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Photochemical Behavior of Cyclopropyl-Substituted Benzophenones and Valerophenones

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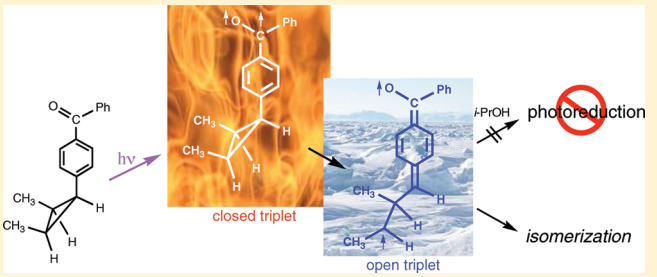
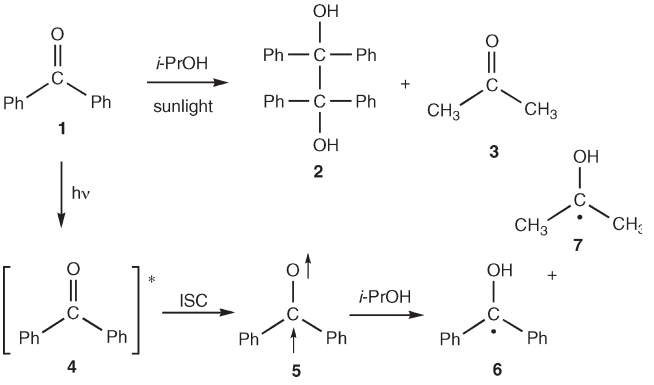
Supporting Information

ABSTRACT: *p*-Cyclopropylbenzophenone, **20**, gives no photoreduction when irradiated in *i*-PrOH solvent. This is a general phenomenon and a number of cyclopropyl-substituted benzophenones, including 4-(*endo*-6-bicyclo[3.1.0]hexyl)benzophenone, **19**, 4-(*cis*-2,3-dimethylcyclopropyl)benzophenone, **21**, 4-(*cis*-2-vinylcyclopropyl)benzophenone, **22**, and 4-(*endo*-7-bicyclo[4.1.0]hept-2-enyl)benzophenone, **23**, also fail to undergo photoreduction. Instead these latter compounds undergo *cis*—*trans* isomerization when irradiated. A mechanism involving formation of an (n, π^*) triplet, which subsequently fragments the strained cyclopropane bond to give a lower energy and unreactive open triplet, has been suggested. *p*-Cyclopropylvalerophenone, **25**, and *p*-(*endo*-6-bicyclo[3.1.0]hexyl)valerophenone, **24**, also undergo photoisomerization and fail to undergo the Norrish Type II photoreactions. Triplet energy dissipation by fragmentation of the cyclopropane bond is also proposed. In addition to the Norrish Type II reaction, *p*-cyclobutylvalerophenone, **27**, undergoes a photofragmentation to give ethylene and *p*-vinylvalerophenone, **60**, by an energy dissipation mechanism involving a 1,4-biradical derived from cyclobutane bond fragmentation.

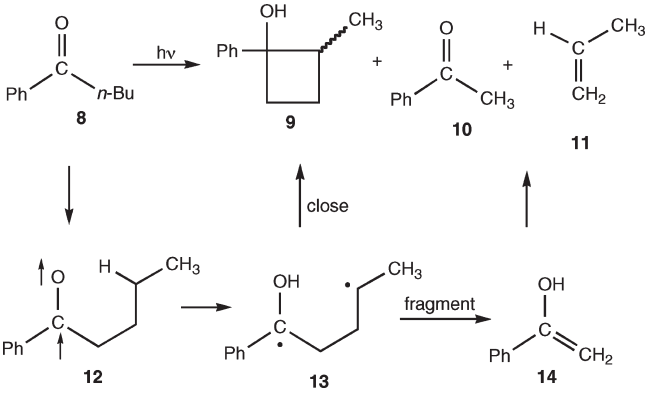


INTRODUCTION

The fledgling field of organic photochemistry was significantly advanced in 1900 when Ciamician and Silber exposed a solution of benzophenone in ethyl alcohol to sunlight.[1] The result was the photoreduction of benzophenone **1** to benzopinacol **2**. A modified version of this photochemical reaction is now the basis of the *Organic Syntheses* preparation of benzopinacol.[2] The photochemistry and photophysics of benzophenone have been thoroughly investigated.[3] The mechanism of this transformation[4] involves formation of the singlet excited state of benzophenone **4**, followed by intersystem crossing to the triplet state **5**. This triplet, which has radical characteristics, abstracts a hydrogen atom from the isopropyl alcohol to generate radicals **6** and **7**. Coupling of **6** gives benzopinacol. A second source of radical **6** is hydrogen atom transfer from radical **7** to benzophenone.



A second major photochemical process that carbonyl-containing compounds undergo is the Norrish Type II transformation.[5] This process is illustrated for the aromatic ketone valerophenone, **8**, which, on irradiation, gives the cyclobutanols **9**, along with fragmentation products acetophenone, **10**, and propene, **11**. Mechanistically, this process involves intramolecular hydrogen atom transfer in the triplet **12** to form the 1,4-biradical **13**. Intersystem crossing and ring closure gives the cyclobutanol **9**, while fragmentation of biradical **13** leads to propene and **14**, the enol tautomer of acetophenone.



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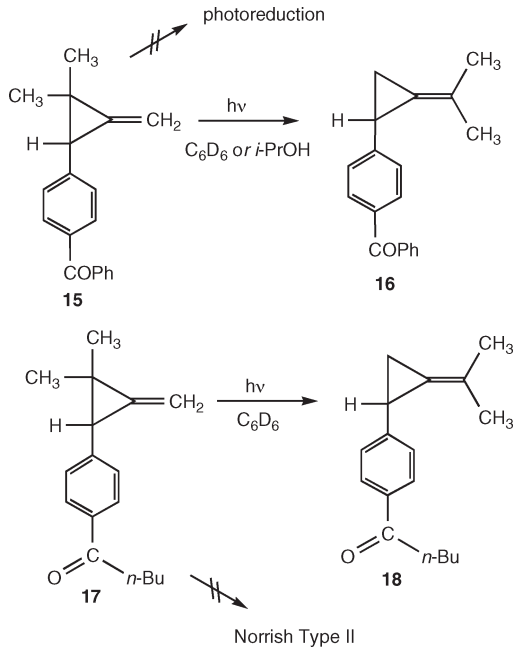
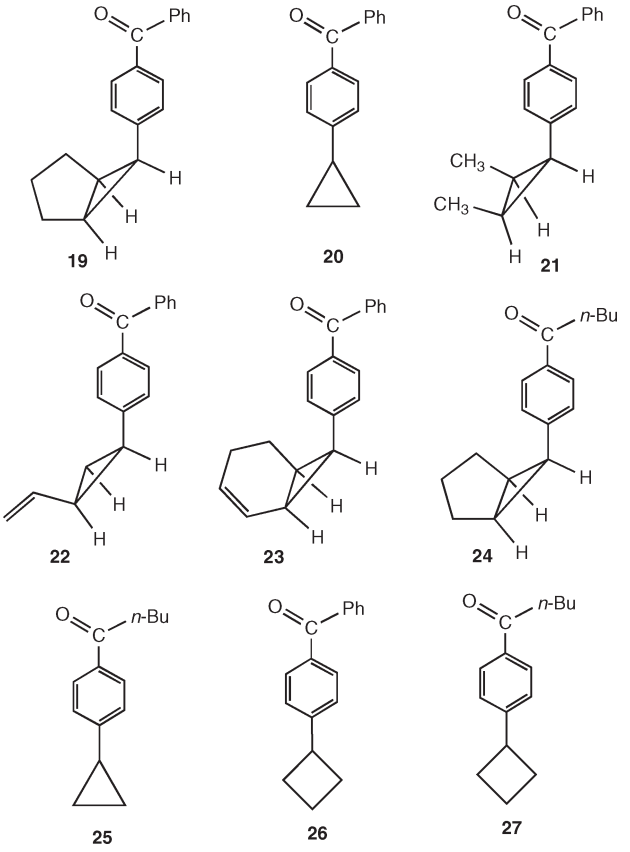
Our interest in carbonyl photochemistry stems from our studies of radical reactions and the methylenecyclopropane rearrangement.[6] During the course of our studies, it was found that substrates **15** and **17** undergo the thermal rearrangement to give **16** and **18**, respectively. We have also found that under photochemical conditions, the same rearrangement products are formed.[7] Interestingly, when **15** was irradiated in *i*-PrOH solvent, the same rearrangement product **16** was observed, with no trace of the corresponding pinacol reduction product. The rearranged product **16** also gave no trace of reduction when irradiated in *i*-PrOH. The lack of photoreduction was attributed to fragmentation of the strained cyclopropane bond of the excited state triplet derived from **15**. This dissipates the triplet energy and renders it incapable of hydrogen atom abstraction from *i*-PrOH. The substrate **17** also rearranges to **18** under photochemical conditions and no trace of Norrish Type II products are observed. The lack of Norrish Type II products is again attributed to rapid dissipation of energy of the triplet derived from **17** by fragmentation of the cyclopropane bond. Hence intramolecular hydrogen atom transfer never occurs.



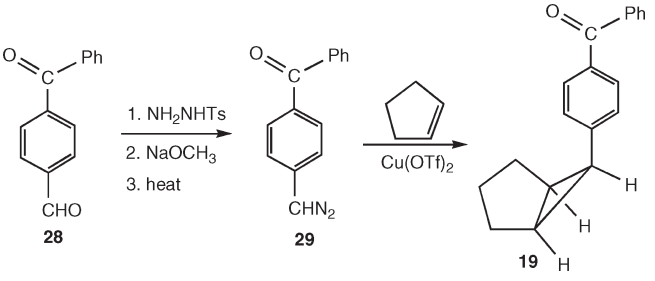
In view of these findings, it was of interest to examine the photochemical behavior of other cyclopropane-containing carbonyl compounds. The carbonyl-containing substrates **19**−**25** were therefore prepared. These substrates are less strained than the previously examined methylenecyclopropanes **15** and **17**. Hence they might be less prone to fragmentation. Additionally, substrates **22** and **23** are substituted vinylcyclopropanes and hence they might be prone to further rearrangements. The cyclobutyl systems **26** and **27** are even less strained (per methylene) than the cyclopropyl analogues. Would these compounds give photoreduction and Norrish Type II reactions? Reported here are the results of qualitative photochemical studies on these substrates.

RESULTS AND DISCUSSION

The diazocompound **29** was the starting material for the preparation of substrates **19**, **21**, **22**, and **23**. Conversion of the



Scheme 1. Synthesis of Substituted Benzophenone 19



known 4-benzoylbenzaldehyde **28** to this diazocompound was accomplished by pyrolysis of the sodium salt of the corresponding tosylhydrazone.[8] The *p*-cyclopropyl-substituted benzophenone **19** was then prepared by the $Cu(OTf)_2$-catalyzed reaction of diazocompound **29** with cyclopentene (Scheme 1). This major product **19** was separated from the minor *exo*-isomer by silica gel chromatography and ^1H NMR spectroscopy was used to establish stereochemistry of these isomers. The *endo*-isomer **19** shows a larger 8.2 Hz coupling constant between the benzylic hydrogen and the *cis*-hydrogens on the cyclopropane ring. Additionally, a B3LYP/6-31G* computational study[9] indicates that *endo*-6-phenylbicyclo[3.1.0]hexane, **30**, adopts a boat-like conformation, where the *endo*-phenyl group shields the *syn*-C_3 hydrogen on the cyclopentane ring (Figure 1). This leads to a GIAO-calculated chemical shift[9] of −0.03 ppm for this hydrogen. The analogous *syn*-C_3 hydrogen in **19** appears far upfield at 0.02 ppm in the ^1H NMR spectrum (C_6D_6). The syntheses of **21**,

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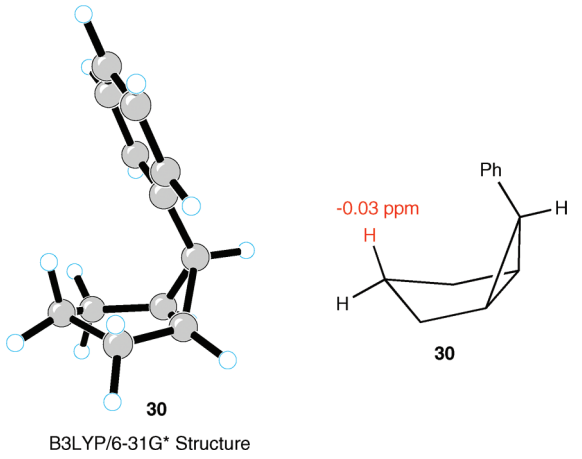

Figure 1. B3YLP/6-31G* calculated structure of 6-phenylbicyclo[3.1.0]-hexane.

22, and **23** utilized the same protocol starting with *cis*-2-butene, 1,3-butadiene, and 1,3-cyclohexadiene, respectively.

Irradiation of a C_6D_6 solution of the *endo*-isomer **19** using a photochemical reactor fitted with lamps emitting light centered at 350 nm led to isomerization to give the *exo*-isomer **31**. This wavelength corresponds to the forbidden (n, π^*) transition of aromatic ketones and the substrates described in this paper weakly absorb in this region of the UV spectrum. A photostationary state (89% of **31**; 11% of **19**) was eventually reached. Figure 2 shows evolving NMR spectra during irradiation of **19** as a function of irradiation time and Figure 3 shows a plot of the amount of remaining **19** as a function of time. When the irradiation was carried out in *i*-PrOH as solvent, the same isomerization of **19** to **31** occurred at a comparable rate and no trace of photoreduction to the corresponding pinacol was observed. Although quantum yields were not precisely measured, the reaction is efficient. Thus irradiation of a 0.071 M solution of benzophenone in *i*-PrOH for 3 min at 350 nm gave 29% reduction to benzopinacol. Under identical conditions 15% of **19** isomerized to **31**.

The photochemical behavior of **19** is reminiscent of the photoisomerization of *cis*- and *trans*-diphenylcyclopropane to reach a photostationary state.[10] A number of additional photochemical rearrangements of carbonyl-containing cyclopropanes, epoxides, and aziridines have also been studied and radical mechanisms have been proposed.[11] The mechanism in Scheme 2 accounts for the observed isomerization of **19**, as well as the lack of photoreduction in *i*-PrOH. Standard photoexcitation followed by intersystem crossing would yield the (n, π^*) triplet **32**.[12] However, it is suggested that the triplet **32**, which has spin density at the para-position, rapidly fragments a cyclopropane bond and forms a lower energy open triplet **33**. This process is suggested to be faster than hydrogen atom abstraction from *i*-PrOH. The new open triplet **33** is not energetic enough to abstract hydrogen from *i*-PrOH and hence no photoreduction is observed. However, **33** can rotate to a different conformation **34**. Intersystem crossing followed by ring closure would generate the observed product **31**.

Previous studies have shown that the effect of substituents on the photochemistry of aromatic ketones can be significant.[3a,13] Substituted benzophenones with lowest lying (n, π^*) triplet states are reduced in *i*-PrOH with high quantum yields. However,

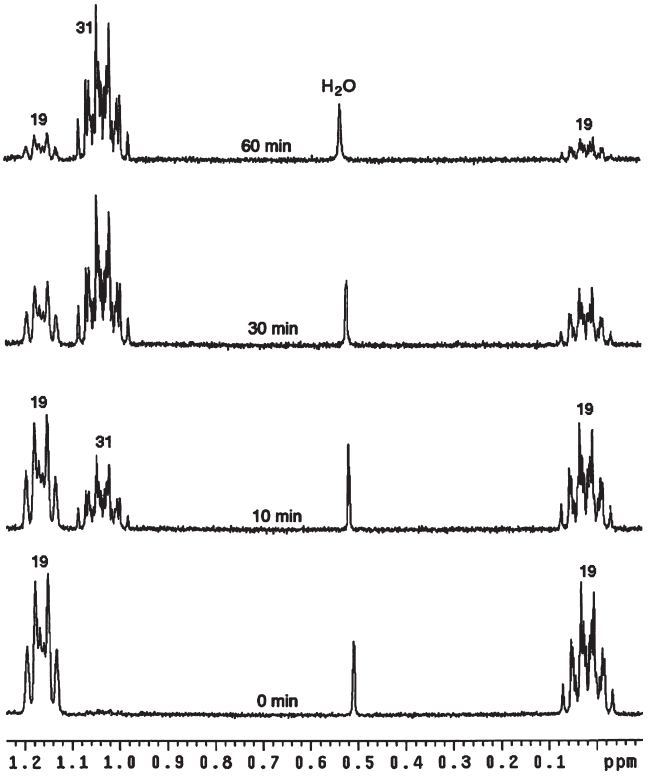

Figure 2. Evolving ^{1}H NMR spectra during irradiation (350 nm) of **19** in C_6D_6.

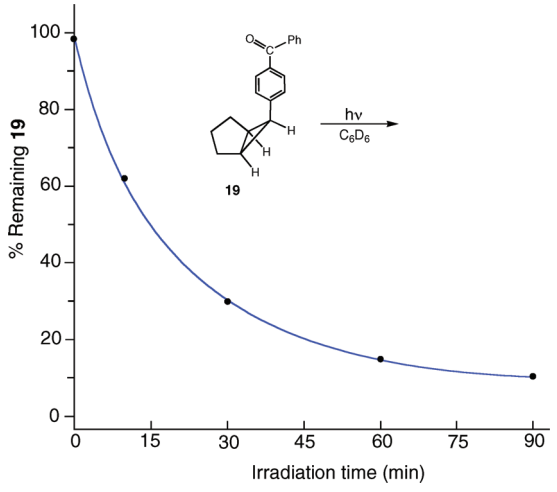

Figure 3. Plot of remaining **19** after irradiation in C_6D_6 versus the irradiation time.

those with low-lying (π, π^*) triplet states are less efficiently reduced (but many are nonetheless reduced to benzopinacols). While the (n, π^*) nature of the lowest triplet state derived from **19** has not been verified, a (π, π^*) triplet should still give slow reduction. The complete lack of reduction of **19** in *i*-PrOH suggests that some other factor (i.e., deactivation by ring-opening) prevents reduction.

To determine whether the high strain energy of the bicyclo-[3.1.0]hexane system **19** was an important feature, the unsubstituted *p*-cyclopropylbenzophenone, **20**, was next examined. Irradiation of **20** in *i*-PrOH gave no observable reaction

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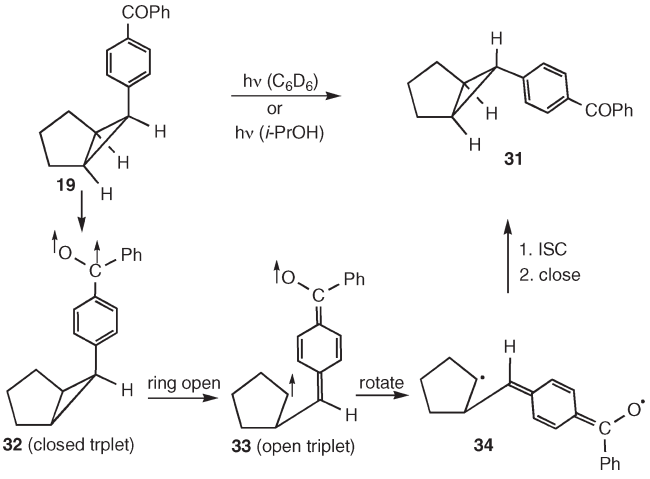
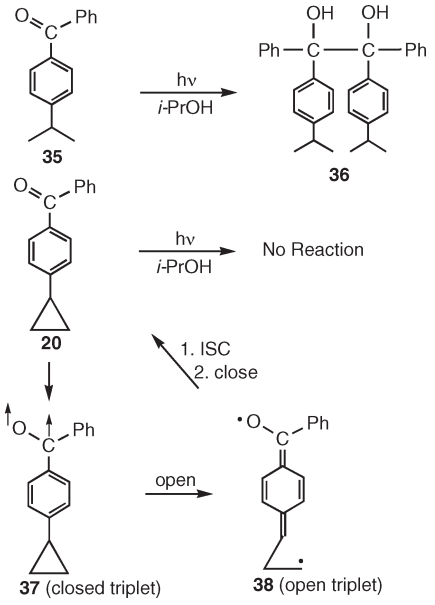
Scheme 2. Photolysis of Substituted Benzophenone 19: Mechanistic Analysis



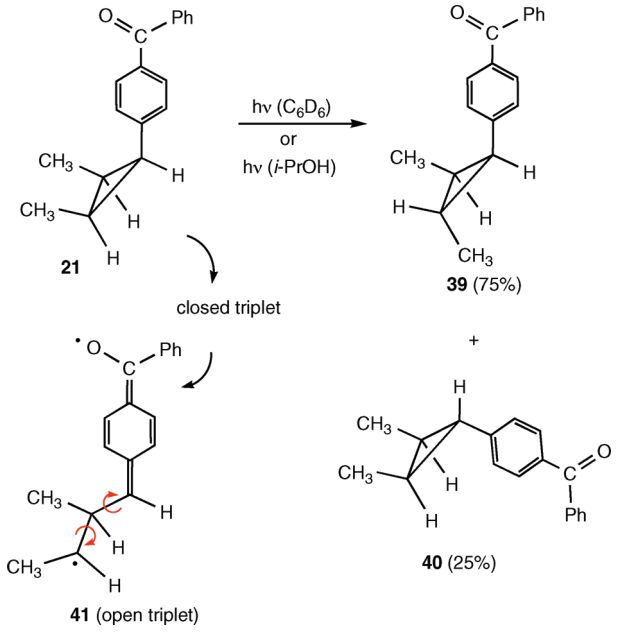
Scheme 3. Photolyses of Substituted Benzophenones 20 and 35



(Scheme 3). This contrasts with *p*-isopropylbenzophenone, **35**, which gave a high yield of the benzopinacol **36** under the same conditions. This suggests that there is no problem in forming the (n, π^*) triplet from **20**, but that this triplet **37** returns to the starting ketone without abstracting a hydrogen atom from *i*-PrOH. It is proposed that the triplet **37** is deactivated by fragmentation of the cyclopropane bond. As in the case of **34**, the open triplet **38** simply returns to **20** after intersystem crossing.

Does the cyclopropane ring of **20** actually fragment during the irradiation process? The substrate **21** can shed light on this suggestion. Irradiation of **21** in C_6D_6 or in *i*-PrOH led to complete conversion to a mixture of isomers **39** and **40** in a 75:25 ratio (Scheme 4). Therefore bond rotation must have occurred about all of the cyclopropane bonds. The open triplet

Scheme 4. Photolysis of Cyclopropyl-Substituted Benzophenone 21



biradical **41** offers a convenient explanation for this isomerization. The analogous biradical **38** is therefore a reasonable intermediate during the photolysis of **20** even though this biradical is "invisible" since **20** lacks a probe for detecting rotation.

The photochemical behavior of **22** and **23** was of interest in view of the known thermal vinylcyclopropane to cyclopentene rearrangement.[14] This process is formally a 1,3-sigmatropic shift that orbital symmetry considerations suggest can be concerted if inversion occurs at the migrating center.[15] The latest mechanistic thinking is that this rearrangement is a concerted process that goes through a transition state that has singlet "biradical character".[14e−g] The substrates **22** and **23** are vinylcyclopropanes and it was of interest to determine whether triplet biradical intermediates generated photochemically could lead to the vinylcyclopropane rearrangement.

Irradiation of both **22** and **23** in C_6D_6 and *i*-PrOH led only to photoisomerization until photostationary states were reached (Scheme 5). Of note is the fact that the *cis*-isomer **22** (62%) predominates over the *trans*-isomer **42** (38%) once the photostationary state is reached. No benzopinacol reduction products were formed in *i*-PrOH. In the case of **22**, no vinylcyclopropane rearrangement to give cyclopentene **43** was observed. No bicyclo[2.2.1]heptene **45** was formed from **23**. This is illustrated in Figure 4, which shows the clean isomerization of **23** to **44** in the ^{1}H NMR spectrum.

These results imply that the intermediates in the photoisomerizations of **22** and **23** are not involved in the thermal vinylcyclopropane rearrangement. In the case of **23**, it is suggested that opening of the initially formed closed triplet followed by rotation leads to **46**. Intersystem crossing and ring closure gives the observed product **44**. Apparently the triplet biradicals derived from **22** and **23**, upon intersystem crossing, do not enter onto the singlet potential energy surface involved in the thermal rearrangements of **22** and **23**. The implication is that the singlet biradical

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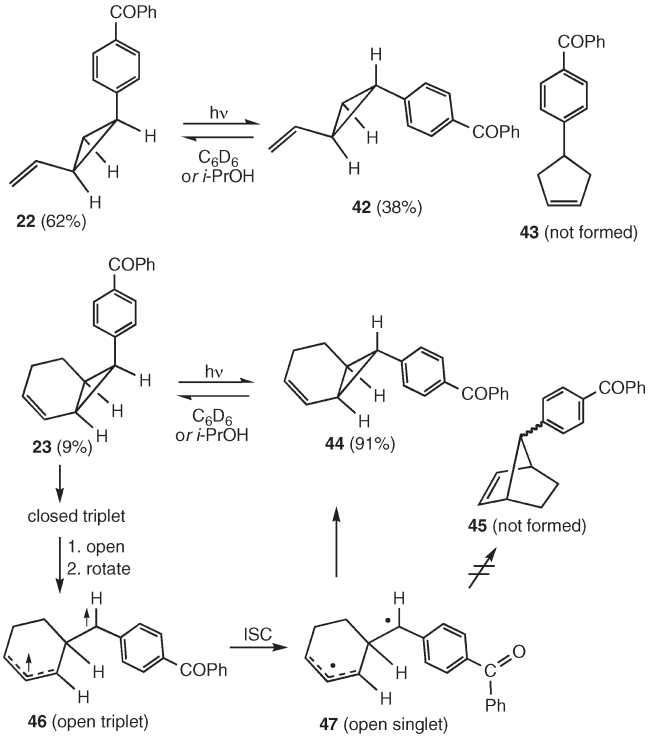
Scheme 5. Photolyses of Vinylcyclopropyl-Substituted Benzophenones 22 and 23



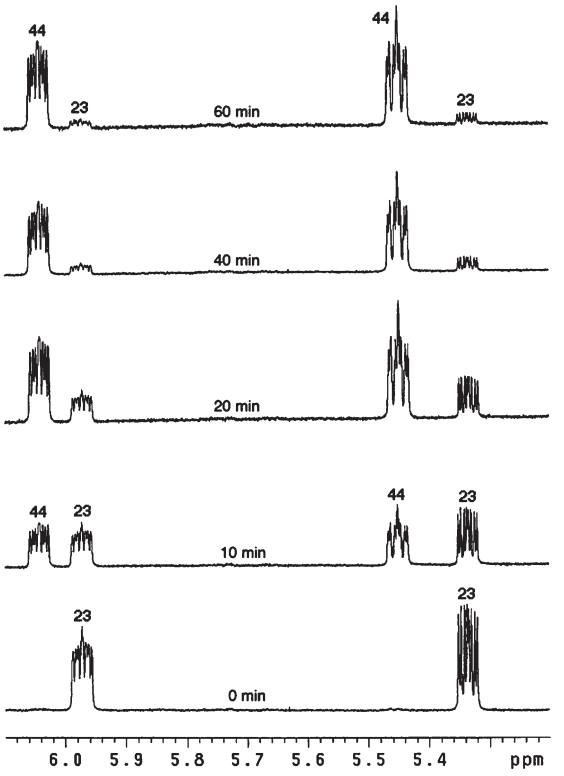


Figure 4. Evolving ^{1}H NMR spectra (alkene region) during irradiation of **23** in C_6D_6.

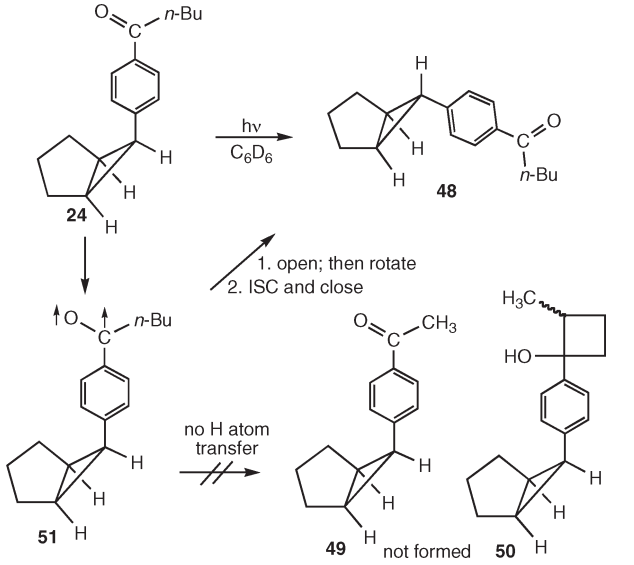
structure represented by **47** has no finite lifetime and hence cannot enter onto the thermal rearrangement energy surface.

Attention was next turned to the Norrish Type II photoreaction. When the cyclopropyl-substituted valerophenone **24** was irradiated in C_6D_6, clean isomerization to the *exo*-isomer **48** occurred (Scheme 6). No traces of the substituted acetophenone **49** or the cyclobutanol **50** were observed, i.e., Norrish Type II processes are completely bypassed. Intramolecular hydrogen atom transfer in the triplet **51**, which would lead to the Norrish Type II products **49** and **50**, is apparently slow relative to cyclopropane ring-opening and rotation, which lead to the observed product **48**.

The behavior of *p*-cyclopropylvalerophenone, **25**, is analogous to that of **24** (Scheme 7). Thus irradiation of **25** in C_6D_6 gave no apparent reaction, while under the same conditions, valerophenone, **8**, readily converted to acetophenone and 1-phenyl-2-methylcyclobutanol. As before, we suggest that the (n, π^*) triplet **52** loses it is ability to abstract hydrogen atoms when it dissipates its energy by cyclopropane ring fragmentation to form **53**. This process is presumably faster than hydrogen atom transfer giving **54**. Intersystem crossing and ring closure returns **53** to starting material.

The photochemistry of the *p*-cyclobutylbenzophenone, **26**, was next examined in order to determine whether or not the cyclobutane ring would fragment and allow standard photoreduction in *i*-PrOH to be circumvented. When irradiated in this solvent, facile photoreduction of **26** to the corresponding pinacol **56** resulted (Scheme 8). This is in stark contrast to the cyclopropyl analogue **20**, which gives no observable photoreduction. The behavior of *p*-cyclobutylvalerophenone, **27**, also contrasts with that of "unreactive" *p*-cyclopropylvalerophenone, **25**. In addition to undergoing the standard Norrish Type II

Scheme 6. Photolysis of Substituted Valerophenone 24



processes (giving **57** and **58**) when irradiated in C_6D_6, **27** also fragments to give *p*-vinylvalerophenone, **59**, and ethylene. Ketone **58** is also photolabile, and fragments under the reaction conditions to give **60**, and ethylene.[16] Figure 5 shows the development of these olefinic products **59** and **60** (as well as propene and ethylene) by ^{1}H NMR spectroscopy during irradiation of **27**. A further control experiment shows that ketone **59** is stable under the photochemical conditions and does not convert (by a Norrish Type II process) to **60**.

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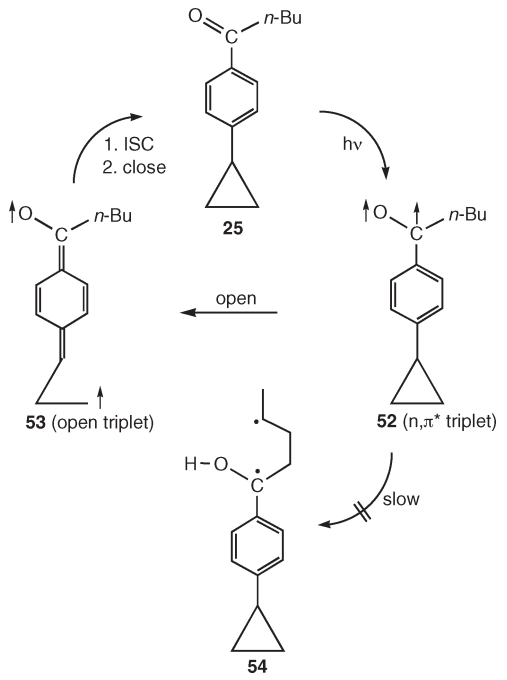
These experiments suggest that (n, π^*) triplet state derived from **26** is "normal" and leads to hydrogen atom abstraction from *i*-PrOH. However, it is suggested that the triplet **61** derived from **27** undergoes competing processes. Competing with Norrish Type II chemistry is opening of the cyclobutane ring of **61** to give biradical **62**, which is the proposed origin of ethylene and the substituted styrene **59**. The fact that triplet biradical **61** can undergo fragmentation of the cyclobutane ring provides indirect

Scheme 7. Photolysis of *p*-Cyclopropylvalerophenone, 25: Mechanistic Analysis



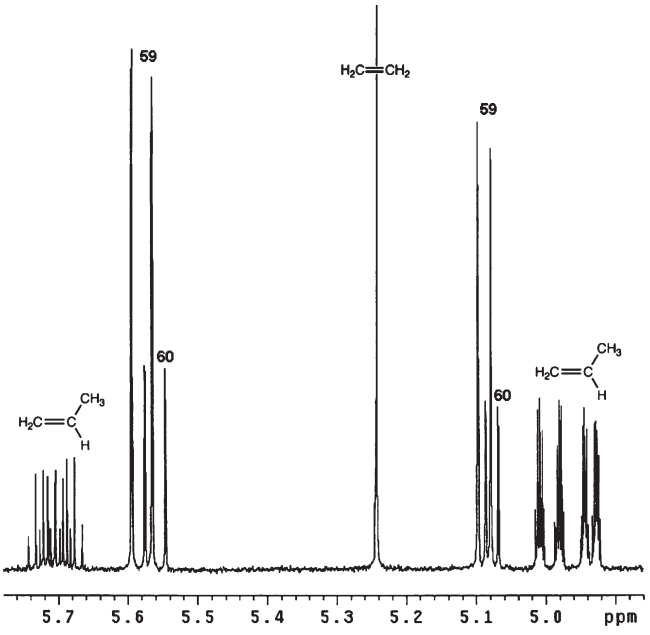
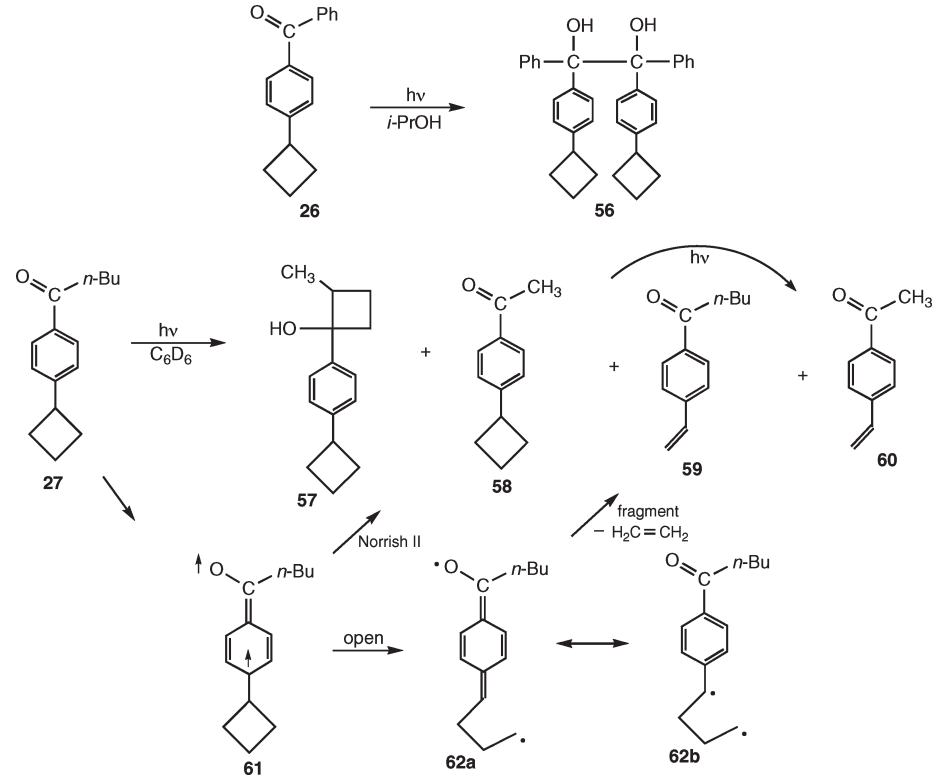


Figure 5. ^{1}H NMR spectrum (alkene region) during irradiation of **27** in C_6D_6.

Scheme 8. Photolyses of *p*-Cyclobutylbenzophenone and *p*-Cyclobutylvalerophenone



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evidence that photoinduced fragmentation of the more strained cyclopropane rings in **19**−**25** to give biradical intermediates is indeed a facile process.

CONCLUSIONS

Cyclopropyl-substituted benzophenones are not photoreduced to benzopinacols when irradiated in *i*-PrOH solution. Instead, cyclopropane bond fragmentation occurs, leading to a lower energy triplet that is incapable of hydrogen atom abstraction. Evidence for cyclopropane bond fragmentation is the observation of *cis*−*trans*-isomerization of the cyclopropane. The Norrish Type II photoreaction is also bypassed when cyclopropyl-substituted valerophenones are irradiated. Fragmentation of the cyclopropane bond again leads to a lower energy triplet and also accounts for the observed *cis*−*trans*-isomerization. The photochemical behavior of *p*-cyclobutylbenzophenone in *i*-PrOH is "normal" in that reduction to the benzopinacol is observed. However, *p*-cyclobutylvalerophenone fragments to give ethylene and *p*-vinylvalerophenone in addition to Norrish Type II photochemical products. The fragmentation products provide evidence for a 1,4-biradical intermediate derived from cleavage of the cyclobutane bond, and further supports the suggestion of facile cyclopropane bond fragmentation during photolyses of cyclopropyl-substituted benzophenones and valerophenones.

EXPERIMENTAL SECTION

Preparation of 4-Benzoylbenzaldehyde, 28. A solution of 2.30 g of *p*-bromobenzaldehyde dimethylacetal[17] in 17 mL of THF was cooled to −78 °C and 7.2 mL of 1.6 M *n*-BuLi in hexanes was added dropwise. After 30 min, at −78 °C, the mixture was warmed to −50 °C for 10 min and then recooled to −78 °C. A solution of 1.505 g of *N*,*N*-dimethylbenzamide in 10 mL of THF was then added over a 10 min period. The mixture was then slowly warmed to 0 °C and water was added with stirring. The mixture was then transferred to a separatory funnel, using ether, and the organic phase was washed with water and saturated NaCl solution, then dried over a mixture of Na_2SO_4 and $MgSO_4$. The solvent was removed with a rotary evaporator and the residue was distilled. After a lower boiling forrun, 2.11 g (71% yield) of *p*-benzoylbenzaldehyde dimethylacetal was collected, bp 150−153 °C (0.2 mm). ^{1}H NMR ($CDCl_3$) δ 7.81 (m, 4 H), 7.58 (m, 3 H), 7.48 (t, J = 7.6 Hz, 2 H), 5.47 (s, 1 H), 3.36 (s, 6 H). ^{13}C NMR ($CDCl_3$) δ 196.4, 142.4, 137.6, 137.5, 132.5, 130.02, 129.98, 128.3, 126.7, 102.4, 52.7.

A solution of 2.112 g of *p*-benzoylbenzaldehyde dimethylacetal in 10 mL of THF was stirred as a solution of 400 mg of H_2SO_4 in 11 mL of water was added dropwise. The mixture was vigorously stirred for 24 h and then transferred to a separatory funnel, using about 30 mL of ether. The ether phase was washed with water, Na_2CO_3 solution, and saturated NaCl solution, and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator. On standing, 1.701 g of 4-benzoylbenzaldehyde, **28**,[18] mp 65−66 °C, solidified. ^{1}H NMR ($CDCl_3$) δ 10.14 (s, 1 H), 8.01 (d, J = 9 Hz, 2 H), 7.93 (d, J = 9 Hz, 2 H), 7.82 (d, J = 9 Hz, 2 H), 7.64 (t, J = 9 Hz), 7.52 (t, J = 9 Hz, 2 H). ^{13}C NMR of **28** ($CDCl_3$) δ 195.9, 191.7, 142.6, 138.5, 136.8, 133.2, 130.4, 130.2, 129.5, 128.6.

Preparation of *p*-Benzoylphenyldiazomethane, 29. A mixture of 1.701 g of 4-benzoylbenzaldehyde, **28**, in 10 mL of methanol was stirred and 1.550 g of tosylhydrazine was added in one portion. The tosylhydrazone product immediately began to crystallize and stirring was continued for 24 h. The mixture was then cooled in an ice bath and the product was collected on a Buchner funnel and washed with a small amount of cold methanol. The yield of tosylhydrazone was 2.730 g (89%).

The crude tosylhydrazone (2.730 g) was placed in a 50 mL flask and 16 mL of freshly prepared 0.50 M $NaOCH_3$ in methanol was added with stirring. After 20 min, the methanol solvent was removed with a rotary evaporator and 20 mL of ethylene glycol was then added. The mixture was warmed in an oil bath at 75 °C to dissolve the salt. The solution was then heated in the oil bath at 90 °C for 6 min and then recooled to room temperature. The red-orange mixture was then extracted with ether and the ether solution of diazocompound **29** was decanted from the ethylene glycol with use of a pipet. The ethylene glycol residue was then reheated to 90 °C for 6 min and cooled to room temperature, then the extraction procedure was repeated. After a third heating and extraction, the combined ether extracts were washed with cold water and saturated salt solution, then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the ether solvent was removed with a rotary evaporator leaving 1.460 g (91%) of solid red-orange *p*-benzoylphenyldiazomethane, **29**, mp 59−62 °C. This diazocompound was stored in the dark at −20 °C. ^{1}H NMR of **29** ($CDCl_3$) δ 7.77 (m, 4 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 6.98 (d, J = 8.4 Hz, 2 H), 5.08 (s, 1 H). ^{13}C NMR of **29** ($CDCl_3$) δ 195.6, 138.1, 135.9, 132.8, 132.1, 131.4, 129.8, 128.2, 120.6, 48.7.

Preparation of 4-(*endo*-6-Bicyclo[3.1.0]hexyl)benzophenone, 19. Cyclopentene (10 mL) was added to 27 mg of dry $Cu(OTf)_2$ (dried at 70 °C and 0.1 mm pressure). A solution of 205 mg of *p*-benzoylphenyldiazomethane **29** in 7 mL of cyclopentene was added dropwise over a period of 1 h with stirring. The solution was stirred for an additional 30 min at room temperature and then filtered. The remaining cyclopentene was removed with a rotary evaporator and the residue was chromatographed on 6.0 g of silica gel. Elution with 3% ether in pentane gave a total of 133 mg of **19** and **31** (55% yield). Pure *endo*-isomer **19** (71 mg) eluted first followed by fractions containing a mixture of **19** and **31** (22 mg). Pure *exo*-isomer **31** eluted last (40 mg). ^{1}H NMR of **19** ($CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 2 H), 7.75 (d, J = 8 Hz, 2 H), 7.58 (t, J = 7.5 Hz, 1 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.35 (d, J = 8 Hz, 2 H), 2.00 (t, J = 8.3 Hz, 1 H), 1.84 (m, 2 H), 1.73 (m, 4 H), 1.29 (m, 1 H), −0.03 (m, 1 H). ^{13}C NMR of **19** ($CDCl_3$) δ 196.7, 144.3, 138.0, 135.2, 132.2, 130.3, 130.0, 129.2, 128.2, 25.8, 23.7, 23.1, 22.7. ESI exact mass ($M + H^+$) calculated for $C_{19}H_{19}O$ 263.1430, found 263.1421. ^{1}H NMR of **31** ($CDCl_3$) δ 7.76 (d, J = 7 Hz, 2 H), 7.70 (d, J = 8 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.09 (d, J = 8 Hz, 2 H), 1.95 (d of d, J = 12.4, 8.3 Hz, 2 H), 1.85 (m, 2 H), 1.71 (t, J = 3.1 Hz, 1 H), 1.67 (m, 3 H), 1.30 (m, 1 H). ^{13}C NMR of **31** ($CDCl_3$) δ 196.4, 149.7, 138.2, 134.3, 132.1, 130.4, 129.9, 128.2, 125.1, 31.0, 28.1, 24.2, 20.9.

Preparation of *p*-Cyclopropylbenzophenone, 20. A solution of 317 mg of *p*-cyclopropylbromobenzene[19] in 7 mL of anhydrous THF was cooled to −78 °C and 1.8 mL of 1.6 M *n*-butyllithium was added. The solution was warmed to −50 °C for 5 min and recooled to −78 °C. A solution of 350 mg *N*,*N*-dimethylbenzamide in 9 mL of anhydrous THF was then added dropwise. After the addition was complete, the solution was slowly warmed to 5 °C. Water (10 mL) was added dropwise 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 Na_2SO_4 and $MgSO_4$ and filtered. The solvent was removed with use of a rotary evaporator and the residue was chromatographed on 8.8 g of silica gel. The column was eluted with increasing amounts of ether in hexanes and 210 mg of **20**[20] (59% yield) eluted with 4% ether in hexanes. ^{1}H NMR of **20** ($CDCl_3$) δ 7.78 (d, J = 8 Hz, 2 H), 7.72 (d, J = 8 Hz, 2 H), 7.57 (t, J = 8 Hz, 1 H), 7.47 (t, J = 8 Hz, 2 H), 7.15 (d, J = 8 Hz, 2 H), 1.97 (m, 1 H), 1.08 (m, 2 H), 0.80 (m, 2 H). ^{13}C NMR of **20** ($CDCl_3$) 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 4-(*cis*-2,3-Dimethylcyclopropyl)benzophenone, 21. Cyclohexane (12 mL) was cooled in an ice/acetone bath under argon as 8.5 g of *cis*-2-butene was condensed into the cyclohexane. Dry $Cu(OTf)_2$ (18 mg) was then added and a solution of 145 mg of *p*-benzoylphenyldiazomethane, **29**, in 13 mL of cyclohexane was added dropwise over 75 min at room temperature. Upon completion of the addition, the mixture was filtered and the solvents were removed under vacuum. Chromatography on 5 g of silica gel and elution with 2% ether in hexanes gave 93 mg (56%) of *cis*-isomer **21** and *trans*-isomer **40**. Pure *cis*-isomer **21** (66 mg; mp 98−99 °C) eluted first followed by a fraction containing a mixture of **21** and **40** (15 mg). Pure *trans*-isomer **40** eluted last (12 mg). ^{1}H NMR of **21** ($CDCl_3$) δ 7.80 (d, J = 8 Hz, 2 H), 7.75 (d, J = 8 Hz, 2 H), 7.58 (t, J = 8 Hz, 1 H), 7.48 (t, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H), 2.05 (t, J = 9 Hz, 1 H), 1.27 (m, 2 H), 0.96 (m, 6 H). ^{13}C NMR of **21** ($CDCl_3$) δ 196.7, 143.5, 137.9, 135.0, 132.2, 131.3, 130.02, 129.98, 128.2, 22.9, 13.9, 9.6. ESI exact mass ($M + H^+$) calculated for $C_{18}H_{19}O$ 251.1430, found 251.1447. ^{1}H NMR of **40** ($CDCl_3$) δ 7.76 (d, J = 8 Hz, 2 H), 7.70 (d, J = 8 Hz, 2 H), 7.56 (t, J = 7.5 Hz, 1 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.07 (d, J = 8 Hz, 2 H), 1.26 (m, 3 H), 1.20 (m, 6 H). ^{13}C NMR of **40** ($CDCl_3$) δ 196.4, 150.4, 138.2, 134.2, 132.1, 130.4, 129.9, 128.2, 125.0, 32.5, 23.8, 12.7.

Preparation of 4-(*cis*-2-Vinylcyclopropyl)benzophenone, 22. As described above, 6.9 g of 1,3-butadiene was condensed into 12 mL of cyclohexane and 12 mg of dry $Cu(OTf)_2$ was added. Addition of 165 mg of *p*-benzoylphenyldiazomethane in 11 mL of cyclohexane gave, after silica gel chromatography, 84 mg (45% yield) of **22** and **42**. Earlier fractions were enriched in the *cis*-isomer **22** while later fractions contained mixtures of the *cis*-isomer **22** and the *trans*-isomer **42**. ^{1}H NMR of **22** ($CDCl_3$) δ 7.79 (d, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H), 7.58 (t, J = 8 Hz, 1 H), 7.48 (t, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 2 H), 5.15 (m, 2 H), 4.90 (m, 1 H), 2.41 (m, 1 H), 1.97 (m, 1 H), 1.35 (t of d, J = 8.3, 5.4 Hz, 1 H), 1.15 (q, J = 5.9 Hz, 1 H). ^{13}C NMR of **22** ($CDCl_3$) δ 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. ESI exact mass ($M + H^+$) calculated for $C_{18}H_{17}O$ 249.1250, found 249.1273.

Preparation of 4-(*endo*-7-Bicyclo[4.1.0]hept-2-enyl)benzophenone, 23. Using a procedure analogous to the preparation of **19**, reaction of *p*-benzoylphenyldiazomethane with $Cu(OTf)_2$ in 1,3-cyclohexadiene gave a mixture of **23** and **44** in 46% yield. ^{1}H NMR of **23** ($CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2 H), 7.70 (d, J = 8 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.37 (d, J = 8 Hz, 2 H), 6.10 (m, 1 H), 5.39 (d of d of d, J = 10, 6, 2.5 Hz, 1 H), 2.34 (t, J = 8.7 Hz, 1 H), 1.97 (m, 1 H), 1.80−1.70 (m, 3 H), 1.64 (m, 1 H), 0.59 (m, 1 H). ^{13}C NMR of **23** ($CDCl_3$) 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. ESI exact mass ($M + H^+$) calculated for $C_{20}H_{19}O$ 275.1430, found 275.1415. ^{1}H NMR of **44** ($CDCl_3$) 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 **44** ($CDCl_3$) 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 *p*-(*endo*-6-Bicyclo[3.1.0]hexyl)valerophenone, 24. Cyclopentene (15 mL) was added to 26 mg of dry $Cu(OTf)_2$ and a solution of 378 mg of *p*-cyanophenyldiazomethane[7] in 20 mL of cyclopentene was added dropwise over a 2 h period. The solution was then warmed to 30 °C for 30 min. The solution was then filtered and the cyclopentene was removed under vacuum. The residue was chromatographed on 7 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. A mixture of *endo*- and *exo*-4-(6-bicyclo-[3.1.0]hexyl)benzonitrile (83 mg; 17% yield) eluted with 3% ether in hexanes.

The mixture of nitriles obtained above was dissolved in 5 mL of anhydrous ether and the solution was cooled to −78 °C. *n*-Butyllithium (1.0 mL of 1.6 M) was then added. The solution was warmed to room temperature and recooled to −78 °C, then 0.25 mL of methanol was added. The mixture was warmed to room temperature, water was added, and the mixture was extracted with ether. The ether extract was vigorously stirred with 5 mL of 3% aqueous HCl solution for 30 min and then transferred to a separatory funnel. The ether phase was washed with water and saturated NaCl solution, then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator. An NMR spectrum showed *endo*-isomer **24** and *exo*-isomer **48** 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. A mixture of **24** and **48** (67 mg; 61% yield) eluted with 4% ether in hexanes. Earlier fractions were enriched in the *endo*-isomer **24** while later fractions were enriched in the *exo*-isomer **48**. ^{1}H NMR of **24** ($CDCl_3$) δ 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 **24** ($CDCl_3$) δ 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. ESI exact mass ($M + H^+$) calculated for $C_{17}H_{23}O$ 243.1743, found 243.1734.

^{1}H NMR of **48** ($CDCl_3$) δ 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 **48** ($CDCl_3$) δ 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.

Preparation of *p*-Cyclopropylvalerophenone, 25. Anhydrous ether (2 mL) was cooled to −78 °C and 0.7 mL of 1.6 M *n*-butyllithium was added. A solution of 78 mg of *p*-cyclopropylbenzaldehyde[21] in 2 mL of ether was then added dropwise. The solution was warmed to room temperature and 5 mL of water was added. The ether phase was washed with water and saturated NaCl solution, and then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator and the residue was dissolved in 3 mL of CH_2Cl_2. Pyridinium chlorochromate (215 mg) was added to the solution and the mixture was stirred at room temperature for 3 h. Pentane (3 mL) was added and the mixture was filtered through a small amount of silica gel. The solvent was removed with a rotary evaporator. The residue was chromatographed on 5 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. A total of 62 mg (62% yield) of **25** eluted with 2% ether in hexanes. ^{1}H NMR of **25** ($CDCl_3$) δ 7.85 (d, J = 8 Hz, 2 H), 7.11 (d, J = 8 Hz, 2 H), 2.92 (t, J = 8 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 **25** ($CDCl_3$) δ 200.3, 150.2, 134.7, 128.5, 125.6, 38.4, 26.9, 22.7, 15.9, 14.2, 10.5. ESI exact mass ($M + H^+$) calculated for $C_{14}H_{19}O$ 203.1430, found 203.1434.

Preparation of 1-Bromo-4-cyclobutylbenzene. A solution of 844 mg of Et_3SiH and 1.318 g of (4-bromophenyl)cyclobutanol[22] in 18 mL of CH_2Cl_2 was cooled to −78 °C and a solution of 1.045 g of boron trifluoride diethyl etherate in 5 mL of CH_2Cl_2 was added dropwise over 5 min. The mixture was warmed slowly to 0 °C and 1.83 g of K_2CO_3 was added followed by 10 mL of water. The solution was transferred with ether to a separatory funnel and the aqueous phase was separated. The organic phase was washed with water and saturated NaCl solution, then dried over a mixture of $NaSO_4$ and $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator and the crude residue was chromatographed on 5 g of silica gel. The product eluted with pentane and the solvent was removed with a rotary evaporator. The residue was distilled by using a short-path distillation head to give 845 mg (69% yield) of 1-bromo-4-cyclobutylbenzene, bp 85 °C (0.8 mm).[23] ^{1}H NMR ($CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 2 H), 7.08 (d, J = 8.4 Hz, 2 H), 3.49 (quintet, J = 8.8 Hz, 1 H), 2.33 (m, 2 H), 2.10 (m 2 H), 2.02 (m, 1 H), 1.85 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 145.2, 131.2, 128.1, 119.3, 39.8, 29.7, 18.2.

Preparation of *p*-Cyclobutylbenzophenone, 26. A solution of 358 mg of 1-bromo-4-cyclobutylbenzene in 6 mL of THF was cooled to −78 °C and 1.1 mL of 1.6 M *n*-butyllithium was added. After 20 min at −78 °C, a solution of 294 mg of *N*,*N*-dimethylbenzamide in 2 mL of THF was added dropwise. After the addition was complete, the solution was slowly warmed to room temperature. Water was added dropwise and the mixture was then extracted into ether. The ether extract was washed with water and saturated NaCl solution, then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator, the residue was chromatographed on 7 g of silica gel, and the column was eluted with increasing amounts of ether in hexanes. The product **26** (251 mg; 63% yield) eluted with 3% ether in hexanes. ^{1}H NMR of **26** ($CDCl_3$) δ 7.79 (d, J = 8 Hz, 2 H), 7.76 (d, J = 8 Hz, 2 H), 7.58 (t, J = 7.5 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.31 (d, J = 8 Hz, 2 H), 3.63 (quintet, J = 8.9 Hz, 1 H), 2.40 (m, 2 H), 2.19 (m, 2 H), 2.7 (m, 1 H), 1.90 (m, 1 H). ^{13}C NMR of **26** ($CDCl_3$) δ 196.5, 151.4, 138.0, 135.1, 132.2, 130.3, 130.0, 128.2, 126.2, 40.3, 29.6, 18.3. ESI exact mass ($M + H^+$) calculated for $C_{17}H_{17}O$ 237.1274, found 237.1265.

Preparation of *p*-Cyclobutylvalerophenone, 27. A solution of 207 mg of 1-bromo-4-cyclobutylbenzene in 5 mL of THF was cooled to −78 °C and 0.7 mL of 1.6 M *n*-butyllithium was added. After 20 min at −78 °C, a solution of 110 mg of distilled valeraldehyde in 2 mL of ether was added dropwise. After the addition was complete, the solution was slowly warmed to room temperature. Water was added dropwise and the mixture was then extracted into ether. The ether extract was washed with water and saturated NaCl solution, dried over a mixture of Na_2SO_4 and $MgSO_4$, and filtered, then the solvent was removed with a rotary evaporator.

The crude residue was dissolved in 5 mL of CH_2Cl_2 and 427 mg of pyridinium chlorochromate was added. The mixture was stirred at room temperature for 2.5 h, 5 mL of pentane was added, and the mixture was filtered through a small amount of silica gel. After solvent removal with a rotary evaporator, the residue was chromatographed on 6 g of silica gel and the column was eluted with increasing amounts of ether in hexanes. The product **27** (187 mg; 80% yield) eluted with 2% ether in hexanes. ^{1}H NMR of **27** ($CDCl_3$) δ 7.90 (d, J = 8 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H), 3.60 (quintet, J = 8.9 Hz, 1 H), 2.94 (t, J = 7.5 H, 2 H), 2.37 (m, 2 H), 2.16 (m, 2 H), 2.05 (m, 1 H), 1.88 (m, 1 H), 1.71 (quintet, J = 7.5 Hz, 2 H), 1.41 (hextet, J = 7.5 Hz, 2 H), 0.95 (t, J = 7.5 Hz, 3 H). ^{13}C NMR of **27** ($CDCl_3$) δ 200.3, 151.7, 134.8, 128.2, 126.5, 40.3, 38.3, 29.6, 26.7, 22.6, 18.3, 14.0. ESI exact mass ($M + H^+$) calculated for $C_{15}H_{21}O$ 217.1587, found 217.1578.

Photolyses in C_6D_6: General Procedures. The following procedure is representative. Benzene-d_6 was deoxygenated by briefly bubbling N_2 through the stock sample. A solution of 4.0 mg of **19** in 270 mg of C_6D_6 was placed in a 3 mm NMR tube under N_2 or argon. The NMR tube was sealed and then placed in a Rayonet Photochemical Reactor fitted with 350 nm lamps.[24] The tube was irradiated for various time periods at ambient temperature (22 °C) using the air-cooling provided by the reactor fan. The tube was periodically analyzed by 600 MHz ^{1}H NMR spectroscopy and typical spectra are shown in Figure 2. Spectra and data for compounds **21**, **22**, and **24** are given as Supporting Information.

Photolysis of *p*-Cyclobutylvalerophenone, 27, in C_6D_6. A solution of 4.0 mg of **27** in 320 mg of C_6D_6 was placed in a 3 mm NMR tube under argon and the solution was irradiated for 2 h. ^{1}H NMR analysis, as shown in the Supporting Information, showed **57**, **58**, **59**, and **60** in an 11:31:11:4 ratio, along with 43% of unreacted **27**. Further analysis of the olefinic region of the spectrum (Figure 5) showed the presence of ethylene and propene. These products were all identified by spectral comparison in C_6D_6 with authentic samples prepared as described below.

Preparation of 1-(4-Cyclobutylphenyl)-2-methylcyclobutanol, 57. A solution of 115 mg of 1-bromo-4-cyclobutylbenzene in 2 mL of THF was cooled to −78 °C and 0.36 mL of 1.6 M *n*-butyllithium in hexanes was added. After 10 min at −78 °C, a solution of 45 mg of 2-methylcyclobutanone[25] in 2 mL of anhydrous ether was added dropwise. The solution was then warmed slowly to room temperature, quenched with water, and then transferred to a separatory funnel with use of ether. The ether extract was washed with water and saturated NaCl solution, then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator. The residue was chromatographed by using a 4.2 g silica gel column packed with pentane. The column was eluted with increasing amounts of ether in pentane to give 96 mg (82%) of alcohols **57**. The major product was 1-(4-cyclobutylphenyl)-2-methylcyclobutanol, **57**, with the 4-cyclobutylphenyl group *trans* to the 2-methyl group, while the minor product was the *cis*-isomer. ^{1}H NMR of **57** ($CDCl_3$) δ 7.36 (d, J = 8 Hz, 2 H), 7.21 (d, J = 8 Hz, 2 H), 3.54 (quintet, J = 8.8 Hz, 1 H), 2.73 (hextet, J = 7.5 Hz, 1 H), 2.42 (m, 1 H), 2.34 (m, 2 H), 2.17 (m, 3 H), 1.99 (m, 2 H), 1.85 (m, 1 H), 1.77 (m, 1 H), 1.16 (d J = 7.5 Hz, 3H). ^{13}C NMR of **57** ($CDCl_3$) δ 145.1, 144.5, 126.3, 124.7, 78.4, 40.1, 40.0, 33.9, 29.8, 23.2, 18.3, 14.1. ESI exact mass ($M + Na^+$) calculated for $C_{15}H_{20}NaO$ 239.1406, found 239.1395.

Preparation of *p*-Cyclobutylacetophenone, 58. The preparation of **61** was analogous to the preparation of *p*-cyclobutylvalerophenone, **27**. Thus, reaction of 261 mg of 1-bromo-4-cyclobutylbenzene in 5 mL of THF at −78 °C with 0.75 mL of 1.6 M *n*-butyllithium followed by addition of 70 mg of acetaldehyde in 2 mL of ether gave the crude alcohol product. This product was dissolved in 5 mL of CH_2Cl_2 and 379 mg of pyridinium chlorochromate was added. After dilution with 5 mL of pentane and filtration through a small amount of silica gel, chromatography on 6 g of silica gel and elution with 3% ether in pentane gave 126 mg (40% yield) of pure **58**.[26] ^{1}H NMR of **58** ($CDCl_3$) δ 7.90 (d, J = 8 Hz, 2 H), 7.29 (d, J = 8 Hz, 2 H), 3.60 (quintet, J = 8.8 Hz, 1 H), 2.58 (s, 3 H), 2.38 (m, 2 H), 2.17 (m, 2 H), 2.05 (m, 1 H), 1.88 (m, 1 H). ^{13}C NMR of **58** ($CDCl_3$) δ 197.9, 152.0, 134.9, 128.4, 126.5, 40.2, 29.5, 26.6, 18.3.

Preparation of *p*-Vinylvalerophenone, 59. The preparation of *p*-vinylvalerophenone, **59**, was analogous to the preparation of *p*-cyclobutylvalerophenone, **27**. Thus reaction of 350 mg of *p*-bromostyrene in 7 mL of THF with 1.2 mL of 1.6 M *n*-butyllithium at −78 °C, followed by addition of 186 mg of valeraldehyde in 3 mL of ether, followed by oxidation with 625 mg of pyridinium chlorochromate in 8 mL of CH_2Cl_2, gave, after chromatography on 7 g of silica gel, 218 mg (61% yield) of **59**.[27] ^{1}H NMR of **59** ($CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 2 H), 6.76 (d of d, J = 17.6, 10.9 Hz, 1 H), 5.87 (d of d, J = 17.6, 0.7 Hz, 1 H), 5.39 (d of d, J = 10.9, 0.7 Hz, 1 H), 2.95 (t, J = 7.4 Hz, 2 H), 1.72 (quintet, J = 7.4 Hz, 2 H), 1.41 (sextet, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.4 Hz, 1 H). ^{13}C NMR of **59** ($CDCl_3$) δ 200.1, 141.9, 136.3, 136.0, 128.5, 126.3, 116.6, 38.4, 26.6, 22.5, 14.0.

Preparation of *p*-Vinylacetophenone, 60. The preparation of *p*-vinylacetophenone, **60**, was analogous to the preparation of *p*-cyclobutylvalerophenone, **27**. Thus reaction of 349 mg of *p*-bromostyrene in 7 mL of THF with 1.2 mL of 1.6 M *n*-butyllithium at −78 °C, followed by addition of 90 mg of acetaldehyde in 2 mL of ether, followed by oxidation with 614 mg of pyridinium chlorochromate in 8 mL of CH_2Cl_2, gave, after chromatography on 7 g of silica gel, 152 mg (55% yield) of **60**.[28] ^{1}H NMR of **60** ($CDCl_3$) δ 7.92 (d, J = 8.3 Hz, 2 H), 7.48 (d, J = 8.3 Hz, 2 H), 6.75 (d of d, J = 17.6, 10.9 Hz, 1 H), 5.88 (d of d, J = 17.6, 0.7 Hz, 1 H), 5.40 (d of d, J = 10.9, 0.7 Hz, 1 H), 2.59 (s, 3 H). ^{13}C NMR of **60** ($CDCl_3$) δ 197.6, 142.1, 136.3, 135.9, 128.7, 126.3, 116.7, 26.6.

Photolyses in *i*-PrOH: General Procedures. The following procedure is representative. A solution of 4.6 mg of **21** in 295 mg of nitrogen-purged *i*-PrOH was sealed in a 3 mm NMR tube under nitrogen or argon. The NMR tube was then irradiated with 350 nm lamps for various time periods at ambient temperature (22 °C), using the air-cooling provided by the reactor fan. The tube was periodically analyzed

by 600 MHz ^{1}H NMR spectroscopy by using No-D NMR techniques[29] and typical spectral data showing isomerizations of **21**, **22**, and **23**, as well as photoreduction of **26**, are given as Supporting Information.

Photolysis of *p*-Isopropylbenzophenone, 35, in *i*-PrOH. A solution of 45 mg of **35** in 2.5 mL of *i*-PrOH was placed in a 5 mm NMR tube under argon. The NMR tube was then irradiated with 350 nm lamps for 70 min at ambient temperature. The solvent was then removed by using a rotary evaporator and the solid residue was slurried with a small amount of pentane. The pentane was decanted and the product **36** (42 mg; 93% yield; 50:50 mixture of meso and threo diastereomers) was dried under vacuum. ^{1}H NMR of **36** ($CDCl_3$) δ 7.40 (m, 2 H), 7.30 (m, 2 H), 7.16 (m, 8 H), 7.08 (m, 2 H), 7.03 (m, 2 H), 3.00 (br s, 2 H), 2.84 (m, 2 H), 1.21 (d, J = 7 Hz, 3 H), 1.20 (d, J = 7 Hz, 3 H), 1.19 (d, J = 7 Hz, 6 H). ^{13}C NMR of **36** ($CDCl_3$) δ 147.6, 147.4, 144.53, 144.49, 141.5, 141.3, 128.7, 128.6, 128.5, 128.4, 127.17, 127.16, 126.8, 126.6, 125.34, 125.32, 83.0, 33.52, 33.51, 23.93, 23.91, 23.99, 23.87. ESI exact mass ($M + Na^+$) calculated for $C_{32}H_{34}NaO_2$ 473.2451, found 473.2443.

■ ASSOCIATED CONTENT

Supporting Information. Complete ref 9, the B3LYP/6-31G* calculated structure, energy, and Cartesian coordinates of **32**, ^{1}H and ^{13}C NMR spectra of compounds **19**, **21**, **22**, **23**, **24**, **25**, **26**, **27**, **36**, **56**, **57**, **58**, **59**, and **60**, evolving ^{1}H NMR spectra during irradiation of **21**, **22**, and **24** in C_6D_6, the ^{1}H NMR spectrum of the aromatic region during photolysis of **27** in C_6D_6, evolving ^{1}H NMR spectra during irradiation of **21**, **22**, **23**, and **26** in *i*-PrOH, as well as UV spectra of **20**, **21**, **25**, and **35**. This material is available free of charge via the Internet at http://pubs.acs.org.

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