SYNTHESIS OF 3,4-(20-CROWN-6)BENZOPHENONE: A POTENTIAL SELECTIVE TRIPLET SENSITIZER

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ABSTRACT

SYNTHESIS OF 3,4-(20-CROWN-6)BENZOPHENONE:
A POTENTIAL SELECTIVE TRIPLET SENSITIZER

By

Sandra Ellen Klassen

3,4-(20-Crown-6)benzophenone was synthesized with the idea that it could be useful as a selective triplet sensitizer. The synthesis was accomplished in five steps, beginning with a literature preparation of 3,4-dimethylbenzophenone. This product was brominated with N-bromosuccinimide, and the dibromide reacted with sodium acetate. The resulting 3,4-bis(acetoxymethyl)benzophenone was treated with potassium hydroxide. The product, 3,4-bis(hydroxymethyl)benzophenone, was reacted with potassium *tert*-butoxide, followed by pentaethylene glycol ditosylate, to yield 3,4-(20-crown-6)benzophenone.

Benzophenone has wide applicability as a triplet sensitizer, and crown ethers are known to complex with hydrochloride salts of primary amines. Some preliminary work toward a study of the sensitized *cis-trans* isomerization of the hydrochloride salt of *p*-aminomethylstilbene, which should be complexed by the crown ether, has been done.

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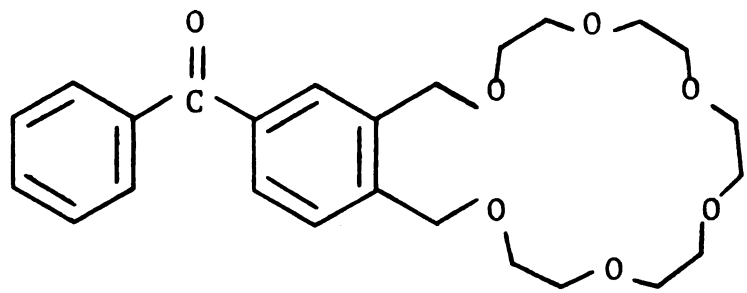
INTRODUCTION

Since triplet-triplet energy transfer in solution occurs upon collision of donor and acceptor,[1] triplet sensitization of a photochemical reaction is generally a random process. The purpose of the present study was to synthesize 3,4-(20-crown-6)benzophenone (*I*), which may act as a selective sensitizer for photochemical reactions which proceed through the triplet state. Compound *I* has two features which are important in a selective sensitization scheme: a portion of the molecule which can transfer



3,4-(20-Crown-6)benzophenone (*I*)

triplet energy, and a portion of the molecule which can complex with suitable substrates.

Because of its wide applicability as a triplet sensitizer, benzophenone was chosen for the sensitizer portion of this molecule. Complexation was the tool chosen to "persuade" the substrate to spend a higher percentage of

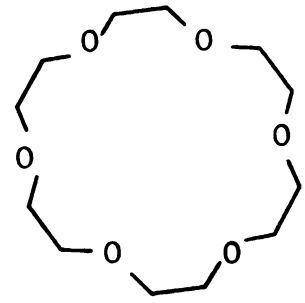
its time near the sensitizer than it ordinarily would in a random process. Thus substrates which are able to complex with the crown ether portion of the molecule are expected to receive a greater amount of triplet energy than substrates which are not able to complex with the crown ether. It is also expected that given a substrate with many sites which could accept triplet energy, those sites nearest the crown ether portion of *I* would be more likely to receive the triplet energy.

Crown ethers, also known as cyclic polyethers, had not received much attention in the literature until 1967 when a paper was published which reported the syntheses of 33 crown ethers and a study of their complexation with certain salts.[2] It was shown that crown ethers could form stable complexes with the cations of Li, Na, K, Rb, Cs, Ca, Sr, Ba, and some other metals, including some transition metals. It was also found that the ammonium ion and salts of primary amines will complex with crown ethers. Results obtained with the hydronium ion were negative, however.

The complexation is believed to be an ion-dipole interaction between the cation and the oxygen atoms in the crown ether, and there are many factors which govern the stability of the complexes. A stable complex involves a cation that will "fit well" into the ring of the crown ether, and a cation that is not too strongly associated with the solvent. The complexes tend to be more stable as

more oxygen atoms are introduced into the ring in a manner such that they are symmetrically disposed about the ring. As the oxygen atoms increase in basicity, the complex becomes more stable.

More recently, complexation constants (also called stability constants[3] or association constants)[4] have been measured for some crown ether-salt complexes. For example, $k = 2.09 \times 10^4$ for sodium chloride and 18-crown-6 (*II*) in methanol at 25°C. When the salt was changed to potassium chloride, $k = 1.26 \times 10^6$.[3] Measurements have also been



18-Crown-6 (*II*)

made with *II* and *tert*-butylammonium thiocyanate in chloroform, and k was reported to be 7.5×10^5.[4]

Many triplet reactions have been sensitized by benzophenone and are possibilities for study. The reaction chosen for initial study with *I* is *cis-trans* isomerization, and the substrate chosen is the hydrochloride salt of *p*-aminomethylstilbene. The *cis-trans* isomerization of stilbenes with various triplet sensitizers, including benzophenone, has been studied extensively,[5] and the

hydrochloride salt of the aminomethyl group should make complexation of the stilbene to the crown ether portion of *I* possible.

The following pages contain a background presentation of the photochemical behavior of phenyl ketones, a discussion of the synthesis of *I*, and a discussion of work done in preparation for a study of *cis-trans* isomerization sensitized by *I*.

BACKGROUND

Compound *I* was synthesized with the idea that it could act as a selective triplet sensitizer, and any experiments to test this idea should be run under conditions such that energy transfer is favorable. Therefore, it is of interest to be familiar with the photochemical behavior of phenyl ketones so as to be aware of photochemical reactions, other than energy transfer, that could occur under a given set of experimental conditions.

The literature concerning the photochemical behavior of phenyl ketones is by no means lacking, since they undergo many kinds of reactions and are also used as sensitizers. The photochemistry of phenyl ketones usually involves the lowest energy triplet state, since the rate of intersystem crossing is rapid and efficient (e.g., $k_{ST} \geq 10^{10}$ sec^{-1} and $\Phi_{ST} = 1.00$ in benzene at 25°C for benzophenone).[6] Thus one would expect to see a reaction involving the lowest energy singlet state only if the rate of reaction could successfully compete with the rate of intersystem crossing. The lowest energy triplet state is usually n,π^*, except in some substituted phenyl ketones where the lowest energy triplet state is π,π^*. Phenyl

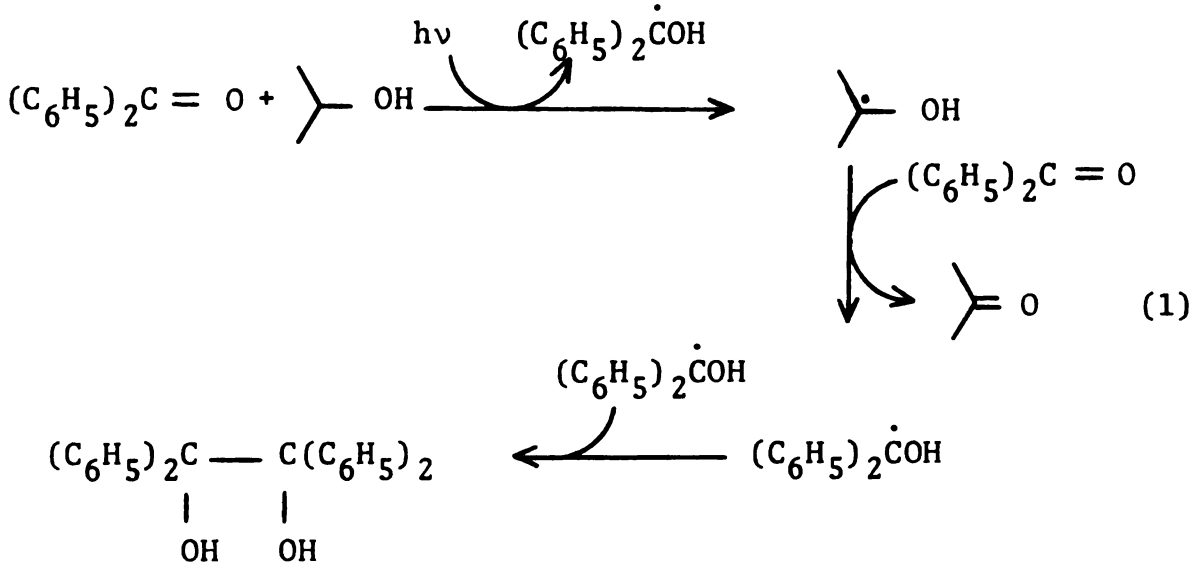
ketones which have an n,π^* state as the lowest energy triplet state will be discussed.

I. Reactions of phenyl ketones

There are, in general, three kinds of photochemical reactions which are typical of ketones and involve the n,π^* triplet: α-cleavage, hydrogen abstraction, and photocycloaddition to olefins. In the vapor phase, acetone will undergo α-cleavage (also called Norrish type I cleavage) to give two kinds of radicals: $CH_3COCH_3 \xrightarrow{h\nu}$ $CH_3\dot{C}O + \cdot CH_3$.[7] The reaction is known to occur from the singlet as well as the triplet excited states of acetone depending upon experimental conditions.[8] In solution lower yields of α-cleavage reaction products are obtained, since there may be other processes available which can compete successfully with the type I process. For example, if the solvent has reactive carbon-hydrogen bonds, acetone will abstract hydrogen atoms, and no type I products are observed.[8] It has also been proposed that the solvent acts as a "cage."[7] Thus, the probability that the radicals will recombine is higher in solution than in the vapor phase, since they cannot separate as quickly in solution.

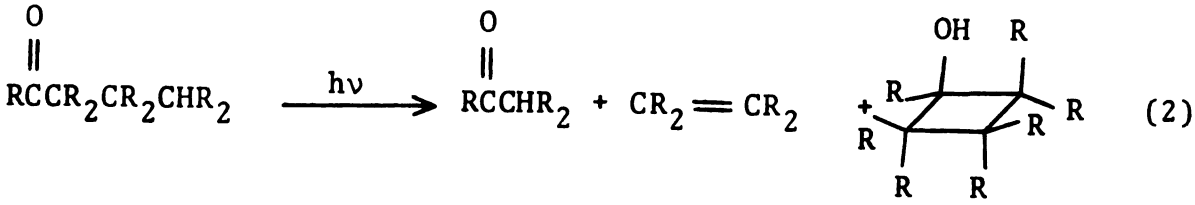
Phenyl ketones do not commonly undergo the type I cleavage reaction, however; and that leaves hydrogen abstraction and photocycloaddition to olefins as the important reactions for this group of ketones.[9] As mentioned earlier, the phenyl ketones, upon irradiation,

undergo rapid and efficient intersystem crossing to the n,π^* triplet state. This leaves an electron deficiency at the carbonyl oxygen[10] which can be relieved by abstraction of a hydrogen atom either in an intermolecular or intramolecular process. One of the best known examples of an intermolecular hydrogen abstraction is the photoreduction of benzophenone in isopropanol to give benzpinacol and acetone.[11] Two molecules of benzophenone are reduced for every one molecule of isopropanol that is oxidized (Equation 1). The ketone undergoing photoreduction need not be



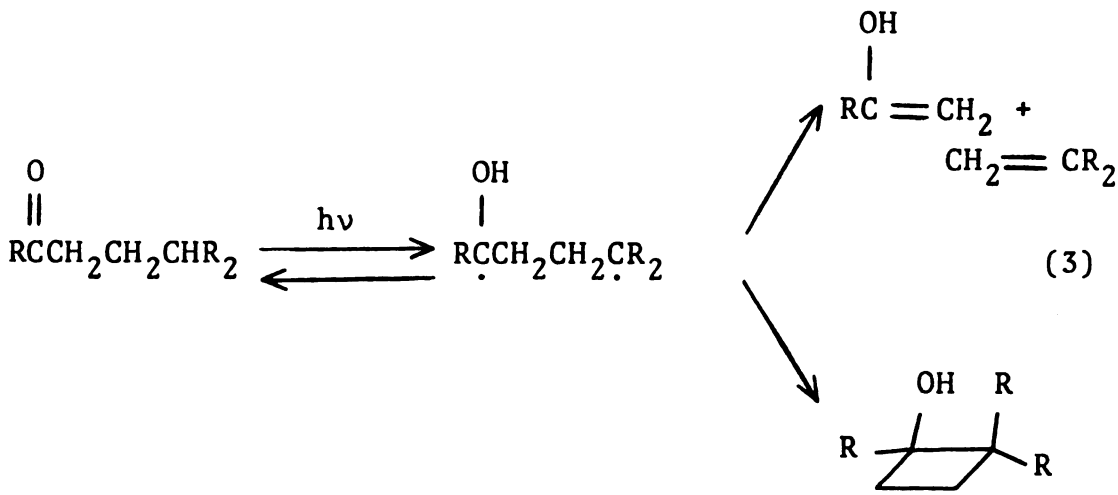
benzophenone, nor need the solvent be isopropanol. The quantum yield for disappearance of benzophenone in ethanol is 1.0; in hexane, 0.67; and in toluene, 0.45.[12] Acetophenone undergoes photoreduction to give a pinacol in isopropanol, toluene, or α-methyl benzylalcohol.[13]

If the phenyl ketone has a γ-hydrogen, intramolecular hydrogen abstraction can also occur and will lead to cleavage products and usually cyclobutanol formation (Equation 2).[14] The process leading to the cleavage products



(2)

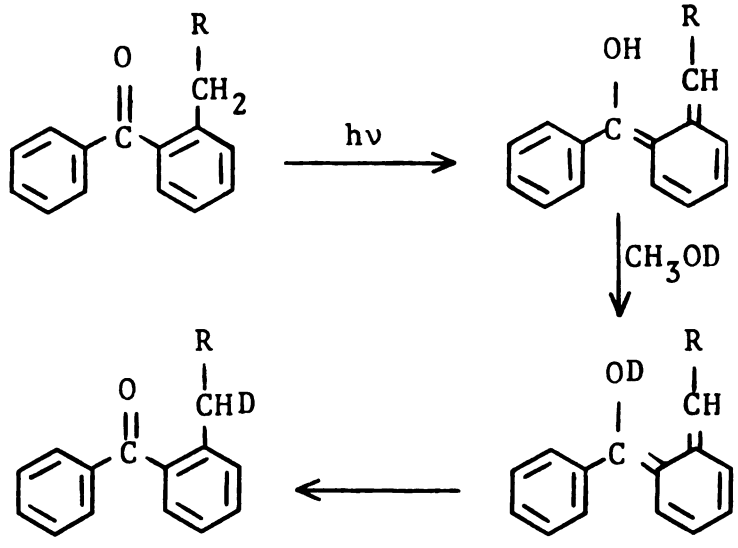
is called the Norrish type II photoelimination. The photoelimination and cyclobutanol formation together are called type II processes. While the type II processes can occur from both the singlet and triplet excited states in aliphatic ketones, they occur only from the n,π^* triplet state in phenyl ketones.[14,15] Evidence has been found for a 1,4 biradical intermediate, and a mechanism can be written as shown in Equation 3.[14,16] The enol tautomerizes to give the ketone. The efficiency of type II processes is very dependent on solvent polarity. For example, when the solvent is hexane, the quantum yield for the disappearance of valerophenone is 0.46. When *t*-butyl alcohol is used, the quantum yield is 1.0.[17] In the nonpolar solvent the intermediate may disproportionate to starting material, and thus the quantum yield for disappearance of starting



(3)

material is low. Polar solvents which can hydrogen bond to the intermediate, however, may suppress the disproportionation reaction thus raising the quantum yield.[14,17]

Certain *ortho*-substituted phenyl ketones can undergo a reversible reaction called photoenolization. In this reaction the n,π^* triplet abstracts a hydrogen atom from an *ortho*-alkyl substituent and forms an enol, which tautomerizes back to starting material. Irradiation of these ketones in CH_3OD results in incorporation of deuterium in the alkyl side chain (Equation 4).[18] If one considers *o*-methylvalerophenone, there are two possible intramolecular hydrogen abstraction processes: photoenolization and type II processes. When it was irradiated, no type II products were obtained, and thus it is thought that photoenolization occurs much faster than the type II processes.[19] A major factor contributing to the faster

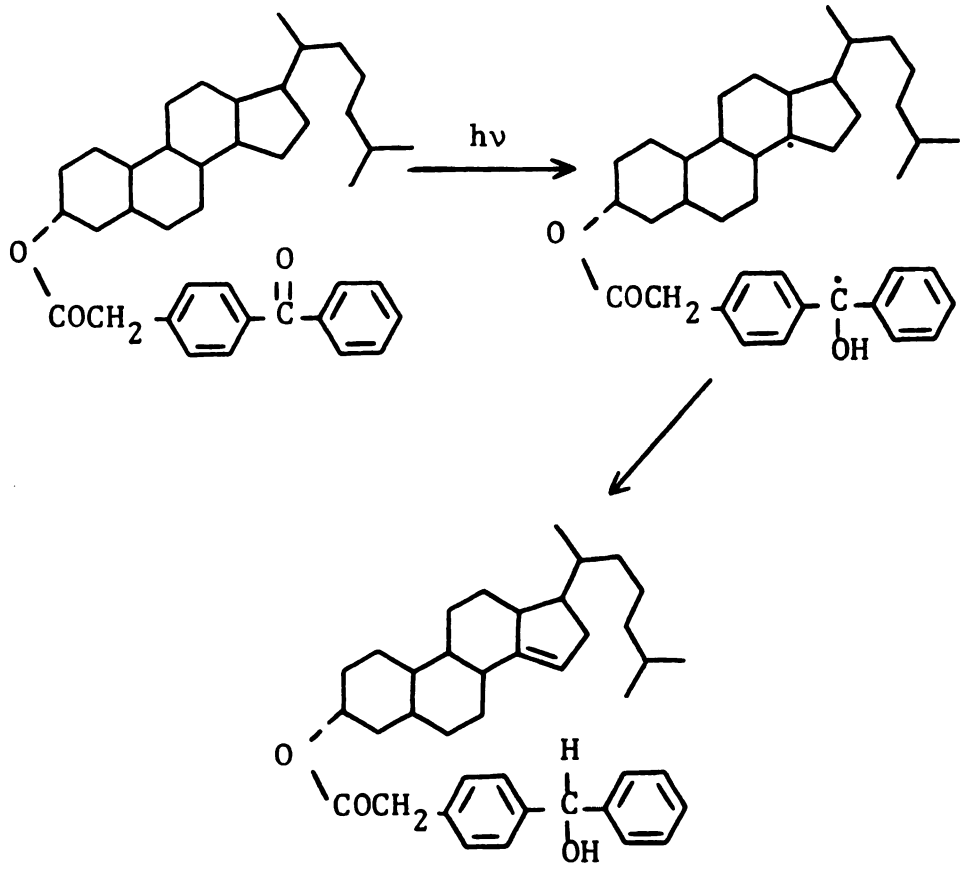


(4)

rate of photoenolization is the relatively rigid position of the γ-hydrogen needed as compared with the relatively free position of the γ-hydrogen needed for type II processes.

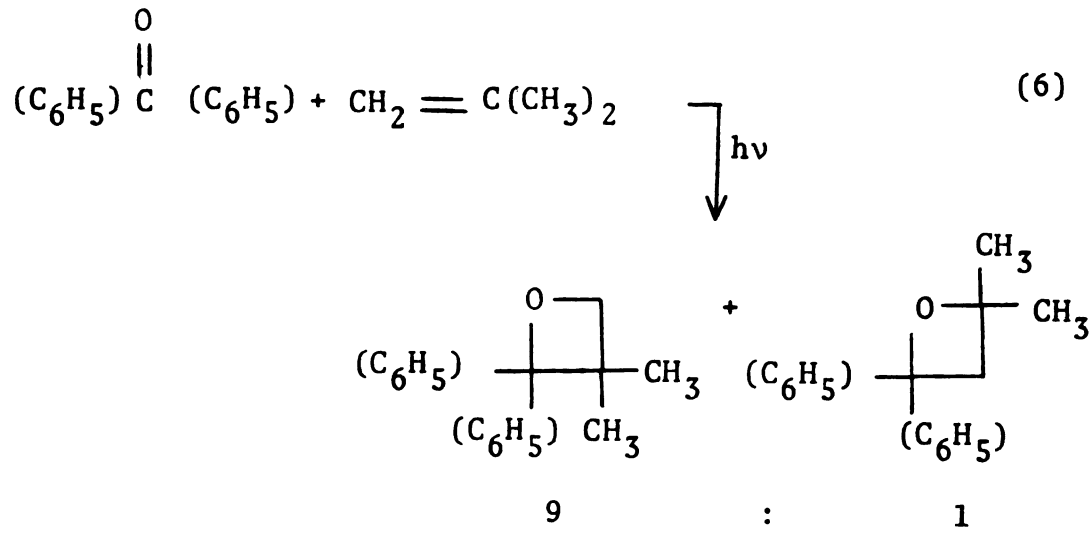
A novel use has been made of the ability of the n,π^* triplet of phenyl ketones to abstract hydrogen atoms. A substituted benzophenone was joined to a steroid in such a way that abstraction of certain steroidal hydrogen atoms was more probable. Using this method a double bond was selectively introduced between carbon atoms 14 and 15 of a steroid as shown in Equation 5.[20] This unique intramolecular hydrogen abstraction has been useful in selectively functionalizing various carbon atoms in steroids.[20-23]

Another way in which the n,π^* triplet of phenyl ketones can relieve the electron deficiency at the carbonyl oxygen is by photocycloaddition to olefins. It is known that this



(5)

reaction can involve the n,π^* triplet, since ketones which undergo photocycloaddition also undergo photoreduction in isopropyl alcohol.[24] As an example, consider the reaction of benzophenone and isobutylene to yield a mixture of photocycloaddition products called oxetanes (Equation 6).[25] This reaction is thought to involve attack of the electron deficient oxygen on the olefin to yield a diradical intermediate which can then close to give product. The diradical intermediate is consistent with the product ratio obtained, since a tertiary radical is more stable than a primary radical.



(6)

9 : 1

Because the reaction commonly occurs from the n,π^* triplet state, there is potential for competition from other reactions of an n,π^* triplet state. In particular, hydrogen abstraction can lower the yield of oxetane formation through photoreduction, type II processes, and photoenolization. For example, irradiation of 2-methylbenzophenone and isobutylene does not yield any oxetane because photoenolization can successfully compete with photocycloaddition.[26]

Another process which can sometimes compete successfully with oxetane formation is energy transfer. If the energy of the olefin triplet state is lower than the energy of the phenyl ketone triplet state, energy can be transferred to the olefin rather than reaction to yield an oxetane.[27] For example, irradiation of acetophenone and norbornene yields dimers of norbornene rather than oxetane. Irradiation of benzophenone and norbornene, however, results in oxetane formation. The triplet state

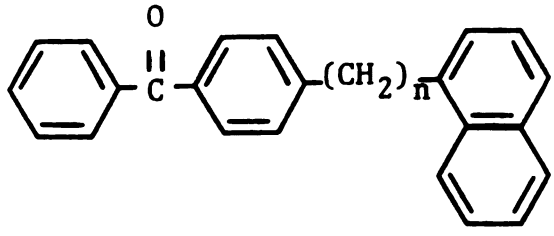
energies of acetophenone, benzophenone, and norbornene are 74 Kcal/mole, 69 Kcal/mole, and 72 Kcal/mole, respectively.[28] The transfer of energy from the n,π^* triplet state of phenyl ketones to suitable acceptor molecules will be discussed further in the next section.

II. Energy transfer from the n,π^* triplet state of phenyl ketones

Besides undergoing the reactions discussed in the previous section, the n,π^* triplet state of phenyl ketones can relieve the electron deficiency at the carbonyl oxygen by transferring excited state energy and returning to the ground state. In the process an acceptor molecule is promoted to its triplet state: $D_T + A_0 \longrightarrow A_T + D_0$.[29] This process is most likely to occur when the lowest energy triplet state of the donor (D_3) lies above the lowest energy triplet state of the acceptor (A_3). The lowest energy excited singlet state of the acceptor (A_1), however, should lie above the lowest energy excited singlet state of the donor (D_1) so that singlet-singlet energy transfer from donor to acceptor is not probable.[29] In solution energy transfer takes place upon collision of the triplet state donor and ground state acceptor.[1] If D_3 is greater than A_3 by 3-4 Kcal/mole, energy transfer occurs nearly every time excited donor and ground state acceptor collide. If D_3 is approximately equal to A_3, then the net rate of energy transfer to the acceptor is less than the rate of collision since the process can be

reversed; that is, the acceptor can transfer energy back to the donor. If D_3 is less than A_3 by 3-4 Kcal/mole, net energy transfer occurs very slowly.[1,30]

Phenyl ketones are often used as donors in energy transfer studies. For example, a study was done on the series of compounds, *III*, *IV*, and *V*, utilizing the benzophenone and naphthalene chromophores.[31] Benzophenone and naphthalene make a good donor-acceptor pair, since D_3 is



III, n = 1

IV, n = 2

V, n = 3

higher energy than A_3 and D_1 is lower energy than A_1. It is also possible to choose a wavelength of light such that either the benzophenone or naphthalene chromophore, but not both, absorb. It was found that irradiation of *III*, *IV*, and *V* with light of 3660 Å wavelength (absorbed by the benzophenone chromophore) was followed by 100% efficient energy transfer to the naphthalene chromophore. Upon irradiation the benzophenone chromophore formed the lowest energy n,π^* singlet state which underwent intersystem crossing to the n,π^* triplet state with 100% efficiency. The triplet was detected by energy transfer to

cis-piperylene, causing its isomerization. (The sensitized isomerization of olefins will be discussed in the next section.) The n,π^* triplet energy of the benzophenone chromophore was then transferred to the naphthalene chromophore to excite it to its lowest energy triplet state also with 100% efficiency. This triplet was detected by observation of a phosphorescence spectrum similar to that of 1-methylnaphthalene. Since all three compounds show the same efficiency of triplet-triplet energy transfer, the role of the methylene bridges, if any exists, is unclear.

The rapid rate of intersystem crossing found in phenyl ketones makes possible their use as donors in triplet-triplet energy transfer even when D_1 is of greater energy than A_1. Consider the donor-acceptor pair of benzophenone and biacetyl.[32] The lowest energy excited singlet state of biacetyl is below the lowest energy excited singlet and triplet states of benzophenone; thus, singlet-singlet transfer from benzophenone to biacetyl is theoretically possible. When a benzene solution of benzophenone and biacetyl were irradiated directly, however, both fluorescence and phosphorescence were observed. If singlet-singlet energy transfer were occurring, one would expect to have seen fluorescence from biacetyl when it was irradiated in the presence of benzophenone. Acetophenone is also known to transfer triplet energy to biacetyl.[33] Thus, the rate of intersystem crossing in phenyl ketones can successfully

compete with the rate of singlet-singlet energy transfer.

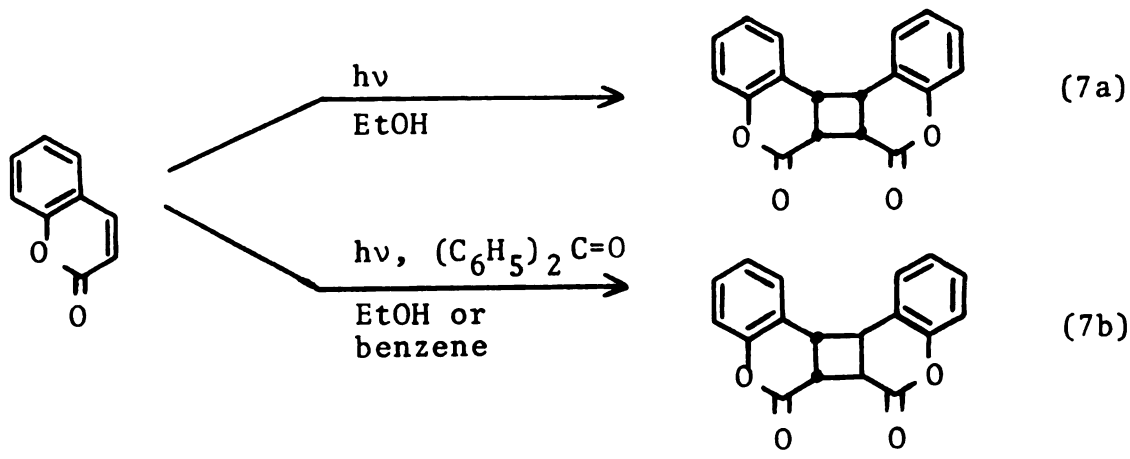
As seen from the previous two examples, triplet-triplet energy transfer can be detected by observation of phosphorescence of the acceptor when irradiation is at a wavelength which produces first the singlet and then the triplet state in the donor. It is also possible that the acceptor triplet state will undergo a reaction instead of phosphorescing. Thus, energy transfer can also be detected by observing a chemical reaction of the acceptor triplet. Indeed, much use has been made of phenyl ketones as triplet sensitizers. A solution of the appropriate phenyl ketone and the acceptor is irradiated at a wavelength which will produce the triplet state of the phenyl ketone. Triplet energy is transferred to the acceptor, thus sensitizing the triplet reaction of the acceptor rather than causing it by direct irradiation of the acceptor. Examples of triplet reactions which have been sensitized by phenyl ketones will be discussed in the next section.

III. Triplet reactions sensitized by phenyl ketones

Phenyl ketones have been used to sensitize a wide variety of reactions. In some cases the sensitized reaction gives a different product than the product resulting from direct irradiation. This has often been interpreted to mean that the sensitized reaction is proceeding through a triplet state, while the unsensitized reaction is proceeding through a singlet state. This is believed to be

true for the decomposition of diazomethane to methylene: $CH_2N_2 \longrightarrow CH_2 + N_2$.[34,35] Singlet and triplet methylene can be differentiated on the basis of their reaction with olefins. Singlet methylene generally adds to double bonds in a stereospecific manner, whereas triplet methylene often does not, since the diradical intermediate which is formed may be able to rotate before spin inversion occurs. When diazomethane was photolyzed in the absence of benzophenone with *cis*-2-butene (or *trans*-2 butene) *cis*-dimethylcyclopropane (or *trans*-dimethylcyclopropane) was obtained as product. In the presence of benzophenone, both *cis*-2-butene and *trans*-2-butene gave a mixture of *cis*- and *trans*-dimethylcyclopropane as products.[34] Thus it is believed that direct photolysis yields singlet methylene.[35] Photolysis in the presence of benzophenone, however, is believed to involve energy transfer to produce the triplet state of diazomethane, which then decomposes to give triplet methylene.[34]

Another photochemical reaction which has been sensitized by a phenyl ketone is the photodimerization of coumarin (Equation 7).[36,37] In ethanol, irradiation of coumarin produced a *cis*-head-to-head dimer (Equation 7a). No dimer was produced in benzene. In either ethanol or benzene, irradiation of coumarin and benzophenone produced the *trans*-head-to-head dimer (Equation 7b). Experiments were done in which coumarin and benzophenone were irradiated with light absorbed mainly by benzophenone or coumarin



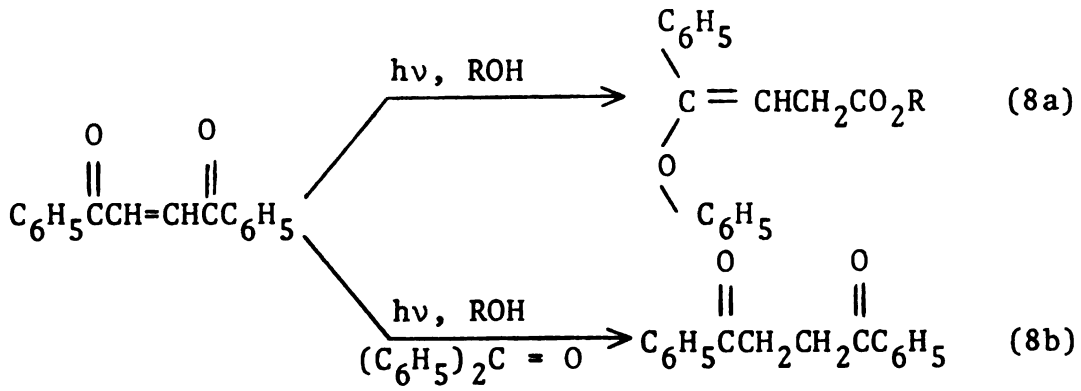
(7a)

(7b)

but not both. In both experiments, the *trans*-head-to-head dimer was formed. The results were explained by energy transfer to produce the coumarin triplet. The triplet energies of coumarin and benzophenone are 62 Kcal/mole and 69 Kcal/mole, respectively. The excited singlet energies are about 82 Kcal/mole and 78 Kcal/mole, respectively. When the light was absorbed by benzophenone, its singlet state was produced and underwent intersystem crossing to the triplet, which in turn transferred energy to coumarin. When the light was absorbed by coumarin, its lowest energy excited singlet state was produced and transferred singlet energy to benzophenone. The benzophenone singlet underwent intersystem crossing and transferred the triplet energy to coumarin. The coumarin triplet produced by either method reacted with ground state coumarin to produce the *trans*-head-to-head dimer.

Since the emission spectrum of coumarin shows both fluorescence and phosphorescence, one might expect that coumarin undergoes intersystem crossing with some efficiency. Therefore, irradiation of coumarin in the absence of benzophenone should show some *trans*-head-to-head dimer. When a dilute solution of coumarin was irradiated, the *trans* dimer was indeed produced. None was produced, however, upon irradiation of a concentrated solution. The explanation given is that in concentrated solution there are two processes which successfully compete with intersystem crossing: reaction of excited singlet coumarin with ground state coumarin to yield either *cis*-head-to-head dimer or unreacted coumarin (a self-quenching reaction). Thus, no *trans*-head-to-head dimer is formed in concentrated solution because the excited singlet reacts at a greater rate than the rate at which it undergoes intersystem crossing.

Another compound which gives a different product when irradiated in the presence of benzophenone is dibenzoylethylene (Equation 8).[38] The rearrangement product was believed to result from an excited singlet state (Equation 8a), and the reduction product was believed to result from a triplet state produced by energy transfer from the benzophenone triplet (Equation 8b). It has been pointed out, however, that one must be careful in assigning triplet states to reactions run in the presence of triplet sensitizers and singlet states to reactions run in their

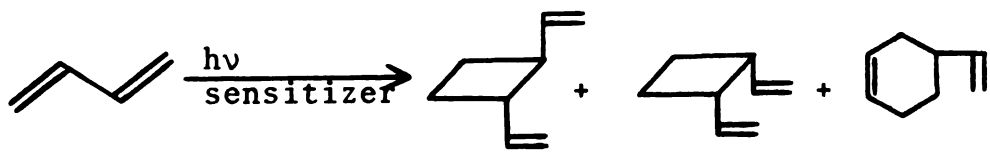


(8a)

(8b)

absence.[39] It was found that when the concentration of dibenzoylethylene was varied (varying the per cent triplet energy transfer), the yield of reduction product remained fairly constant. In the presence of a nonhydrogen abstracting triplet sensitizer, rearrangement product was observed; however, no reduction product was observed. This would suggest that the rearrangement was occurring through a singlet or triplet state, and that the reduction was occurring through some process other than energy transfer from a triplet sensitizer. It was suggested that the benzophenone triplet abstracted a hydrogen atom from the solvent and then transferred it to dibenzoylethylene. Thus it seems that benzophenone was participating chemically rather than sensitizing the reaction through energy transfer.

Unsaturated hydrocarbons are also known to undergo photosensitized reactions in the presence of phenyl ketones. For example, benzophenone or acetophenone will transfer triplet energy to butadiene, which can in turn react with ground state butadiene to produce dimers (Equation 9).[40,41] Photodimerization is also known to occur for isoprene[40] and cyclohexadiene.[41]



(9)

Phenyl ketones can also sensitize the photodimerization of simple alkenes if the triplet energy of the alkene is less than the triplet energy of the phenyl ketone. Phenyl ketones will add to the alkene to give an oxetane if the triplet energy of the alkene is higher than that of the phenyl ketone. Examples of these reactions were given previously in the section dealing with reactions of phenyl ketones.

Perhaps one of the most well-known photosensitized reactions of simple alkenes, however, is *cis-trans* isomerization. When simple alkenes are irradiated directly, the singlet state is produced, which undergoes very inefficient

intersystem crossing to the triplet state. Since isomerization occurs from the triplet state, triplet sensitizers are used to produce the alkene triplet in a more efficient manner.[42] The use of the photosensitized reaction also allows one to by-pass the singlet state and its reactions, which may complicate the study of isomerization.[43]

Isomerization can occur in either direction (*cis* to *trans* or *trans* to *cis*), and irradiation for a long period of time will give the photostationary state mixture, a mixture of *cis* and *trans* isomers whose composition does not change upon further irradiation. The composition has been found to depend on the energy of the triplet sensitizer used. As an example, consider *cis*- and *trans*-stilbene.[5,44] The triplet energies of *cis*- and *trans*-stilbene are 57 Kcal/mole and 50 Kcal/mole, respectively. If the triplet energy of the sensitizer lies above about 62 Kcal/mole, the composition of the photostationary state does not vary with the sensitizer. The triplet states formed from *cis*- and *trans*-stilbene are thought to stabilize themselves by rotation to form a twisted triplet which is common to both. The twisted or "phantom" triplet then decays to *cis*- or *trans*-stilbene. Since the isomerization occurs through an intermediate which is common to both isomers, similar results are expected with triplet sensitizers of energy above 62 Kcal/mole. Acetophenone and benzophenone are two phenyl ketones which are included in this group of sensitizers.

As the triplet energy of the sensitizer drops below 60 Kcal/mole, the composition of the photostationary mixture changes. Triplet-triplet energy transfer occurs as usual to *trans*-stilbene; however, a slower nonvertical energy transfer to *cis*-stilbene is postulated. This involves energy transfer coupled with rotation to produce the triplet state of *trans*-stilbene. Thus, as the rate of reaction of *cis*-stilbene becomes slower relative to *trans*-stilbene, the photostationary mixture becomes enriched in *cis*-stilbene.

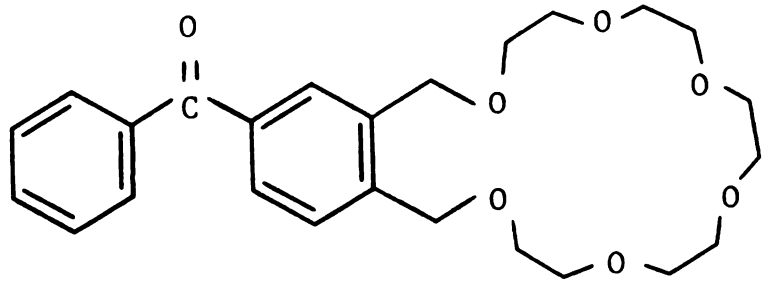
When sensitizers are used that have triplet energies less than that of either *cis*- or *trans*-stilbene, isomerization still occurs. It is believed that both *cis*- and *trans*-stilbene are undergoing nonvertical excitation to the "phantom" triplet, which then decays. Since the ground state energy of *cis*-stilbene is greater than that of *trans*-stilbene, the energy required to form the "phantom" triplet is less than that for *trans*-stilbene. Thus *cis*-stilbene isomerizes at a greater rate, and the photostationary mixture becomes enriched in *trans*-stilbene as the energy of the sensitizer drops.

Thus, phenyl ketones exhibit a wide variety of photochemical behavior which must be considered when planning a synthesis and study of *I* as a selective sensitizer. The synthesis of *I* and preliminary work done to test the feasibility of *I* as a selective sensitizer are discussed in the next section.

RESULTS AND DISCUSSION

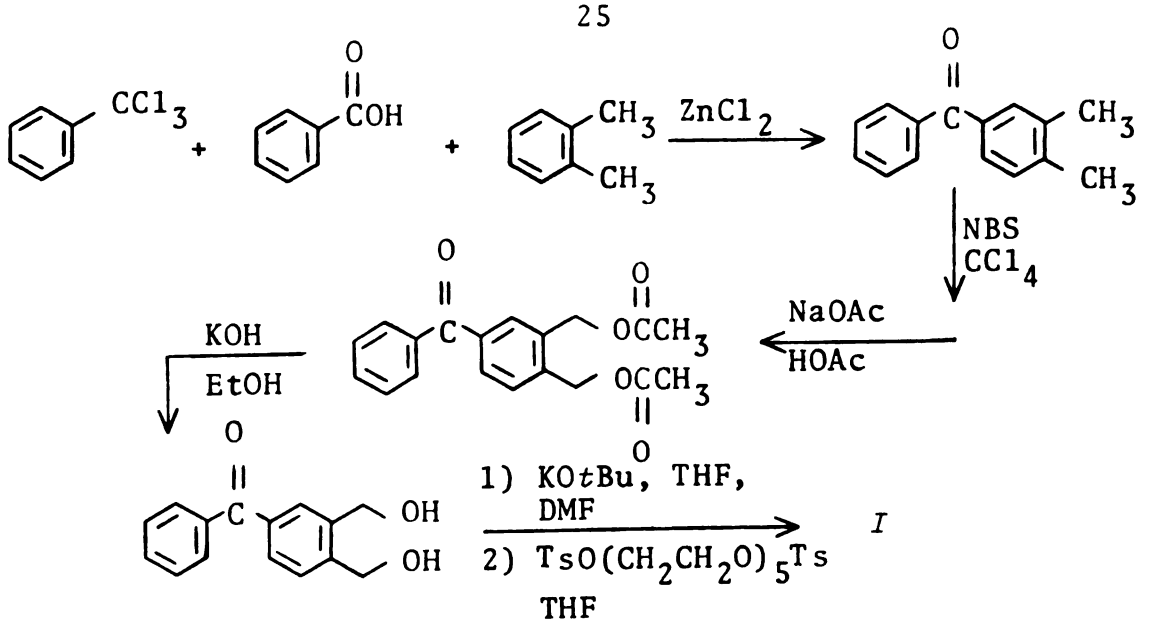
I. Synthesis of 3,4-(20-Crown-6)benzophenone (*I*)

The purpose of the present study was to synthesize 3,4-(20-crown-6)benzophenone (*I*) for use as a selective sensitizer. The molecule can be divided into a ketone portion and a crown ether portion, and syntheses can be



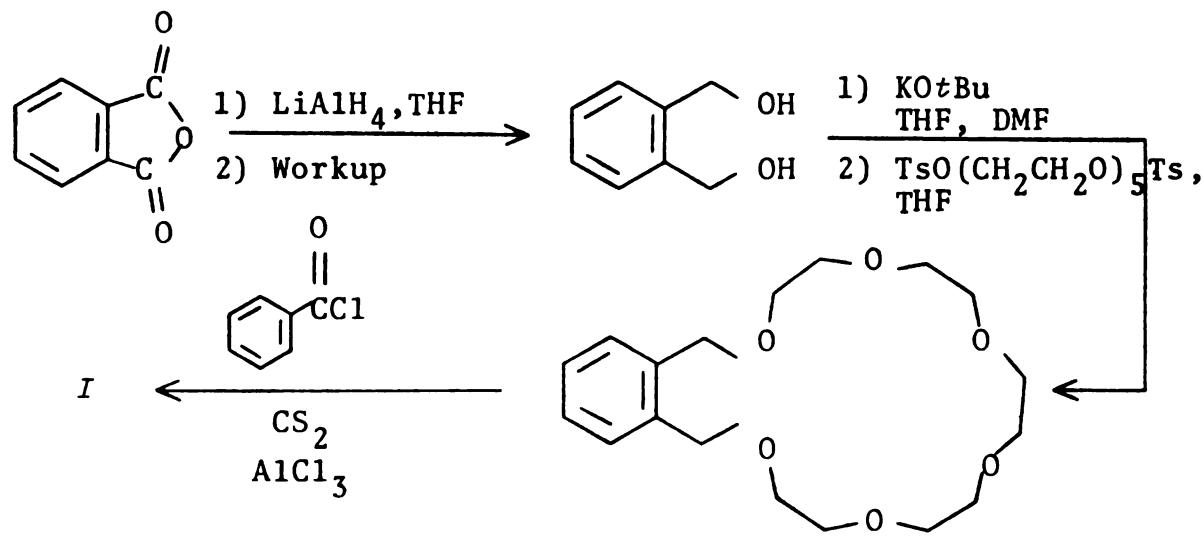
I

devised which involve two approaches: synthesis of the ketone portion with subsequent attachment of the crown ether, and synthesis of the crown ether portion with subsequent attachment of the ketone. Both approaches were tried, and the approach which was successful is outlined in Scheme I.



Scheme I

Initially it was decided to synthesize *I* as outlined in Scheme II, which involved synthesis of the crown ether portion of the molecule and later attachment of the ketone. This approach, however, was unsuccessful. The first step of Scheme II proceeded in 70% yield; however, the second

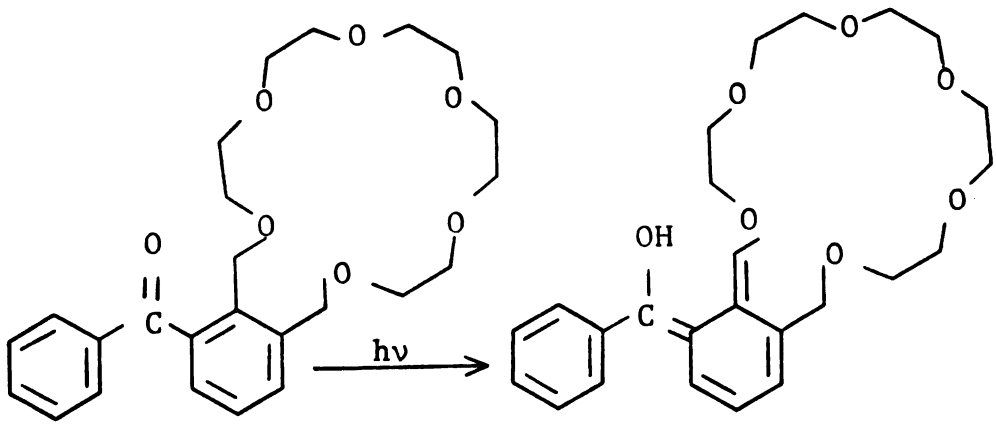


Scheme II

step proceeded in low yield (about 10%), and isolation of the pure product (column chromatography) proved long and tedious. Furthermore, when the third step of Scheme II was attempted at 0°C, the nmr spectrum of the crude reaction mixture indicated the presence of much starting material. Because the isolation of pure product from the second step was time-consuming and tedious, and because this product may have been susceptible to cleavage (benzylic ether) in the presence of aluminum trichloride at higher temperatures,[45] Scheme II was abandoned for Scheme I.

The first step of Scheme I, the synthesis of 3,4-dimethylbenzophenone, was accomplished by following an interesting patented preparation.[46] The ir and nmr spectra of the product were identical with known spectra (Sadtler Research Laboratories, Inc., nmr 18835M; ir 23905). Importantly, the ir spectrum was different than the ir spectrum of a known sample of 2,3-dimethylbenzophenone. If the product were 2,3-dimethylbenzophenone instead of 3,4-dimethylbenzophenone, *VI* would have been synthesized by following the rest of Scheme I. This molecule would be a poor choice for triplet sensitization studies since photoenolization would be likely to compete with energy transfer (Equation 10).

Attempts were made to isolate 3,4-bis(bromomethyl)-benzophenone; however, none were successful. Since this compound is also suspected to be carcinogenic, no further



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VI

attempts were made to isolate it, and the oil from the reaction was reacted with sodium acetate directly. Use of silica gel column chromatography allowed isolation of 3,4-bis(acetoxymethyl)benzophenone as a crystalline solid. This compound was then reacted with potassium hydroxide. The reaction mixture was neutralized carefully and poured over ice to obtain 3,4-bis(hydroxymethyl)benzophenone as a crystalline solid.

In preparation of *I* from 3,4-bis(hydroxymethyl)benzophenone, it was noticed that the nmr spectra of crude product from reactions run at 0°C showed a more complete reaction than the spectra of crude product from reactions run at room temperature. It was also noticed that a dark brown color of unknown origin developed in reactions run at room temperature upon addition of base. If an ice bath was used and base added slowly, sometimes the dark color did not develop. Once pentaethylene glycol ditosylate was

added to the reaction mixture, the reaction was allowed to warm up to room temperature.

Isolation of *I* required careful column chromatography on alumina. Alumina was chosen since it allows separation of *I* from any unreacted starting materials. Alcohols move very slowly, if at all, on alumina, and if the column is run slowly, tosylates will hydrolyze on alumina. Large amounts of pure *I* were difficult to obtain since an unknown impurity followed *I* very closely. This impurity showed up as a spot of slightly lower R_f value by tlc on alumina. Some pure *I* could be obtained from an initial column, and more could be obtained by rechromatographing fractions which contained impure *I*.

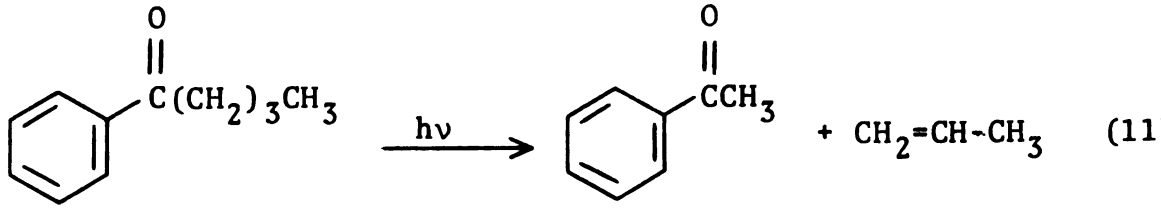
Attempts made to crystallize *I* were unsuccessful. The compound froze in various combinations of ether and pentane at -78°C. The solvent system ethanol and water was also tried without success. Thus *I* remained an oil and was stored in a freezer in the dark, since it was suspected that *I* decomposed in the presence of heat and light.

II. Preliminary work done in preparation for a study of *cis-trans* isomerization sensitized by *I*

The quantum yield for a photochemical reaction can be defined as the number of molecules undergoing a reaction per number of quanta of light absorbed by the system.[47] Therefore, to calculate the quantum yield of *cis-trans*

isomerization sensitized by *I*, it is necessary to know the the number of molecules of substrate (*p*-aminomethylstilbene hydrochloride) undergoing isomerization and the quanta of light absorbed by a solution of *I* and the substrate.

Work has been done on an actinometer so that the amount of light absorbed by this system can be determined. Identical benzene solutions, each containing valerophenone and *n*-pentadecane, were irradiated in a "merry-go-round" apparatus. Valerophenone undergoes a Norrish type II cleavage (Equation 11) upon irradiation, and the quantum



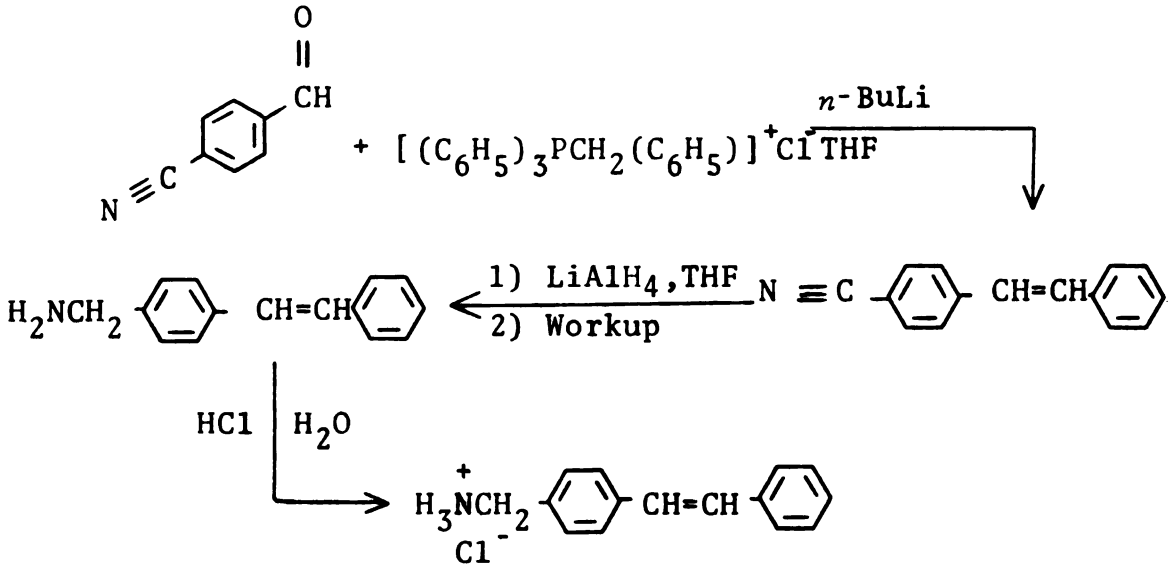
(11)

yield of acetophenone formation for various concentrations of valerophenone is known.[48] Therefore, if the amount of acetophenone formed is also known, the amount of light absorbed can be calculated. The amount of acetophenone present in the actinometer solutions was measured relative to a known amount of *n*-pentadecane by vapor phase chromatography. A flame ionization detector was used, and since the relative response of the detector is not identical with the relative molar amounts of *n*-pentadecane and

acetophenone, the instrument was calibrated with solutions containing known amounts of *n*-pendadecane and acetophenone.

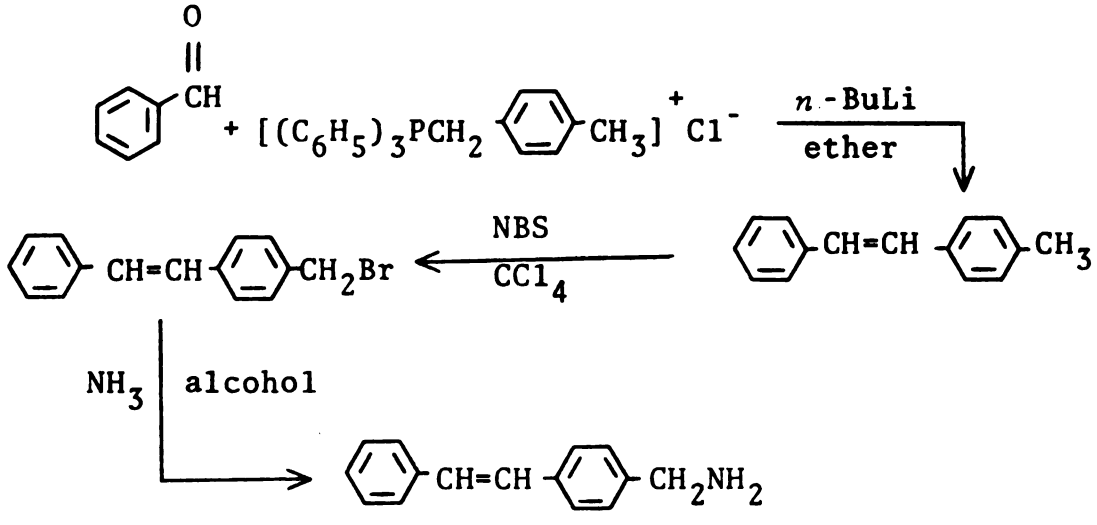
Benzene, suitable for use in photochemical experiments, was purified by photochlorination. The object was to photochlorinate hydrocarbon impurities so that they could be easily separated from benzene upon distillation. Benzene was saturated with chlorine and irradiated until almost colorless. This procedure was to be repeated until the benzene remained dark yellow, indicating that the impurities were no longer reacting with chlorine. The benzene used in the present study, however, did not remain dark yellow upon repeated saturation with chlorine and irradiation. When precipitate was obtained, it was assumed that enough irradiations had been done, and the benzene was washed, dried over magnesium sulfate, and distilled. The precipitate was very likely polychlorinated hydrocarbons.

The hydrochloride salt of *p*-aminomethylstilbene can be synthesized by following Scheme III. The first step of this scheme has been attempted, and indications are that the product is indeed *p*-cyanostilbene. The reduction of *p*-cyanostilbene could be accomplished by following a published procedure for the reduction of *o*-tolunitrile to *o*-xylylamine.[49] The hydrochloride salt could be made by adding *p*-aminomethylstilbene to an aqueous solution of hydrogen chloride which contains one equivalent of acid for every one equivalent of base added.



Scheme III

Alternatively Scheme IV could be used to synthesize *p*-aminomethylstilbene. The hydrochloride salt could be made in the same manner as Scheme III. Triphenyl-*p*-xylylphosphonium chloride is a known compound,[50] and the second step of Scheme IV is a known reaction.[51] The



Scheme IV

product of this reaction could be reacted with alcoholic ammonia to give the amine. *n*-Butylamine was prepared from *n*-butyl bromide in this manner,[52] as was *n*-heptylamine from *n*-heptyl bromide.[53] Although Scheme IV involves one more step, the starting material is not as costly.

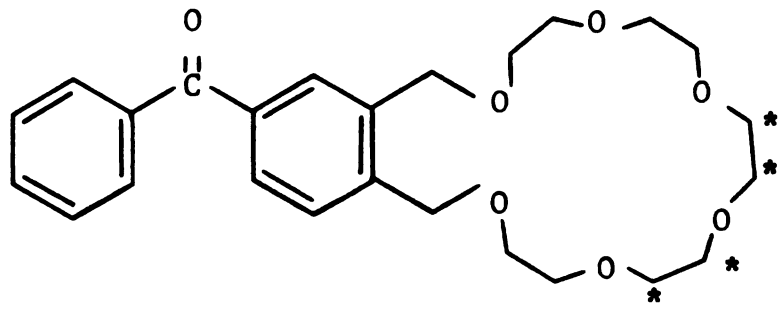
III. Problems that may be encountered in the study of *cis-trans* isomerization sensitized by *I*, and work which remains to be completed

Other processes involving the carbonyl group or the n,π^* triplet of phenyl ketones may compete with energy transfer to the substrate and may complicate a study of *cis-trans* isomerization sensitized by *I*. The substrate chosen is a salt of a primary amine. If the salt dissociates a significant amount in the solvent chosen for the photochemical reactions, two reactions could occur: Schiff base formation and reduction of the carbonyl group. Schiff base formation can be followed by infrared spectroscopy by noting the disappearance of a peak due to a carbonyl group and the appearance of a peak due to a carbon-nitrogen double bond. Photoreduction of benzophenone by amines is known;[11] thus, it is very likely that photoreduction of *I* by amines is also possible.

The benzophenone n,π^* triplet is well known for its ability to abstract hydrogen atoms, and since the uv spectrum of *I* is very similar to that of benzophenone, one would expect that *I* also has the same capability. There are two possible hydrogen abstraction processes upon

irradiation of a solution of *I*: intermolecular and intramolecular. It is possible that the n,π^* triplet of one molecule could abstract a hydrogen atom from the crown ether portion of another molecule. This would be expected to be a favorable process since the radical produced would be stabilized by an adjacent oxygen atom. The intermolecular abstraction process could be minimized by using dilute solutions of *I*.

The problem which remains is intramolecular hydrogen abstraction. Molecular models (Corey, Pauling, Koltun) show that the carbon atoms marked with an asterisk are susceptible to having their hydrogen atoms abstracted. This would be a favorable process for the same reason as with the intermolecular process.



One could test the extent of intramolecular hydrogen abstraction by measuring the triplet lifetimes of *I* and the dimethyl ether of 3,4-bis-(hydroxymethyl)benzophenone in dilute solution. If similar results are obtained, little intramolecular hydrogen abstraction is probably occurring.

It is also possible that the alkylammonium portion of the substrate might quench the n,π^* triplet before it can transfer energy to the olefin portion. One could measure the triplet lifetimes of dilute solutions of *I* with and without the hydrochloride salt of benzylamine. Similar results would indicate little quenching of the n,π^* triplet of *I* by the alkylammonium group.

In addition to consideration of reactions which may preclude or compete with energy transfer to substrate, much work remains before a study of *cis-trans* isomerization sensitized by *I* is completed. After the substrate has been synthesized, a preparative and analytical method are needed for separating the *cis-trans* isomers. Ultraviolet spectra should be taken of each isomer and compared with the spectrum of *I*. It should be possible to choose a wavelength of light such that *I* will absorb it, and the substrate will not. The appropriate filter system is then needed.

The following four solutions should be made up and irradiated (low conversion): solution A, *I* and *trans* substrate; solution B, *I* and *trans*-stilbene; solution C, benzophenone and *trans* substrate; and solution D, benzophenone and *trans*-stilbene. The solutions should be analyzed and quantum yields calculated. If the crown ether portion of *I* does indeed "hold" the substrate close to the sensitizer, one would expect the quantum yields to indicate this. Solution A should have the highest quantum

yield since the process of energy transfer in the other solutions should be more random. If solutions A and B or solutions A and C have similar quantum yields, then one could conclude that either complexation is not raising the quantum yields or that complexation is not occurring. Solutions C and D should have similar quantum yields. If the quantum yield of solution C were less than that of D, this might indicate that some quenching of the n,π^* triplet by the alkylammonium group was occurring.

Another set of experiments might also be run on the following solutions: solution E, *I*, *trans* substrate, and *trans*-stilbene; and solution F, benzophenone, *trans* substrate, and *trans*-stilbene. One might expect the quantum yields for the substrate (*trans* to *cis*) and stilbene (*trans* to *cis*) to be similar for solution F, since energy transfer to both *trans* substrate and *trans*-stilbene should be random. This would not be the expected results for solution E, however. The quantum yield for the substrate (*trans* to *cis*) should be larger than the quantum yield for stilbene (*trans* to *cis*), since the substrate can be complexed next to the benzophenone portion of *I*. Energy transfer to *trans*-stilbene, however, should be random.

These experiments could be repeated with *cis* substrate in the place of *trans* substrate. It would be interesting to determine whether the same photostationary state was reached using *I* or benzophenone as the sensitizer.

EXPERIMENTAL

Reactions were run in appropriate size 3-neck round bottom flasks fitted with stopper, condensor, and gas inlet tube. All reactions were run under a N_2 atmosphere. Solvents were removed by rotary evaporation under aspirator pressure or vacuum pump pressure as required by the particular solvent. Melting points were taken on a Thomas Hoover capillary melting point apparatus and were not corrected.

The ultraviolet (uv) spectrum was taken on a Cary 17 spectrophotometer. Infrared (ir) spectra were taken on a Perkin-Elmer Grating Infrared Spectrophotometer, Model 237B, and were calibrated with the 3027.1 and 1601.4 cm^{-1} bands of polystyrene film. The intensity of each band is given in parentheses (s = strong, m = medium, w = weak). Nuclear Magnetic Resonance (nmr) spectra were taken on a Varian T-60 Spectrometer. All spectra were recorded in delta (δ) units relative to tetramethylsilane. The information given in parentheses is as follows: the multiplicity of the signal (s = singlet, m = multiplet), the number of hydrogen atoms represented by the signal (obtained from the relative integrated signal intensity), and the kind of hydrogen atoms represented by the signal.

Mass spectra were taken on a Hitachi, Model RMU-6, Mass Spectrometer by Mrs. Lorraine Guile, Department of Chemistry, Michigan State University.

Elemental analyses were performed by Instranal Laboratory, Inc., Rensselaer, New York.

3,4-Dimethylbenzophenone

3,4-Dimethylbenzophenone was prepared according to instructions in a patented preparation.[46] The oil obtained from this preparation was crystallized from ether-pentane at -78°C, and the white solid was used without further purification (41%, 86 g): m.p. 44-45$\frac{1}{2}$°C; ir (Nujol) 1660 (s), 1610 (m), 1595 (m), and 1575 cm^{-1} (w); nmr ($CDCl_3$) δ 2.20 (s, 6, methyl), 6.90-7.73 ppm (m, 8, aromatic).

3,4-Bis(acetoxymethyl)benzophenone

3,4-Dimethylbenzophenone (12.60 g, 0.06 mole), N-bromosuccinimide (21.75 g, 0.12 mole; recrystallized and dried under vacuum for 20 to 24 hours), and dibenzoyl peroxide (0.1 g) were added to 160 ml of sieve dried carbon tetrachloride and brought to 60-70°C. Dibenzoyl peroxide (0.1 g) was added again, and the reaction was refluxed. A vigorous reaction was observed 15-30 minutes after the second addition of dibenzoyl peroxide. The reaction was allowed to reflux until a white solid (succinimide) floated on top and no more N-bromosuccinimide settled at the bottom of the flask. Upon completion of

the reaction, it was cooled on ice and filtered to remove the succinimide. The filtrate was washed with water (2 x about 100 ml), saturated sodium chloride (1 x about 100 ml), dried (sodium sulfate), and carbon tetrachloride removed. The oil (crude 3,4-bis(bromomethyl)benzophenone) which remained was dissolved in 100 ml glacial acetic acid and added to a solution of anhydrous sodium acetate (16 g, 0.195 mole) in 100 ml glacial acetic acid. This was kept at 92-98°C for about 15 hours. The reaction mixture was filtered to remove a solid (sodium bromide), and the glacial acetic acid was removed from the filtrate. The oily solid residue was dissolved in diethyl ether and water, and the layers were separated. The ether layer was washed with water (1 x about 100 ml), approximately 0.01N sodium hydroxide (1 x about 100 ml), again with water (1 x about 100 ml), and then dried (sodium sulfate) before removal of the diethyl ether to leave an oil. The oil was purified by column chromatography with 150 g SilicAR CC-7 (Mallinckrodt, Inc.) and methylene chloride. A yellow band was allowed to move through the column, and the eluate was discarded. The column packing was then emptied into a sintered glass funnel and washed with 10% methanol-90% methylene chloride (3 x about 300 ml). Removal of the solvent from the filtrate gave an oil which crystallized from cold diethyl ether. The product was then recrystallized from ethanol and water (13.2%, 2.58 g): m.p. 85-86°C; ir (Nujol), 1738 (s), 1662 (s), 1610 (m), 1590 (m), 1575 (w),

1275-1200 cm^{-1} (s); nmr ($CDCl_3$) δ 2.02 (s, 3, methyl), 2.05 (s, 3, methyl), 5.08 (s, 2, methylene), 5.12 (s, 2, methylene), 7.03-7.70 ppm (m, 8, aromatic); mass spectrum m/e (rel intensity) 326 (1, molecular ion), 266(20), 224(100), 196(35), 165(6), 147(18), 119(7), 105(70), 91(7), 77(38), 51(8), 43(89).

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.92; H, 5.57. Found: C, 69.85; H, 5.48.

3,4-Bis(hydroxymethyl)benzophenone

3,4-Bis(acetoxymethyl)benzophenone (1.44 g, 4.42 mmole) was added to 45 ml 100% ethanol and heated until all the solid had dissolved. Potassium hydroxide (0.59 g, 10.5 mmole) was dissolved in 5 ml water and added dropwise. After refluxing for about 15 hours, the reaction mixture was cooled, neutralized with dilute hydrochloric acid, and poured over ice. After about 2 hours crystals had formed (67.3%, 0.72 g); m.p. $97\frac{1}{2}$-100°C. The solid product can be recrystallized from ethanol and water: m.p. $99\frac{1}{2}$-101°C; ir ($CHCl_3$) 3500-3200 (m), 1657 (s), 1610 (m), 1600 (m), 1575 (m), 1450 (m), 1320 (m), 1275 (s), (Nujol) 3400-3200 (s), 1635 (s), 1605 (m), 1590 (m), 1560 (w), 1300 (m), 1280-1260 cm^{-1} (s); nmr ($CDCl_3$) δ 2.30-2.77 (s, 2, exchangeable hydrogens), 4.70 (s, 2, methylene), 4.73 (s, 2, methylene), 7.10-7.83 ppm (m, 8, aromatic); mass spectrum m/e (rel intensity) 242 (1, molecular ion), 240(1), 239(1), 224(29), 195(7), 165(11), 147(25), 119(11),

105(36), 91(11), 77(19), 65(6), 51(11), 43(11), 32(48), 31(11), 28(100), 18(19).

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.35; H, 5.84. Found: C, 74.10; H, 5.81.

3,4-(20-Crown-6)benzophenone

3,4-Bis(hydroxymethyl)benzophenone (0.5 g, 2.06 mmole) was added to 200 ml of undried tetrahydrofuran and 25 ml of N,N-dimethylformamide. An ice bath was placed around the flask, and the flask was also flushed with N_2 for 1 hour. Potassium *tert*-butoxide (0.55 g, 4.91 mmole) was added slowly. The reaction mixture turned yellow and then became very dark. Pentaethylene glycol ditosylate (1.13 g, 2.06 mmole) was dissolved in 150 ml of undried tetrahydrofuran and added dropwise through an addition funnel over a period of 2 hours. The reaction mixture was stirred under N_2 until it was neutral (about 48 hours) as tested with pH paper. The reaction was then filtered through Celite and washed with tetrahydrofuran (1 x about 150 ml), chloroform (1 x about 150 ml), and again with tetrahydrofuran (1 x about 150 ml). The solvent was removed from the filtrate, and the oil which remained was purified by column chromatography on alumina (A-540, 80-200 mesh, Fisher Scientific Company). The amount of alumina used was 100 times the weight of the oil (0.77 g). The column was packed using methylene chloride, and the first 25 ml eluted with methylene chloride. The solvent was then

changed to 0.4% methanol in methylene chloride. One hundred 15 ml fractions were collected, and product was located by tlc in fractions 47-54. Fractions 47-49 (0.12 g) showed one spot, and fractions 50-54 (0.16 g) showed two spots. The product has resisted all efforts to crystallize it: uv (100% C_2H_5OH) max 38,700 (ε17,600), 30,000 (ε193), min 43,200 (ε7,120), 30,800 cm^{-1} (ε190); ir 3020 (w), 2950-2850 (s), 1660 (s), 1610 (m), 1600 (m), 1575 (m), 1450 (m), 1325-1250 (m), 1150-1100 cm^{-1} (s); nmr ($CDCl_3$) δ 3.60-3.77 (m, 20, methylene), 4.67 (s, 2, methylene), 4.73 (s, 2, methylene), 7.17-7.80 (m, 8, aromatic); mass spectrum m/e (rel intensity) 445 (4, molecular ion), 400 (<1), 358(2), 313(<1), 281(<1), 268(<1), 250(<1), 237(1), 225(4), 223(3), 208(8), 196(2), 181(3), 165(4), 138(8), 131(4), 105(19), 89(20), 87(5), 77(12), 73(4), 59(3), 51(2), 45(67), 32(22), 28(100).

Anal. Calcd for $C_{25}H_{32}O_7$: C, 67.54; H, 7.27.
Found: C, 67.49; H, 7.26.

Materials for valerophenone actinometry

Benzene (1400 ml, SpectrAR, Mallinckrodt) was saturated with chlorine gas and irradiated with fluorescent lamps until clear (about 20 min). This procedure was repeated several times (at least 10) until a white solid precipitated. At this time the benzene was light yellow. The benzene was washed with water (2 x about 1 liter), sodium carbonate solution until neutral as tested with pH paper (3 x about

1 liter), and again with water (1 x about 1 liter). The benzene was then dried over magnesium sulfate and distilled to free it from water and chlorinated hydrocarbons. The first 300 ml were discarded and 650 ml of pure benzene were collected and stored over 3 Å molecular sieves. Valerophenone (Chemical Samples Co.) was passed through an alumina column and then distilled under vacuum. Acetophenone (Mallinckrodt) was used directly from the bottle. *n*-Pentadecane was an Analabs standard.

Calibration of Varian aerograph series 1400 gas chromatograph

The following benzene solutions were prepared in 10 ml volumetric flasks: A, 0.0218 g *n*-pentadecane; B, 0.0234 g *n*-pentadecane; C, 0.0134 g acetophenone; and D, 0.0130 g acetophenone. From these solutions 6 benzene solutions were prepared in 10 ml volumetric flasks: 1, 1 ml B and 1 ml C; 2, 1 ml A and 2 ml D; 3, 1 ml B and 3 ml C; 4, 2 ml B and 1 ml C; 5, 3 ml B and 1 ml C; and 6, 1 ml A and 6.5 ml D. These 6 solutions were analyzed on a 15' x $\frac{1}{8}$" column packed with 3% FFAP on 100-120 Chromasorb W (HMDS treated). Gas flow rates were set as recommended in the manual (carrier gas-nitrogen), and the temperatures of the injector and detector were 220°C and 230°C, respectively. A temperature program was used (initial temperature-100°C, final temperature-170°C), and the rate was 8°C/minute. The column was held at 170°C until acetophenone was eluted. The retention times for

benzene, *n*-pentadecane, and acetophenone were 3, 8, and $10\frac{1}{2}$ minutes, respectively. A ratio of the peak area of *n*-pentadecane to the peak area of acetophenone (1:y) for each solution was obtained from the integrator trace. An actual molar ratio of *n*-pentadecane to acetophenone (1:x) was also calculated for each solution. The results are (y,x): 1, (0.48, 1.01); 2, (0.94, 2.12); 3, (1.39, 3.03); 4, (0.22, 0.50); 5, (0.15, 0.34); and 6, (3.16, 6.88). These results were graphed into a calibration curve.

Valerophenone actinometry

Three milliliters of solution A were put into a 25 ml volumetric flask which contained 1.4557 g valerophenone. This was made up to volume with benzene. Three 3 ml samples were each placed into a 13 x 100 mm pyrex test tube which had been constricted 3 cm from the top. The samples were degassed using four freeze-pump-thaw cycles and sealed under vacuum. The solutions were irradiated in a "merry-go-round" apparatus with a Hanovia 450 W medium pressure mercury lamp for 40 minutes, including a 10 minute warm-up period for the lamp. The light was filtered through pyrex and a solution of 5 g potassium carbonate and 0.194 g potassium chromate in 1000 ml water. The samples were then analyzed in a manner identical to the analysis of the solutions for calibration. The retention time of valerophenone was 16 minutes. The number of moles of acetophenone formed in each tube was calculated (2.30×10^{-5}, 2.71×10^{-5}, and 2.04×10^{-5} moles). From data contained in reference 48,

the quantum yield for formation of acetophenone using 0.36M valerophenone was calculated to be 0.38. Therefore, the light absorbed by the samples was 6.05×10^{-5}, 7.13×10^{-5}, and 5.37×10^{-5} moles, respectively.

p-Cyanostilbene

Benzyltriphenylphosphonium chloride (3 g, 7.7 mmole; prepared according to a literature preparation[54] and dried under vacuum for 6 hours) was added to 50 ml dried tetrahydrofuran to form a white slurry. As *n*-butyl lithium (4.3 ml, 1.8M) was added, the reaction mixture turned orange-red and then became very dark. The ylide was allowed to stir for 30 minutes, and then 4-cyanobenzaldehyde (1.01 g, 7.7 mmole) in 50 ml dried tetrahydrofuran was added dropwise. After about 48 hours, 10 ml isopropyl alcohol was added to kill any unreacted base, and the reaction was rotovapped to leave a dark oil. Petroleum ether (about 300 ml) was poured into the flask and a gummy orange solid precipitated. The mixture was filtered and the flask washed with petroleum ether. The filtrate was rotovapped to leave an oil which crystallized from ethanol and water. Recrystallization from ethanol and water, and then from 80% acetic acid gave 0.12 g product (8%): m.p. 108-112°C; ir (Nujol) 2230 (s), 1700-1650 (s), 1600 (m), and 1500 cm^{-1} (m); nmr ($CDCl_3$) δ 7.0-7.5 ppm (m, has larger peaks at 7.0 and 7.5); mass spectrum m/e (rel intensity) 205 (molecular ion, 100), 190(31), 177(14),

165(13), 151(6), 140(3), 127(4), 102(11), 89(16), 76(14), 63(7), 51(13), 39(7).

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