PHOTOCHEMICAL PROCESSES IN CYCLOPROPYL CONTAINING CARBONYL COMPOUNDS

A Thesis

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Master of Science

by

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December 2008
To my family and friends with love
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ACKNOWLEDGMENTS

In the next few moments I would like to give my thanks to so many who have made this entire experience possible. I first wish to thank my chemistry undergraduate professor, Dr. Steve Wathen. Over the years your kind words of encouragement spoke volumes. Your enthusiasm for organic chemistry always inspired me to develop a profound interest in the field. Thank you so much for your unwavering support.

I would also like to thank fellow group members Beth Willis-Kochly, Kyle Chormanski, Caitlin Hildebrand, and Jason Forbush. Beth, I could not have done it without your assistance and lab expertise. You were always there to mentor me and to lend a hand when I needed something. I really appreciate your help. Kyle, you always found a way to make the lab experience more worthwhile. I truly enjoyed and continue to value your persistent humor and your friendship. Caitlin and Jason, thank you for taking the time to listen to me. It was a pleasure to work with both of you in the lab.

Dr. Creary, I simply can’t thank you enough for all you’ve done for me. Sometimes when it seemed like a long, tough road ahead, somehow you always managed to “coach” me through it. You never stopped believing in me. Thank you so very much for inviting me to be a member of your chemistry “team” and for all of your baseball pep talks. I truly appreciate your relentless dedication to helping me reach my potential.

I would also like to thank my committee members, Dr. Marvin Miller, Dr. Brad Smith, and Dr. Olaf Wiest for taking the time to read this thesis. Thank you for all of your help.
Lastly, I wish to thank my family, friends, and boyfriend John Markiewicz for their constant patience, endless encouragement, and abundant support. You all were there for me every step of the way, though thick and thin. Thank you.
CHAPTER 1
AN INTRODUCTION TO PHOTOCHEMICAL REACTIONS

1.1 The Beginning

It truly is no secret that over the course of the last century free radical chemistry has developed into one of the most important areas of organic chemistry. Contributing to the early establishment of free radical chemistry was Moses Gomberg in 1900. Gomberg announced a discovery which was initially viewed with much skepticism. In his early experiments, Gomberg attempted to synthesize hexaphenylethane 6. Triphenylmethyl chloride 1 dissolved in benzene and was treated with several metals, including zinc at various temperatures. Instead of isolating hexaphenylethane 6, Gomberg observed bistriphenylmethyl peroxide 2. The peroxide 2 was proposed to be derived from the first stable radical, triphenylmethyl radical 3. Additional support for the formation of this trivalent carbon compound was obtained in several ways. In the absence of molecular oxygen, the yellow radical 3 was stable over the period of many weeks. Upon deliberate introduction of either O₂, or a halogen such as bromine, the respective peroxide 2, or the bromide 5 was formed. These experiments initiated the development of free radical chemistry, one of the most fascinating and important areas of chemistry over the past century.
1.2 The Photoreduction of Benzophenone

Also in 1900, Ciamician, an Italian chemist, along with Silber, carried out a reaction initiated by sunlight,\(^2\) that we now recognize as involving a radical similar to Gomberg’s triphenylmethyl radical \(3\). They discovered that by harnessing sunlight and using it as a simple energy source, they could promote a chemical change. This began the area which is known today as photochemistry. Perhaps the most notable reaction which led to the development of the field of photochemistry was the photoreduction of benzophenone \(7\) to benzopinacol \(8\) shown in Scheme 2. This reaction, originally carried out on a roof top in sunny Italy, used isopropyl alcohol as a solvent and gave useful amounts of benzopinacol. It is now described in an Organic Syntheses preparation of benzopinacol.\(^3\)

_Scheme 1. Gomberg’s Generation of Triphenylmethyl Radical_
This reaction is now recognized as proceeding via a photoexcited state of benzophenone, 10. This excited state singlet 10 rapidly converts to triplet 11, which readily abstracts a hydrogen atom from isopropyl alcohol. The 2-hydroxypropyl radical 13 donates a hydrogen atom to unreacted benzophenone 7, forming acetone, 9, as well as more of the radical 12. Coupling of the radical 12 forms the benzopinacol 8.

1.3 The Photochemistry of Carbonyl Containing Compounds

Our understanding of the photoreduction of benzophenone has progressed extensively since the pioneering studies of Ciamician and Silber. While isopropyl alcohol is an ideal solvent for photoreductions, other solvents have been used. In 1963, Beckett and others\(^4\) illustrated not only the utility of various solvents, but also showed that the rate of benzophenone disappearance was solvent dependent. For example, while photoreduction in alcoholic solvents occurs readily, use of solvents such as benzene gave no photoreduction.

To explain the reactivity of benzophenone and its ability to be photoreduced, something must be said about the energetics of benzophenone photochemistry. The
carbonyl functional group is the key to benzophenone photochemistry. A Jablonski diagram shown in Figure 1 is useful for understanding these processes.

Figure 1. Jablonski Diagram Illustrating Benzophenone Photochemical Processes

Benzophenone 7 is a singlet in the ground state (S₀). Upon irradiation, benzophenone absorbs a single photon, which serves to excite the molecule to a higher energy singlet excited state, S₁. The singlet exited electronic state of benzophenone quickly relaxes to the lowest vibrational level which lies 75 kcal/mol above the ground
The small energy difference between the excited singlet state and the triplet state of benzophenone, $T_1$, which lies 69 kcal/mol above the ground state, allows intersystem crossing (ISC) to occur rapidly. Electron spin flip followed by relaxation to the lowest vibrational level gives the excited triplet state, $T_1$. This excited triplet state behaves like a biradical and it is often written as $\text{11}$.

The excited benzophenone triplet $\text{11}$ can transfer up to 69 kcal/mol of energy to an acceptor molecule through collision in order to return to the singlet ground state, $S_0$. This process is called sensitization. Another way for benzophenone in the triplet state to return to the ground state is phosphorescence or emission of a photon. Despite being a forbidden process, phosphorescence can eventually occur, thereby returning triplet benzophenone to the ground state. Phosphorescence generally takes place over a relatively long period of time. Scheme 3 illustrates the processes by which triplet benzophenone can return to the ground state, $S_0$.

\[
\left[ \begin{array}{c} O \\ \text{Ph-C-Ph} \end{array} \right]^3 \text{11} = \left[ \begin{array}{c} O \\ \text{Ph-C-Ph} \end{array} \right] = \left[ \begin{array}{c} O^- \\ \text{Ph-C-Ph} \end{array} \right]
\]

*Scheme 3. Return of Triplet Benzophenone $T_1$ to the Ground State $S_0$*

**1.4 Norrish Type II Chemistry: $\gamma$-Hydrogen Abstraction**

The early investigations of benzophenone and its interesting photochemistry certainly paved the way for what was to come in the photochemistry of carbonyl
containing compounds. In 1923, Ronald Norrish, perhaps one of the most influential experimentalists in the history of photochemistry, began his scientific career. Over several decades, Norrish became well known for the photochemical experiments that he and his cohorts performed on carbonyl containing compounds. The first substantial discovery involved bond cleavage at the carbonyl carbon. This process is known as the Norrish Type I process, or $\alpha$–cleavage. Another photochemical process of carbonyl compounds that has been investigated in detail is the Norrish Type II photochemical transformation. This process is illustrated in Scheme 4 for the aromatic ketone valerophenone, 14. Irradiation of 14 gave acetophenone 15, propene 16, and cyclobutanols 17. These products are believed to be derived from excitation of the ketone 14 to a triplet excited state. The excited state 18 contains enough energy to abstract a $\gamma$ hydrogen atom. Following hydrogen abstraction, the ensuing biradical 19 undergoes bond cleavage between the $\alpha$ and $\beta$ carbons. The resulting enol 20 tautomerizes to form acetophenone, 15. The other product of this cleavage process is propene, 16. An additional pathway by which the biradical 19 can react involves ring closure to form the cyclobutanols 17. Finally it has been shown that 19 can reform the starting ketone 14 by transferring a hydrogen atom back to the $\gamma$ carbon.
Scheme 4. The Norrish Type II Photochemical Process for Valerophenone

1.5 The Methylene cyclopropane Rearrangement

The methylene cyclopropane rearrangement is a process that has been intensively investigated, primarily under thermal conditions. Scheme 5 shows a general methylene cyclopropane rearrangement that our laboratory has studied extensively since the 1980’s. The thermal rearrangement of 21 is proposed to involve rate limiting fragmentation of the strained cyclopropane bond to give the singlet biradical 23. This benzylic radical can reclose at the primary end of the allylic radical to give the observed product 22, which is about 3.5 kcal/mol more stable than the starting methylene cyclopropane 21.
A factor which has been shown to affect the rearrangement rate is the substituent present at the \textit{para}-position of 21. Numerous methylenecyclopropanes 21 were examined and the vast majority with both electron-withdrawing and electron-donating substituents in the \textit{para}-position gave rate enhancements relative to the unsubstituted analog (X=H). To explain these observations, the substituents were proposed to stabilize the developing radicals 23 through spin-delocalization. Scheme 6 shows typical rate enhancements due to substituents in the \textit{para}-position of the aromatic ring.

\textit{Scheme 5. Thermal Methylenecyclopropane Rearrangement}
Of particular interest are the \( p \)-substituted carbonyl compounds such as \( 27 \) and \( 28 \). The carbonyl groups of \( 27 \) and \( 28 \) stabilize the biradical \( 23 \) and thereby lead to enhanced thermal rearrangement rates. With the availability of carbonyl containing substrates such as \( 27 \) and \( 28 \), it was of interest to examine potential photochemical variants of the methylenecyclopropane rearrangement. Although isolated examples are known, photochemical versions of the methylenecyclopropane rearrangement have not been examined to the same extent as their thermal counterparts. With this in mind, the methylenecyclopropane \( 27 \), which is an analog of benzophenone, was irradiated with 350 nm light in \( \text{C}_6\text{D}_6 \) as well as in \( \text{i-PrOH} \) as shown in Scheme 7. The reaction in either of the solvents provided only the rearranged product, \( 29 \). Photoreduction of \( 27 \) to the corresponding pinacol did not occur when \( 27 \) was irradiated in isopropyl alcohol. This is in stark contrast to what has been observed for the parent molecule, benzophenone, \( 7,9 \).

![Scheme 7. Photochemical Rearrangement of a Substituted Methylenecyclopropane in \( \text{C}_6\text{D}_6 \) and \( \text{i-PrOH} \)](image_url)

The proposed mechanism for the photochemical rearrangement of \( 27 \) involves photoexcitation to the higher energy, excited singlet state \( 27^* \). This singlet excited state rapidly undergoes intersystem crossing to the excited triplet state, \( 30 \). This closed triplet state \( 30 \) should have enough energy to abstract a hydrogen atom from isopropyl alcohol. However, it has been proposed that \( 30 \) rapidly fragments to give the open triplet state \( 31 \).
The fragmentation of the highly strained cyclopropane ring releases 40 kcal/mol of energy which disperses the triplet energy of 30. The resultant triplet 31 does not have enough energy for hydrogen atom abstraction from i-PrOH. Instead of hydrogen abstraction, the triplet 31 simply undergoes intersystem crossing followed by closure to form the lower energy product, 29.9

Scheme 8. Proposed Mechanism of the Photochemical Methylene-cyclopropane Rearrangement of 27

With the photochemical behavior of 27 in mind, substrates such as 32 to 33 were next irradiated with 350 nm light. All of these underwent a photochemical methylene-cyclopropane rearrangement to give product 22. The key to these rearrangements appeared to be the ability to access the triplet excited state of 32 and 33 by direct irradiation with 350 nm light. These triplet states fragment in processes analogous to fragmentation of 30.
Finally compounds 34 and 35 were examined under photochemical conditions. When irradiated with 350 nm light, they failed to rearrange since they do not readily absorb light at that wavelength. However, both of these compounds have predicted triplet energies which should be accessible through the use of the sensitizer benzophenone, 7. The triplet energies for the naphthyl containing molecule 34 and the biphenyl containing compound 35 are 61 kcal/mol and 66 kcal/mol respectively. To achieve the desired methylenecyclopropane rearrangements, benzophenone was added to the solutions of 34 and 35 in C₆D₆. Both were irradiated with 350 nm light. The triplet benzophenone produced by the irradiation lies 69 kcal/mol above the ground state. Transfer of this energy to the acceptor molecules, 34 and 35, occurs through a collision, which excites the methylenecyclopropanes to a closed triplet state (such as 36) and returning benzophenone to the singlet ground state. This photosensitization process is illustrated in Scheme 9.

Scheme 9. The Methylenecyclopropane Rearrangement of Photosensitized 34
After sensitization, the closed triplet 36 undergoes ring fragmentation and again releases approximately 40 kcal/mol of energy. The resulting open triplet 37 then undergoes intersystem crossing, and ring closure to form 38. An analogous sensitized mechanism accounts for the rearrangement of 35.

1.6 Concluding Remarks

Substrates 32 are several examples where methylenecyclopropanes have been shown to rearrange under photochemical conditions. A common factor which appears to be important in these rearrangements is the ring strain present in these cyclopropyl systems. Based on the rearrangements of these methylenecyclopropanes 32, it is of interest to investigate the behavior of less strained cyclopropyl systems such as 39. The intent of this thesis is to explore several less strained cyclopropyl systems and to determine to what extent traditional photochemical processes can be bypassed. In other words, will less strained cyclopropyl systems such as 39 simply rearrange much like the methylenecyclopropanes 32 when irradiated? Will they undergo photoreduction in i-PrOH by a process analogous to that of benzophenone 7? Will less strained cyclopropyl systems such as 39 and 40 (R = n-Bu) undergo Norrish Type II processes analogous to that of valerophenone 14? The following studies will attempt to answer these questions.
CHAPTER 2
THE PHOTOCHEMISTRY OF CYCLOPROPYL CONTAINING SUBSTRATES

2.1 Benzoyl Containing Substrates

As previously discussed in Chapter 1, the photochemistry of benzophenone 7 has been studied extensively and its photochemical behavior is well understood. The substituted methylenecyclopropane 27, an analog of benzophenone, has also been investigated under photochemical conditions and was shown to rearrange to the isomeric substrate 29. Based on the photochemistry of the model compounds 7 and 27, it was of interest to explore the behavior of the less strained cyclopropyl systems 41-44. One goal of this research was to determine whether or not substrates 41-43 would isomerize by a mechanism analogous to that of the benzophenone substituted methylenecyclopropane analog 27. Another objective was to determine if substrates 41-44 would photoreduce in an analogous process to that of benzophenone when irradiated in i-PrOH.

The first of these substrates to be studied was the substituted cyclopropyl system, 41. The synthesis of this substrate 41 involved the cyclopropanation of cyclopentene using the carbene precursor \(\rho\)-benzoylphenylidiazomethane 45 and copper triflate as a catalyst.
The reaction, carried out by J. Forbus in our laboratory, produced the *endo*-isomer 41 in addition to the *exo*-isomer 46 shown in Scheme 10. These products were separable using column chromatography.

![Scheme 10. Synthesis of Substrates 41 and 46](image)

Stereochemistry of these isomers was established using $^1$H NMR spectroscopy. Computational studies$^{11}$ suggest that 41 and 46 exist in a boat-like conformation. The C3 *endo*-hydrogen of 41 is far upfield at $\delta$ 0.02 due to the shielding nature of the aromatic ring. The C3 *exo*-hydrogen is also upfield at $\delta$ 1.17. On the other hand, the *exo*-isomer 46 shows the C3 *endo*-hydrogen at $\delta$ 1.06. This upfield shift is probably due to a weak shielding effect of the cyclopropane ring.

![Chemical structures showing hydrogen shifts](image)

The photochemical behavior of substrate 41 was investigated in both C$_6$D$_6$ and i-PrOH solvents. Figure 2 shows evolving $^1$H NMR spectra when 41 was irradiated in C$_6$D$_6$ using a Rayonet Photochemical Reactor fitted with 350 nm lamps, and illustrates the disappearance of the *endo*-isomer 41. Over time, the *endo*-isomer 41 isomerized to
the exo-isomer 46 until a photostationary state (90% 41; 10% 46) was reached. Figure 3 shows the time dependence of this photoisomerization.

Figure 2. Evolving $^1$H NMR Spectra During Irradiation of 41 in C$_6$D$_6$

Figure 3. Plot of Percent Isomerization of 41 to 46 vs. Irradiation Time in C$_6$D$_6$
Figures 4 and 5 show the photochemical behavior of substrate 41 in i-PrOH. Once again, photoisomerization to the exo-isomer 46 is observed and approximately the same photostationary ratio of 41 and 46 is reached. Photoreduction of 41 to the corresponding pinacol is not observed.

Figure 4. Evolving $^1$H NMR Spectra During Irradiation of 41 in i-PrOH

Figure 5. Plot of Percent Isomerization of 41 to 46 vs. Irradiation Time in i-PrOH
The proposed mechanism accounting for the photoisomerization of the endo-isomer 41 to the exo-isomer 46 is shown in Scheme 11. Much like benzophenone 7, substrate 41 also absorbs a photon when irradiated with 350 nm light. The light promotes the molecule to the higher energy, singlet excited state, 41*. Intersystem crossing proceeds quickly, giving the closed excited triplet 48. The strained cyclopropane ring fragments, releasing approximately 28 kcal/mol of ring strain to afford the open triplet 49. Due to the fragmentation, rotation can now take place to give 50. Upon intersystem crossing, the ring closes, producing the exo-isomer 46.

Scheme 11. Proposed Mechanism of the Photoisomerization of 41 in C₆D₆ and i-PrOH

Why is photoreduction not observed when 41 is irradiated in i-PrOH? Removing a hydrogen atom from i-PrOH requires an energetic triplet such as 48. However, cyclopropane ring fragmentation lowers the energy of the triplet state 49. The less energetic triplet 49 (or 50) no longer has sufficient energy to abstract a hydrogen atom from i-PrOH. The only reasonable pathway remaining is spin inversion and ring closure.
Another substrate of interest was the bicyclic cyclopropane 42. Adduct 42 was also prepared by reacting p-benzoylephenyldiazomethane 45 with 1,3-cyclohexadiene using copper triflate as a catalyst. The endo-isomer 42 and the exo-isomer 51 were separated using column chromatography. The synthesis is shown in Scheme 12.

Scheme 12. Synthesis of Substrates 42 and 51

The photochemical behavior of 42 was of interest based on the known thermal rearrangement of vinylcyclopropane 52 to cyclopentene 53\(^\text{12}\) shown in Scheme 13. This process is formally a 1,3-sigmatropic shift which orbital symmetry considerations suggest can be concerted if inversion occurs at the migrating center. Scheme 13 shows an alternative biradical mechanism.

Scheme 13. Thermally Induced Vinylcyclopropane Rearrangement of 52 to 53

The substrate 42 is also a vinylcyclopropane and it was investigated in order to determine if an analogous rearrangement to a cyclopentene would occur under photochemical conditions. When substrate 42 was irradiated (350 nm light) in C\(_6\)D\(_6\) or in \(i\)-PrOH, the vinylcyclopropane rearrangement to 54 did not occur. Photoreduction to the
corresponding pinacol in \textit{i}-PrOH was also bypassed. Instead, substrate 42 photoisomerized to the \textit{exo}-isomer 51 until a photostationary state (91\% of 51; 9\% of 42) was reached. Scheme 14 along with Figure 6 illustrates this photoisomerization process in C$_6$D$_6$. Behavior in \textit{i}-PrOH is analogous.

\begin{center}
\textbf{Scheme 14. The Photoisomerization of 42 in C$_6$D$_6$ and \textit{i}-PrOH}
\end{center}

\begin{center}
\textbf{Figure 6. Evolving $^1$H NMR Spectra During Irradiation of 42 in C$_6$D$_6$}
\end{center}
Irradiation of the \textit{exo}-isomer 51 was also carried out in C₆D₆. Photoisomerization occurred and approximately the same photostationary state was obtained as during irradiation of the \textit{endo}-isomer 42. Figure 7 shows the approach of substrates 42 and 51 to the photostationary state.

![Figure 7. Plot Showing Isomerization of 42 and 51 vs. Irradiation Time in C₆D₆](image)

The vinylcyclopropane 43 (along with the \textit{trans}-isomer 55) was also prepared by carbene addition to 1,3-butadiene as shown in Scheme 15. Under photochemical conditions adduct 43 also isomerized to 55 when irradiated in C₆D₆ or \textit{i}-PrOH. Again, photoreduction was precluded during the irradiation of 43 in \textit{i}-PrOH. The rearrangement of the vinylcyclopropane 43 to the corresponding cyclopentene was also bypassed.

![Scheme 15. Synthesis of Substrates 43 and 55](image)
The ring expanded product (the cyclopentene) is not observed. This suggests that the mechanism for the observed photoisomerization is different from that of the vinylcyclopropane rearrangement. Scheme 16 illustrates the proposed mechanism for the isomerization. The cyclopropane ring of the \((n,\pi^*)\) triplet 56 fragments to give 57. As before, rotation, intersystem crossing, and ring closure gives the observed product 55. Much like the other benzoyl containing substrates examined previously, a photostationary state is attained for the photoisomerization of cis-isomer 43 (62%) to the trans-isomer 55 (38%). Finally, these results suggest that singlet biradical intermediates analogous to 57 and 58 are not involved in the vinylcyclopropane rearrangement.

**Scheme 16. Proposed Mechanism for the Photoisomerization of 43 in C\(_6\)D\(_6\) and i-PrOH**

The final benzoyl containing compound of interest was substrate 44, which is the simplest benzoyl substituted cyclopropane. This compound was prepared as shown in Scheme 17. The bromide 59 underwent lithium-halogen exchange upon addition of \(n\)-butyllithium to give 60. This aryllithium reagent was then converted to ketone 44 using \(N,N\)-dimethylbenzamide.
The photochemical behavior of substrate 44 was investigated in i-PrOH. When irradiated, substrate 44 did not undergo photoreduction to form the pinacol. Ketone 44 was recovered unchanged. This behavior contrasts with that of the isopropyl analog 61, which undergoes facile photoreduction to form pinacol 62 as shown in Scheme 18. This process is completely analogous to the photoreduction of benzophenone illustrated in Scheme 2.

The fact that photoreduction of substrate 44 does not occur is undoubtedly due to the presence of the cyclopropane. It is suggested that, as before, cyclopropane ring fragmentation occurs in the triplet 64. The lower energy triplet 65 no longer has enough energy to abstract a hydrogen atom from i-PrOH. Eventually it recloses to form 44. The i-Pr analog 61 differs in that the triplet energy of 63 cannot be dissipated. The higher
energy intermediate 63 readily abstracts a hydrogen atom from \textit{i}-PrOH leading to the formation of the pinacol 62.

Scheme 19. Photochemical Process for 44

2.2 Norrish Type II Substrates

The next compounds studied have the potential to undergo Norrish Type II photochemistry. It was of interest to determine whether or not this traditional photochemical process would be bypassed when these substrates were irradiated in C\textsubscript{6}D\textsubscript{6}. The first of these compounds studied was 68. Preparation involved reaction of carbene precursor 66\textsuperscript{13} with cyclopentene which gave a mixture of isomers 67. The nitriles 67 were treated with \textit{n}-butyllithium followed by dilute acid to give the isomeric substrates 68 and 69 which were separated by column chromatography. Scheme 20 illustrates this synthesis.

Scheme 20. Synthesis of Substrates 68 and 69
The photochemical behavior of 68 was investigated in C₆D₆. Continued irradiation gave only the isomerized product 69 until a photostationary state (86% 69; 14% 68) was reached. The Norrish Type II products 70 and 71 shown in Scheme 21 were not observed. This lack of Norrish Type II behavior suggests that intramolecular hydrogen atom transfer to give 72 is slow relative to bond fragmentation of 73 leading to 74. These processes are shown in Scheme 22.

Scheme 21. The Photoisomerization of 68 in C₆D₆

Scheme 22. Potential Reaction Pathways for 73
Another simpler substrate studied was ketone 77. The synthesis of 77 is shown in Scheme 23. Addition of \( n \)-butyllithium to the known aldehyde 75\(^{14} \) gave the alcohol 76. Subsequent oxidation using pyridinium chlorochromate gave ketone 77.

\[
\begin{align*}
\text{Scheme 23. Synthesis of Substrate 77}
\end{align*}
\]

When substrate 77 was irradiated in C\(_6\)D\(_6\) at 350 nm, the Norrish Type II products 78 and 79 were not formed and substrate 77 was recovered unchanged. Once again, the presence of the cyclopropane ring appears to have prevented this traditional photochemical process from occurring. As shown in Scheme 24, it is suggested that the excited triplet 80 does not abstract a \( \gamma \) hydrogen due to competing fragmentation of the cyclopropane ring. The fragmentation of the cyclopropane ring of 80 disperses the energy required for intramolecular hydrogen abstraction and therefore Norrish Type II processes are bypassed.

\[
\begin{align*}
\text{Scheme 24. Photochemical Behavior of 77 in C\(_6\)D\(_6\)}
\end{align*}
\]
2.3 Photosensitized Processes

Our group has shown\(^9\) that certain methylenecyclopropanes which do not readily absorb light can attain triplet energy states, and subsequently rearrange, when the sensitizer benzophenone is used in photochemical reactions. The following studies involved cyclopropyl systems that are less strained than methylenecyclopropanes. They were investigated to determine whether or not isomerization would occur under benzophenone sensitized conditions. The first of these substrates to be examined was \(82\), the synthesis of which is illustrated in Scheme 25. Addition of lithium tetramethylpiperidide to cyclopentene and chloride \(81\) gave the isomeric substrates \(82\) and \(83\). These products were then separated using column chromatography.

\[
\text{Scheme 25. Synthesis of Substrates 82 and 83}
\]

Direct irradiation of \(82\) in \(C_6D_6\) resulted in no change. This is presumably due to the fact that \(82\) does not absorb light at 350 nm. The irradiation of \(82\) in \(C_6D_6\) containing the sensitizer benzophenone, however, promoted the photoisomerization of \(82\) to the isomeric substrate \(83\). Continued irradiation established a photostationary state (34% \(82\); 66% \(83\)). Next, the pure \(exo\)-isomer \(83\) was irradiated in a solution of \(C_6D_6\) containing benzophenone. Over time, the same photostationary state was reached. Figure 8 illustrates the sensitized and unsensitized irradiation of \(82\) and the establishment of the photostationary state.
The proposed mechanism for the sensitized rearrangement is shown in Scheme 26. Transfer of energy from the excited benzophenone triplet to 82 gives triplet 84. Ring opening of 84 followed by rotation of 85, intersystem crossing, and ring closure gives the observed isomerized product 83.

Scheme 26. Proposed Mechanism of the Sensitized Isomerization of 82
The next substrate investigated was the naphthyl containing compound 86. The preparation of this compound was previously described.\textsuperscript{15} When 86 was directly irradiated in C\textsubscript{6}D\textsubscript{6} with 350 nm light, no change was observed. Surprisingly, even when substrate 86 was irradiated in a solution of C\textsubscript{6}D\textsubscript{6} containing benzophenone, isomerization did not occur. The reasons for the lack of isomerization in the sensitized irradiation of 86 illustrated in Scheme 27 are unclear. By way of contrast, the analogous methylenecyclopropane 87 undergoes facile benzophenone sensitized isomerization to 88.

Scheme 27. Sensitized Irradiation of Substrates 86 and 87 in C\textsubscript{6}D\textsubscript{6}

The next compound investigated involved the more strained tricyclic system, 89, the synthesis of which has been previously described.\textsuperscript{15} When substrate 89 was irradiated in C\textsubscript{6}D\textsubscript{6} without benzophenone, isomerization to the \textit{exo}-isomer 90 was very slow. Addition of the sensitizer, however, promoted isomerization until a photostationary state was reached (20\% 89; 80\% 90). The sensitized attainment of this photostationary state is illustrated in Scheme 28. As before, the triplet 91 is probably involved in this rearrangement. The greater strain in 91, relative to the triplet derived from 86, may offer an explanation for the lack of rearrangement of 86.
Scheme 28. Sensitized Reaction of Substrate 89 in C₆D₆

The final compounds of interest included the nitro containing substrates 92 and 93. The syntheses of 92 and 93 involved carbene additions to cyclopentene and norbornene respectively using copper triflate as a catalyst. Substrates 92 and 93 were of interest because the photochemistry of the nitro group is similar to that of the carbonyl group. It is also known that the triplet energy of nitrobenzene is only 58 kcal/mol above the ground state. When methylenecyclopropane 94 was directly irradiated in C₆D₆, rearrangement to 96 occurred through the triplet intermediate 95 as shown in Scheme 29. It was initially thought that isomerization of the less strained analogs 92 and 93 could occur with direct irradiation since the triplet states of these nitro systems should be attainable. The bicyclic systems 92 and 93 were therefore irradiated in C₆D₆. Interestingly, neither substrate isomerized (Scheme 29). The reasons behind the failure of substrates 92 and 93 to isomerize are not immediately clear.
Scheme 29. Photochemical Behavior of 92, 93, and 94 in C₆D₆

2.4 Final Remarks

Conclusively, based on the studies carried out in this thesis, it has been shown that a number of strained cyclopropyl systems do not undergo traditional photochemical processes involving hydrogen atom abstraction when irradiated with 350 nm light in C₆D₆ and i-PrOH. A common thread linking the substrates together is the presence of the cyclopropane ring. Attainment of the triplet state of these substrates was achieved either by direct irradiation or through the use of a sensitizer. Fragmentation of the cyclopropane releases approximately 30 kcal/mol of strain energy, lowering the triplet energy of the excited state of the respective substrate. The lower energy triplet no longer has enough energy to abstract a hydrogen atom. The only reasonable pathway remaining for the intermediate following ring fragmentation was rotation, intersystem crossing, and subsequent ring closure. This explains the observed isomerizations and lack of photoreduction or Norrish Type II photochemistry.
APPENDIX A:

EXPERIMENTAL

**General.** All $^1$H and $^{13}$C spectra were acquired on either a Varian 500 MHz or Varian 600 MHz Spectrometer. Photolyses of the studied compounds were carried out in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company) fitted with lamps emitting wavelengths centered at 350 nm. Chromatographic separations were carried out using EM Science 230-400 mesh silica gel 60.
Preparation of 41. A sample of this compound (prepared by Cu(OTf)\textsubscript{2} catalyzed reaction of PhCOC\textsubscript{6}H\textsubscript{4}CHN\textsubscript{2} with cyclopentene) was supplied by J. Forbush.

Preparation of 42 and 51. 1,3-Cyclohexadiene (1 mL) was added to 12 mg of dry Cu(OTf)\textsubscript{2} in a round-bottom flask fitted with an addition funnel. A solution of 99 mg of \textit{p}-benzoylphenyldiazomethane\textsuperscript{10} in 4 mL of 1,3-cyclohexadiene was added dropwise over a 2 h period. On completion of the addition, the mixture was stirred for an additional 30 min at room temperature. The 1,3-cyclohexadiene was then removed at aspirator pressure and the crude residue was chromatographed on 9.6 g silica gel. The column was eluted with increasing amounts of ether in hexanes. Mixtures of 42 and 51 eluted with 4% ether in hexanes. A total of 56 mg of 42 and 51 were isolated (46% yield). Earlier fractions were enriched in the \textit{endo}-isomer 42 while later fractions were enriched in the \textit{exo}-isomer 51. \textsuperscript{1}H NMR of 42 (CDCl\textsubscript{3}) \(\delta\) 7.78 (d, \(J = 8.4\) Hz, 2 H), 7.70 (d, \(J = 8.3\) Hz, 2 H), 7.57 (t, \(J = 7.4\) Hz, 1 H), 7.47 (t, \(J = 8.0\) Hz, 2 H), 7.37 (d, \(J = 8.4\) Hz, 2 H), 7.28 (d, \(J = 8.0\) Hz, 2 H), 7.19 (t, \(J = 7.4\) Hz, 1 H), 7.17 (d, \(J = 8.0\) Hz, 2 H), 7.10 (d, \(J = 8.0\) Hz, 2 H), 7.00 (d, \(J = 8.3\) Hz, 2 H), 6.80 (t, \(J = 7.4\) Hz, 1 H), 5.78 (m, 2 H), 5.60 (m, 2 H), 4.45 (m, 2 H), 3.90 (m, 2 H), 2.60 (m, 2 H), 2.30 (m, 2 H), 1.90 (m, 2 H), 1.60 (m, 2 H), 1.30 (m, 2 H), 1.00 (m, 2 H).
Hz, 2 H), 6.10 (m, 1 H), 5.39 (d of d of d, J = 9.3, 5.4, 2.4 Hz, 1 H), 2.34 (t, J = 8.7 Hz, 1 H), 1.97 (m, 1 H), 1.8-1.70 (m, 3 H), 1.64 (m, 1 H), 0.59 (m, 1 H). $^{13}$C NMR of 42 (CDCl$_3$) δ 196.9, 144.2, 138.2, 135.4, 132.4, 130.4, 130.2, 130.1, 128.4, 126.5, 124.9, 29.0, 22.3, 18.5, 17.3, 14.6. $^1$H NMR of 51 (CDCl$_3$) δ 7.77 (m, 2 H), 7.72 (d, J = 8.3 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.12 (d, J = 8.2 Hz, 2 H), 6.13 (m, 1 H), 5.57 (m, 1 H), 2.19 (t, J = 4.2 Hz, 1 H), 2.15-2.07 (m, 2 H), 1.96 (m, 1 H), 1.82 (m, 1 H), 1.72 (m, 1 H), 1.64 (m, 1 H). $^{13}$C NMR of 51 (CDCl$_3$) δ 196.5, 148.7, 138.3, 134.8, 132.3, 130.7, 130.1, 128.4, 127.1, 125.3, 124.1, 28.8, 26.7, 24.1, 21.0, 18.3.

**Preparation of 43 and 55.** Cyclohexane (12 mL) in a round-bottom flask was cooled to approximately -10 °C as 6.9 g of 1,3-butadiene was condensed into flask. Dry Cu(OTf)$_2$ (12 mg) was added to the flask. A solution of 165 mg of $p$-benzoylphenyldiazomethane in 11 mL of cyclohexane was added dropwise using an addition funnel over a 4 h period. On completion of the addition, the mixture was stirred for an additional 2 days. The solution was filtered and the solvent was removed using a rotary evaporator. The crude mixture was chromatographed on 10 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. Mixtures of 43 and 55
eluted with 3% ether in hexanes. A total of 84 mg of 43 and 55 were isolated (45% yield). Earlier fractions were enriched in the cis-isomer 43 while later fractions contained mixtures of the cis-isomer 43 and the trans-isomer 55 (approximately 40:60 ratio). \(^1\)H NMR of 43 (CDCl₃) \(\delta 7.79 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.74 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.58 (t, J = 8.4 \text{ Hz}, 1 \text{ H}), 7.48 (t, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.30 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 5.15 (m, 2 \text{ H}), 4.90 (m, 1 \text{ H}), 2.41 (m, 1 \text{ H}), 1.97 (m, 1 \text{ H}), 1.35 (m, 1 \text{ H}), 1.15 (m, 1 \text{ H}). \(^{13}\)C NMR of 43 (CDCl₃) \(\delta 196.6, 144.5, 138.1, 137.4, 135.4, 132.4, 130.24, 130.16, 129.0, 128.4, 115.2, 24.0, 23.7, 12.3.\(^{1}\)H NMR of 55 (CDCl₃) \(\delta 7.77 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.73 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.57 (t, J = 8.4 \text{ Hz}, 1 \text{ H}), 7.47 (t, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.15 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 5.55 (m, 1 \text{ H}), 5.14 (m, 1 \text{ H}), 4.98 (m, 1 \text{ H}), 2.02-1.98 (m, 1 \text{ H}), 1.80 (m, 1 \text{ H}), 1.30 (m, 1 \text{ H}), 1.22 (m, 1 \text{ H}). \(^{13}\)C NMR of 55 (CDCl₃) \(\delta 196.5, 148.1, 140.2, 138.2, 135.1, 132.4, 130.7, 130.1, 128.4, 125.5, 113.5, 28.6, 25.6, 17.8.

**Preparation of 44.** A solution of 317 mg of \(p\)-cyclopropylbromobenzene\(^{16}\) in 7 mL of anhydrous THF was cooled to -78 °C. After cooling, 1.8 mL of 1.6 M \(n\)-butyllithium was added. The solution was warmed to -50 °C for 5 min and re-cooled to -78 °C. A solution of 350 mg \(N,N\)-dimethylbenzamide in 9 mL of anhydrous THF was added dropwise over a 15 min period. After the addition was complete, the solution was
slowly warmed to 5 °C. Water (10 mL) was added dropwise to the round-bottom flask over a 5 min period. The mixture was extracted with ether and the ether extract was washed with water and saturated NaCl solution. The ether solution was dried over a mixture of Na₂SO₄ and MgSO₄ and filtered. The solvent was removed by rotary evaporator. The crude material was chromatographed on 8.8 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. Ketone 44 eluted with 4% ether in hexanes. A total of 210 mg of 44 was isolated (59% yield). ¹H NMR of 44 (CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.47 (t, J = 8.1 Hz, 2 H), 7.15 (d, J = 8.2 Hz, 2 H), 1.97 (m, 1 H), 1.08 (m, 2 H), 0.80 (m, 2 H). ¹³C NMR of 44 (CDCl₃) δ 196.6, 150.0, 138.2, 134.9, 132.3, 130.6, 130.1, 128.4, 125.4, 15.9, 10.6.

Preparation of 67a and 67b. Cyclopentene (15 mL) was added to 26 mg of dry Cu(OTf)₂ in a round bottom flask fitted with an addition funnel. A solution of 378 mg of p-cyanophenyl diazomethane¹² in 20 mL cyclopentene was added dropwise over a 2 h period. The solution was then warmed to 30 °C using a water bath for 30 min. The solution was then filtered and the cyclopentene was removed at aspirator pressure. The residue was chromatographed on 6.7 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. Pure isomer 67a eluted with 2% ether in
hexanes followed by mixtures of \textbf{67a} and \textbf{67b}. The total yield of \textbf{67a} and \textbf{67b} was 83 mg (17\% yield). \textsuperscript{1}H NMR of \textbf{67a} (CDCl\textsubscript{3}) \(\delta\) 7.57 (d, \(J = 8.4\) Hz, 2 H), 7.34 (d, \(J = 8.4\) Hz, 2 H), 1.97 (t, \(J = 8.3\) Hz, 1 H), 1.85 (m, 2 H), 1.76-1.64 (m, 4 H), 1.29 (m, 1 H), -0.16 (m, 1 H). \textsuperscript{13}C NMR of \textbf{67a} (CDCl\textsubscript{3}) \(\delta\) 145.0, 132.3, 130.2, 119.5, 109.8, 25.9, 23.9, 23.3, 22.7.

A solution of nitriles \textbf{67a} and \textbf{67b} (83 mg) in 5 mL of anhydrous ether was cooled to -78 °C. A solution of 1.0 mL of 1.6 M \(n\)-butyllithium (diluted with 1 mL of pentane) was added over a 2 min period. The solution was then warmed to room temperature and the solution was re-cooled to -78 °C. Methanol (0.25 mL) was added. The mixture was then warmed to room temperature and water was added. A 4 mL portion of ether was added to the round bottom flask and the aqueous layer was removed. Dilute HCl (5 mL of 3\%) was added to the organic phase and the solution was vigorously stirred for an additional 30 min. The mixture was transferred to a separatory funnel and the ether extract was washed with water and saturated NaCl solution. The ether was dried over a mixture of Na\textsubscript{2}SO\textsubscript{4} and MgSO\textsubscript{4} and filtered. The solvent was removed by rotary evaporator. An NMR spectrum showed endo-isomer \textbf{68} and exo-isomer \textbf{69} in a 75:25 ratio. This mixture was chromatographed on 8 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. Mixtures \textbf{68} and \textbf{69} (67 mg; 61\% yield)
eluted with 4% ether in hexanes. Earlier fractions were enriched in the endo-isomer 68 while later fractions were enriched in the exo-isomer 69. $^1$H NMR of 68 (CDCl$_3$) $\delta$ 7.88 (d, $J = 8.2$ Hz, 2 H), 7.32 (d, $J = 8.3$ Hz, 2 H), 2.95 (t, $J = 7.3$ Hz 2 H), 1.97 (t, $J = 8.2$ Hz, 1 H), 1.83 (m, 2 H), 1.75-1.68 (m, 6 H), 1.41 (hextet, $J = 7.5$ Hz, 2 H), 1.26 (m, 1 H), 0.95 (t, $J = 7.3$ Hz, 3 H), -0.10 (m, 1 H). $^{13}$C NMR of 68 (CDCl$_3$) $\delta$ 200.7, 144.8, 135.1, 129.6, 128.3, 38.5, 26.8, 26.0, 23.8, 23.3, 22.8, 22.7, 14.2. $^1$H NMR of 69 (CDCl$_3$) $\delta$ 7.83 (d, $J = 8.5$ Hz, 2 H), 7.06 (d, $J = 8.3$ Hz, 2 H), 2.91 (t, $J = 7.3$ Hz, 2 H), 1.93 (m, 2 H), 1.83 (m, 2 H), 1.73-1.64 (m, 4 H), 1.62 (m, 2 H), 1.40 (hextet, $J = 7.5$ Hz, 2 H), 1.29 (m, 1 H), 0.94 (t, $J = 7.4$ Hz, 3 H). $^{13}$C NMR of 69 (CDCl$_3$) $\delta$ 200.4, 150.1, 134.2, 128.3, 125.5, 38.4, 31.1, 28.2, 26.9, 24.3, 22.8, 21.1, 14.2.

![Image](image.png)

**Preparation of 77.** Anhydrous ether (2 mL) was cooled to -78 °C in a 3-neck round-bottom flask fitted with an addition funnel and 0.7 mL of 1.6 M n-butyllithium was added. A solution of 78 mg of p-cyclopropylbenzaldehyde$^{13}$ in 2 mL of ether was then added dropwise. After addition of the aldehyde, the solution was warmed to room temperature and 5 mL of water was added. The mixture was extracted with ether and the ether extract was washed with water and saturated NaCl solution. The ether extract was then dried over a mixture of Na$_2$SO$_4$ and MgSO$_4$ and filtered. The solvent was removed using a rotary evaporator. The crude residue was dissolved in 3 mL of methylene
chloride and pyridinium chlorochromate (215 mg) was added to the solution. The mixture was stirred at room temperature for a 3 h period. Pentane (3 mL) was added and was filtered through a small amount of silica gel. The solvent was removed using a rotary evaporator. The residue was chromatographed on 5.1 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. A total of 62 mg (62% yield) of 77 eluted with 2% ether in hexanes. \( ^1H \) NMR of 77 (CDCl\(_3\)) \( \delta \) 7.85 (d, \( J = 8.3 \) Hz, 2 H), 7.11 (d, \( J = 8.2 \) Hz, 2 H), 2.92 (t, \( J = 7.5 \) Hz, 2 H), 1.94 (m, 1 H), 1.70 (m, 2 H), 1.40 (m, 2 H), 1.05 (m, 2 H), 0.95 (t, \( J = 7.4 \) Hz, 3 H), 0.77 (m, 2 H). \( ^{13}C \) NMR of 77 (CDCl\(_3\)) \( \delta \) 200.3, 150.2, 134.7, 128.5, 125.6, 38.4, 26.9, 22.7, 15.9, 14.2, 10.5.

![82](image1)

Preparation of 82 and 83. Cyclopentene (5 mL) was added to 293 mg of 4-(chloromethyl)biphenyl in a 3-neck round-bottom flask. A 2.1 mL portion of 1.5 M methyllithium in ether was added to a solution of 425 mg of 2,2,6,6-tetramethylpiperidine in 4 mL of anhydrous ether cooled to -15 °C. The solution was slowly warmed to room temperature as methane gas evolved. After liberation of the methane gas ceased, the solution of lithium tetramethylpiperidide was added to the 3-neck flask dropwise over a period of 10 min using a cannula. After 30 min, water was added and the solution was extracted into ether. The ether extract was washed with cold, dilute HCl solution, water, and saturated NaCl solution. The ether extract was dried over a mixture of Na\(_2\)SO\(_4\) and
MgSO₄ and filtered. The solvent was removed using a rotary evaporator. The crude mixture containing 82 and 83, was chromatographed on 9.6 g of silica gel and the column was eluted with hexanes. A total of 236 mg of 82 and 83 was isolated. Earlier fractions were enriched in the endo-isomer 82 while later fractions were enriched in an inseparable mixture of the exo-isomer 83 and uncharacterized by-products. ¹H NMR of 82 (CDCl₃) δ 7.59 (d, J = 7.4 Hz, 2 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.42 (t, J = 7.5 Hz, 2 H), 7.32 (m, 3 H), 1.98 (t, J = 8.1 Hz, 1 H), 1.83 (m, 2 H), 1.76 (m, 2 H), 1.69 (m, 2 H), 1.28 (m, 1 H), 0.05 (m, 1 H). ¹³C NMR of 82 (CDCl₃) δ 141.4, 138.7, 138.1, 129.8, 128.9, 127.2, 127.1, 127.1, 26.1, 23.4, 23.13, 23.05. ¹H NMR of 83 (CDCl₃) δ 7.56 (d, J = 9.6 Hz, 2 H), 7.46 (d, J = 9.6 Hz, 2 H), 7.41 (t, J = 9.6 Hz, 2 H), 7.30 (t, J = 9.6 Hz, 1 H), 7.08 (d, J = 9.6 Hz, 2 H), 1.93 (m, 2 H), 1.82 (m, 2 H), 1.67 (m, 2 H), 1.59 (m, 2 H), 1.30 (m, 1 H).

**Preparation of 89.** The preparation of 89 has previously been described.¹⁵

Preparation of 86. The preparation of 86 has previously been described.¹⁵
Preparation of 92a and 92b. Cyclopentene (10 mL) was added to 16 mg of dry Cu(OTf)$_2$ in a round-bottom flask fitted with an addition funnel. A solution of 190 mg of $p$-nitrophenyldiazomethane$^{18}$ in 17 mL of cyclopentene was added drop wise over a 1.5 h period. On completion of the addition, the mixture was stirred for an additional 30 min in a 33 °C water bath. The solution was filtered and the cyclopentene was then removed at aspirator pressure. The crude mixture was chromatographed on 9.4 g of silica gel. The column was eluted with increasing amounts of ether in hexanes. Mixtures of endo-isomer 92a and exo-isomer 92b, eluted with 3% ether in hexanes. The earlier fractions were enriched with the endo-isomer 92a, while the later fractions were enriched with the exo-isomer. $^1$H NMR of 92a (CDCl$_3$) δ 8.15 (d, $J = 9.0$ Hz, 2 H), 7.39 (d, $J = 9.0$ Hz, 2 H), 2.0 (t, $J = 8.4$ Hz, 1 H), 1.86 (m, 2 H), 1.76 (m, 2 H), 1.70 (m, 2 H), 1.29 (m, 1 H), -0.15 (m, 1 H). $^{13}$C NMR of 92a (CDCl$_3$) δ 147.3, 146.5, 130.2, 123.7, 25.8, 23.8, 23.5, 22.7. $^1$H NMR of 92b (CDCl$_3$) δ 8.08 (d, $J = 9.0$ Hz, 2 H), 7.10 (d, $J = 9.0$ Hz, 2 H), 1.95 (m, 2 H), 1.86 (m, 2 H), 1.74 (m, 2 H), 1.67 (m, 2 H), 1.29 (m, 1 H). $^{13}$C NMR of 92b (CDCl$_3$) δ 152.7, 145.6, 125.8, 123.7, 32.0, 28.2, 24.4, 20.9.
Photolyses in $\text{C}_6\text{D}_6$. General Procedures. The following procedure is representative. Approximately (5.0 mg) of the appropriate substrate was dissolved in approximately 375 mg of $\text{C}_6\text{D}_6$. A portion of the solution was placed in a 3 mm NMR tube and purged with N$_2$. The NMR tube was sealed and then irradiated for various periods of time in a Rayonet Photochemical Reactor$^9$ fitted with 350 nm lamps. The irradiations were carried out at ambient temperature (22 °C) which was maintained through the use of the reactor fan. Periodic $^1\text{H}$ analysis was performed on a 600 MHz NMR. Typical evolving spectral data are provided in Figure 2 and in Appendix B.

Photolyses in $\text{C}_6\text{D}_6$ with Benzophenone. General Procedures. The following procedure is representative. Benzophenone (5.0 mg) was dissolved in 375 mg of $\text{C}_6\text{D}_6$. The solution was added to 5.0 mg of the appropriate substrate and a portion of the mixture was placed in a 3 mm NMR tube. The NMR tube was purged with N$_2$, sealed, and irradiated with 350 nm light for various periods of time. The irradiations were carried out at ambient temperature (22 °C) as the tubes were cooled with the reactor fan. The tube was periodically analyzed by 600 MHz $^1\text{H}$ NMR spectroscopy. Typical data are shown in Figure 8 and in Appendix B.

Photolyses in $i$-PrOH. General Procedures. The following procedure is representative. A solution of 4 mg of appropriate substrate in approximately 260 mg of $i$-PrOH was placed in a 3 mm NMR tube and purged with N$_2$. The NMR tube was then sealed and irradiated for various periods of time using 350 nm lamps. The irradiations were carried out at ambient temperature (22 °C) which was maintained through the use of
the reactor fan. Periodic $^1$H analysis was performed using a 500 MHz NMR. Typical spectral data are provided in Figure 4 and in Appendix B.
APPENDIX B:

TYPICAL KINETIC PLOTS

The following pages show typical kinetic plots and corresponding evolving $^1$H NMR spectra for compounds discussed in the text.
Evolving $^1$H NMR spectra and the corresponding kinetic plot.
Evolving $^1$H NMR spectra and the corresponding kinetic plot
Evolving $^1$H NMR spectra and the corresponding kinetic plot.
Evolving $^1$H NMR spectra and the corresponding kinetic plot

![NMR Spectra](image)

![Kinetic Plot](image)

$$
\begin{array}{c}
\text{O} = C - n-\text{Bu} \\
\text{H} \quad \text{hv} (\text{C}_6\text{D}_6) \\
\text{H} \quad 69 \\
\end{array}
$$
Evolving $^1$H NMR spectra under Ph$_2$CO sensitized irradiation and the corresponding kinetic plot for the direct vs. sensitized reactions.
Evolving $^1$H NMR spectra under direct irradiation and Ph$_2$CO sensitized
APPENDIX C:

NMR SPECTRA

The following pages show $^1$H and $^{13}$C NMR spectra of new compounds discussed in the text.
$^{1}H$ NMR in CDCl$_3$
^13C NMR in CDCl\textsubscript{3}
$^{13}\text{C NMR in CDCl}_3$

43  87%

55(*)  13%
$^{13}$C NMR in CDCl$_3$
$13C$ NMR in CDCl$_3$
$^{13}\text{C} \text{NMR in CDCl}_3$
REFERENCES


10. Compound 45 was prepared (unpublished work from our laboratory) using the following procedure:

\[
\begin{align*}
\text{Br} & \quad \text{CH(OCH}_3\text{)}_2 \\
& \quad 1. n-\text{BuLi} \quad 2. \text{PhCON(CH}_3\text{)}_2 \\
& \quad 3. \text{H}_2\text{O}^+ \quad 4. \text{NH}_2\text{NHTs} \\
& \quad 5. \text{NaOCH}_3 \quad 6. \text{heat} \\
& \quad \text{COPh} \\
45
\end{align*}
\]

11. Unpublished B3LYP/6-31G* calculations from our laboratory.


