio of 1.5:1.0 (by $^1$H NMR) in 5.7% yield.

Scheme 2-2

The structures were determined by spectroscopic analysis. The GC-MS spectra of both products showed the same parent peak at m/e 178 indicative of acetylated methyl benzoates. The $^1$H NMR spectrum (CDCl$_3$) of the mixture clearly showed 1,3- and 1,4-disubstituted benzene patterns in the aromatic proton region. Compound 25 shows a triplet at 7.56 ppm for $H_b$, a singlet at 8.61 ppm for $H_d$, and two doublets at 8.23 and 8.16 ppm for the $H_a$ and $H_c$, respectively. The isomer 26 gives a doublet at 7.78 ppm for $H_a$ and $H_a'$ and another doublet at 8.12 ppm for...
Hb and Hb' with a coupling constant of 8.4 Hz. The chemical shifts of two methyl groups are identical for the two isomers with the signals occurring at 2.69 ppm for the acetyl methyl and 3.96 ppm for the ester methyl. IR spectroscopy (neat film) of the mixture revealed two strong absorption bands at 1734 and 1698 cm\(^{-1}\), which suggests an ester carbonyl and conjugated carbonyl groups.

Other Benzene Derivatives

Irradiation of ACHBF\(_2\) and t-butyl benzene in acetonitrile for 5 hours yielded a slightly purple solution. Isomeric acetylated products were formed as the major products. Two minor dehydration products were also detected by GC analysis. GC-MS of the acetylated t-butylbenzenes gave a molecular ion peak of m/e = 176 and a base peak of m/e = 161 (M\(^+\)-CH\(_3\)). The minor products were shown by their GC-MS to have a molecular ion peak of m/e = 256 and a base peak of m/e = 241 (M\(^+\)-CH\(_3\)). These masses indicated these were enol ethers similar to 17.

Similar to the photoaddition of ACHBF\(_2\) to methyl benzoate (24), the photolysis with chlorobenzene and benzonitrile gave acetylated benzene derivatives as the major products. These were identified by GC-MS. However, under similar conditions, ACHBF\(_2\) failed to photolytically add to anisole. After 6 hours irradiation, analysis of the yellow photolysate showed that 96% of ACHBF\(_2\) survived.

2.2.2 ACPBF\(_2\) to Benzene

Photolysis of \((2\text{-acetyl)cyclopentanonoato})\)boron difluoride (ACPBF\(_2\), 0.052 M, 2.1 mmol) in benzene and ether (2:3 by volume) for 45 min under
nitrogen using a 200 W medium pressure mercury lamp gave a mixture of acetophenone (18), one minor (Rt 2.12 min), and one major (Rt 2.39 min) products in a 5:1:5 GC (160°C) peak area ratio. The minor product was not isolated but the parent ion peak, m/e = 186, and base peak, m/e = 171(M+-CH3), from its GC-MS spectra (CI and EI mode) suggested that it has an enol ether structure (27). From GC-MS, the major product was shown to have a molecular weight of 204, which corresponded to a 1:1 adduct of 2-acetylcyclopentanone (ACP) to benzene such as 6-acetyl-5-(2-oxocyclopentyl)-1,3-cyclohexadiene (28), as shown in Scheme 2-2. The GC-MS (CI) of 28 shows an M+1 peak of 205 (78) and a base peak of mass 121 (C6H5COCH3+1), which indicates it as a photoadduct between benzene and ACPBF2 and also reveals the propensity to form acetophenone. The yield of acetophenone was increased if the photolysate was left at room temperature; this could be prevented by washing with water. When the photolysis was carried out in the presence of tributylamine, work-up of the photolysate gave 28, 27 and acetophenone in a 12:1:1 GC ratio. 1H NMR studies (100 MHz, CDCl3) of the crude product clearly showed signals attributable to allylic protons. They occurred as one doublet of a doublet (3.49 ppm) and one multiplet (3.05 ppm) with a coupling constant of 8.3 Hz for cis-geometry. Four additional signals corresponding to olefinic protons around 5.95 ppm. Flash column chromatography of the photolysate gave no primary adduct 28 but one new compound, 2-(2-acetylphenyl)cyclopentanone (29, Rt 2.98 min at 160°C), as presented in Scheme 2-2, in 17% yield. It is clear that 29 is derived from dehydrogenation of 28 in the presence of oxygen. The identification of the structure of 29 was based on its spectroscopic data (Table 4-1 to Table 4-4). The GC-MS data give its molecular weight to be 202 [EI, 202
The $^1$H NMR spectrum (in CDCl$_3$) shows a singlet at 2.81 ppm corresponding to the methyl group adjacent to a carbonyl group, and a doublet of doublets at 3.92 ppm ($J = 9.0$ and 1.3 Hz) for the quaternary hydrogen $H_a$. The chemical shift of 217.6 ppm in its $^{13}$C NMR spectrum (CDCl$_3$) and the absorption band of 1741 (vs) cm$^{-1}$ in its IR spectrum are typical of a 5-membered ring ketone. This indicates the presence of a cyclopentanone moiety. Meanwhile, the chemical shift of 202.0 ppm in the $^{13}$C NMR spectrum and the band of 1690 (vs) cm$^{-1}$ in the IR spectrum are common for an acetophenone carbonyl.

**Scheme 2-3**

**2.2.3 AABF$_2$ to Benzene**

Photolysis of AABF$_2$ (1) and benzene in ether was carried out in Apparatus II using a 200 W medium pressure mercury lamp. GC analysis showed a rapid formation of a product corresponding to a 1:1 primary adduct 31 (M$^+$, 178). The mixture was irradiated until GC showed the peak
area of 31 started to decrease. Flash column chromatography of the photolysate afforded 5-acetyl-6-(2-oxopropyl)-1,3-cyclohexadiene (31, isolated yield 3%), a small amount of (2-acetylphenyl)-2-propanone (32, Rt 3.81 min at 120°C) and acetophenone, as presented in Scheme 2-4.

**Scheme 2-4**

![Scheme 2-4 diagram](image)

The structural assignment of 31 was based on its spectroscopic data (Table 4-1 to Table 4-4). Two NMR signals from the allylic protons, H_a and H_b, could be located easily in the ^1H NMR spectrum. They gave rise to signal with chemical shifts at 3.56 (multiplet) and 3.19 (multiplet) ppm with a coupling constant of 7.2 Hz; this indicates cis-geometry of the two protons. The two methylene protons give rise to a doublet at 2.52 ppm (J = 7.0 Hz) by coupling with H_b. The two methyl group signals occur as singlets at 2.08 and 2.19 ppm. The four olefinic proton signals appear between 5.87-6.04 ppm. The existence of two unconjugated carbonyls was clearly shown by the ^13C NMR spectrum since signals were observed at 208.69 and 207.26 ppm; this was also supported by an IR band at 1730 (broad, vs) cm⁻¹.
The structure of \textit{32}^6,67 was deduced from its GC-MS and $^1$H NMR spectra. The GC-MS (EI) spectrum gave m/e (relativity): 176(M$^+$, 14), 161(M$^+$-CH$_3$, 30), 134(M$^+$-COCH$_2$, 37), 119(M$^+$-CH$_2$COCH$_3$, 100) and 91(21); CI, 177(M$^+$+1, 100) and 159(12). The $^1$H NMR spectrum (CDCl$_3$) of the aromatic proton region showed two doublets of a triplet at 7.40 and 7.49 ppm with a mutual coupling constant 7.5 Hz, and two doublets of a doublet at 7.19 and 7.86 ppm, which are typical for ortho-substituted benzenes. The singlet from the methylene protons was found at 4.02 ppm.

Prolonged irradiation of the above photolysate containing AABF$_2$, benzene and the product 31 as well as acetophenone in ether using the same light source resulted in the decomposition of 31 to acetophenone. In order to determine whether the formation of acetophenone is catalyzed by acids produced in the photolysate, the above reaction was carried out in the presence of pyridine. The formation of acetophenone was reduced to some extent which is summarized in Table 2-2. However, the amount of product 31 was not increased significantly upon prolonged irradiation.

In an independent experiment, photolysis of AABF$_2$ (0.052 M, 2.09 mmol) and benzene (10 mL) in ether (30 mL) using a 200 W medium pressure mercury lamp for 125 min gave adduct 31 (Rt 2.69 min, 41%), acetophenone (8%) and unreacted AABF$_2$ (46%) as analyzed by GC (120°C). Flash column chromatography of the photolysate yielded a 1:1 mixture of two other products 32 (Rt 3.81 min) and 33 (Rt 6.45 min).
Table 2-2  Effect of Pyridine on the Photoaddition of AABF₂ to Benzene in Ether.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>[Pyridine] (M)</th>
<th>Time (h)</th>
<th>AABF₂</th>
<th>CH₃COPh</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.5</td>
<td>0.2922</td>
<td>0.0792</td>
<td>0.1646</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.1083</td>
<td>0.1373</td>
<td>0.0294</td>
</tr>
<tr>
<td>2</td>
<td>0.038</td>
<td>1.5</td>
<td>0.3463</td>
<td>0.0175</td>
<td>0.1735</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>0.1918</td>
<td>0.0271</td>
<td>0.1785</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The solutions containing AABF₂ (0.030 M), dodecane (as I.S., 0.015 M) in benzene/ether (2 mL, 1:1 by volume) were irradiated in Apparatus I using RPR-3000 Å lamps.

\textsuperscript{b} R is the GC peak area ratio of AABF₂ or product over the internal standard.

It was found that the above photolysate containing 31 slowly gave 32 and 33 when kept in the dark as shown by GC analysis. The GC-MS spectra of both 32 and 33 give the molecular weights as 176 (EI and CI), which implies that they are dehydrogenation products from 31. The \textsuperscript{1}H NMR spectrum of the mixture (Table 4-3) shows a typical AA'BB' system at 7.30 and 7.93 ppm (J = 8.3 Hz) for 33 in the aromatic region. In addition, there are other signals from the ortho product 32; this indicates that 33 is a \textit{para} isomer of 32.\textsuperscript{68} The mechanism for the formation of 33 is uncertain at this stage.
2.2.4 Naphthalene Derivatives to AABF$_2$

Naphthalene and AABF$_2$

Photolysis of a mixture of naphthalene (Np, 11) and AABF$_2$ (1) in ether with RPR-3000 Å lamps for 28 hours yielded a single product (Scheme 2-5) identified as 1-acetyl-1,2-dihydro-2-(2-oxopropyl)-naphthalene (34, isolated yield 36% based on 28% conversion of Np).

Scheme 2-5

![Scheme 2-5](image)

The spectroscopic data for 34 are given in Tables 4-1 to 4-4. The GC-MS (CI) of 34 gives an M$^+$$+$1 peak of 229, which is the molecular weight of an adduct between Np and AAH. The $^1$H NMR spectrum (in CDCl$_3$) shows a doublet at 3.84 ppm ($J = 7.6$ Hz) for $H_a$ and a multiplet at 3.43 ppm for $H_b$ indicating there is an acetyl group at the 1-position of naphthalene. Two sets of doubletted doublets at 5.78 ppm and 6.45 ppm with a coupling constant of 9.6 Hz imply there are two olefinic protons conjugated to an aromatic ring. The two diastereotopic methylene protons resonate at 2.65 ppm ($J = 17.8$ and 8.0 Hz) and 2.86 ppm ($J = 17.8$ and 7.8 Hz) as two sets of doubletted doublets. The existence of two unconjugated carbonyl groups is characterized by chemical shifts at 208.46 and 207.03 ppm in the $^{13}$C NMR spectrum (Table 4-4) and a strong band at 1716 cm$^{-1}$ in the IR spectrum (Table 4-2).
1-Chloronaphthalene and AABF₂

Photolysis of 1-chloronaphthalene (1-NpCl) and AABF₂ (1) in ether for 15.5 hours with RPR-3000 Å lamps resulted in one major product that was identified as 1-acetyl-8-chloro-1,2-dihydro-2-(2-oxopropyl)-naphthalene (35, yield 21% based on 48% 1-NpCl consumed) according to its spectroscopic data (Tables 4-1 to 4-4).

The GC-MS (CI) of 35 shows an M⁺+1 peak at m/e = 263 (100) for 35Cl and 265 (34) for 37Cl. Its ¹H NMR spectrum (in CDCl₃) shows there are three aromatic protons that give signals in the region of 7.03-7.25 ppm. This indicates there is addition to a unsubstituted aromatic ring. A doublet at 4.09 ppm (J = 7.3 Hz) assigning to Hₐ and a multiplet at about 3.40 ppm corresponding to Hₖ indicate the acetyl group is on the 1-position of naphthalene. The methylene proton signals occur as two sets of doubletted doublets at 2.75 ppm (J = 18.2 and 7.7 Hz) and 2.92 ppm (J = 18.2 and 7.2 Hz). The ¹³C NMR spectrum shows chemical shifts of 207.37 and 206.74 ppm for the two unconjugated carbonyl groups which also give a strong absorption band at 1712 cm⁻¹ in IR spectrum (Table 4-2).

Methyl 2-Naphthalenecarboxylate and AABF₂

Photolysis of a solution of 2-NpCO₂CH₃ (12) and AABF₂ (1) in ether using RPR-3500 Å lamps for 6 hours gave two adducts identified as methyl
2-acetyl-1,2-dihydro-1-(2-oxopropyl)-2-naphthalenecarboxylate (13, yield 10%) and methyl 1-acetyl-1,2-dihydro-2-(2-oxopropyl)-2-naphthalene-carboxylate (14, yield 15%) and a by-product of methyl 1-acetyl-2-naphthalenecarboxylate (36, 8%), which have been isolated by flash column chromatography.

The \(^1\)H NMR spectrum of 13 corresponds to two olefinic protons resonating at 6.17 and 6.58 ppm with a mutual coupling constant of 9.6 Hz. Four aromatic protons give signals in the region of 7.03 to 7.19 ppm. This clearly indicates addition at the 1,2-positions. The \(^1\)H NMR spectrum of 14 shows a similar pattern to that of 13. The signals of the two diastereotopic methylene protons of 13 have the same chemical shift, a doublet at 2.56 ppm (\(J = 6.5\) Hz), while \(H_a\) gives a triplet at 4.33 ppm. This indicates that the acetonil group adds to the 1-position of naphthalene ring. For compound 14, the \(^1\)H NMR shows two doublets at 3.04 ppm and 3.19 ppm (\(J = 18.2\) Hz) for the two diastereotopic methylene protons, and a singlet at 3.59 ppm for \(H_b\). Both 13 and 14 show the ester methyl signal at about 3.6 ppm in their \(^1\)H NMR spectra. The existence of two unconjugated carbonyl and one ester carbonyl is confirmed by \(^{13}\)C chemical shifts at 206.34, 203.58 and 170.02 ppm for 13 and 207.51, 205.80 and 173.57 ppm for 14. The structure of 36 was assigned based on its GC-MS [CI, m/e = 229 (M\(^+\)+1, 100)] and \(^1\)H NMR (100 MHz).
2.2.5 Phenanthrene Derivatives to AABF₂

Phenanthrene and AABF₂

Photolysis of an ether solution containing phenanthrene (PN, 37) and AABF₂ (1) with RPR-3000 Å lamps for 11 hours afforded two products as shown in Scheme 2-6. These are assigned as cis-9-acetyl-9,10-dihydro-10-(2-oxopropyl)-phenanthrene (38, isolated yield 46%) and trans-9-acetyl-9,10-dihydro-10-(2-oxopropyl)-phenanthrene (39, isolated yield 5.6%) on the basis of their spectroscopic data (Table 4-1 to Table 4-4). Similar yields were obtained using RPR-3500 Å lamps.

Scheme 2-6

\[
\begin{align*}
\text{37} + \text{1} & \xrightarrow{\text{hv}} \text{Et₂O} \rightarrow \text{38} + \text{39}
\end{align*}
\]

The GC-MS of both 38 and 39 gave their parent masses as m/e = 278 indicating that both of them are photoadducts between PN and AABF₂. The \(^1\text{H}\) NMR spectrum (CDCl₃) of 38 gave a doublet at 3.99 ppm (J = 4.6 Hz) for \(H_a\) and a doublet of a doublet of a doublet at 3.85 ppm (J = 4.6, 5.8 and 6.8 Hz) for \(H_b\). This evidently indicates a 9,10-addition. The methylene protons give two sets of doubletted doublets at 2.86 and 3.02 ppm with a coupling constant equal to 18.0 Hz. The chemical shifts of 208.79 and 207.04 ppm in the \(^{13}\text{C}\) NMR spectrum combined with a strong
absorption band at 1708 cm$^{-1}$ in the IR spectrum clearly reflect the
existence of two unconjugated carbonyl groups. Product 39 was shown to
have a 9,10-addition on the basis of its $^1$H NMR spectrum. The $^1$H NMR
spectrum (CDCl$_3$) of 39 gives a doublet at 3.70 ppm ($J = 1.3$ Hz) for H$_C$
and a doublet of a doublet of a doublet at 4.00 ppm ($J = 1.3$ and 6.0 and
8.8 Hz) for H$_D$. Two sets of doublet-doublet doublets at 2.51 ppm ($J = 17.0$
and 6.0 Hz) and 2.55 ppm ($J = 17.0$ and 8.8 Hz) are assigned to the two
diastereotopic methylene protons. The existence of two carbonyl groups
in 39 is supported by the $^{13}$C chemical shifts of 206.90 and 206.68 ppm
as well as by its IR absorption at 1713 cm$^{-1}$ (vs).

Treatment of a mixture of 38 and 39 (2:1 GC ratio) with NaOCH$_3$
in methanol gave an aldol condensation product 40. It was found that 39
remained unchanged by this treatment as determined by GC analysis (30%
before reaction and 34% after the reaction, GC peak area ratio). This
result supports the above stereochemical assignments for 38 and 39.

The spectroscopic data of 40 are given in Table 4-1 to Table 4-4. The
GC-MS (CI) of 40 gives a base peak at m/e = 261 ($M^+1$) indicating the
loss of one water molecule from 38. The $^1$H NMR spectrum (in C$_6$D$_6$) of 40
shows a doublet at 3.80 ppm for H$_A$ with $J = 5.0$ Hz, a doublet of a
triplet at 2.96 ppm for H$_B$ ($J = 11.0$ and 5.0 Hz) and a singlet at 6.05
ppm for the olefinic hydrogen H. Two diastereotopic methylene protons give signals at 1.59 and 1.90 ppm with a geminal coupling constant of 18.2 Hz. The chemical shift of 199.44 ppm in the $^{13}$C NMR spectrum (CDCl$_3$) and the absorption band at 1664 cm$^{-1}$ in its IR spectrum strongly support the presence of one conjugated carbonyl group in 40.

A mixture of 38 (43%) and 39 (52%) was treated with hydrochloric acid to give a mixture of 38, 39 and 40 in a 1:18:1 ratio.

9-Cyanophenanthrene and AABF$_2$

Irradiation of 9-cyanophenanthrene (9-PNCN, 15) and AABF$_2$ (1) in ether for 47 hours with RPR-3000 Å lamps led to the formation of two major photoadducts which were identified as 9-acetyl-9-cyano-9,10-dihydro-10-(2-oxopropyl)-phenanthrene (41, yield 21%) and 10-acetyl-9-cyano-9,10-dihydro-9-(2-oxopropyl)-phenanthrene (42, yield 18%) based on the spectroscopic data (Tables 4-1 to 4-4).

![Chemical Structures](image)

The $^1$H NMR spectrum of 41 shows a doubleted doublet at 4.20 ppm ($J = 7.4$ and 4.1 Hz) for the allylic proton and two doublets of a doublet at 3.17 ppm ($J = 18.6$ and 7.4 Hz) and 3.21 ppm ($J = 18.6$ and 4.1 Hz) for the methylene protons. This indicates that the acetonyl group is attached to the 10-position of phenanthrene. The presence of two
carbonyl groups in 41 is shown by signals at 205.25 and 199.29 ppm in the $^{13}$C NMR spectrum. The presence of the cyano group was indicated by the carbon signal at 77.21 ppm. The GC-MS (CI) of 42 shows a base peak of m/e = 304 ($M^+1$), the same as that of 41, indicating a second photoaddition product. The $^1$H NMR spectrum confirms 42 as the regioisomer of 41. Two doublets for the methylene protons at 3.22 and 3.67 ppm with a coupling constant of 17.8 Hz and a singlet at 4.67 ppm for the allylic proton indicated that the acetonyl group is at the 9-position and the acetyl group at the 10-position. The two methyl singlets at 2.14 and 2.17 ppm in the $^1$H NMR spectrum also prove that there are two ketone side chains in 42.

2.2.6 Other Aromatic Compounds to AABF$_2$

The irradiation of the following naphthalene derivatives with AABF$_2$ in ether was carried out by using RPR-3000 Å lamps. Under the GC detection limit, no photoproduct could be detected.

In acetonitrile, the photolyses of AABF$_2$ and aromatic compounds such as phenanthrene, 1-NpCl and 2-NpCO$_2$Me, under similar conditions using RPR-3000 Å lamps also gave no cycloaddition product by GC analyses. Similar results were obtained for 1-NpOMe and 2-NpOMe.
2.3 Photolysis of Benzene and Some 1,3-Diketones

A solution of 2-acetylcyclohexanone (ACHH, 21 mg, 0.15 mmol) in benzene (5 mL) was irradiated in a Pyrex tube with RPR-3000 Å lamps in Apparatus I. After irradiation for 10 hours, GC analysis (at 170°C) of the colorless photolysate showed no product. Similar results were obtained for photolyses of 2-acetylcyclopentanone (ACPH) and 1,3-pentanедione (AAH) in benzene. The above experiments were also performed using the same concentrations of 1,3-diketones and 2.0 M benzene in acetonitrile. Again, no product could be detected by GC upon irradiation for 10 hours.

2.4 Mechanistic Studies for the Photoaddition of ACHBF₂ to Benzene

2.4.1 Triplet Sensitization and Triplet Quenching

To investigate the possibility of a triplet pathway in the photoaddition of ACHBF₂ (2, \( E_T = 67 \text{ kcal/mol} \)) to benzene, xanthone (\( E_T = 74.1 \text{ kcal/mol} \)) and benzophenone (\( E_T = 69 \text{ kcal/mol} \)) were used as triplet sensitizers. In these experiments, enough sensitizer (0.050 M) was added to a dioxane solution of ACHBF₂ (0.020 M) and benzene (2.0 M) to absorb more than 90% of incident light (RPR-3500 Å lamps). GC analyses of the photolysates gave no cycloaddition product 17 in the presence of xanthone and 3.7% of 17 in the case of benzophenone as the sensitizer while the corresponding control reaction (i.e., in the absence of a sensitizer) showed 32% yield of 17.
1,3-Cyclohexadiene (CHDE, $E_s = 97$ kcal/mol, $E_T = 52.4$ kcal/mol) and 1,3-pentadiene (PDE, $E_T = 59$ kcal/mol) were employed as triplet quenchers for the photoaddition of ACHBF$_2$ (0.030 M) to benzene (2.0 M) in 1,4-dioxane. Both 1,3-cyclohexadiene and 1,3-pentadiene in the concentration range of 0.002-0.012 M failed to quench the photoaddition on irradiation with RPR 300 nm light source in Apparatus I. Under these conditions, the quantum yields for the formation of 17 were determined as a function of CHDE and PDE concentrations, and shown to be virtually unchanged in the plot of $\Phi_p^*/\Phi_p$ against [CHDE] and [PDE] in Figure 2-7, where $\Phi_p^*$ and $\Phi_p$ are the quantum yields for the formation of 17 in the absence and presence of the quencher.

The failure of both triplet sensitization and triplet quenching indicates that the photocycloaddition of ACHBF$_2$ to benzene occurs from the singlet excited state of ACHBF$_2$ rather than its triplet state.

2.4.2 Heavy Atom Effect

The dependence of quantum yield for the formation of 17 from the photocycloaddition of ACHBF$_2$ to benzene on 1,2-dibromoethane was determined. The reaction was carried out in dioxane at fixed concentrations of ACHBF$_2$ (0.030 M) and benzene (2.35 M), and various concentrations of 1,2-dibromoethane (0.02 to 0.10 M) using RPR-3000 Å lamps. It was found that the relative quantum yield $\Phi_p^*/\Phi_p$ ($\Phi_p^*$ is the quantum yield in the absence of BrCH$_2$CH$_2$Br and $\Phi_p$ is that in the presence of BrCH$_2$CH$_2$Br) increased with increasing concentration of BrCH$_2$CH$_2$Br, which implies that 17 is a product from a singlet state (Table 2-3 and Figure 2-8).
Figure 2-7  The Stern-Volmer plots for quenching of the photoaddition of ACHBF₂ to benzene by 1,3-cyclohexadiene and 1,3-pentadiene in 1,4-dioxane. [ACHBF₂] = 0.030 M, [benzene] = 2.0 M, [C₁₄H₃₀] = 0.010 M (as I.S.).
Table 2-3  Heavy Atom Effect of 1,2-Dibromoethane on the Formation of 17 in 1,4-Dioxane.\textsuperscript{a}

<table>
<thead>
<tr>
<th>[BrCH\textsubscript{2}CH\textsubscript{2}Br] (M)</th>
<th>R/R\textsubscript{I.S.} (ACHBF\textsubscript{2})</th>
<th>unreacted [ACHBF\textsubscript{2}] (M)</th>
<th>R/R\textsubscript{I.S.} (17)</th>
<th>[17]\texttimes10\textsuperscript{-3} (M)</th>
<th>(\Phi p^*/\Phi p^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.2986</td>
<td>0.027</td>
<td>0.3517</td>
<td>4.43</td>
<td>1.0</td>
</tr>
<tr>
<td>0.020</td>
<td>1.3081</td>
<td>0.027</td>
<td>0.3377</td>
<td>4.26</td>
<td>1.04</td>
</tr>
<tr>
<td>0.040</td>
<td>1.3288</td>
<td>0.028</td>
<td>0.2732</td>
<td>3.44</td>
<td>1.28</td>
</tr>
<tr>
<td>0.060</td>
<td>1.3266</td>
<td>0.028</td>
<td>0.1810</td>
<td>2.28</td>
<td>1.94</td>
</tr>
<tr>
<td>0.080</td>
<td>1.3310</td>
<td>0.028</td>
<td>0.0364 \textsuperscript{c}</td>
<td>0.46</td>
<td>9.6</td>
</tr>
<tr>
<td>0.10</td>
<td>1.4155</td>
<td>&gt;0.029</td>
<td>0.0196 \textsuperscript{c}</td>
<td>0.25</td>
<td>17.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a.} The solutions containing ACHBF\textsubscript{2} (0.030 M), benzene (2.4 M), tetradecane (as I.S., 0.010 M) and various 1,2-dibromoethane were irradiated for 60 min in Apparatus I with RPR-3000 Å lamps.

b. \(\Phi p^*/\Phi p\) values were the R/R\textsubscript{I.S.} in the absence of BrCH\textsubscript{2}CH\textsubscript{2}Br over the corresponding R/R\textsubscript{I.S.} in the presence of BrCH\textsubscript{2}CH\textsubscript{2}Br.

c. Error for the values from GC analyses were at least 50%.
Figure 2-8 The plot for the quenching of the photoaddition of ACHBF₂ to benzene by BrCH₂CH₂Br in 1,4-dioxane. [ACHBF₂] = 0.030 M, [benzene] = 2.4 M, [C₁₄H₃₀] = 0.01 M (as I.S.).
2.4.3 Quantum Yield Determination

Quantum yields for the formation of 17 from the photoaddition of ACHBF\textsubscript{2} to benzene in dioxane solvent were measured at various concentrations of benzene (1.12-2.47 M) using RPR-3000 Å lamps. With a fixed concentration of ACHBF\textsubscript{2} (0.030 M), the quantum yields increased with increasing concentration of benzene as shown in Table 2-4.

From the expressions for reaction efficiency under steady-state excitation, the quantum yield \( \Phi \) for enol ether 17 formation can be expressed by the following equations (eq 2-1 and eq 2-2):

\[
\Phi = a \frac{k_2[Bz]}{k_q[Bz] + k_D} \quad (eq \ 2-1)
\]

where \( a \) = efficiency of formation of (ACHBF\textsubscript{2})\textsuperscript{+}, \( k_2 \) is the rate constant for bimolecular reaction, \( k_q \) is the rate constant for all bimolecular quenching and \( k_D \) is the rate constant for unimolecular deactivation of (ACHBF\textsubscript{2})\textsuperscript{+}.

\[
1/\Phi = \frac{k_q[Bz] + k_D}{ak_2[Bz]} = \frac{1}{a} \left( \frac{k_q}{k_2} + \frac{k_D}{k_2[Bz]} \right) \quad (eq \ 2-2)
\]

The experimental plots of 1/\( \Phi \) versus 1/[benzene] gave a straight line with slope equal to \( s = k_D/(ak_2) \) and intercept of \( i = k_q/(ak_2) \), as shown in Figure 2-9. From this figure, \( k_q \)\textsuperscript{T} is equal to 0.067 (i/s = 5.4/81) and the limiting quantum yield is equal to 1/i = 1/5.4 or 0.19 in dioxane. In acetonitrile solution, \( k_q \)\textsuperscript{T} = 0.032 (i/s = 8/247) and \( \Phi_{\text{limiting}} = 0.12 \) (1/i = 1/8) were obtained (Table 2-4 and Figure 2-9).
Table 2-4 Quantum Yields as a Function of the Concentration of Benzene for the Photoaddition of ACHBF$_2$ to Benzene.a

<table>
<thead>
<tr>
<th>Expt. No</th>
<th>[Benzene] (M)</th>
<th>R</th>
<th>( \Phi )</th>
<th>[Benzene]$^{-1}$ (M$^{-1}$)</th>
<th>( \Phi^{-1} )</th>
<th>( k_q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>In 1,4-dioxane b</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.12</td>
<td>0.1571</td>
<td>0.0082</td>
<td>0.893</td>
<td>122.0</td>
<td>0.067</td>
</tr>
<tr>
<td>2</td>
<td>1.34</td>
<td>0.2684</td>
<td>0.0150</td>
<td>0.746</td>
<td>66.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.57</td>
<td>0.3326</td>
<td>0.0175</td>
<td>0.640</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.79</td>
<td>0.3437</td>
<td>0.0193</td>
<td>0.560</td>
<td>51.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.01</td>
<td>0.3273</td>
<td>0.0215</td>
<td>0.498</td>
<td>46.5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.47</td>
<td>0.4046</td>
<td>0.0266</td>
<td>0.406</td>
<td>37.6</td>
<td></td>
</tr>
<tr>
<td>In acetonitrile c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.032</td>
</tr>
<tr>
<td>1</td>
<td>1.12</td>
<td>0.0709</td>
<td>0.0044</td>
<td>0.893</td>
<td>228.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.34</td>
<td>0.0842</td>
<td>0.0052</td>
<td>0.746</td>
<td>192.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.68</td>
<td>0.1071</td>
<td>0.0064</td>
<td>0.595</td>
<td>155.4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.01</td>
<td>0.1224</td>
<td>0.0076</td>
<td>0.498</td>
<td>132.2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.47</td>
<td>0.1557</td>
<td>0.0096</td>
<td>0.406</td>
<td>103.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.91</td>
<td>0.1879</td>
<td>0.0116</td>
<td>0.344</td>
<td>86.1</td>
<td></td>
</tr>
</tbody>
</table>

a. The six 5 mL sample solutions (Pyrex) containing ACHBF$_2$ (0.030 M), tetradecane (as I.S., 0.010 M) and various amount of benzene were bubbled with nitrogen for 15 min and then irradiated in Apparatus I with RPR-3000 Å lamps.

continued
b. The irradiation time was 75 min for No. 1 to 3, 70 min for No. 4 and 60 min for No. 5 and 6. The quantum yields in 1,4-dioxane were determined by Method II using No. 5 as a control.

c. The irradiation time was 60 min. The quantum yields in CH₃CN were determined by Method I.

Figure 2-9 The Stern-Volmer plots of $\Phi^{-1}$ versus $[\text{benzene}]^{-1}$ for the photoaddition of ACHBF₂ to benzene in 1,4-dioxane ($r = 0.998$) and acetonitrile ($r = 0.999$). $[\text{ACHBF₂}] = 0.030 M$, $[\text{C}_{14}\text{H}_{30}] = 0.010 M$. 
The quantum yields for the formation of 17 from the photoaddition of ACHBF₂ to benzene (fixed at 2.0 M) in dioxane were determined as a function of concentration of ACHBF₂ (0.020, 0.024, 0.030, 0.034, and 0.040 M) by irradiating the solutions in Apparatus I with RPR-3000 Å lamps for 60 min. At this fixed concentration of benzene, the quantum yields were essentially constants within the experiment error of changing the concentration of ACHBF₂. At [benzene] = 2.0 M, the quantum yield for the formation of 17 was measured to be 0.021 (see Table 2-5 and Figure 2-10).

![Figure 2-10](image)

Figure 2-10 The plot of $\Phi^{-1}$ against $[\text{ACHBF}_2]^{-1}$ for the photoreaction of ACHBF₂ to benzene in 1,4-dioxane. [benzene] = 2.0 M, $[\text{C}_{14}\text{H}_{30}] = 0.010$ M (as I.S.).
Table 2-5  Determination of Quantum Yields as a Function of the Concentration of ACHBF$_2$ for the Photoaddition of ACHBF$_2$ to Benzene.$^a$

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>[ACHBF$_2$] (M)</th>
<th>R</th>
<th>$\Phi^b$</th>
<th>[ACHBF$_2$]$^{-1}$ (M$^{-1}$)</th>
<th>$\Phi^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.020</td>
<td>0.3175</td>
<td>0.0208</td>
<td>50.0</td>
<td>48.0</td>
</tr>
<tr>
<td>2</td>
<td>0.024</td>
<td>0.3152</td>
<td>0.0207</td>
<td>41.7</td>
<td>48.4</td>
</tr>
<tr>
<td>3</td>
<td>0.030</td>
<td>0.3482</td>
<td>0.0228</td>
<td>33.3</td>
<td>43.9</td>
</tr>
<tr>
<td>4</td>
<td>0.030</td>
<td>0.3218</td>
<td>0.0211</td>
<td>33.3</td>
<td>47.4</td>
</tr>
<tr>
<td>5</td>
<td>0.034</td>
<td>0.3292</td>
<td>0.0216</td>
<td>29.4</td>
<td>46.3</td>
</tr>
<tr>
<td>6</td>
<td>0.040</td>
<td>0.3354</td>
<td>0.0220</td>
<td>25.0</td>
<td>45.4</td>
</tr>
</tbody>
</table>

a. The six 5 mL sample solutions in 1,4-dioxane (Pyrex) containing benzene (2.0 M), tetradecane (as I.S., 0.010 M) and various ACHBF$_2$ (0.020-0.040 M) were purged with nitrogen for 15 min and then irradiated together with actinometer solutions for 60 min (5 min for the actinometers) in Apparatus I using RPR-3000 Å lamps.

b. The quantum yields $\Phi$ were determined by Method I and calculated according to equation 4-3. The $f$ value for ACHBF$_2$ is 1.26. The intensity of incident light was $1.6 \times 10^{-5}$ einstein/min calculated by equation 4-1.
CHAPTER 3 DISCUSSION

3.1 Photocycloaddition of BF$_2$ Complexes to Benzenes

3.1.1 Primary Photoaddition

As shown in Schemes 2-3 and 2-4, the photoaddition of ACPBF$_2$ or AABF$_2$ to benzene gives 1:1 adducts of ACPH or AAH and benzene as the primary products. The 1,5-diketones 28 and 31 are examples of this addition. Although this type of 1,5-diketone compound often easily undergoes other transformations, 31 has been isolated and was stable enough for analysis by $^1$H NMR spectroscopy. The primary product is assumed to be formed by a [2+2] photocycloaddition of the substrate to a BF$_2$ complex to form a cyclobutane intermediate such as 30 (Scheme 2-4) or 43 (Scheme 3-1). Spontaneous ring opening of the cyclobutane ring and subsequent hydrolysis of the BF$_2$ moiety can then lead to the primary cycloadduct, 1,5-diketone 31 or 44. This mechanism is proposed to occur in a manner analogous to the photoaddition of DBMBF$_2$ to olefins.$^{29}$ The hydrolysis of the BF$_2$ moiety by trace amounts of water in the solvent or the moisture encountered during the work-up generates an acid which may promote acid catalyzed thermal reactions to be described below.

It should be pointed out that the proposed mechanism would predict the cis-geometry of the ketone substituents in 1,5-diketones 28, 31 and 44 if the [2+2] photoaddition is concerted. The cis-geometry is confirmed for both 28 and 31 by their $^1$H NMR spectra. The coupling constant of two allylic protons is found to be 8.3 Hz in 28, and 7.2 Hz in the case of 31.
Scheme 3-1  [2+2] Photocycloaddition of ACHBF\textsubscript{2} to benzene and the subsequent thermal reactions.
Based on the above mechanism, the unisolated 1:1 adduct of ACHBF$_2$ and benzene is deduced to be 1,5-diketone 44. This is in agreement with the structures of subsequent products shown in Scheme 3-1. The stereochemistry is lost in aromatization of the ring in the subsequent reactions of 44.

As described in Chapter 1, the 1,3-diketonatoboron difluorides exist in their resonance forms. For the unsymmetrical ACHBF$_2$ or ACPBF$_2$, two primary photoaddition products are expected owing to the position of the double bond as shown in Scheme 3-2. It is obvious that transformation of 48 would not give enol ether 17. The photoaddition products arising from the alternative enol isomer (endocyclic double bond) of ACHBF$_2$ or ACPBF$_2$ to benzene was not formed to a detectable extent as shown by careful GC analysis. Should such photoaddition occur, naphthoquinone derivatives could not be obtained. It appears that these unsymmetrical BF$_2$ complexes preferentially react from their exocyclic olefin isomers. Similar results were reported by H. Nozaki and co-workers in the photocycloaddition of corresponding 2-acetylcyclohexanone (ACHH) or 2-acetylcylopentanone (ACPH) and 2-acetyl-1-decalone to olefins. These 1,3-diketones enolized to give an equilibrium mixture of enols with exo- and endocyclic double bonds as indicated by NMR. It was found that ACPH exists mainly as enol form (60%) in carbon tetrachloride. The ratio of the endo/exo enol forms is 0.43 in benzene.

The observed substitution patterns of the photoaddition products (21 to 23) from ACHBF$_2$ and toluene and the lack of ortho substituted product could be explained in that ACHBF$_2$ reacts with monosubstituted
Scheme 3-2  Two possible ways of the photoaddition of ACHBF₂ to benzene.

 benzene at the 3,4-position exclusively. If the photocycloaddition also occurs at the 2,3-position, the production of ortho substituted compounds corresponding to 21-23 would be expected, since the approach of ACHBF₂ to a monosubstituted benzene would not be expected to occur under regiospecific control. The lack of the ACHBF₂ attack on the 2,3-position may arise from the steric factor of the monosubstituted group. Although [2+2] cycloadducts from ACHBF₂ in the presence of methyl benzoate (24) were not obtained, the 3,4-addition is expected to be formed based on the two acetylated products (25 and 26), which should be derived from the primary adducts between ACHBF₂ and methyl benzoate, by the same argument as for toluene. Chlorobenzene and benzonitrile gave similar results to methyl benzoate. The lack of regiospecificity in the photoaddition of these BF₂ complexes is a major impediment in their synthetic applications.
As shown in Scheme 3-1, the enol ether 17 undergoes photooxygenation to give lactone 19. The X-ray crystal structure (Figure 2-5) of 19 shows that the carbonyl is nearly perpendicular to the benzene ring. The conformation of the lactone ring is similar to that in oxacyclodeca-2,7-dione, with the ring oxygen and carbonyl groups so situated as to minimize a number of non-bonded interactions.

3.1.2 Secondary Thermal Reactions

The primary 1,5-diketone photoadducts, 28, 31 and 44, from the \([2+2]\) photoaddition exhibit a wide range of reactivities. 28 and 31 are obviously more stable than 44 and similar adducts of ACHBF₂ to monosubstituted benzenes. While the adducts of the latter group undergo thermal reactions during photolysis, 28 and 31 do survive under the experimental conditions. One of the thermal reactions is the elimination of a ketone fragment (cyclohexanone for ACHBF₂, cyclopentanone for ACPBF₂, and acetone for AABF₂) as aromatization occurs to generate acetophenone. This is evidently an acid-catalyzed reaction since the addition of pyridine or tributylamine to neutralize the acid formed during the photolysis reduces the formation of acetophenone. It should be pointed out that acetophenone might also be obtained by photoinitiated Norrish Type II process of the primary product. The Norrish Type II photoreaction appears to contribute insignificantly to the formation of acetophenone in the present study since it was found that the yield of acetophenone is not changed significantly in the photolysis of ACHBF₂ and benzene by using either longer wavelength irradiation source (RPR-3500 Å lamps) or a high concentration of ACHBF₂ complex. Photoaddition of other BF₂ complexes should follow the same
pattern. This acid-catalyzed elimination changes the primary photoadduct 1,5-diketones to acetophenone derivatives, a process that is particularly serious for the relatively stable 1,5-diketones such as 28 and 31. However, as noted previously, such a process can be controlled with the addition of a tertiary amine or pyridine.

The 1,5-diketone, 44, efficiently undergoes thermal reactions, most likely acid-catalyzed, hence there is little buildup of concentrations of 44 and acetophenone during the photoaddition as shown by GC examinations. The 1,5-diketone 8, the product from the de Mayo reaction,73 underwent aldol condensation readily in the presence of an acid or a base, yielding enone type compounds 49 and 50.

![Chemical structures](image)

The possibility of this type of thermal reaction has been ruled out based on the spectroscopic data of the product 17. If 44 underwent aldol condensation, it would give two products (51 and 52), as shown below.

![Chemical structures](image)
Both 51 and 52 should show signals of carbonyl and allylic proton in their spectroscopic spectra. The lack of characteristic signals for a ketone in both the IR and $^{13}$C NMR spectra of 17 strongly suggest a structure other than 51 and 52. An enol ether structure for 17 is indicated by its NMR and IR spectra. The formation of an enol ether during the course of photoaddition has been reported in the literature. Tada et al. found that [2+2] photoaddition of 3-cyano-2,4-pentanedione to cyclohexene gave enolized 1,5-diketone 53, which underwent spontaneous hemiketal formation giving enol ether 54 in analogy to 45 or 46 in Scheme 3-1.

The proposed mechanisms for the formation of 17 and 20 are presented in Scheme 3-1. The enolization of 44 in either site, followed by hemiketal formation, proceeds readily to give 45 and 46, probably arising from the 6-membered structural feature (as opposed to 28 and 31). It is speculated that the 1,5-diketone, 44, can easily assume conformations convenient for intramolecular enol ether formation because the formation of six-membered rings are involved. The process of 44$\rightarrow$45 is probably faster than that of 44$\rightarrow$46 because of the possibility of achieving extended conjugation in the enolization step. The subsequent transformations of 45$\rightarrow$17 and 46$\rightarrow$17 are facilitated by the driving force of aromatization and conjugation. In the presence of oxygen, the
lactone, 19, and the enol acetate, 20, are obtained. Since 19 is the sole product of photooxygenation of 17 as shown by an independent experiment, 20 should be derived from the hemiketal intermediate 46. The dehydrogenation of 46 to 20 may require lower energy than required for the dehydration/aromatization step to give 17 in the presence of oxidative species. The direct dehydrogenation of 44 does not occur easily, probably owing to its fast enolization/hemiketal formation process. It seems that certain subtle conformation factors lower the energy barriers for enolization-cyclization process in 44, consequently favoring this pathway over others. Isolation of the 1,5-diketone 28 was not successful because of the extremely facile dehydrogenation to the corresponding ortho-substituted benzene, 29, during the work-up. The 1,5-diketone, 31, is the most stable primary adduct in the benzene system since it survives during the isolation process. It does, however, give dehydrogenation products (32 and 33) easily. It seems that the driving force for dehydrogenation of these cyclohexadienes which have two ketone substituents to benzene ring is very strong compared to the 1,5-diketone products from naphthalene and phenanthrene systems described later in this thesis.

The finding of 4-acetonylacetoephone (33), formed in the photoaddition of AABF$_2$ to benzene, has caused considerable uncertainty concerning the occurrence of the otherwise straightforward mechanistic proposal. The para isomer 33 could arise from a [4+2] cycloaddition followed by dehydrogenation. The photoaddition of an excited state olefin to benzene or a similar addition involving a cyano substituted substrates generally gives 1,2-adducts.$^{76,77}$ A photoaddition involving excited state benzenes to an olefin can give all possible 1,2-, 1,3- and
1,4-adducts with retention of stereochemistry.\textsuperscript{78,79} In the present photocycloaddition, the excited singlet state of AABF\textsubscript{2} is not expected to be able to sensitize benzene by energy transfer nor to follow the [4+2] addition pattern. The photolysate has been carefully examined by GC-MS and \textsuperscript{1}H NMR analysis to show the absence of primary photoadducts other than 31. For a heavily functionalized system such as 31, many possible mechanisms can be considered for this transformation. We tentatively conclude that the para-isomer 33 is derived from 31 by an acid-catalyzed reaction.

\textbf{3.1.3 Mechanistic Aspect of the Photoaddition}

Having defined the overall reaction pattern, we wish to discuss the primary photoreaction step of the BF\textsubscript{2} complex photoaddition to benzene derivatives. As indicated by the absorption curves of ACHBF\textsubscript{2} and other complexes (Figure 2-1), it seems clear that the excitation of the BF\textsubscript{2} complexes is the primary step in the initiation of the photoreaction under the irradiation conditions with a Pyrex filter (cut off at 290 nm). ACHBF\textsubscript{2} shows only weak fluorescence emission. This poses a severe limitation to fluorescence quenching experiments. The weak fluorescence of these BF\textsubscript{2} complexes suggests a fast intersystem crossing or internal conversion and therefore a short singlet excited state lifetime.

The quantum yields for the formation of the enol ether, 17, can be measured readily by GC analysis. The lack of diene quenching of the quantum yield and the failure to sensitize the reaction by benzophenone suggest that the excited singlet state of BF\textsubscript{2} complex undergoes the photoaddition. This is confirmed by the heavy atom effect. 1,2-
Dibromoethane promotes the intersystem crossing of the singlet state of ACHBF₂ to its triplet state and thereby reduces the quantum yield of 17.

The plots (Figure 2-9) of the reciprocal of the quantum yields of the formation of 17 against the reciprocal of the concentrations of benzene give straight lines for both acetonitrile and dioxane solvents. The $k_{qt}$ values obtained should represent the product of the reaction rate constant and lifetime of the singlet excited ACHBF₂. The low $k_{qt}$ values of 0.032 in CH₃CN and 0.067 in dioxane means that both $k_q$ and $\tau$ or one of them are small. As mentioned above, a short lifetime for the singlet excited state of ACHBF₂ is suggested by the weak fluorescence. While $k_{qt}$ values are small, quantum yields in the presence of high concentrations of benzene are reasonably good as shown by the limiting quantum yields of 0.12 and 0.19. The UV spectrum of a mixture of ACHBF₂ and benzene does not show any evidence for the formation of a ground state complex. Taken together, these results suggest that the observed limiting quantum yield arises from a long lifetime of the exciplex between ACHBF₂ and benzene ($E_{1/2}^{OX} = 2.11 \text{ V}^{36}$). The attempted photoreaction of ACHBF₂ and anisole ($E_{1/2}^{OX} = 1.34 \text{ V}^{36}$) does not give any photoadduct but only a color change; hence, it is considered that the exciplex is dissociated into a radical-ion pair by an electron transfer process.

3.2 Photocycloaddition of AABF₂ to Naphthalenes and Phenanthrenes

In analogy to the photocycloaddition of AABF₂ to benzene, all the primary photoproducts obtained from the photolyses of AABF₂-polycyclic
arene systems are 1,5-diketone products. The initial photoreaction gives a cyclobutane adduct that undergoes a spontaneous ring opening, leading to the 1,5-diketone product. As the resonance structure of the chelate ring no longer exists in such an intermediate (cyclobutane), the BF₂ complex is hydrolyzed readily by trace amounts of water in the reaction mixture or during the work-up. These 1,5-diketone products are, however, thermally stable and can be isolated.

The chemical outcome of the photolysis is the same as that from the irradiation of acetylacetone (AAH) and the corresponding arenes. For example, methyl 2-naphthalenecarboxylate (2-NpCO₂Me, 12) was reported⁵⁴ to regiospecifically add to AAH to give the cycloadduct, 14. (Scheme 1-13). Compound 14 was also obtained from the photoaddition of AABF₂ to 2-NpCO₂Me.

In contrast to AAH,⁵⁵ AABF₂ exhibits some significant features in its photocycloaddition to polycyclic arenes. These are summarized below: i) the reaction takes place in ether, while no photocycloaddition is observed when acetonitrile is used as the solvent; ii) the rate of the photoaddition is much faster using AABF₂ but there is lack of regiospecificity; iii) some naphthalene derivatives, such as 1-NpOMe and 2-NpOMe which undergo facile photoaddition to AAH, are found to be photochemically unreactive towards AABF₂ in ether and acetonitrile.

Naphthalenes

It was observed that the photocycloaddition of naphthalene to AABF₂ gave a major product, 34, with acetyl at the 1-position (Scheme 2-5). The coupling constant between the two allylic protons Ha and Hb is
7.6 Hz, which indicates a cis-geometry for the two protons.\textsuperscript{80} This is in agreement with a concerted mechanism. The stereochemistry with regard to AABF\textsubscript{2} (cyclobutane ring) is totally lost during the ring opening.

Similar to the reported photoadditions\textsuperscript{55} of 1-substituted naphthalenes to AAH, the cycloaddition of AABF\textsubscript{2} to 1-NpCl also occurs preferentially at the 7,8-position of 1-NpCl giving one major product, 35, (page 34). The regiochemistry of compound 35 was determined according to the previous work in our lab.\textsuperscript{81} Again the acetyl group is located at the 1-position. The stereochemistry of 35 is cis for the two allylic protons as indicated by their coupling constant of 7.3 Hz.

In contrast to the addition pattern to 1-NpCl, AABF\textsubscript{2} undergoes [2+2] cycloaddition to 2-NpCO\textsubscript{2}CH\textsubscript{3} at the 1,2-position of 2-NpCO\textsubscript{2}CH\textsubscript{3} upon photolysis. Two photoproducts 13 and 14 (regioisomers, page 35) were obtained in a ratio of 2:3. Although the coupling constant is not available, the stereochemistry of products 13 and 14 is assumed to be cis of the two ketone chains on the basis of the previously proposed concerted mechanism.

The absorption spectra of naphthalenes and AABF\textsubscript{2} overlap in the studied range, which makes selective irradiation impossible.

Phenanthrenes

The photocycloaddition of AABF\textsubscript{2} to phenanthrene (PN) and 9-cyanophenanthrene (9-PNCN) yields 9,10-addition products exclusively. 9-PNCN gives two regioisomers, 41 and 42, (page 38) in a 1:1 ratio. In the case of PN, two stereoisomers (cis and trans) were formed in a ratio of about 8:1 and their structures were assigned by comparison of the H-H
coupling constants \((J_{9,10})\) between the two benzylic protons \((J = 4.6 \, \text{Hz for one isomer and } 1.3 \, \text{Hz for the other})\) with literature values for 9,10-disubstituted 9,10-dihydrophenanthrene.\(^{82,83}\) The large coupling constant is reported for the cis geometry and the smaller coupling constant for the trans analog. Treatment of a mixture of cis (38) and trans (39) products with NaOCH\(_3\) showed that only the cis-isomer gave an aldol condensation product 40 while trans-isomer 39 remained unchanged during the reaction. When the same mixture was treated with hydrochloric acid, the cis-isomer was converted to the trans analog and 40 was only formed in a small amount. The mechanism for the formation of 40 is presented in Scheme 3-3. Although there is a possibility that the aldol condensation product may be 55, the observed coupling, which appeared as a line broadening, between olefin hydrogen \((\delta = 6.05 \, \text{ppm})\) and one of the methylene protons \((\delta = 3.80 \, \text{ppm})\) favors structure 40.

Scheme 3-3
The photoaddition of phenanthrene (PN) to AABF$_2$ also occurred in the same efficiency when RPR-3500 Å lamps were used. When the solution of PN (0.020 M) and AABF$_2$ (0.040 M) was irradiated with RPR-3500 Å lamps, more than 95% of the incident light was absorbed by phenanthrene ($\epsilon \approx 220$ in the 310-345 nm region$^{84}$), therefore the reaction occurs most probably from the excited state of PN since energy transfer from PN ($E_S = 83.5$ and $E_T = 62$ kcal/mol)$^{69}$ to AABF$_2$ is impossible. At this stage we can not rule out the possibility that the trans-isomer 39 is formed through an acid-catalyzed isomerization of the cis-isomer 38. The control experiment showed that 39 could be detected by GC during the early stage of the photoreaction. In fact, the photoreaction of PN to AAH afforded the trans-isomer 39 as the predominant photoproduct,$^{55}$ presumably via a non-concerted mechanism, in the less acidic system. Therefore, we suggest that the trans-isomer 39 in the photoaddition of PN to AABF$_2$ is formed as a primary photoadduct through a non-concerted mechanism.
CHAPTER 4 EXPERIMENTAL

4.1 General Conditions

If not otherwise stated, the experimental procedures were used under the following conditions. Melting points (m.p.) were measured on a Fisher-Johns melting point apparatus and were uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer 559B spectrophotometer (neat film or KBr pellet). Ultraviolet and visible spectra (UV/VIS) were recorded on a Varian Cary-210 spectrophotometer. Gas chromatography-mass spectra (GC-MS) were recorded on a Hewlett-Packard 5985 GC-MS system, equipped with a DB-1 capillary column (30 m x 0.25 mm), by either electron impact (EI) or chemical ionization (CI). Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker WM-400 spectrometer. Chemical shifts ($\delta$) are reported in parts per million (ppm) using tetramethylsilane (TMS) as a standard and coupling constants (J) in Hz. The coupling patterns are presented as s (singlet), d (doublet), t (triplet), q (quartet), dd (doubletted doublet), dt (doubletted triplet) and m (multiplet). The chemical shifts of $^{13}$C NMR spectra are also reported as $\delta$ value in ppm relative to TMS. Elemental analyses were carried out by Mr. M. K. Yang on a Carlo Erba Model-1106 Elemental Analyzer. Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5790A gas chromatograph (FID), equipped with an HP-1 capillary column (12 m x 0.2 mm) and a Hewlett-Packard 3390A chart integrator. Retention times (Rt) are reported in minutes (min). Phosphorescence and fluorescence spectra were taken on a Perkin-Elmer MFP 44B spectrophotometer and were uncorrected. All sample solutions for
quantitative studies were deaerated as follows: a sample solution placed in a test tube or a fluorescence cuvette was sealed with a rubber septum and purged with nitrogen for 15 min through a syringe needle. Flash column chromatography was carried out using 230-400 mesh silica gel (Merck) with ethyl acetate/hexanes as eluant.

4.2 Chemicals

For photochemical reactions, reagent grade solvents were distilled prior to use. 1,4-Dioxane was distilled from sodium. Benzene and toluene were distilled in the presence of sodium after being washed with concentrated H$_2$SO$_4$, water and dried over CaCl$_2$. Commercial spectroscopic grade or distilled solvents (over P$_2$O$_5$) were used for spectroscopic analysis.

Methyl 2-naphthalenecarboxylate (2-NpCO$_2$Me) was prepared by esterification of 2-naphthalenecarboxylic acid (Aldrich).$^{85}$

Commercially available reagents, 1-methoxynaphthalene (1-NpOMe, Aldrich), 2-methoxynaphthalene (2-NpOMe, Aldrich), 2-acetylnaphthalene (Matheson), phenanthrene (PN, Matheson) and 9-xanthone (Aldrich) were purified by distillation, recrystallization or vacuum sublimation prior to use. 1,3-Cyclohexadiene (Aldrich), 1,3-pentadiene (Matheson), tributylamine (Matheson), pyridine (Fischer), 1,2-dibromoethane (Aldrich), and all benzene derivatives were distilled before use. 1,3-Pentanedione (AAH, Aldrich), 2-acetylcyclohexanone (ACHH, Aldrich), 2-acetylcyclopentanone (ACPH, Aldrich), benzophenone (Fischer), benzhydrol (Matheson), naphthalene (Np, Bake & Adamson), 1-chloronaphthalene (1-
NpCl, Matheson), 1-methylnaphthalene (Kodak), 9-cyanophenanthrene (9-PNCN, Aldrich), acetone (Fischer), hexadecane (Sigma), tetradecane (Kodak), dodecane (Matheson) and boron trifluoride-ether (BF$_3$OEt$_2$, BDH) were used as supplied.

### 4.3 Photolysis Apparatus and Methods for Quantum Yield Determination

Three different types of photolysis apparatus were employed in the experiments.

**Apparatus I**

This apparatus consists of a 12-tube merry-go-round (a Rayonet Photochemical Reactor) equipped with RPR-3000 Å lamps (16 x 21 watt) or RPR-3500 Å lamps (16 x 24 W) and a fan to circulate the air providing a constant temperature at 31 ± 1°C. Quartz tubes (1.1 x 11 cm, made by the glass blowing shop at SFU) or Pyrex tubes (No. 9820, 1.2 x 10 cm) were used as photoreaction cells.

**Apparatus II**

This apparatus consists of a long cylindrical fused-Pyrex vessel (40 mL) fitted with two side arms (inlet) as shown in Figure 4-1. The light source was a 200 W Hanovia medium pressure mercury lamp (645A 36) inserted into the water-cooled jacket. Nitrogen or oxygen was bubbled 30 min before and during the irradiation.
Figure 4-1  Apparatus II: a cylindrical fused-Pyrex photoreactor.
Apparatus III

This apparatus was a long cylindrical reaction vessel (180 mL, Pyrex glass) fitted with a side arm, into which a condenser was inserted. A Pyrex water-cooled lamp housing was inserted into the vessel. Nitrogen or oxygen was bubbled into the photolysate through an inlet tube. The light source was a 200 W Hanovia medium pressure mercury lamp (645A 36).

Methods for quantum yield determination

Unless specified, the following procedures were followed for preparation of actinometer solution, light intensity determination and quantum yield determination.

Actinometer

The actinometer solution was prepared as follows. Benzophenone (456 mg, 2.50 mmol) and benzhydrol (921 mg, 5.00 mmol) were dissolved in 25 mL of benzene, respectively. An aliquot (3.0 mL) from each of the above stock solutions was pipetted into a test tube to give the actinometer solution. 5.0 mL of the actinometer solution containing benzophenone (0.050 M) and benzhydrol (0.10 M) were purged with nitrogen for 10 min and then irradiated with sample solutions in Apparatus I for 5 min. This benzophenone/benzhydrol actinometer system is known to have the quantum yield of 0.74.86 The absorbance of benzophenone at 342 nm was measured in 0.10 cm optical path cells before and after the irradiation, respectively. The light intensity $I_0$ was calculated using absorbance change ($\Delta A$) by equation 4-1.
where \( \varepsilon_{342} = 140 \text{ M}^{-1} \text{ cm}^{-1} \) is the extinction coefficient of benzophenone at 342 nm, \( \Delta t \) is the elapsed irradiation time in minute, and \( L = 0.10 \) cm, \( V \) is volume in mL.

Quantum yield was determined as follows.

**Method I**

Photolysates were analyzed by GC with tetradecane (\( C_{14}H_{30} \), for benzene system) or hexadecane (\( C_{16}H_{34} \), for phenanthrene system) as an internal standard (I.S., added into sample solution before irradiation). Concentration of a product (P) or a starting material (S.M.) was calculated according to equation 4-2 and the corresponding quantum yield \( \Phi \) was calculated from equation 4-3.

\[
[P] = R \cdot f \cdot [I.S.] \tag{4-2}
\]

where, \( R \) is the GC peak area ratio of the product over I.S. and \( f \) is the GC response factor for the product (P) which is determined from the slope of the corresponding calibration curve.

\[
\Phi = \frac{\text{Moles of P formed}}{I_0 \cdot \Delta t} = \frac{[P] \cdot V \cdot 10^{-3}}{I_0 \cdot \Delta t} \tag{4-3}
\]
where $I_0$ is the light intensity from equation 4-1, $\Delta t$ (min) is irradiation time and $V$ (mL) is volume of the solution.

Method II

In the case of photoreaction of ACHBF$_2$ and benzene, a control solution (5.0 mL) as a secondary actinometer as well as one of the sample solutions was prepared containing ACHBF$_2$ (0.030 M), benzene (2.01 M), and tetradecane (0.010 M, as I.S.) in 1,4-dioxane. The quantum yield $\Phi_{sec}$ of this secondary actinometer for product formation was determined to be 0.021 according to Method I in Apparatus I using RPR-3000 Å lamps and Pyrex tubes. The sample solutions were irradiated with this secondary actinometer and the photolysates were analyzed by GC to give $R_{sec}$ (GC peak area ratio of product over I.S. for the secondary actinometer solution) and $R_{sample}$ (GC peak area ratio of product over I.S. for the sample solution), which should be proportional to their quantum yields. The quantum yield of a sample solution $\Phi_{sample}$ based on product formation was calculated from equation 4-4.

$$\Phi_{sample} = \Phi_{sec} \frac{R_{sample}}{R_{sec}} \quad (4-4)$$

4.4 Spectroscopic Studies

4.4.1 Preparation of 1,3-Diketonatoboron Difluorides

1,3-Diketonatoboron difluorides, e.g. acetylacetonatoboron difluoride (AABF$_2$), (2-acetylcyclohexanonato)boron difluoride (ACHBF$_2$) and (2-acetylcyclopentanonato)boron difluoride (ACPBF$_2$), were prepared from the corresponding 1,3-diketones.
(a) (2-Acetylcylohexanonato)boron Difluoride (ACHBF₂, 2)

ACHBF₂ was prepared according to the method described by Smith.⁸⁷

BF₃.OEt₂ (18.5 g, 0.13 mol) was added to a stirred solution of 2-acetylcyclohexanone (ACHH, 10.6 g, 0.076 mol) in methylene chloride (130 mL) at room temperature under nitrogen. After 2 hours, the resulting orange solution was washed with water until pH = 7 and dried over MgSO₄. The solvent was removed under reduced pressure. The crystalline product was then recrystallized twice from CH₂Cl₂/hexanes to afford white prism crystals of (2-acetylcylohexanonato)boron difluoride⁸⁸ (9.9 g, yield 70%). m.p., 79-79.5°C. MS (EI), m/e (relative intensity): 188(M⁺, 31), 173(M⁺-CH₃, 100), 169(M⁺-F, 17) and 145(M⁺-COCH₃, 27). IR (KBr), νmax: 2962(s), 2877(m), 1587(vs), 1521(vs), 1412(s), 1368(vs), 1335(vs), 1307(s), 1205(vs), 1151(vs), 1050(vs), 825(s) and 669(m) cm⁻¹. ¹H NMR (400 MHz, CDC1₃), δ: 1.76(m, 4H), 2.29(s, 3H, COCH₃), 2.38(t, 2H, CH₂, J = 7 Hz) and 2.57(t, 2H, CH₂, J = 7 Hz) ppm. ¹³C NMR (CDC1₃), δ: 191.85, 189.97, 108.95, 32.37, 23.06, 22.13, 21.85 and 20.83 ppm.

(b) (2-Acetylcylopentanonato)boron Difluoride (ACPBF₂, 4)

To a stirred solution of 2-acetylcylopentanone (ACPH, 7.14 g, 0.056 mol) in methylene chloride (60 mL) was added BF₃.OEt₂ (12.7 g, 0.089 mol) in portions under nitrogen sweeping. The resulting red solution was stirred at ambient temperature for 2 hours, and then washed with water until free of boron trifluoride. After dried over MgSO₄, the solvent was removed under reduced pressure. The yellow crystals obtained were recrystallized twice from Et₂O-hexanes giving yellowish crystals of (2-acetylcylopentanonato)boron difluoride⁸⁹ (6.2 g, yield 63%). m.p., 65.5-66°C. MS (EI), m/e (relative intensity): 174(M⁺, 24), 159(M⁺-CH₃,
105, 155(M⁺-F, 16), 131(M⁺-COCH₃, 14), 118(16), 79(17), 65(15) and 43(32). IR (KBr), vmax: 2968(m), 2921(m), 1606(vs), 1543(vs), 1386(vs), 1348(vs), 1313(vs), 1197(vs), 1154(vs), 1028(vs), 970(s), 814(m) and 783(m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃), δ: 2.11(m, 2H), 2.28(s, 3H, CH₃), 2.68(t, 2H, CH₂, J = 7 Hz) and 2.77(t, 2H, CH₂, J = 7 Hz) ppm. ¹³C NMR (CDCl₃), δ: 199.13, 186.96, 112.72, 34.45, 25.13, 22.24 and 20.00 ppm.

(c) Acetylacetonatoboron Difluoride (AABF₂, 1)

AABF₂ was prepared according to the literature.¹³ Into a 100 mL round-bottom flask equipped with a condenser, a dropping funnel and nitrogen sweep, was placed boron trifluoride-ether (BF₃·OEt₂, 35.5 g, 0.25 mol). Acetylacetone (AAH, 25 g, 0.25 mol) was then added dropwise to the stirred solution. While hydrogen fluoride was evolved, the reaction mixture became warm and brown in color. After the evolution of HF ceased, the mixture was distilled under reduced pressure to give an orange liquid, bp 163-167°C (3 mmHg), which solidified upon scratching. Recrystallization four times from anhydrous ether gave white crystals of AABF₂ (16.6 g, 45%). m.p., 42.5-43°C (lit.¹¹ 43°C).

4.4.2 Absorption Spectra

Solutions of ACHBF₂ (1.0 x 10⁻⁴ M) in various solvents such as hexanes, ether, chloroform, acetonitrile and benzene (0.95 x 10⁻⁴ M) were prepared and the absorption spectra were measured. The absorption spectra of ACPBF₂ (1.0 x 10⁻⁴ M in acetonitrile) and AABF₂ (1.0 x 10⁻⁴ M in ether) were also recorded. The spectra are shown in Figure 2-1. Similarly, UV spectra of the corresponding 1,3-diketones (1.0 x 10⁻⁴ M
in acetonitrile) were measured. The absorption data are given in Table 2-1.

4.4.3 Attempts to Detect Ground State Complex

A stock solution of ACHBF$_2$ (0.060 M) and a stock solution of benzene (4.02 M) were prepared in 1,4-dioxane and kept in dark prior to use. Differential absorption spectrum was recorded using a pair of double compartment cells. A typical run is shown in Figure 4-2. No absorption peak was observed.

For recording baseline

Reference cell
[ACHBF$_2$]=0.060 M
[Benzene]=4.02 M

For recording spectrum

Sample cell
[ACHBF$_2$]=0.060 M
[Benzene]=4.02 M

[ACHBF$_2$]=0.030 M
[Benzene]=2.01 M

Figure 4-2 A pair of double compartment cells for differential absorption spectra.
4.4.4 Emission Spectra of ACHBF₂

A solution of ACHBF₂ (0.030 M), ACPBF₂⁻ (0.030 M) or AABF₂ (0.030 M) in ether was prepared. Phosphorescence spectra of ACHBF₂ (Figure 4-3) and ACPBF₂ were measured at 77 K in a quartz phosphorescence tube using undegassed solution. No phosphorescence was observed for AABF₂. Sample solutions for fluorescence measurements of ACHBF₂ and ACPBF₂ were prepared in acetonitrile (2.0 x 10⁻⁴ M) and purged with nitrogen for 10 min prior to use.

![Figure 4-3 Phosphorescence spectrum of ACHBF₂ (0.03 M) in ether at 77 K. λ_ex = 330 nm, S_ex = 6 nm, S_em = 3 nm.](image-url)

Figure 4-3 Phosphorescence spectrum of ACHBF₂ (0.03 M) in ether at 77 K. λ_ex = 330 nm, S_ex = 6 nm, S_em = 3 nm.
4.5 The Photocycloadditions of 1,3-Diketonatoboron Difluorides to Aromatic Compounds

4.5.1 General Procedures

Unless specified, the following procedures were followed. A solution of 1,3-diketonatoboron difluoride and an aromatic compound was irradiated in Apparatus II under nitrogen. Alternatively, a solution was placed in tubes and purged with nitrogen for 10 min, then irradiated in Apparatus I. During the irradiation, a sample of the photolysate was withdrawn at intervals for GC analysis. The irradiation was stopped when all the starting material was consumed or the yield of the product did not increase by GC analysis. The photolysate was washed with water twice and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the residue was flash chromatographed to afford products.

4.5.2 ACHBF₂ to Benzene

Under nitrogen

A solution of ACHBF₂ (760 mg, 4.0 mmol) in benzene (80 mL) was divided into two portions and each of which was irradiated separately in Apparatus II for 2.5 hours to give a cloudy yellow solution. The photolysate was shown to give four GC peaks (at 170°C) at Rt 0.91, 1.99 (ACHBF₂), 2.38 and 3.43 min in a GC peak area ratio of 15:1:69:2. The product at Rt 0.91 min (parent mass: 120) was identified to be acetophenone by a co-injection in GC with an authentic sample and by GC-
MS \((M^+ = 120)\). The photolysate was washed successively with 2 x 25 mL water and 25 mL saturated aqueous sodium chloride solution; then it was dried over MgSO₄. The yellow residue was flash chromatographed by using 5% ethyl acetate in hexanes as the eluant to give a yellowish oily compound of 6-methyl-2,3,4,6-tetrahydro-1H-dibenzo[b,d]pyran (17, 256 mg, 32%). UV (n-heptane), \(\lambda_{\text{max}}\): 285 nm \((\varepsilon, 13000)\). Anal. Calcd. for 17 \((C_{14}H_{16}O)\): C, 83.96; H, 8.05. Found: C, 84.26; H, 8.13. The spectroscopic data of 17 are listed in Table 4-1 to Table 4-4.

Photolysis under air

A solution of ACHBF₂ (670 mg, 3.56 mmol) in 43 mL benzene and 90 mL acetonitrile was placed in Apparatus III and irradiated for 4 hours resulting an orange solution. GC analysis \((170^\circ C)\) showed three major peaks at Rt 0.91 (acetophenone, 40%), 1.55 (10%) and 3.43 min (37%). The photolysate was treated according to the general procedures. Flash column chromatography of the residue by using 7% ethyl acetate in hexanes and 20% ethyl acetate in hexanes, respectively, gave two fractions. The first fraction contained 2-phenyl-1-cyclohexen-1-ol acetate\(^\text{63}\) (20, Rt 1.55 min, 12 mg, yield 1.6%) as shown by its spectroscopic data (Tables 4-1 to 4-4). The second fraction contained 1-methyl-3,4,5,6,7,8-hexahydro-1H-2-benzoxecin-3,8-dione (19, Rt 3.43 min, 130 mg, 15%), which was recrystallized from ether/hexanes to afford white crystals, m.p., 116.5-117.5°C. UV (MeOH), \(\lambda\) (nm): 258 (\(\varepsilon\) 323), 264 (\(\varepsilon\) 288), 295 (\(\varepsilon\) 73). Anal. Calcd. for 19 \((C_{14}H_{16}O_3)\): C, 72.39; H, 6.94. Found: C, 72.34; H, 6.88. The spectroscopic data of 19 are listed in Table 4-1 to Table 4-4. The structure of 19 was confirmed by X-ray crystallographic analysis as shown in Figure 2-5.
Photooxygenation of 17 to 19

A solution of 17 (298 mg, 1.49 mmol) in CH₃CN/CH₃OH (3:1 by volume, 40 mL) containing small amount of methylene blue (1 x 10⁻⁵ M, used as a sensitizer) was irradiated under an oxygen atmosphere for 75 min in Apparatus II equipped with a 200 watt medium pressure mercury lamp and a GWV filter to cut off light of λ<350 nm. GC analysis (170°C) of the photolysate showed one peak at Rt 3.43 min corresponding to 19. Upon removal of the solvent, the dark blue residue was dissolved in 10 mL ethyl acetate, and passed through a pipette filled with one inch silica gel to give a yellow solution. Evaporation of the solvent yielded 310 mg (yield 90%) of a yellow solid. Flash column chromatography of this crude product afforded white crystals of 19 (238 mg).

Material Balance

Material balance analysis is shown in Figure 2-4. A stock solution of ACHBF₂ (282 mg, 1.5 mmol), benzene (7.85 g, 0.1 mol) and tetradecane (as I.S., 99 mg, 0.5 mmol) in 1,4-dioxane (50 mL) was prepared. Nine sample solutions (5 mL each) containing ACHBF₂ (0.030 M), benzene (2.01 M) and tetradecane (0.010 M) were purged with nitrogen for 15 min and irradiated in Apparatus I using RPR-3000 Å lamps for various times (0.5 to 5.5 hours). GC analyses (170°C) showed four peaks for acetophenone (Rt 0.91 min), tetradecane (Rt 1.25 min), ACHBF₂ (Rt 1.99 min) and 17 (Rt 2.38 min). The relative response factor (f) for acetophenone, ACHBF₂ and 17 with respect to the internal standard were determined to be 2.10, 2.32 and 1.26, respectively, using the plot of A_S/A_I.S. against [S]/[I.S.] based on equation 4-6.
\[ \frac{A_S}{A_{I.S.}} = f \cdot \frac{[S]}{[I.S.]} \]  \hspace{1cm} (4-6)

where \( A_S \) and \( A_{I.S.} \) are the peak areas of the sample and the internal standard, respectively; \([S]\) and \([I.S.]\) are the concentrations of the sample and the internal standard, respectively.

4.5.3 \textit{ACHBF}_2 \textit{to Toluene}

\textbf{ACHBF}_2 \textit{to Toluene under Nitrogen}

A solution of \textit{ACHBF}_2 (932 mg, 4.96 mmol) in 120 mL toluene was divided into three portions; each was irradiated for 7 hours in Apparatus II. The yellow photolysate was analyzed by GC (180°C) to show three major peaks: Rt 1.01 (12%), 1.79 (ACHBF\(_2\), 19%) and 2.63 min (63%). The photolysate was treated according to the general procedures to give a yellow-green oily mixture (924 mg), which was flash column chromatographed on silica gel eluting with 5% EtOAc in hexanes to give two fractions. The first fraction provided an oil (249 mg, 24%) of Rt 2.63 min which was characterized to be a mixture of 6,8-dimethyl-2,3,4,6-tetrahydro-1H-dibenzo[b,d]pyran (21a) and 6,9-dimethyl-2,3,4,6-tetrahydro-1H-dibenzo[b,d]pyran (21b) in a ratio of ca. 1:1 by \( ^1\)H NMR analysis. For their spectroscopic data, see Tables 4-1 to 4-4.

The second fraction (Rt 1.01 min at 180°C) provided a mixture (42 mg, 6.3%) of 4-methyl acetophenone (22a) and 3-methyl acetophenone (22b). GC analysis at 100°C of the mixture gave two peaks at Rt 2.14 min (22a) and Rt 2.24 min (22b) in a ratio of ca. 1:1. The identifications of the two isomers were based on the spectroscopic data (see Table 4-1 to Table 4-3).
Photooxygenation of 21a and 21b

A solution of 21a and 21b (249 mg, 1.16 mmol) in 40 mL of CH$_3$CN/CH$_3$OH (3:1) containing methylene blue (1 x 10^{-5} M, used as a sensitizer) was irradiated under an oxygen atmosphere for 1.5 hours in Apparatus II equipped with a 200 W medium pressure mercury lamp and a GWV glass filter to cut off light of $\lambda<350$ nm. GC analysis (at 180°C) of the photolyzate showed one major peak at Rt 3.74 min and a minor peak at Rt 3.49 min in an area ratio of 8:1. After removal of the solvent, the dark blue residue was dissolved in 10 mL ethyl acetate and passed through a silica gel column (2 x 3 cm) to remove methylene blue. The yellow solution obtained was evaporated and the residue (295 mg) was flash chromatographed using 18% ethyl acetate in hexanes as the eluant to afford a mixture of 23a and 23b (171 mg, 59%), which were shown by $^1$H NMR to be 1,11-dimethyl-3,4,5,6,7,8-hexahydro-1H-2-benzoxecin-3,8-dione (23a) and 1,10-dimethyl-3,4,5,6,7,8-hexahydro-1H-2-benzoxecin-3,8-dione (23b) in a ratio of ca. 1:1. The spectroscopic data of 23a/23b are summarized in Tables 4-1 to 4-4.

4.5.4 ACHBF$_2$ to Methyl Benzoate

A solution of ACHBF$_2$ (205 mg, 1.09 mmol) and methyl benzoate (24, 5 mL) in acetonitrile (35 mL) was placed in Apparatus II equipped with nitrogen sweep and irradiated for 12.5 hours using a 200 W medium pressure mercury lamp. The yellow photolysate was analyzed by GC at 200°C to give a product peak at Rt 1.18 min (72%) in addition to ACHBF$_2$ peak at Rt 1.43 min (24%). After removal of the solvent under reduced pressure, the residue was flash chromatographed by first using 13% and
then 17% ethyl acetate in hexanes as eluants to afford a fraction (11 mg, yield 5.7%) with Rt 1.18 min at 200°C. GC analysis of this fraction at 110°C showed two peaks of Rt 5.87 min (25) and 6.03 min (26) in 1.5:1 ratio in addition to methyl benzoate (Rt 1.38 min, 9%). The products were determined to be methyl 3-acetyl benzoate (25) and methyl 4-acetyl benzoate (26) (Tables 4-1 to 4-3).

4.5.5 ACPBF₂ to Benzene

A solution of ACPBF₂ (371 mg, 2.13 mmol) and benzene (16 mL) in 24 mL anhydrous ether was placed in Apparatus II and irradiated for 45 min under nitrogen. GC analysis (at 160°C) of the cloudy yellowish photolysate gave no ACPBF₂ peak (Rt 1.68 min) but three product peaks at Rt 0.92, 2.22 and 2.39 min in a GC area ratio of 5:1:5. The peak of Rt 0.92 min was identified to be acetophenone by co-injection with an authentic sample. GC-MS (EI) analysis of the peak at Rt 2.22 min showed m/e (relative intensity): 186(M⁺, 27) and 171(M⁺-CH₃, 100), 128(13) and 115(11) suggesting a dehydration product (27) from the primary photoadduct of benzene to ACPBF₂. GC-MS of the unknown product peak at Rt 2.39 min gave its mass spectrum as follows: EI, m/e (relative intensity): 204(M⁺, 0.2), 186(M⁺-H₂O, 0.4), 161(M⁺-COCH₃, 9), 143(15), 126(47), 117(39), 105(M⁺-91, 39), 91(29), 84 (100) and 77 (20); CI, m/e (relative intensity): 205(M⁺+1, 78), 187(M⁺+1-H₂O, 44) and 121(100). These suggested that this product is a primary photoadduct (28) between benzene and ACPBF₂.

The above photolysate was filtered through silica gel (230-400 mesh, 2 x 3 cm), then the filtrate was washed with 2 x 25 mL water, 20
mL saturated aqueous NaCl solution and dried with MgSO₄. The residue, which gave an additional small peak on GC at Rt 2.58 min (2%) besides the two major peaks (Rt 0.92 and Rt 2.39 min), was flash chromatographed using 20% ethyl acetate in hexanes to give two fractions. The first fraction contained acetophenone (75 mg, yield 29%) and the second one contained 72 mg (yield 17%) of 2-(2-acetylphenyl)-cyclopentanone (29, Rt 2.98 min at 160°C). The spectroscopic data of 29 are given in Table 4-1 to Table 4-4.

**In the Presence of Tributylamine**

A solution of ACPBF₂ (330 mg, 1.9 mmol), tributylamine (0.5 mL, 2.1 mmol) and benzene (10 mL) in ether (30 mL) was irradiated in Apparatus II for 55 min under nitrogen sweep. GC analysis (160°C) of the cloudy photolysate showed three product peaks at Rt 0.92 (CH₃COPh), 2.22 (27) and 2.39 (28) min in an area ratio of 1:2:7. The photolysate was washed with water (2 x 25 mL), saturated aqueous sodium chloride solution (25 mL) and dried over MgSO₄. Upon removal of the solvent under reduced pressure, GC analysis of the residue showed 79% of 28 in the mixture. ¹H NMR was taken immediately for this crude product. It showed four protons at δ 5.97 ppm for the olefinic hydrogens and two allylic protons at chemical shifts 3.05 and 3.45 ppm.

**4.5.6 Photolysis of AABF₂ to Benzene**

A solution of AABF₂ (620 mg, 4.19 mmol) and benzene (20 mL) in anhydrous ether (60 mL) was divided into two portions and each of which was irradiated under nitrogen in Apparatus II with a 200 W medium
pressure Hanovia lamp. GC analysis (at 120°C) of the reaction mixture during the irradiation (every 20 min) showed three major peaks at Rt 1.17 (acetophenone), 1.46 (AABF₂) and 2.69 min (31). The irradiation was stopped at 120 min when the peak area ratio of Rt 2.69 min started to decrease and that of acetophenone (Rt 1.17 min) started to increase. GC analysis of the final colorless photolysate showed 50% AABF₂ survived and 39% of 31 formed along with 11% acetophenone (GC peak area ratio). The photolysate, to which 0.3 mL Bu₃N was added, was washed with water (2 x 25 mL) and saturated aqueous sodium chloride solution (25 mL), and dried over MgSO₄. The solvent was removed under vacuum, and ¹H NMR was taken immediately for this crude product. GC showed there was a major peak of 31 accompanied by a small new peak at Rt 3.81 min (32). The residue was flash chromatographed by using 27% ethyl acetate in hexanes as eluant to afford 5-acetyl-6-(2-oxopropyl)-1,3-cyclohexadiene (31, 23.5 mg, yield 3%); this fraction was contaminated by 12% (2-acetylphenyl)-2-propanone (32) as shown by GC and ¹H NMR analyses. The spectroscopic data of 31 are listed in Table 4-1 to Table 4-4.

A similar photolysis was run using a solution of AABF₂ (310 mg, 2.09 mmol) in 10 mL benzene and 30 mL anhydrous ether under the same conditions as described above. GC analysis of the colorless photolysate showed that 46% of AABF₂ was survived and 41% of Rt 2.69 min was formed along with 8% acetophenone (GC peak area ratio). The photolysate was treated according to the general procedures. Upon removal of the solvent, the brown residue (110 mg) was subjected to flash column chromatography. When 40% ethyl acetate in hexanes was used, a fraction (7.8 mg, yield 2%) containing two GC peaks of Rt 3.81 and 6.45 min (120°C) was obtained in a 1:1 ratio (by ¹H NMR spectroscopy). The
mixture were identified to be (2-acetylphenyl)-2-propanone\textsuperscript{67} (32) and (4-acetylphenyl)-2-propanone\textsuperscript{68} (33) based on their spectroscopic data (Table 4-1 to Table 4-4).

Two solutions containing AABF\textsubscript{2} (8.8 mg, 0.059 mmol) and dodecane (as I.S., 5.0 mg, 0.029 mmol) in benzene/ether (2 ml, 1:1 by volume) were prepared in Pyrex tubes; No. 2 solution also contained pyridine (6 mg, 0.076 mmol). The solutions were irradiated with RPR-3000 Å lamps in Apparatus I for 3 hours and analyzed by GC (120°C) at 1.5 hour interval. GC showed three major peaks at Rt 1.17 (acetophenone), 1.46 (AABF\textsubscript{2}) and 2.69 (31) min; the R value (GC peak area ratio of product or starting material over I.S.) was calculated for each peak and given in Table 2-2.

4.5.7 Naphthalene to AABF\textsubscript{2}

A solution of naphthalene (Np, 210 mg, 1.64 mmol) and AABF\textsubscript{2} (480 mg, 3.24 mmol) in ether (50 mL) placed in 8 quartz tubes was irradiated for 28 hours in Apparatus I equipped with RPR-3000 Å lamps. GC analysis (at 180°C, 25 m x 0.2 mm HP-1 capillary column) of the photolysate showed a peak of Np (73%, Rt 1.90 min), a major product peak at Rt 4.90 min (34, 17%) and additional two peaks at Rt 3.03 and 3.24 min (2.4% and 4.5%, respectively). The residue was flash chromatographed by using 25% ethyl acetate in hexanes as eluant to give a yellow oily compound (36 mg, yield 36% based on the consumed Np) of 1-acetyl-1,2-dihydro-2-(2-oxopropyl)-naphthalene (34, Table 4-1 to Table 4-4). GC-MS (CI) spectra of both peaks at Rt 3.03 and 3.24 min gave 171 (M\textsuperscript{+}+1, 100) suggesting 1- and 2-acetylnaphthalenes.
4.5.8 1-Chloronaphthalene to AABF₂

A solution of 1-chloronaphthalene (1-NpCl, 181 mg, 1.11 mmol) and AABF₂ (296 mg, 2 mmol) in ether (25 ml) was placed in 5 quartz tubes and irradiated for 15.5 hours in Apparatus I using RPR-3000 Å nm lamps. The yellow photolysate was analyzed by GC (at 200°C, 25 m x 0.20 mm HP-1 capillary column) giving a mixture with Rt 2.05 (1-NpCl, 34%), 3.26 (unknown, 7%), 3.37 (unknown, 10%), 4.75 (35, 26%) and 5.01 min (unknown, 10%). The residue was flash chromatographed with 18% ethyl acetate in hexanes as eluant to afford a yellow oil (35) (41 mg, yield 21% based on the consumed 1-NpCl) of 1-acetyl-8-chloro-1,2-dihydro-2-(2-oxopropyl)-naphthalene. The spectroscopic data of 35 are given in Tables 4-1 to 4-4. GC-MS analyses (CI) of the products at Rt 3.26 and Rt 3.37 min both gave m/e = 205 (M⁺+1, 100) as their parent masses, which suggested that the acetylation products of 1-NpCl were formed. GC-MS (CI) of the unknown peak at Rt 5.01 min gave m/e 265 (M⁺+1, Cl₁₃⁰, 8), 263(M⁺+1, Cl₁₃⁵, 26), 207(M⁺+1-CH₃COCH₃, Cl₁₃⁷, 32), 205(M⁺+1-CH₃COCH₃, Cl₁₃⁵, 100), suggesting another photoadduct between 1-NpCl and AABF₂.

4.5.9 Methyl 2-Naphthalenecarboxylate to AABF₂

A solution of 2-NpCO₂CH₃ (341 mg, 1.83 mmol) and AABF₂ (467 mg, 3.16 mmol) in ether (65 mL) was placed in 11 quartz tubes and was irradiated in Apparatus I with RPR-3500 Å lamps. Upon irradiation for six hours, the resulting yellowish photolysate was analyzed by GC (200°C, 25 m x 0.20 mm HP-1 capillary column) giving four major peaks at Rt 2.76 (2-NpCO₂CH₃, 10%), 4.93 (13, 17%), 5.15 (14, 31%) and 5.89 min (36, unknown, 13%); in addition, several other peaks (trace amount)
between Rt 8 and 11 min were detected. The residue was flash chromatographed by using 30% ethyl acetate in hexanes as the eluant to afford the following compounds, a yellow oil (78 mg, 15%) of methyl 2-acetyl-1,2-dihydro-1-(2-oxopropyl)-2-naphthalenecarboxylate (14), a slightly yellow powder (53 mg, 10%) of methyl 1-acetyl-1,2-dihydro-2-(2-oxopropyl)-2-naphthalenecarboxylate (13), and a white solid compound 36 (35 mg, 8%). 13 was recrystallized from cyclohexane to afford white crystals, m.p. 84-85°C. The GC-MS of 36 [CI, m/e = 229 (M+1, 100)] and its 1H NMR spectrum [100 MHz, CDCl3, 2.75(s, 3H), 4.00(s, 3H), 7.89-8.26(m, 4H) and 8.49-8.73 (m, 2H) ppm] suggested its structure as methyl 1-acetyl-2-naphthalenecarboxylate. The spectroscopic data of 13 and 14 are summarized in Table 4-1 to Table 4-4.

4.5.10 Phenanthrene to AABF2

Photocycloadditions

A solution of phenanthrene (PN, 191 mg, 1.1 mmol) and AABF2 (302 mg, 2.0 mmol) in anhydrous ether (50 mL) was placed into 8 quartz tubes and purged with nitrogen for 10 min before irradiation. The solution was irradiated in Apparatus I equipped with RPR-3000 Å lamps for 11 hours. GC analysis (at 230°C, 25 m x 0.2 mm HP-1 capillary column) of the colorless photolysate showed that 16% of PN (Rt 2.59 min) was survived and one major product of Rt 5.14 min (38, 81%) was formed along with a minor product of Rt 4.53 min (39, 2%). After ether was evaporated under vacuum, the residue was flash chromatographed by using 15% and 17% ethyl acetate in hexanes as eluants to give two fractions. The first one afforded 141 mg (46%) white crystals of cis-9-acetyl-9,10-dihydro-10-(2-
oxopropyl)-phenanthrene (38), which was recrystallized from EtOAc/hexanes to give colorless crystals, m.p. 119-120°C. Anal. Calcd. for 38 (C_{19}H_{18}O_{2}): C, 81.98; H, 6.52. Found: C, 81.77; H, 6.45. The second fraction contained 17 mg (5.6%) of trans-9-acetyl-9,10-dihydro-10-(2-oxopropyl)-phenanthrene (39). A mixture (40 mg, 13%) of 38 and 39 was also obtained in a 1:2 ratio. The spectroscopic data of the two compounds are listed in Table 4-1 to Table 4-4.

This experiment was repeated using PN (230 mg, 1.29 mmol) and AABF_{2} (220 mg, 1.49 mmol) in 55 mL ether (9 quartz tubes, nitrogen purged). The solution was irradiated for 6.5 hours with RPR-3500 Å lamps in Apparatus I. GC analysis under the same conditions showed PN (10.5%), 38 (65.7%) and 39 (22.1%). Work-up as the above gave a mixture of 38 and 39 (258 mg, yield 72%) in a 1.0:1.3 ratio.

Aldol condensation

To a stirred solution of 38 (62%) and 39 (30%) (82 mg, 0.29 mmol) in methanol (40 mL), sodium methoxide (NaOMe) solution was added. After 1.5 hours, 40 mL water was added and the resulting solution was extracted with methylene chloride (3 x 20 mL). The combined CH_{2}Cl_{2} extract was washed with saturated sodium chloride solution and dried with MgSO_{4}. GC analysis (at 230°C, 25 m x 0.2 mm HP-1 capillary column) of the solution showed peaks of 39 (Rt 4.53 min, 34%), 38 (Rt 5.14 min, 1%), and one major new compound (40, Rt 6.46 min, 60%) as well as a minor new peak at Rt 6.96 min (5%). Flash column chromatography of the residue provided 4a,12b-dihydro-3-methyl-phenanthro[9,10-b]-2-cyclohexen-1-one (40, 29 mg, yield 38%, 15% ethyl acetate in hexanes as
the eluant). 39 was recovered (8 mg). The spectroscopic data of 40 are listed in Table 4-1 to Table 4-4.

4.5.11 9-Cyanophenanthrene to AABF₂

A solution of 9-cyanophenanthrene (9-PNCN, 304 mg, 1.5 mmol) and AABF₂ (906 mg, 6.1 mmol) in ether (60 mL) was placed into 9 quartz tubes and purged with nitrogen for about 5 min before irradiation. The solution was irradiated for 47 hours in Apparatus I equipped with RPR-3000 Å lamps. GC analysis (at 230°C, 25 m x 0.2 mm HP-1 capillary column) of the yellow photolysate gave three major peaks at Rt 3.80 min (9-PNCN, 32%), Rt 6.43 min (41, 26%) and Rt 7.09 min (42, 24%). Upon removal of the solvent, the residue was flash chromatographed by using 15% ethyl acetate (giving fraction 1) and 25% ethyl acetate (giving fraction 2). The first fraction (140 mg), which contained 9-PNCN (14%) and 41 (70%), was rechromatographed to give a colorless oil of 9-acetyl-9-cyano-9,10-dihydro-10-(2-oxopropyl)-phenanthrene (41, 100 mg, 21%). The spectroscopic data of 41 are given in Tables 4-1, 4-3 and 4-4. The second fraction, containing a mixture of AABF₂ (major) and 42, was rechromatographed by using 25% ethyl acetate in hexanes but failed to separate 42 from AABF₂.

This experiment was repeated using 9-PNCN (219 mg, 1.08 mmol) and AABF₂ (594 mg, 4.01 mmol) in 54 mL ether (non-degassed solutions in 8 quartz tubes). The mixture was irradiated for 23 hours with RPR-3500 Å lamps in Apparatus I. The resulting yellow solution was analyzed by GC under the same conditions as mentioned above to give 9-PNCN (27%), 41 (15%) and 42 (34%). The irradiated solution was flash chromatographed to
give two mixtures as described above. Further chromatography of the mixture of AABF$_2$ and 42 by using 40% ethyl acetate in hexanes as the eluant provided a compound of 10-acetyl-9-cyano-9,10-dihydro-9-(2-oxopropyl)-phenanthrene (42, 59 mg, 18%). Spectroscopic data of 42 are given in Tables 4-1 to 4-3.

4.5.12 The Photoaddition to Other Aromatic Compounds

A solution of ACHBF$_2$ (7.5 mg, 0.04 mmol) and methyl phenyl ether (0.7 mL) in acetonitrile (1.4 mL) in a quartz tube was irradiated in Apparatus I using RPR-3000 Å lamps for 6 hours. GC analysis of the yellow photolysate showed that 96% of ACHBF$_2$ survived.

A solution of ACHBF$_2$ (7.5 mg, 0.04 mmol) and t-butyl benzene (0.7 mL) in CH$_3$CN (1.4 mL) in a Pyrex tube was irradiated for 5 hours in Apparatus I with RPR-3000 Å lamps. GC analysis (at 180°C, 25 m x 0.2 mm HP-1 capillary column) of the slightly purple photolysate showed that ACHBF$_2$ was consumed and four products at Rt 2.23 min (38.7%), Rt 2.35 min (38.3%), Rt 8.14 min (11.7%) and Rt 8.72 min (8.7%) were detected. GC-MS (EI) of both Rt 2.23 and Rt 2.35 min gave parent peaks 176 (M$^+$) and base peaks 161 (M$^+$-CH$_3$), which suggested acetylated t-butyl benzene structures. No further study was made on this reaction.

Photolyses of ACHBF$_2$ (7.5 mg, 0.04 mmol) with chlorobenzene (0.7 mL) and benzonitrile (0.7 mL) in acetonitrile (1.4 mL) were carried out under the similar conditions to give acetylated benzene derivatives as the major products as shown by GC-MS analysis.
An ether solution (5 mL) of 2-methoxynaphthalene (2-NpOMe, 27 mg, 0.17 mmol) and AABF$_2$ (37.8 mg, 0.26 mmol) in a quartz tube was irradiated in Apparatus I with RPR-3000 Å lamps. Upon irradiation for 10 hours, no product peak was detected by GC (at 200°C). Similar results were obtained for the photolyses of 1-methylnaphthalene and 2-acetyl naphthalene with AABF$_2$ in ether.

An acetonitrile (4 mL) solution of phenanthrene (PN, 22 mg, 0.12 mmol) and AABF$_2$ (22 mg, 0.15 mmol) in a quartz tube was irradiated in Apparatus I for 21 hours using RPR-3000 Å lamps. No product was detected by GC (at 230°C). Similar results were obtained for photoreactions of AABF$_2$ with 1-methoxynaphthalene, 2-methoxynaphthalene, 1-chloronaphthalene, methyl 2-naphthalenecarboxylate and 2-acetyl naphthalene in acetonitrile.
### Table 4-1  GC-Mass Spectroscopic Data of Photoaddition Products.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/e (relative intensity)</th>
</tr>
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<tbody>
<tr>
<td>17</td>
<td>EI 200 (M⁺, 21), 185 (M⁺-CH₃, 100), 128 (12), 115 (19).</td>
</tr>
<tr>
<td></td>
<td>CI 201 (M⁺+1, 100), 185 (9).</td>
</tr>
<tr>
<td>19</td>
<td>EI 232 (M⁺, 10), 204 (4), 149 (100), 131 (31), 103 (15), 77 (25), 55 (37).</td>
</tr>
<tr>
<td></td>
<td>CI 233 (M⁺+1, 100), 149 (19).</td>
</tr>
<tr>
<td>20</td>
<td>EI 216 (M⁺, 4), 174 (M⁺-42, 100), 157 (8), 146 (18), 115 (21), 91 (42), 77 (17), 43 (30).</td>
</tr>
<tr>
<td></td>
<td>CI 217 (M⁺+1, 100), 199 (M⁺+1-H₂O, 4), 175 (75).</td>
</tr>
<tr>
<td>21a,21b</td>
<td>EI 214 (M⁺, 15), 199 (M⁺-CH₃, 100), 141 (17), 128 (32), 115 (23), 91 (8), 77 (17).</td>
</tr>
<tr>
<td></td>
<td>CI 215 (M⁺+1, 100).</td>
</tr>
<tr>
<td>22a</td>
<td>EI 134 (M⁺, 86), 119 (M⁺-CH₃, 100), 91 (M⁺-COCH₃, 44).</td>
</tr>
<tr>
<td>22b</td>
<td>EI 134 (M⁺, 49), 119 (M⁺-CH₃, 100), 91 (M⁺-COCH₃, 60).</td>
</tr>
<tr>
<td>23a,23b</td>
<td>EI 246 (M⁺, 5), 218 (6), 163 (100), 145 (57), 119 (47), 91 (19), 77 (6), 55 (17).</td>
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<td>CI 247 (M⁺+1, 100).</td>
</tr>
</tbody>
</table>

to be continued
<table>
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<th>Table 4-1 continued</th>
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<tbody>
<tr>
<td>25</td>
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<tr>
<td>26</td>
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<td>29</td>
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<tr>
<td>31</td>
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<tr>
<td>32</td>
</tr>
</tbody>
</table>
Table 4-1 continued

| 33 | EI 176 (M⁺, 5), 134 (M⁺-COCH₂, 100), 119 (M⁺-CH₂COCH₃, 6), 105 (12). | CI 177 (M⁺+1, 100). |
| 34 | EI 228 (M⁺, 2), 185 (M⁺-COCH₃, 17), 171 (M⁺-CH₂COCH₃, 47), 141 (42), 128 (68), 115 (28), 43 (100). | CI 229 (M⁺+1, 100), 171 (58). |
| 35 | EI 262 (M⁺, 1), 219 (M⁺-COCH₃, 22), 205 (M⁺-CH₂COCH₃, 45), 164 (M⁺-92, 37Cl, 32), 162 (M⁺-92, 35Cl, 100), 141 (51), 127 (14), 115 (16). | CI 265 (M⁺+1, 37Cl, 34), 263 (M⁺+1, 35Cl, 100), 245 (6), 229 (M⁺+1-Cl, 25), 205 (M⁺+1-CH₃COCH₃, 31). |
| 13 | EI 286 (M⁺), 254 (1), 211 (11), 186 (100), 155 (62), 141 (23), 127 (28), 115 (16). | CI 287 (M⁺+1, 100), 269 (M⁺+1-H₂O, 15). |
| 14 | EI 286 (M⁺, 1), 268 (M⁺-H₂O, 1), 211 (10), 186 (100), 155 (35), 141 (48), 115 (24). | CI 287 (M⁺+1, 89), 269 (M⁺+1-H₂O, 27), 241 (100). |
| 38 | EI 278 (M⁺, 3), 220 (M⁺-CH₃COCH₃, 26), 217 (25), 178 (PN⁺, 100), 165 (14), 43 (54). | CI 279 (M⁺+1, 100), 221 (M⁺+1-CH₃COCH₃, 52). |

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Table 4-1 continued

<table>
<thead>
<tr>
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<th>EI</th>
<th>CI</th>
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</thead>
<tbody>
<tr>
<td>39</td>
<td>278 (M⁺, 7), 220 (M⁺-CH₃COCH₃, 53), 217 (46), 205 (19), 178 (PN⁺, 50), 165 (13), 43 (100).</td>
<td>279 (M⁺+1, 12), 221 (M⁺+1-CH₃COCH₃, 100).</td>
</tr>
<tr>
<td>40</td>
<td>260 (M⁺, 4), 178 (PN⁺, 100), 152 (6).</td>
<td>261 (M⁺+1, 100), 178 (PN⁺, 13).</td>
</tr>
<tr>
<td>41</td>
<td>303 (M⁺, &lt;1), 260 (M⁺-COCH₃, 4), 203 (9-PNCN⁺, 100), 177 (5), 43 (CH₃CO⁺, 52).</td>
<td>304 (M⁺+1, 100), 286 (M⁺+1-H₂O, 9), 277 (M⁺+1-HCN, 47), 204 (9-PNCN⁺+1, 100).</td>
</tr>
<tr>
<td>42</td>
<td>303 (M⁺, 1), 203 (9-PNCN⁺, 100), 177 (5), 43 (CH₃CO⁺, 69).</td>
<td>304 (M⁺+1, 100), 246 (M⁺-CH₃COCH₃, 50), 204 (9-PNCN⁺+1, 50).</td>
</tr>
</tbody>
</table>
Table 4-2  Infrared Spectroscopic Data of Photoaddition Products.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_{\text{max}}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>3072(w), 3040(w), 2940(s), 2867(m), 2845(m), 1658(s, C=C-O), 1607(m), 1495(s), 1384(m), 1195(s, C-O), 1166(m), 1150(m), 760(s, o-C$_6$H$_4$RR')</td>
</tr>
<tr>
<td>19</td>
<td>3000(m), 2978(s), 2882(w), 1738(vs, COO-), 1709(C=O, vs), 1500(m), 1372(s), 1244(vs), 1226(vs), 1167(s), 1080(vs), 1025(s), 782(s, o-C$_6$H$_4$RR')</td>
</tr>
<tr>
<td>20 a</td>
<td>3072(m), 3040(m), 2954(vs), 2879(s), 1760(vs, COO-), 1690(m), 1500(s), 1451(s), 1376(vs), 1229(vs), 1172(vs), 1110(vs), 1075(vs), 770(vs) and 712(vs)</td>
</tr>
<tr>
<td>21a, 21b</td>
<td>3040(m), 2984(s), 2940(vs), 2870(s), 1657(vs), 1503(s), 1450(s), 1373(s), 1200(vs), 1171(vs), 836, 820</td>
</tr>
<tr>
<td>22a, 22b</td>
<td>2955(s), 1690(vs), 1617(m), 1369(s), 1286(s), 830(s), 800(s), 705(s)</td>
</tr>
<tr>
<td>23a, 23b</td>
<td>3012(m), 2960(s), 2902(m), 1750(vs, COO-), 1720(vs, C=O), 1628(m), 1468(s), 1439(s), 1380(s), 1292(s), 1254(s), 1172(s), 1087(s), 875(w), 838(s), 820(m), 768(m)</td>
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Table 4-2 continued

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<tbody>
<tr>
<td>25, 26</td>
<td>3020 (w), 2978 (m), 1734 (vs), 1698 (vs), 1613 (m), 1443 (s), 1368 (s), 1314 (vs), 1293 (vs), 1246 (vs), 1120 (s), 780 (m), 766 (s), 710 (m), 700 (s).</td>
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<tr>
<td>29</td>
<td>2978 (s), 2796 (m), 1741 (vs), 1690 (vs), 1362 (s), 1260 (vs), 1150 (s), 770 (s).</td>
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<tr>
<td>31</td>
<td>3020 (w), 2970 (w), 1730 (vs, broad), 1580 (m), 1430 (s), 1365 (vs), 1270 (s), 1255 (s), 1174 (s), 776 (m), 725 (s).</td>
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<tr>
<td>32, 33</td>
<td>3010 (w), 2925 (s), 1721 (vs, shoulder), 1713 (vs), 1682 (vs), 1606 (s), 1573 (m), 1419 (s), 1359 (vs), 1267 (vs), 1162 (s), 959 (m), 861 (w), 840 (w), 763 (m), 609.</td>
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<tr>
<td>34</td>
<td>3040 (w), 2942 (m), 1716 (vs), 1602 (w), 1497 (m), 1364 (s), 1170 (s).</td>
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<tr>
<td>35 a</td>
<td>1712 (vs), 1462 (s), 1381 (s).</td>
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<tr>
<td>13</td>
<td>3020 (w), 2980 (m), 1748 (vs, -COO), 1721 (vs, C=O), 1498 (m), 1443 (s), 1370 (s), 1238 (vs), 1190 (s), 815 (s), 800 (s).</td>
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<tr>
<td>14</td>
<td>3020 (w), 2900 (m), 1745 (vs, -COO-), 1723 (vs, C=O), 1498 (m), 1441 (s), 1369 (s), 1210 (s), 1176 (s), 810 (s), 778 (m).</td>
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<tr>
<td>38 b</td>
<td>3026, 2995 (m), 2874 (m), 1708 (vs), 1567 (s), 1485 (s), 1400 (s), 1371 (s), 1354 (s), 1161 (s).</td>
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</tbody>
</table>

to be continued
Table 4-2 continued

| 39 | 3067(m), 2923(m), 1713(vs), 1485(s), 1450(s), 1440(s), 1356(s), 1160(s), 760(s), 738(s). |

| 40 | 3084(m), 2998(m), 2940(m), 1664(vs, C=C-C=O), 1495(s), 1461(s), 1450(s), 1388(s), 1134(s), 770(vs), 751(vs). |

a. In CHCl₃ solution.

b. IR spectra were recorded on Perkin-Elmer 1710 Fourier Transform infrared spectrophotometer, KBr pellet for 38, neat film for 39.
Table 4-3  $^1$H NMR Data of Photoaddition Products (CDCl$_3$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1.61 (d, 3H, $J = 6.4$ Hz), 1.70-1.83 (m, 4H), 2.10-2.31 (m, 2H), 2.33-2.44 (m, 2H), 5.08 (q, 1H, $J = 6.4$ Hz), 7.03 (d, 1H, $J = 7.6$ Hz), 7.06 (d, 1H, $J = 7.5$ Hz), 7.15 (dt, 1H, $J = 7.6$ and 1.3 Hz), 7.25 (dt, 1H, $J = 7.5$ and 1.5 Hz).</td>
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<tr>
<td>19</td>
<td>1.48-1.55 (m, 1H), 1.57 (d, 3H, $J = 6.6$ Hz), 1.66-1.73 (m, 1H), 2.13-2.31 (m, 3H), 2.56-2.66 (m, 2H), 2.71-2.80 (m, 1H), 6.05 (q, 1H, $J = 6.6$ Hz), 7.06 (dd, 1H, $J = 7.5$ and 1.5 Hz), 7.21 (dd, 1H, $J = 7.5$ and 0.8 Hz), 7.27 (dt, 1H, $J = 7.5$ and 0.8 Hz), 7.34 (dt, 1H, $J = 7.5$ and 1.5 Hz).</td>
</tr>
<tr>
<td>20</td>
<td>1.75-1.87 (m, 4H), 1.91 (s, 3H), 2.25-2.29 (m, 2H), 2.39-2.43 (m, 2H), 7.20-7.23 (m, 3H), 7.28-7.30 (m, 2H).</td>
</tr>
<tr>
<td>21a or 21b $^a$</td>
<td>1.563 (d, 3H, $J = 6.5$ Hz), 1.68-1.79 (m, 4H), 2.08-2.29 (m, 2H), 2.331 (s, 3H), 2.34-2.39 (m, 2H), 5.06 (q, 1H, $J = 6.5$ Hz), 6.87 (s, broad, 1H), 6.91 (d, 1H, $J = 7.3$ Hz), 6.96 (d, 1H, $J = 7.3$ Hz).</td>
</tr>
</tbody>
</table>

*to be continued*
Table 4-3 continued

| 21b or 21a \(^a\) | 1.560 (d, 3H, \(J = 6.5\) Hz), 1.68-1.79 (m, 4H), 2.08-2.29 (m, 2H), 2.324 (s, 3H), 2.34-2.39 (m, 2H), 5.06 (q, 1H, \(J = 6.5\) Hz), 6.84 (s, broad, 1H), 6.95 (d, 1H, \(J = 7.4\) Hz, became a singlet when decoupled at 7.06 ppm), 7.06 (d, 1H, \(J = 7.4\) Hz). |
| 22a | 2.41 (s, 3H), 2.60 (s, 3H), 7.26 (dd, 2H, \(J = 8.3\) Hz), 7.86 (d, 2H, \(J = 8.3\) Hz). |
| 22b | 2.41 (s, 3H), 2.59 (s, 3H), 7.36 (m, 2H), 7.77 (m, 2H). |
| 23a or 23b \(^b\) | 1.45-1.55 (m, 1H), 1.54 (d, 3H, \(J = 6.7\) Hz), 1.63-1.72 (m, 2H), 2.13-2.19 (m, 1H), 2.22-2.28 (m, 3H), 2.32 (s, 3H), 2.52-2.64 (m, 2H), 2.69-2.77 (m, 1H), 6.02 (q, 1H, \(J = 6.7\) Hz), 6.84 (s, broad, 1H), 6.95 (d, 1H, \(J = 8.6\) Hz), 7.06 (d, 1H, \(J = 8.6\) Hz). |
| 23b or 23a \(^b\) | 1.45-1.55 (m, 1H), 1.56 (d, 3H, \(J = 6.7\) Hz), 1.67-1.77 (m, 2H), 2.13-2.19 (m, 1H), 2.22-2.28 (m, 3H), 2.35 (s, 3H), 2.52-2.64 (m, 2H), 2.69-2.77 (m, 1H), 5.99 (q, 1H, \(J = 6.7\) Hz), 7.01 (s, broad, 1H), 7.09 (d, 1H, \(J = 8.6\) Hz), 7.14 (d, 1H, \(J = 8.6\) Hz). |
| 25 | 2.69 (s, 3H), 3.96 (s, 3H), 7.56 (t, 1H, \(J = 8.0\) Hz), 8.16 (dt, 1H, \(J = 8.0\) and 1 Hz), 8.23 (dt, 1H, \(J = 8.0\) and 1 Hz), 8.61 (s, 1H). |

*to be continued*
Table 4-3 continued

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<td>26</td>
<td>2.69 (s, 3H), 3.96 (s, 3H), 7.78 (d, 2H, J = 8.4 Hz), 8.12 (d, 2H, J = 8.4 Hz).</td>
</tr>
<tr>
<td>29</td>
<td>1.95 (m, 1H), 2.20 (m, 2H), 2.45 (m, 3H), 2.61 (s, 3H), 3.92 (dd, 1H, J = 8.0 and 1.3 Hz), 7.34 (dt, 1H, J = 8.0 and 1.3 Hz), 7.45 (dt, 1H, J = 8.0 and 1.3 Hz), 7.75 (dd, 1H, J = 8.0 and 1.3 Hz).</td>
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<td>31</td>
<td>2.08 (s, 3H), 2.19 (s, 3H), 2.52 (d, 2H, J = 7.0 Hz), 3.19 (m, 1H), 3.56 (m, 1H), 5.87-5.94 (m, 4H), 5.99-6.04 (m, 1H).</td>
</tr>
<tr>
<td>32</td>
<td>2.29 (s, 3H), 2.59 (s, 3H), 4.02 (s, 2H), 7.19 (dd, 1H, J = 7.5 and 1.5 Hz), 7.40 (dt, 1H, J = 7.5 and 1.5 Hz), 7.49 (dt, 1H, J = 7.5 and 1.5 Hz), 7.86 (dd, 1H, J = 7.5 and 1.5 Hz).</td>
</tr>
<tr>
<td>33</td>
<td>2.19 (s, 3H), 2.58 (s, 3H), 3.78 (s, 2H), 7.30 (d, 2H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.0 Hz).</td>
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<tr>
<td>34</td>
<td>2.03 (s, 3H), 2.20 (s, 3H), 2.65 (dd, 1H, J = 17.8 and 8.0 Hz), 2.86 (dd, 1H, J = 17.8 and 7.8 Hz), 3.43 (m, 1H), 3.84 (d, 1H, J = 7.6 Hz), 5.78 (dd, 1H, J = 9.6 and 3.0 Hz), 6.45 (dd, 1H, J = 9.6 and 2.8 Hz), 7.10 (d, 1H, J = 7.4 Hz), 7.15-7.21 (m, 3H).</td>
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to be continued
Table 4-3 continued

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<thead>
<tr>
<th>Compound</th>
<th>Spectroscopic Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>1.91 (s, 3H), 2.22 (s, 3H), 2.75 (dd, 1H, J = 18.2 and 7.7 Hz), 2.92 (dd, 1H, J = 18.2 and 7.2 Hz), 3.40 (m, 1H), 4.09 (d, 1H, J = 7.3 Hz), 5.75 (dd, broad, 1H, J = 9.6 and 2.0 Hz), 6.55 (dd, 1H, J = 9.6 and 3.2 Hz), 7.03 (d, 1H, J = 7.2 Hz), 7.21 (t, 1H, J = 7.7 Hz), 7.25 (dd, 1H, J = 9.0 and 1.4 Hz).</td>
</tr>
<tr>
<td>13</td>
<td>1.93 (s, 3H), 2.23 (s, 3H), 2.56 (d, 2H, J = 6.5 Hz), 3.62 (s, 3H), 4.33 (t, 1H, J = 6.5 Hz), 6.17 (dd, 1H, J = 9.6 and 1.0 Hz), 6.58 (d, 1H, J = 9.6 Hz), 7.03-7.05 (m, 1H), 7.13-7.19 (m, 3H).</td>
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<tr>
<td>14</td>
<td>2.10 (s, 3H), 2.11 (s, 3H), 3.04 (d, 1H, J = 18.2 Hz), 3.19 (d, 1H, J = 18.2 Hz), 3.59 (s, 3H), 4.47 (s, 1H), 5.82 (d, 1H, J = 9.6 Hz), 6.51 (d, 1H, J = 9.6 Hz), 7.07-7.13 (m, 2H), 7.18-7.24 (m, 2H).</td>
</tr>
<tr>
<td>38 (CDCl₃)</td>
<td>1.94 (s, 3H), 2.20 (s, 3H), 2.86 (dd, broad, 1H, J = 18.0 and 5.8 Hz), 3.02 (dd, 1H, J = 18.0 and 6.8 Hz), 3.85 (m, 1H, J = 4.6, 5.8 and 6.8 Hz), 3.99 (d, 1H, J = 4.6 Hz), 7.15-7.44 (m, 6H), 7.55 (dd, 1H, J = 7.5 and 1.1 Hz), 7.81 (d, 1H, J = 7.4 Hz).</td>
</tr>
<tr>
<td>(C₆D₆)</td>
<td>1.68 (s, 3H), 1.70 (s, 3H), 2.41 (dd, 1H, J = 18.0 and 5.8 Hz), 2.91 (dd, 1H, J = 18.0 and 6.8 Hz), 3.85-3.92 (m, 2H), 7.09-7.24 (m, 6H), 7.61 (d, 1H, J = 7.4 Hz), 7.66 (d, 1H, J = 7.5 Hz).</td>
</tr>
</tbody>
</table>

To be continued
Table 4-3 continued

39 (CDCl\textsubscript{3}) 1.97 (s, 3H), 2.00 (s, 3H), 2.51 (dd, 1H, J = 17.0 and 6.0 Hz), 2.55 (dd, 1H, J = 17.8 and 8.8 Hz), 3.70 (d, 1H, J = 1.3 Hz), 4.00 (m, 1H, J = 1.3 and 6.0 and 8.8 Hz), 7.23-7.34 (m, 5H), 7.39 (t, 1H, J = 6.2 Hz), 7.73 (d, 1H, J = 7.5 Hz), 7.79 (d, 1H, J = 7.8 Hz).

(C\textsubscript{6}D\textsubscript{6}) 1.42 (s, 3H), 1.68 (s, 3H), 2.09 (dd, 1H, J = 17.8 and 6.0 Hz), 2.16 (dd, 1H, J = 17.8 and 8.5 Hz), 3.62 (d, 1H, J = 1.7 Hz), 4.23 (m, 1H, J = 1.7 Hz, 6.0 and 8.5 Hz), 6.96 (dd, 1H, J = 7.8 and 1.2 Hz), 7.07-7.27 (m, 5H), 7.58 (dd, 1H, J = 7.0 and 1.7 Hz), 7.63 (dd, 1H, J = 7.8 and 0.8 Hz).

40 (CDCl\textsubscript{3}) 1.89 (s, 3H), 2.25 (s, broad, 2H), 3.49 (m, 1H), 3.79 (d, 1H, J = 5.1 Hz), 6.04 (d, 1H, J = 0.5 Hz), 7.10 (d, 1H, J = 7.7 Hz), 7.24-7.33 (m, 3H), 7.36-7.40 (m, 2H), 7.81 (d, 1H, J = 8.0 Hz), 7.82 (dd, 1H, J = 8.0 and 1.0 Hz).

(C\textsubscript{6}D\textsubscript{6}) 1.17 (s, 3H), 1.59 (dd, broad, 1H, J = 18.2 and 5.2 Hz), 1.90 (dd, broad, 1H, J = 18.2 and 11.0 Hz), 2.96 (dt, 1H, J = 11.0 and 5.0 Hz), 3.90 (d, broad, 1H, J = 5.0 Hz), 6.05 (s, broad, 1H), 6.89 (dd, 1H, J = 7.4 and 1.5 Hz), 7.09-7.17 (m, 5H), 7.65 (dd, 1H, J = 7.8 and 1.2 Hz), 7.67 (dd, 1H, J = 7.8 and 1.2 Hz).

---
to be continued
Table 4-3 continued

| 41 | 2.16 (s, broad, 3H), 2.26 (s, 3H), 3.17 (dd, broad, 1H, \( J = 18.6 \) and 7.4 Hz), 3.21 (dd, 1H, \( J = 18.6 \) and 4.1 Hz), 4.20 (dd, 1H, \( J = 7.4 \) and 4.1 Hz), 7.02 (d, 1H, \( J = 7.5 \) Hz), 7.32 (dt, 1H, \( J = 7.8 \) and 1.3 Hz), 7.38 (dt, 1H, \( J = 7.3 \) and 1.0 Hz), 7.43 (dt, 1H, \( J = 7.4 \) and 1.5 Hz), 7.52 (dt, 1H, \( J = 7.4 \) and 1.5 Hz), 7.64 (d, 1H, \( J = 7.5 \) Hz), 7.74 (dd, 1H, \( J = 7.7 \) and 1.3 Hz), 7.86 (dd, 1H, \( J = 7.7 \) and 1.3 Hz). |

| 42 | 2.14 (s, broad, 3H), 2.17 (s, 3H), 3.22 (d, broad, 1H, \( J = 17.8 \) Hz), 3.67 (d, 1H, \( J = 17.8 \) Hz), 4.67 (s, 1H), 7.31 (d, broad, 1H, \( J = 7.5 \) Hz), 7.38 (dt, 2H, \( J = 7.7 \) and 1.3 Hz), 7.44 (dt, 1H, \( J = 7.5 \) and 1.6 Hz), 7.47 (dt, 1H, \( J = 7.5 \) and 1.4 Hz), 7.63 (d, broad, 1H, \( J = 7.4 \) Hz), 7.77 (d, broad, 1H, \( J = 7.6 \) and 1.6 Hz), 7.80 (dd, 1H, \( J = 7.7 \) and 1.0 Hz). |

a. \( \textsuperscript{1}H \) NMR was measured for a mixture of 21a and 21b.

b. \( \textsuperscript{1}H \) NMR was measured for a mixture of 23a and 23b.
### Table 4-4  \(^{13}\text{C}\) NMR Data of Photoaddition Products (CDCl\(_3\)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>150.57, 132.68, 132.43, 127.59, 125.69, 122.86, 119.13, 107.03, 73.01, 27.73, 23.36, 22.84, 22.78, 19.40.</td>
</tr>
<tr>
<td>19</td>
<td>207.48, 171.79, 140.45, 138.16, 128.73, 127.22, 126.46, 124.74, 71.64, 41.53, 34.29, 23.50, 22.54, 20.68.</td>
</tr>
<tr>
<td>20</td>
<td>169.31, 143.42, 139.45, 128.59, 128.17, 127.97, 127.48, 126.66, 125.42, 30.06, 27.44, 22.77, 22.60, 20.69.</td>
</tr>
<tr>
<td>21a,21b</td>
<td>150.58, 149.55, 137.09, 135.35, 132.79, 132.40, 129.67, 128.08, 126.24, 123.70, 122.79, 119.96, 119.16, 107.40, 73.01, 72.91, 27.76, 27.68, 23.40, 22.85, 22.79, 21.39, 21.20, 19.50.</td>
</tr>
<tr>
<td>23a,23b</td>
<td>208.0, 172.0, 138.5, 138.2, 136.9, 135.2, 130.7, 129.3, 127.8, 126.9, 126.3, 125.1, 124.7, 122.2, 121.6, 71.5, 41.57, 41.43, 34.24, 23.45, 23.38, 22.49, 21.05, 20.66.</td>
</tr>
<tr>
<td>29</td>
<td>217.6, 202.0, 137.7, 137.6, 131.7, 130.6, 129.4, 126.7, 54.5, 38.1, 31.4, 29.1, 20.9.</td>
</tr>
<tr>
<td>31</td>
<td>208.69, 207.26, 130.28, 125.43, 128.92, 123.69, 51.28, 42.11, 30.44, 30.05, 28.92.</td>
</tr>
</tbody>
</table>

to be continued
### Table 4-4 continued

|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 34 | 208.46, 207.03, 133.59, 132.57, 131.52, 128.66, 128.07, 127.61, 127.41, 126.92, 54.72, 44.55, 32.09, 30.38, 29.27. |
| 35 | 207.37, 206.74, 135.85, 134.16, 132.89, 131.54, 128.68, 127.13, 125.46, 54.91, 51.05, 44.78, 32.52, 30.40, 29.52. |
| 13 | 206.34, 203.58, 170.02, 136.86, 130.65, 129.27, 128.58, 127.87, 127.35, 126.99, 124.45, 64.93, 52.79, 44.40, 37.72, 30.74, 26.93. |
| 14 | 207.51, 205.80, 173.57, 131.93, 131.59, 129.08, 128.52, 128.35, 128.15, 128.00, 127.24, 56.25, 52.49, 47.59, 47.12, 30.06 (2C, overlap). |
| 38 | 208.79, 207.04, 137.80, 134.34, 134.20, 133.76, 128.59, 128.24, 128.18, 127.94, 127.41, 125.82, 124.43, 124.21, 55.29, 43.49, 35.44, 30.52, 30.33. |
| 39 | 206.90, 206.68, 137.73, 133.83, 132.55, 132.28, 130.91, 128.91, 128.53, 128.42, 128.13, 127.76, 124.18, 123.94, 57.33, 37.49, 36.13, 30.50, 28.45. |

*to be continued*
Table 4-4 continued

<table>
<thead>
<tr>
<th></th>
<th>199.44, 162.80, 137.53, 134.08, 133.25, 130.48, 129.79, 128.33, 128.11, 128.02, 127.40, 127.26, 126.26, 124.35, 123.70, 49.37, 37.95, 34.74, 24.18.</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>205.25, 199.29, 134.58, 133.79, 132.35, 130.18, 129.79, 129.07, 128.72, 128.22, 128.14, 126.46, 125.10, 124.46, 77.21, 58.22, 43.75, 39.87, 29.91, 28.27.</td>
</tr>
</tbody>
</table>

a. $^{13}$C NMR was measured as a mixture of 21a and 21b.

b. $^{13}$C NMR was measured as a mixture of 23a and 23b.
4.6 Sensitization and Quenching

4.6.1 Triplet Sensitization

Three 1,4-dioxane solutions (5 mL), each containing ACHBF$_2$ (0.020 M, 0.10 mmol), benzene (2.01 M, 10.05 mmol), and tetradecane (as I.S., 0.0066 M, 0.033 mmol), were prepared in Pyrex tubes. No. 1 solution which contained no sensitizer served as the control. No. 2 solution further contained 9-xanthone (49 mg, 0.25 mmol, 0.05 M adsorbed >95% of light) and No. 3 contained benzophenone (45 mg, 0.25 mmol, 0.05 M, absorbed 90% of light).

The above solutions were purged with nitrogen for 15 min, and then irradiated for 3 hours in Apparatus I using RPR-3500 Å lamps. GC analysis (at 170°C) of No. 1 solution showed that adduct 17 was formed in 32% yield while no product 17 could be detected by GC for No. 2 solution and 3.7% 17 was formed in No. 3 solution.

4.6.2 Triplet Quenching

1,3-Cyclohexadiene

Sample solutions of ACHBF$_2$ (0.030 M), benzene (2.01 M), tetradecane (as I.S., 0.010 M) and various concentrations of 1,3-cyclohexadiene (0 to 0.012 M) in 1,4-dioxane were prepared by the general procedure described below. A stock solution A (10 mL) containing ACHBF$_2$ (188 mg, 1.0 mmol), benzene (5.233 g, 0.067 mol) and tetradecane (as I.S., 66 mg, 0.33 mmol) in 1,4-dioxane was prepared. 1,3-Cyclohexadiene (20 mg, 0.25 mmol) was dissolved in 1,4-dioxane (5 mL)
to provide solution B. A 1.5-mL aliquot of solution A was pipetted into
each of six 5-mL volumetric flasks, and various aliquots (0, 0.20, 0.50,
0.80, 1.0 and 1.2 mL) of solution B were pipetted into each of the above
six flasks. After diluting with dioxane to 5 mL, the sample solutions
were transferred into Pyrex tubes and purged with nitrogen for 15 min.
The deaerated solutions were irradiated in Apparatus I with RPR-3000 Å
lamps for 60 min. The photolysates were analyzed by GC at 170°C. Quantum
yields were determined according to Method II (see section 4.3). The
results were plotted in Figure 2-7.

1,3-Pentadiene

1,3-Pentadiene (34 mg, 0.5 mmol) was dissolved in 1,4-dioxane (10
mL) to provide solution B (0.05 M). Six sample solutions (5 mL)
containing ACHBF₂ (0.030 M), benzene (2.01 M), tetradecane (as I.S.,
0.010 M) and various concentrations of 1,3-pentadiene (0-0.12 M) were
prepared and irradiated in a similar way to that described above. The
results are shown in Figure 2-7.

4.7 Heavy Atom Effect on the Photocycloaddition of ACHBF₂
to Benzene

A stock solution A containing ACHBF₂ (188 mg, 1.0 mmol), benzene
(6.12 g, 0.078 mol) and tetradecane (as I.S., 66 mg, 0.33 mmol) and a
solution B containing 1,2-dibromoethane (396 mg, 2.1 mmol) in 1,4-
dioxane were prepared in two 10 mL volumetric flasks, respectively. An
aliquot (1.5 mL) of solution A was pipetted into each of six 5 mL
volumetric flasks, into which various aliquots of solution B (0, 0.50,
1.0, 1.5, 2.0, 2.5 mL) were pipetted. After diluting with 1,4-dioxane to 5 mL, six sample solutions containing ACHBF$_2$ (0.030 M), benzene (2.36 M), tetradecane (0.010 M) and 1,2-dibromoethane (0.0-0.10 M) were transferred into six Pyrex tubes and purged with nitrogen for 15 min. The samples were irradiated in Apparatus I with RPR-3000 Å lamps for 60 min. $R$ values (GC peak area ratio of 17 over I.S.), which were proportional to the quantum yield, were obtained by GC analyses of the photolysates. The results of this experiment are given in Table 2-3.

4.8 Quantum Yield Determination

4.8.1 Concentration Dependence on ACHBF$_2$

A stock solution A (10 mL) containing benzene (7.866 g, 0.10 mol) and tetradecane (as I.S., 99.6 mg, 0.50 mmol) in 1,4-dioxane was prepared. A stock solution B was prepared by dissolving ACHBF$_2$ (188 mg, 1.0 mmol) in 10 mL 1,4-dioxane. A 1.0 mL aliquot of solution A was pipetted into each of six 5 mL volumetric flasks, and various amounts of solution B (1.0, 1.2, 1.5, 1.5, 1.7, 2.0 mL) were pipetted into each of the six flasks followed by diluting with 1,4-dioxane to 5 mL. The six sample solutions, which contained benzene (2.01 M), tetradecane (0.010 M) and ACHBF$_2$ (0.020, 0.024, 0.030, 0.030, 0.34, 0.040 M), were transferred into Pyrex tubes. After purged with nitrogen for 15 min, the sample solutions were sealed. The deaerated solutions were irradiated for 60 min in Apparatus I using RPR-3000 Å lamps. Two actinometer solutions (5-mL) each containing benzophenone (0.05 M) and benzhydrol (0.10 M) were prepared (see Section 4.3, page 68) and irradiated with the sample solutions for 5 min (one at the beginning of the irradiation,
the other at the end of the irradiation). GC analyses showed that the formation of 17 was 10-20% (based on ACHBF$_2$). The quantum yields (calculated by equation 4-3 on page 69) and the Stern-Volmer parameters are summarized in Table 2-5. The Stern-Volmer plot is given in Figure 2-10.

4.8.2 Concentration Dependence on Benzene

In 1,4-Dioxane

A stock solution containing ACHBF$_2$ (188 mg, 1.0 mmol) and tetradecane (as I.S., 66 mg, 0.33 mmol) in 1,4-dioxane was prepared in a 10 mL volumetric flask. 1.5 mL of aliquot of the ACHBF$_2$ stock solution was pipetted into each of the six volumetric flasks (5 mL), into which various amounts of benzene (0.50, 0.60, 0.70, 0.80, 0.90, 1.10 mL) were added. After diluting with 1,4-dioxane to give six 5-mL sample solutions containing ACHBF$_2$ (0.030 M), benzene (1.12-2.47 M) and tetradecane (0.010 M), the solutions were transferred into Pyrex tubes and purged with nitrogen for 15 min prior to irradiation. The deaerated solutions were then irradiated in Apparatus I using RPR-3000 Å lamps for 60 to 75 min. The formation of product 17 ranged 6-17% and the quantum yields were calculated by Method II. The Stern-Volmer plot is shown in Figure 2-9. All the results are summarized in Table 2-4.

In Acetonitrile

A stock solution of ACHBF$_2$ (188 mg, 1.0 mmol) in acetonitrile (10 mL) was prepared. 1.5 mL of the solution were pipetted into each of six 5 mL volumetric flasks followed by adding various amounts of benzene
(0.50, 0.60, 0.75, 0.90, 1.10, 1.30 mL) into each of the flasks. After diluting to 5 mL with acetonitrile to give six sample solutions containing ACHBF₂ (0.030 M) and benzene (1.12-2.91 M), the solutions were transferred to six Pyrex tubes and bubbled with nitrogen for 15 min. The deaerated samples and an actinometer solution of benzophenone/benzhydrol (0.05 M /0.10 M) were irradiated in Apparatus I with RPR-3000 Å lamps for 60 min (5 min for the actinometer). After irradiation, 13 µL (10 mg, 0.05 mmol) pure tetradecane (as I.S., d = 0.763) was injected into each of samples and mixed well. The photolysates were analyzed by GC (at 170°C) to show that 17 was formed in 3-8% yield. The quantum yields (calculated from equation 4-1, page 69) and other parameters are summarized in Table 2-4. The Stern-Volmer plot is shown in Figure 2-9.
References


60. Chow, Y. L.; Cheng, X. E, unpublished result.
70. Nozaki, H; Kurita, M; Mori, T; Noyori, R. Tetrahedron 1968, 24, 1821.


