# The Effect of Wavelength on Organic Photoreactions in Solution. Reactions from Upper Excited States

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## I. Introduction

One of the most widely held and useful generalizations in solution phase photochemistry has been that reaction and luminescence occur from vibrationally relaxed molecules in their lowest singlet or triplet states. The conventional picture holds that excitation to vibrationally excited levels of the lowest electronic state, or to higher electronic states, is followed by rapid radiationless deactivation to an equilibrium distribution of vibronic states of $S_1$ or $T_1$ prior to emission or photochemical events (Figure 1a). For emission, this generalization has often been verified experimentally, and has led to the formulation of the well-known rules of Kasha and Vavilov as follows.[1a]

*Kasha's Rule:* In solution, emission occurs from $S_1$ or $T_1$ independent of the state which is initially excited.

*Vavilov's Rule:* The fluorescence quantum yield is independent of the excitation wavelength.

For photochemical reactions, although not formally codified as rules, most investigations have similarly corroborated this picture. A particularly elegant example is the work of Zimmerman and co-workers on diphenylcyclohexenone.[1b] Over the last several years, however, a number of examples contrary to the general mechanism illustrated in Figure 1a have been demonstrated or proposed. It will be our purpose in this review to summarize these examples and examine the possible reasons for deviation from this generalized model of fast higher excited state relaxation followed by photochemistry or luminescence.

One might expect that a molecule containing excess electronic and vibrational energy can undergo any of a variety of relaxation processes including radiative decay, nonradiative intramolecular or intermolecular decay, energy transfer, or photochemistry. That most photochemical and luminescent events in solution do seem to occur from the lowest vibrational levels of the lowest electronic states simply means that the nonradiative decay route is ordinarily faster than competing radiation or photochemistry from highly excited states. This conclusion is by no means absolute. For example, at low pressures where collisions are relatively rare, and thus energy removal is relatively slow, it has long been accepted that photochemistry and emission from higher excited states are fairly common. In fact, a recent investigation suggests that the quantum yield for $S_2$ fluorescence in thiophosgene (vapor at low pressure) may be 1.0.[2] In condensed phases, then, one may expect that higher excited state photochemistry will be most easily observed when radiationless deactivation rates are unusually slow or when radiative or photochemical rates are unusually fast. Two cases may be differentiated.

In one case, photochemistry occurs from higher vibrational levels of a given electronic state in competition with energy removal by collisions (Figure 1b). Rate constants for vibrational relaxation in polyatomic molecules in both ground and excited states in solution have been determined by a number of workers using picosecond laser techniques. Values ranging from $1 \times 10^{11}$ to $1 \times 10^{12}\ \mathrm{s}^{-1}$ have ordinarily been obtained.[3] Even such a fast rate constant as $10^{11}$ does not seem to exclude simple chemical events like bond dissociation, which could presumably occur within a single vibrational period in the absence of an activation barrier. The rate constant for a unimolecular reaction from an excited vibrational level of energy $E^*$ above the ground vibrational level may be described qualitatively by the RRK expression

$$k = A\left(\frac{E^* - E_a}{E^*}\right)^{s-1}$$

where $A$ is the Arrhenius preexponential factor, $E_a$ is the activation energy, and $s$ is a parameter related to the total number of vibrational modes of the reactant. Since $E_a$ for excited state reactions is often small, the photochemical rate constant may approach its limiting value ($A \cong 10^{12}$) at fairly modest levels of vibrational excitation. Fluorescence rate constants, on the other hand, seldom exceed $\sim 10^9\ \mathrm{s}^{-1}$. Thus there is reason to believe that the grounds for Kasha's or Vavilov's rules may be less universally applicable to photochemical reactions than to luminescent processes. Furthermore, since quantum yields of 1% or less may be quite readily detected, the appropriate rate

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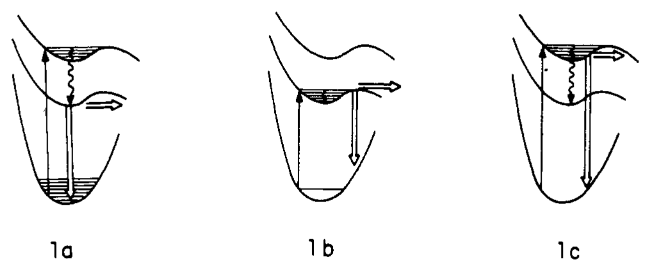


**Figure 1.** General state diagrams for reactions from (a) $S_1$ state, (b) higher vibrational levels of $S_1$, and (c) higher excited state.

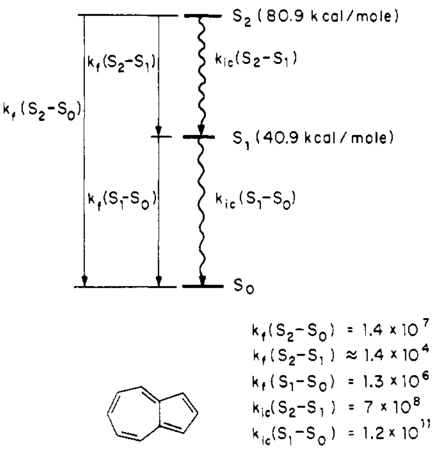


**Figure 2.** Spectroscopic data for azulene.

constant for effective competition with vibrational relaxation need only be $10^9-10^{10}$ $s^{-1}$ which makes even the observation of activated bimolecular processes a possibility. Case one type photochemistry has been proposed by Becker[4] and Pitts.[5] This work will be described in more detail in later sections.[6]

In the second case (Figure 1c), vibrational relaxation within a given higher electronic state occurs rapidly, but internal conversion $S_n \rightarrow S_{n-1}$ is slow enough to permit photochemical or emission events to compete. Theoretically, the rate of internal conversion from the 0 vibrational level of an upper excited state ($S_2$) to the lower excited state ($S_1$) with $m$ isoenergetic vibrational levels is given by[7]

$$k_{ic} \propto |\langle\Psi_2|J|\Psi_1\rangle|^2 \Sigma_m \langle\chi_{20}|\chi_{1m}\rangle|^2 = C_{12}F \qquad (1)$$

In this equation $\Psi_1$ and $\Psi_2$ are the electronic wave functions of $S_1$ and $S_2$, respectively, while $\chi_{20}$, $\chi_{1m}$ are the nuclear wave functions for the appropriate vibrational levels of $S_1$ and $S_2$, respectively. The operator $J$ is the nuclear kinetic energy operator. The first term is an electronic factor ($C_{12}$) that results from a coupling of the electronic wave functions, while the second is the familiar Franck-Condon factor between the two states. Decay rates of higher excited singlet states of aromatic systems in solution have been determined by fluorescence, absorption line width, and picosecond laser techniques, and are typically $1 \times 10^{11} \rightarrow 1 \times 10^{14}$ $s^{-1}$ [8] with the notable exceptions of azulene[9] and benzopyrene.[10] Clearly these rates are sufficiently fast that competitive processes will be observable only rarely or in low yield. However, there are well-characterized examples in which $k_{ic}$ is not nearly as fast, azulene being the best known ($k_{ic} = 7 \times 10^8$). This, then, permits observation of fluorescence from $S_2$. As will be discussed in more detail below, the peculiarity of azulene arises from a particularly poor Franck-Condon factor for the $S_2 \rightarrow S_1$ internal conversion. In a similar way, one might expect photochemical processes from higher excited states to be most readily observable when internal conversion is slow. From eq 1 it is clear that slow internal conversion may result either from a poor Franck-Condon factor, as when the energy gap between $S_2$ and $S_1$ is large, or a poor electronic factor, as when $\Psi_2$ and $\Psi_1$ are orthogonal.

In practice it is extremely difficult to experimentally distinguish case I from case II, just as the distinction between an $S_1$ or $T_1$ mechanism and a "hot" ground state mechanism in "normal" photochemical processes is often obscure. More often, what is observed phenomenologically is a dependence of $\Phi_{reac}$ or $\Phi_{emission}$ on wavelength. Therefore, this review will be more concerned with differentiating spurious $\lambda$ effects due to ground state properties from $\lambda$ effects implying higher excited state or vibronic photochemistry, than with assigning the observed reactions to the latter two categories. We will, however, attempt to account for those features (fast reaction, or slow internal conversion) which make the photochemical route observable in any particular case.

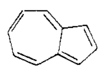
## *II. Emission and Energy Transfer*

### A. Emission

In this section some specific examples of fluorescence from higher excited states will be examined. The aim is not to provide a complete review of this field of spectroscopy but rather to illustrate the factors which allow emission from higher electronically excited states to be detected.

#### *1. Anomalous Emission*

The best documented example of anomalous fluorescence is that of azulene (**1**).[9,11-15] In 1955, Beer and Longuet-Higgins reported the emission and absorption spectra of **1**.[11] The first two absorption maxima occur at 340 and 585 nm. However, the emission spectrum contains only one band located at 374 nm. Simply from energetic considerations, one may conclude that the emission occurs from $S_2$ rather than $S_1$. Furthermore, the 0–0 bands of the emission and $S_2$ absorption overlap and the spectra display the expected mirror image relationship. Consequently, the emission is unambiguously assigned to fluorescence from $S_2$. This conclusion was quickly confirmed by several other groups.[12,13] The known photophysical data for azulene are shown in Figure 2.[9,16] Judging from the $S_0$–$S_1$ and $S_1$–$S_2$ energy gaps alone, the rates of internal conversions of $S_1$ and $S_2$ would be expected to be similar. However, the geometries of $S_1$ and $S_2$ are expected to be similar while $S_0$ will have a substantially different geometry. This will reduce the FC factor for the $S_2$–$S_1$ internal conversion. This reduction of several orders of magnitude in $k_{ic}(S_2-S_1)$ allows the rather slow processes of fluorescence [$k_f(S_2-S_0) = 1.4 \times 10^7$] to compete with internal conversion.

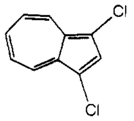
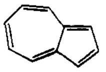
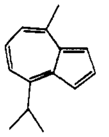
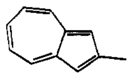
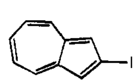
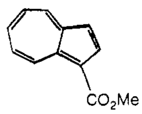
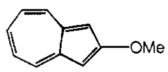
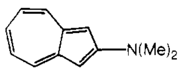


*1*

The study of substituent effects on the anomalous fluorescence of azulene has further confirmed the emission to be from $S_2$.[17-20] When substituents replace the hydrogens of azulene, the $S_2$ absorption maximum is shifted to longer wavelength (red shifted). Some representative examples are shown in Table I.[20] While every substituent causes a red shift in the $S_2$ band, there is no such trend apparent in the $S_1$ absorption maximum. Some substituents bring about a red shift while others cause a blue shift. In all cases, the emission maxima also show a red shift upon substitution. Furthermore, the 0–0 bands of $S_2$ absorption and emission overlap in most cases. This provides further justification for assigning the fluorescence as occurring from the $S_2$ state.

A consideration of the data in Table I also illustrates the dependence of the FC factor on the energy gap. As shown in the last column of Table I, the entries are in order of decreasing energy gap between $S_2$ and $S_1$. The fluorescence quantum yields

**TABLE I. Fluorescence Quantum Yields and the Energies of the First Two Excited Singlet States of Substituted Azulenes**[a]

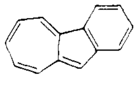
|  | $\Phi_{fl}$ | $E_{S_1}$, kcal/mol | $E_{S_2}$, kcal/mol | $\Delta E$, kcal/mol |
|---|---|---|---|---|
|  | 0.058 | 36.3 | 77.0 | 40.9 |
|  | 0.031 | 40.9 | 80.9 | 40.0 |
|  | 0.014 | 39.5 | 77.8 | 38.3 |
|  | 0.0081 | 42.6 | 79.5 | 36.9 |
|  | 0.0034 | 42.9 | 77.5 | 34.6 |
|  | ~$10^{-4}$ | 44.3 | 77.2 | 32.9 |
|  | ~$10^{-4}$ | 46.9 | 76.9 | 30.0 |
|  | ~$10^{-5}$ | 47.8 | 68.4 | 20.6 |

[a] Adopted from S. Murata, C. Iwanaga, T. Toda, and H. Kokubun, *Ber. Bunsenges. Phys. Chem.*, **76**, 1176 (1972).

($\Phi_{fl}$) are shown in the second column. Clearly, as the energy gap decreases, the amount of fluorescence decreases. This is due to the increased rates of the internal conversion from $S_2$ to $S_1$. By examining some 30 azulene derivatives, Kokubun and coworkers concluded that $\Phi_{fl}$ decreases exponentially with respect to the energy difference between $S_2$ and $S_1$.[20]

An additional piece of information may be gleaned from Table I. The major deactivating pathway of $S_2$ is not intersystem crossing to a higher triplet state but internal conversion. This is illustrated by comparing iodoazulene with, for example, methoxyazulene. If intersystem crossing were important, the iodo derivative should have a small fluorescence. Since this derivative does have appreciable fluorescence and is in accord with the energy gap hypothesis, the intersystem crossing rate may be considered very slow.

Besides azulene and its derivatives, anomalous fluorescence has been observed for several other hydrocarbons. For example, the benzene annulated azulene derivatives (**2**–**4**) all show anomalous fluorescence.[14,18] Furthermore, derivatives of Hafner's hydrocarbon (**5**) have been shown to exhibit anomalous fluorescence.[21]



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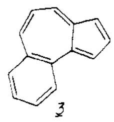

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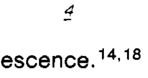

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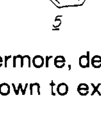

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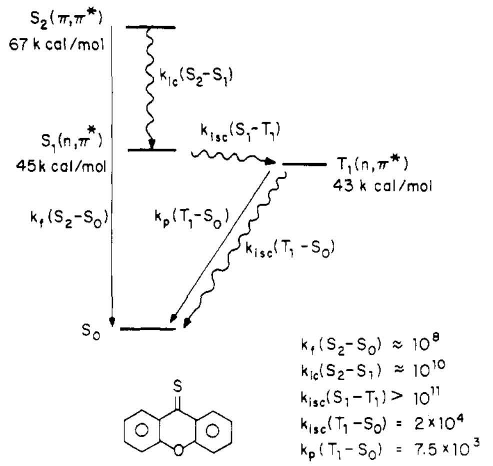
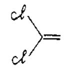


**Figure 3.** Spectroscopic data for xanthione.

In addition to the above examples, emission from higher excited states of benzene, toluene, and *p*-xylene has recently been observed.[22] The emission maxima occur at ≃235, ≃240, and ≃245 nm, respectively. In all these cases the quantum yield was less than $10^{-5}$. Likewise, fluorescence from $S_3$ in naphthalene and pyrene has been observed.[22] In the case of naphthalene (deoxygenated isooctane) the emission occurred at 227 nm, $\Phi_{fl} = 2.2 \times 10^{-5}$. The assignment of $S_3$ fluorescence is based upon the proximity of the fluorescence to the $S_3$ absorption band. From the $\Phi_{fl}$ and absorption strengths, the rate constant for $S_3$ radiationless deactivation was calculated to be $1 \times 10^{14}\ s^{-1}$. Finally, the $S_3$ emission of pyrene occurs at 284 nm, $\Phi_{fl} = 5 \times 10^{-5}$, and the $S_3$ radiationless deactivation rate constant was determined to be $1 \times 10^{14}\ s^{-1}$.

Thiones represent another general class of molecules displaying anomalous fluorescence. For example, thiophosgene (**6**) in the vapor phase displays fluorescence from $S_2$[2,23] with a very high quantum yield ($\Phi \sim 1$). The absorption spectrum consists of two maxima at 475 and 254 nm. The low-energy band is assigned to a n,$\pi^*$ transition and the higher energy one to a $\pi,\pi^*$ transition. The emission consists of a broad, structureless band extending from 290 nm down to 530 nm. This emission has been assigned to fluorescence from $S_2$. The fascinating aspect of this molecule is that fluorescence will occur only if absorption results in population of one of the first three vibrational levels of $S_2$. Thus, while radiation of wavelength greater than 277 nm will result in fluorescence, higher energy radiation ($\lambda < 277$ nm) results in a decrease in fluorescence efficiency. This wavelength effect on fluorescence quantum yields has been noted for normal fluorescence (from $S_1$) as well. Further discussion of its causes will be deferred until section C.



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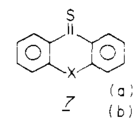
Other thiones displaying anomalous fluorescence include xanthione (**7a**) and thioxanthione (**7b**). The known photophysics for **7a** are displayed in Figure 3.[24] The absorption spectrum consists of a n,$\pi^*$ ($\lambda$ 633 nm) and a $\pi,\pi^*$ ($\lambda$ 428 nm) transition. The energy difference between $S_1$ and $S_2$ is sufficiently large to allow fluorescence from $S_2$ to compete with internal conversion. The excitation of the $S_2$ band, in fact, results in emission from $S_2$, whereas excitation into $S_1$ band leads to emission from $T_1$.



7 (a) X = O (b) X = S

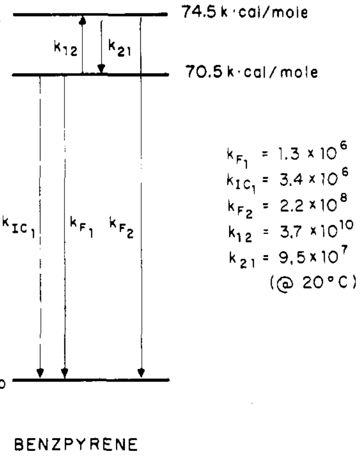
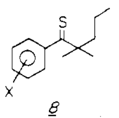


**Figure 4.** Spectroscopic data for 1,2-benzopyrene.

The same general pattern is displayed by thioxanthione.[24] However, both emission and absorption maxima are shifted by 40–50 nm. Furthermore, the $S_2$–$S_1$ energy gap is decreased so that the quantum yield of fluorescence decreases from 0.0051 in **7a** to 0.0015 in **7b.**

Another important series of thiones, especially from the view point of reactivity of upper excited states, is the arylalkylthiones shown below.[25] In a later section the reactivity patterns resulting from population of $S_1$ and $S_2$ will be discussed. Only the photophysical data will be considered in this section.



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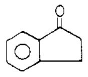
These thiones have absorption spectra consisting of two bands in the range of 200–300 nm ($\pi,\pi^*$) and 400–500 nm ($n,\pi^*$). The emission spectrum consists of a fluorescence band, assigned to $S_2$ fluorescence and a phosphorescence band occurring from $T_1$.

While a number of examples of fluorescence from upper excited states have been fairly well characterized, the same cannot be said of upper excited state phosphorescence. There have been a number of reports of dual phosphorescence occurring in matrices. However, in most cases the dual phosphorescence has been attributed to different solvent–solute interactions[26] or different molecular conformations.[27] Indanone (**9**) appears to be an authentic example of dual phosphorescence although this interpretation is still a controversial matter.[26–30]



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## 2. Temperature-Dependent Anomalous Fluorescence

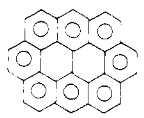
When the first and second excited electronic states of a molecule are energetically proximate, it is possible to thermally populate the second excited state. However, the population of $S_2$ has to compete with the other processes which deactivate $S_1$. For example, if the lifetime of $S_1$ is $10^{-9}$ s, the thermal population rate has to be at least $10^9$ s$^{-1}$ which is possible at room temperature only if the energy gap is less than ~5.5 kcal/mol (assuming the *A* factor in the Arrhenius expression to be $10^{13}$). In addition, to observe emission or reaction from the thermally populated $S_2$, the rates of emission and reaction must be able to compete with other processes deactivating $S_2$ including the radiationless return to $S_1$. In this section we describe the emission from $S_2$ upon thermal population from $S_1$; the reactions under these conditions are discussed in a later section.

One of the first reported cases of thermally induced "anomalous fluorescence" involved benzopyrene.[10,31,32] At low temperatures (−73 °C), the emission consists of a set of sharp bands around 400 nm. The 0–0 band for $S_1$ fluorescence occurs at 403 nm. On the high energy side of this 0–0 band are several very weak bands. These have been ascribed to anomalous fluorescence from $S_2$ and the 0–0 band has been assigned to the band at 384 nm. As the temperature is raised, the intensity of the $S_2$ 0–0 band increases relative to the $S_1$ 0–0 band. In fact, a semilogarithmic plot of the ratio of the $S_2$ and $S_1$ fluorescence intensities vs. $1/T$ is nearly linear. This procedure yields an energy difference between the two excited states of 2.7 kcal/mol. Hence, the thermal population of $S_2$ is readily achieved at room temperature.

More recently, Van Voorst and co-workers have pointed out that not all the higher energy bands are due to fluorescence from $S_2$.[33] By a careful analysis of the temperature response of each band, these workers were able to identify fluorescence from $S_2$ as well as from a vibrationally hot $S_1$ state. Thus, care must be taken when assigning luminescence from thermally populated fluorescent states.

Similar to the case of 3,4-benzopyrene, it is found that 1,12-benzoperylene shows thermally dependent fluorescence from $S_2$.[34,35] This system has been thoroughly studied and some of the pertinent data are displayed in Figure 4.[34,33] The data indicate that the rate constant for the thermal population of $S_2$ is an order of magnitude larger than those for fluorescence or internal conversion from $S_1$.

Besides the above well-characterized examples, a number of other molecules do show temperature-dependent anomalous fluorescence. Generally, these molecules are large aromatic systems. The molecule ovalene (**10**) is a typical example.[36] Other examples are 1,2-benzanthracene,[32] 3,4-benzotetraphene,[32] and fluoranthrene.[36]



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## 3. Wavelength-Dependent Fluorescence

In the previous sections, we discussed emission from higher electronic states wherein radiative decay was able to compete with other processes which deplete these states. When higher electronic states do not emit measurably, the ability of reaction and intersystem crossing to a triplet manifold to compete with internal conversion can be measured in terms of the variation of fluorescence yield from $S_1$ with respect to varying wavelength. Such wavelength-dependent fluorescence from $S_1$ is due to slow internal conversion from higher electronic states and slow vibrational relaxation within a single electronic manifold or fast competing radiationless processes.

A variety of aromatic hydrocarbons including 9,10-dibromoanthracene have been shown to exhibit wavelength-dependent fluorescence quantum yields from $S_1$.[37] In all of these cases fluorescence yields decreased if the excitation resulted in $S_2$ population. The variation is attributed to the ability of predissociation (C–Br bond) and/or intersystem crossing to the triplet manifold to compete with the internal conversion.

A well characterized system showing wavelength-dependent fluorescence is benzene.[38] Benzene displays a temperature-dependent relaxation mechanism from the $S_1$ state which has been referred to as the "channel 3" relaxation process. Consequently, excitation to higher vibrational levels of $S_1$ can lead to decreases in fluorescence quantum yield as the channel 3 process begins to become significant. Furthermore, Lipsky reported that benzene, toluene, *p*-xylene, and mesitylene show poor emission from $S_1$ ($\Phi \sim 10^{-4}$) upon irradiation in the $S_2$

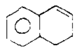
band. This has been attributed at least in part to the ability of photoreaction (to form benzvalene) to compete with internal conversion from $S_2$ to $S_1$. Reaction from higher excited states of benzene is discussed in detail in later sections.

Another interesting system displaying wavelength-dependent fluorescence is that of phenol and its derivatives.[39] In hydrocarbon solvents, the fluorescence quantum yield depends upon the wavelength of excitation. Irradiation into the $S_2$ band causes a decrease in the $S_1$ fluorescence and a concomitant increase in the formation of $H_2$. Apparently, excitation into $S_2$ enhances the homolytic cleavage of the O–H bond. In support of this, the decrease in $\Phi_{fl}$ can be suppressed by addition of solvents capable of forming hydrogen bonds. Thus, in a solution of 15% methanol and 85% cyclohexane, $\Phi_{fl}$ is essentially independent of the excitation wavelength.

As alluded to in a previous section, the rate of internal conversion between $S_2$ and $S_1$ may also be wavelength dependent. Recall that the fluorescence from $S_2$ of thiophosgene showed a wavelength dependence.[23] In particular, excitation into the first three vibronic levels of $S_2$ resulted in fluorescence, but excitation into higher vibronic levels resulted in rapid internal conversion. Such a behavior has been explained by assuming that the rate of internal conversion is dependent upon the vibronic level of the excited state.

Several examples wherein photoreaction or intersystem crossing compete with vibrational relaxation ($S_1$) have been investigated by Becker and co-workers.[4,40,41] The two cyclic systems **11** and **12** were studied.

The dihydronaphthalene derivative (**11**) was shown to be "normal" in that its fluorescence quantum yield ($\Phi_{fl}$) was independent of the wavelength of excitation. This was not the case for 2,2-dimethyl-5,6-benzo-2*H*-chromene (**12**). As the excitation wavelength is varied from 329 to 303 nm $\Phi_{fl}$ decreases by a factor of 3. In this case, the process competing with relaxation among the vibronic levels of $S_1$ is photoreaction producing the cyclic ketone **13**.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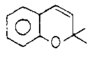

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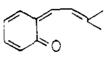

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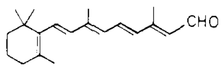
An interesting aspect of this study was identification of vibrational modes which promoted the photoreaction. Two vibrational sequences, one having a spacing of 280 $cm^{-1}$ and the other 1300 $cm^{-1}$, were identified in the absorption spectrum of **12.** These workers were able to demonstrate that the ratios of vibrational relaxation to photochemical conversion were 2.8 and 0.7 for the 280- and 1300-$cm^{-1}$ sequences, respectively. In other words, the 1300-$cm^{-1}$ mode promoted reaction efficiently while the less energetic mode promoted internal conversion. This is readily understandable since the 1300-$cm^{-1}$ vibration is assigned to a C–O–C asymmetric stretching mode.

Similar wavelength dependence has been noted for several other systems. One of the most studied is the series of retinal isomers.[40-42] While none of the isomers fluoresces at room temperature, the all-trans, 9-cis- and 13-cis isomers all fluoresce at 77 K in a hydrocarbon glass. This fluorescence has been found to be wavelength dependent. For example, the all-trans isomer has a fluorescence quantum yield of 0.044 when excited with 440-nm light. However, when the wavelength is reduced to 300 nm, $\Phi_{fl}$ decreases to 0.005. Precisely the same trend has been observed in the other isomers that fluoresce.



all-trans retinal

Table II. Rate Constants for Fluorescence Quenching by 1,3-Cyclohexadiene and Quantum Yields for Anthracene Fluorescence, Intersystem Crossing, and Sensitized Dimerization of 1,3-Cyclohexadiene

| Anthracene | $k_q$ $(M^{-1}\ s^{-1})^a$ $(\times 10^6)$ | $\Psi_{fl}$ | $\phi_{isc}^{rel}$ | $\phi_{reac}^{rel}$ [c] |
|---|---|---|---|---|
| 9,10-Diphenyl | 1.20 | 0.76[b] | (0.24) | 0.0295 |
| 9,10-Dichloro | 1.35 | 0.56 | 0.48 | 0.0302 |
| 9,10-Dibromo | 2.06 | 0.1 | (0.90) | 0.0336 |

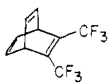
[a] Quenching by 1,3-cyclohexadiene. [b] V. L. Ermolaev and An. Terenin, *Sov. Phys. Usp.*, **3**, 423 (1960). [c] Relative quantum yields for sensitized dimerization of 1,3-cyclohexadiene (0.0726 M).

The causes of this wavelength dependence are somewhat unclear. It is possible that isomerization competes with internal conversion. However, it is also possible that there are two low-lying singlet excited states. If the lowest excited state was a $\pi\pi^*$ state with a large $\Phi_{fl}$ and a $n\pi^*$ state with a small $\Phi_{fl}$ was slightly higher in energy, the observed wavelength dependence could be accounted for. Furthermore, the fact that little or no wavelength dependence of fluorescence has been observed for the Schiff bases of these retinals[41] and closely related unsaturated hydrocarbons[42] tends to support this interpretation.

## B. Energy Transfer

From the previous discussion, one may conclude that in certain cases higher excited states may have lifetimes approaching the nanosecond range. The possibility of bimolecular processes occurring from these states then becomes very real. In this section the bimolecular process of energy transfer will be discussed. This section will be devoted to energy transfer from higher excited triplet states.

The most thoroughly studied example of energy transfer from higher excited triplet states involves anthracene derivatives.[43-47] Evidence for energy transfer comes from an investigation of the triplet-sensitized rearrangement of rigid diene systems such as **14** and **15.** For example, compound **14** rearranges to the expected di-$\pi$-rearranged products when sensitized by triplet donors with triplet energies greater than 68 kcal/mol. Hence, benzophenone ($E_T$ = 68.5) will efficiently sensitize the reaction while 2-acetonaphthone ($E_T$ = 59.3) will not. However, anthracene ($E_T$ = 42) is capable of sensitizing the reaction. Since it could be shown that the anthracene $T_1$ state did not sensitize the reaction, the only remaining states which may be responsible for sensitizing the rearrangement are the $S_1$ and $T_2$ states.



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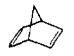
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If the singlet state were involved, a spin-forbidden energy transfer typified by the following equation

$$D(S_1) + A(S_0) \rightarrow D(S_0) + A(T_1) \qquad (2)$$

would be required. This type of process has indeed been implicated in the fluorescence quenching of anthracene derivatives by naphthalene.[48] In contrast, if the $T_2$ state were involved, a spin-allowed energy transfer occurs but limitations are imposed on the $T_2$ lifetime.

In order to differentiate these two possibilities, Liu and Campbell investigated the fluorescence quenching of anthracene derivatives by 1,3-cyclohexadiene.[49] The results are shown in Table II. Also shown in this table are the quantum yields for fluorescence and intersystem crossing of the anthracene derivatives and the quantum yield for the sensitized dimerization of 1,3-cyclohexadiene. This dimerization occurs only from the triplet manifold of the diene and so acts as a "triplet counter". As can be seen from Table II, $k_q$ and $\Phi_{isc}$ follow the same trend

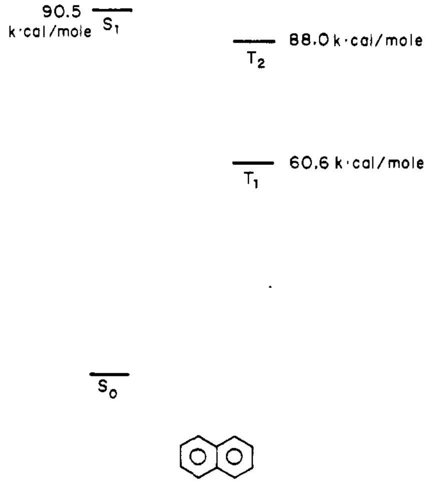


**Figure 5.** State energy levels of naphthalene.

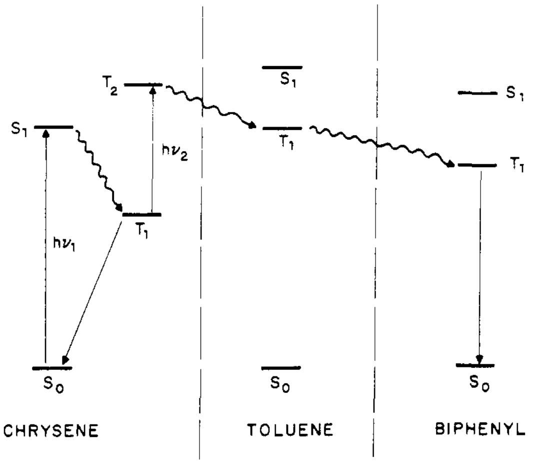


**Figure 6.** State energy levels for chrysene, toluene, and biphenyl.

as $\Phi_{reac}$. However, since the dimerization is characteristic of triplet states, a significant amount of $T_2$ must be trapped by the diene. Further support for involvement of $T_2$ comes from the fact that $\Phi_{fl}$ decreases as $\Phi_{reac}$ increases. In conclusion, it appears that a significant amount of $T_2$ is produced and readily trapped. Also, even though fluorescence is quenched by the diene, this energy transfer contributes little if any to the triplet reaction.

From detailed studies of both cyclic and acyclic dienes[44,45] the lifetimes of the $T_2$ states for several monosubstituted anthracene derivatives have been determined. These lifetimes lie in the range of $2\text{-}5 \times 10^{-10}$ s[49] and have been attributed to a large $T_1$–$T_2$ energy gap. Furthermore, a fluorescence assigned to $T_2$ to $T_1$ emission has been observed.[50] The energy of $T_2$ for anthracene was determined to be 74 kcal/mol. Thus $T_2$ should certainly be capable of sensitizing the reactions of many diene systems.

Using similar experimental techniques Ladwig and Liu were able to observe energy transfer from the $T_2$ state of naphthalene.[51] The pertinent data for naphthalene are shown in Figure 5. The lifetime of the second excited triplet state was estimated to be $1.7 \times 10^{-11}$ s, i.e., an order of magnitude less than that of the anthracene $T_2$ state. Interestingly, the lifetime of naphthalene $T_2$ increased as hydrogen was replaced by deuterium.[52] In contrast, the $T_2$ lifetime of dibromoanthracene showed no deuterium isotope effect.[49]

In the previous examples, direct excitation led to population of a higher triplet state via intersystem crossing. An alternative method for producing these higher triplet states involves direct excitation via $T_1 \rightarrow T_2$ absorption. A population of the lowest triplet state is first produced in a matrix at 77 K. Then a second light source is switched on and this results in the production of higher triplet states. Using such a process, it has been possible to observe energy transfer from higher triplet states.[48,53,54] For example, chrysene and biphenyl were frozen in a toluene matrix and the chrysene was irradiated. The state energy levels for these three compounds are shown in Figure 6. Population of the chrysene lowest singlet resulted in phosphorescence from the $T_1$ state. However, in the presence of a second light source, the phosphorescence of chrysene decreased, but now phosphorescence from the lowest triplet state of biphenyl was observed. As can be seen from Figure 6, this is consistent with the $T_2$ state of chrysene transferring energy to the toluene matrix. Exciton transfer occurs through the matrix until the energy is trapped by a biphenyl molecule. The excited biphenyl emits and a new phosphorescence is observed.

**TABLE III. Escape Efficiency ($\beta$) of Selected Triplet States**[a]

| Molecule | $\beta$ | $\Delta(T_n - T_1)$,[b] kcal/mol |
|---|---|---|
| Biphenyl | 0.18 | 77.2 |
| Naphthalene-$d_8$ | 0.13 | 68.6 |
| Carbazole | 0.04 | 57.2 |
| Diphenylamine | 0.02 | 51.5 |
| Chrysene | 0.02 | 42.9 |
| Phenanthrene | 0.02 | 37.2 |

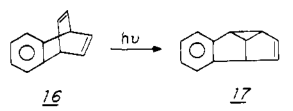
[a] V. I. Alfinn, I. G. Batekta, Y. B. Sheck, and V. I. Gerko, *Spectrochim. Acta, Part A*, **27**, 329 (1971).

The higher excited triplet states of a molecule may either transfer energy to the surrounding matrix or decay back to the lowest triplet state. A method for determining the probability for energy transfer ($\beta$) has been developed by Alfinov and coworkers[55] Some of their results are shown in Table III. The quantity $\beta$ is proportional to the lifetime of $T_2$ in a toluene matrix. The decrease in the $T_2$ lifetime as the $T_2$–$T_1$ energy gap decreases is exactly that expected from the previous discussion of azulene and its derivatives.

This procedure has also been useful in sensitizing reactions in the matrix. For example, the photochemical decomposition of $CH_3I$ to the methyl radical and an iodine atom may be sensitized by higher excited triplet states of naphthalene.[56,57] This process has been shown to involve two photons by demonstrating that the concentration of methyl radicals depends upon the square of the light intensity. Furthermore, by the use of two monochromatic light sources, the second excited triplet state of naphthalene was definitely implicated in the reaction sequence.

Further work showed that not only naphthalene but many other sensitizers brought about the decomposition of $CH_3I$.[56,57] Some examples are diphenylamine, phenanthrene, benzophenone, and $H^+$-fluorescein. Finally, the cleavage of C–C[57] as well as C–H bonds[58] has also been achieved by energy transfer from higher excited triplet states.

Recently, a possible example of an intramolecular trapping of $T_2$ has been reported. This example involves the photochemical di-$\pi$-methane rearrangement of arylbarrelenes. Benzobarrelene (**16**) and naphthobarrelene (**18**) produce the



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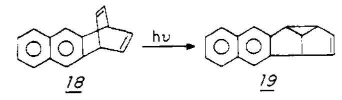

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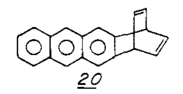


rearrangement from $T_2$
no rearrangement from $T_1$

corresponding products **17** and **19**.[59] The reactions occur from triplet manifolds with quantum yields approaching 0.5.

In the case of the anthracene derivative **20**, the reaction again occurs upon direct irradiation.[59b] However, population of the lowest triplet state (~42 kcal/mol) by triplet sensitization does not produce any rearranged product. Since the reaction is characteristic of triplet states, these results suggest that the $T_2$ state of the anthracene is responsible for the rearrangement.

## *III. Reaction*

A general experimental manifestation of higher or hot excited state photochemistry is wavelength-dependent product ratios or quantum yields. Wavelength effects in solution photochemistry could arise either from excited state or ground state properties. The simplest classification of these reactions may be as follows: (i) reactions from higher electronic states, i.e., $S_n{}^*$ or $T_n{}^*$ ($n >$ 1), (ii) reactions from higher vibrational states (hot) of the lowest excited electronic states, i.e., $^*S_1{}^{\ddagger}$ or $^*T_1{}^{\ddagger}$, (iii) reactions from $T_1$ through population from $S_n{}^*$ or $S_1{}^{\ddagger}$, (iv) wavelength dependence due to ground state properties.

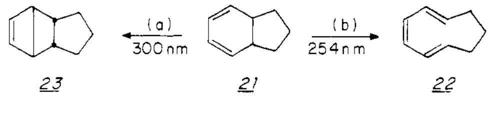
In this section we review *organic reactions in solution* which show wavelength dependence. We have organized them according to the chromophore responsible for photochemical reaction but have attempted where possible to assign them to one of the above classification and attempted to illustrate the factors which allow them to show reactions from higher or hot excited states.

### A. Olefins

Even though the experimental observation of a wavelength dependence of some property of a photoreaction commonly implies the occurrence of a higher excited state reaction, it is not in itself a sufficient condition for such a conclusion. In fact the origin of the wavelength dependence can often be assigned to ground state properties or spurious effects. For example, olefins and especially polyenes undergo a variety of photochemical reactions, some of which have been shown to be wavelength dependent, but none of which has been demonstrated to originate from higher electronic or vibrational states. The wavelength effects observed in polyenes will be used to illustrate the importance of ground state properties.

#### *1. Effects due to Secondary Photoreactions by the Primary Photoproduct*

Wavelength effects may be observed as an artifact of experimental conditions if secondary reactions of photoproducts having different absorption characteristics occur. An interesting example of this kind has been observed in the case of bicyclo[4.3.0]nona-2,4-diene (**21**).[60] When **21** is irradiated in pentane using 254-nm light, a photostationary state is reached between **21** and **22**. On the other hand, irradiation with 300-nm light gives **23** and not **22**. Even though these results are consistent with reactions a and b originating from two different electronic states of **21**, this wavelength effect can be readily explained without invoking higher excited states. **21** can undergo two primary photoreactions: (a) ring closure to give **23** and (b) ring opening to give **22**. Process a is much slower than process b. Similarly **22** can undergo photochemical ring closure to give **21**. At 254 nm the ratio $\epsilon_{21}/\epsilon_{22} \simeq 30$ and hence the stationary state is in favor of **22**. At 300 nm the ratio of $\epsilon$ drops to about 0.02 ($\epsilon_{21}{}^{300} \sim 50$, $\epsilon_{22}{}^{300} \sim 2000$) so the photostationary state is greatly displaced to favor **21**, thus allowing the less efficient **23** formation to proceed from **21** at a significant rate. The observed wavelength effect is therefore purely due to the secondary photoreaction of **22** and the absorption properties of **21** and **22**.

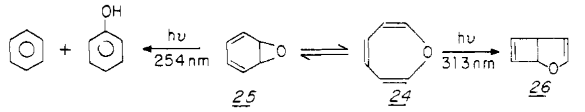


(5)

#### *2. Effects due to Thermal Equilibrium in the Ground State*

If the thermal energy barrier between interconvertible molecular structures is less than ~17 kcal/mol, they would for normal chemical purposes be considered to be in rapid thermal equilibrium at room temperature. Nevertheless, since photon absorption is virtually an instantaneous event on the timescale of nuclear motion, they may be independently excited. Furthermore, equilibrium may not be attained within the lifetime of the excited state. Therefore excitation of these species may result in their independent photochemistry. Such a mechanism could lead to wavelength-dependent photochemistry as illustrated by the following example.

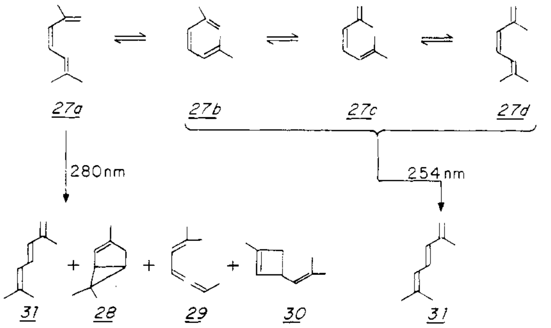
Irradiation of benzene oxide (**25**) in ether solution (>310 nm) gave **26** as the only product.[61] But, irradiation with 253.7-nm light at −80 °C gave 74% phenol and 15% benzene. This wavelength dependence has been explained as follows. At room temperature **24** and **25** exist in equilibrium, but since $\epsilon$ for **24** greatly exceeds that of **25**, the photochemistry observed at room temperature is largely that of **24**. On the other hand, at −80 °C the equilibrium lies strongly in favor of **25** and photochemistry results from excitation of this structure.



(6)

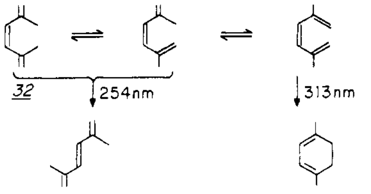
The interconverting structures need not be structural isomers as in the preceding example, but could in fact be conformational isomers. Although little is known about the magnitude of rotational barriers in excited states, examples like the ready photoracemization of biphenyl systems suggest that they may be vastly different from the barriers in the ground state. If excited state conformational barriers are relatively high, or even if they are not significantly different from the ground state barriers, as the excited state lifetime is short, the conformational isomers may exhibit independent photochemistry. This situation could lead to wavelength-dependent photochemistry if the absorption spectra of the conformers are significantly different. This effect is illustrated in the photochemistry of dienes and trienes.

Irradiation of the triene **27** at >280 nm results in several competitive processes leading to a mixture of products **28–31**.[62] If the irradiation of **27** is performed with 254-nm light cis–trans isomerization is highly favored, yielding a high proportion of the *E* triene **31** (>70%). The effect is thought to arise from differential absorption properties of the various conformers of **27**. As shown below, **27** could exist in several conformations and they could be individually excited. The excitation of **27a** results in **28–31**, whereas excitation of **27b–d** results predominantly in geometric isomerization.



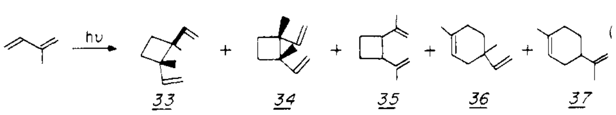
(7)

A similar wavelength effect is also observed in the case of 2,5-dimethyl-1,3,5-hexatriene.[63] When irradiation is conducted at 313 nm, (*Z*)-hexatriene **32** preferentially undergoes photocyclization to yield cyclohexadiene, whereas irradiation at 254 nm results in *Z*-*E* isomerization and no photocyclization. The wavelength dependence in these polyenes is governed solely by the ratio of the ground state conformers in conjunction with their extinction coefficients at the wavelengths of excitation.



(8)

Wavelength dependence in the triplet manifold may be hard to detect experimentally for most compounds since $S_0 \rightarrow T_1$ absorption is extremely weak. But an equivalent effect may be observed in the energy dependence of triplet photosensitization. This has been achieved in the case of dienes. For example, isoprene (2,3-dimethylbutadiene) undergoes photodimerization upon triplet sensitization to give cyclobutanes (**33–35**) and cyclohexenes (**36–37**).[64]



(9)

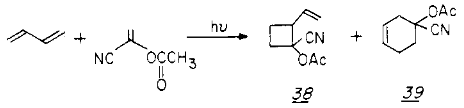
$E_T > 60$ kcal/mol $\Sigma$ **33, 34, 35** ~ 90%

$\Sigma$ **36, 37** ~ 10%

$E_T < 50$ kcal/mol $\Sigma$ **33, 34, 35** ~ 35%

$\Sigma$ **36, 37** ~ 65%

The ratio of cyclobutanes to cyclohexenes is found to be sensitive to the excitation energy of the triplet sensitizers. Sensitization of isoprene in the presence of $\alpha$-acetoxyacrylonitrile gave photoadducts. The distribution of products was again dependent on the triplet energy of the sensitizer in much the same manner as dimerization.[65]

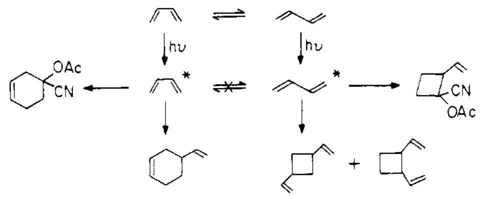


(10)

$E_T > 60$ kcal/mol **38/39** ≈ 45

$E_T < 50$ kcal/mol **38/39** ≈ 2

These variations in product composition are suggested to be the result of excitation of s-cis and s-trans conformers of the dienes which undergo independent photochemistry from their triplet states before thermal equilibrium is achieved[64,65] on the triplet surface.

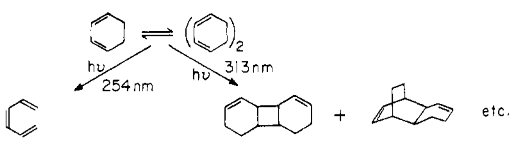


(11)

### 3. Effects due to Ground State Complexation

Similar to equilibrium between conformational isomers and structural isomers, equilibrium between isomers and dimers could exist at room temperature. This fast thermal equilibrium could result in wavelength-dependent photochemistry as illustrated with 1,3-cyclohexadiene.

1,3-Cyclohexadiene upon irradiation with 254-nm light gives 1,3,5-hexatriene as the only product,[66] but irradiation at 313 nm produces several dimers as in eq 12.[67] This wavelength-dependent product distribution has been shown to be the result of ground state complexation. Upon irradiation at 254 nm, the absorption is mainly by the monomer whereas 313-nm irradiation excites mainly the dimers. That such complexation does occur in the ground state is indicated by the observation that the Beers law plot for 1,3-cyclohexadiene in cyclohexane shows substantial curvature at 313 nm.



(12)

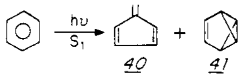
In summary, wavelength-dependent photochemistry may arise from a variety of ground state effects including (a) secondary reaction of the photoproduct, (b) independent excitation of structural or conformational isomers, and (c) excitation of ground state complexes.

## B. Aromatics

### 1. Benzene Isomers

Because of the considerable literature on the spectroscopy and photophysics of benzene, it constitutes one of the best defined wavelength-dependent photochemical systems. However, the picture is still rather complicated and as yet unclear. One-electron transitions from the highest occupied molecular orbitals (MO's) to the lowest unoccupied MO's in benzene lead to three excited singlet states as follows: 38 000–48 000 cm$^{-1}$ (260–225 nm) $^1B_{2u}$, 48 000–57 000 cm$^{-1}$ (~220–190 nm) $^1B_{1u}$, and 57 000–66 000 cm$^{-1}$ (~190–160 nm) $^1E_{1u}$.[68] In addition, there exists an $^1E_{2g}$ state whose energy is not known with certainty. It has recently been suggested that a band observed in matrices at 46 000 cm$^{-1}$ may in fact correspond to $^1E_{2g}$ excitation. Further complication results from the consideration of Rydberg series which are expected to appear in the region of the $S_0 \rightarrow S_2$ transition.[70] Therefore, the electronic configuration of the populated states, especially for excitation at short wavelengths, cannot be assigned with certainty. However, most authors have adopted the three-state convention and have discussed the singlet photochemistry and photophysics in terms of transitions between these states. A state diagram with rate constants for the various interconversions is shown in Figure 7. A review of the photochemistry of benzene has recently been published, to which the reader may refer for more detailed experimental information than space permits us to include here.[71]

Excitation within the $S_1$ band of benzene leads to the formation of two products, fulvene (**40**) and benzvalene (**41**) in solution, neat liquid or vapor phases.[72,75] Some if not all of the fulvene appears to arise from a secondary reaction of benzvalene.[71]



(13)

Limiting quantum yields are very sensitive to experimental conditions, primarily because of secondary processes taking benzvalene both to fulvene and back to benzene. There is no apparent wavelength dependence of the photochemical quantum yield in solution over the range from 237 to 253 nm.[73,76] However, in the gas phase quantum yields increase with decreasing wavelength over the same range (Table IV).[73] Table IV also provides evidence that triplet states are not involved in the photoisomerization since benzvalene is formed during the vapor phase irradiation at 237 nm where $\Phi_{isc}$ is virtually zero.

Two interpretations have been offered for these results. In one, rearrangement is postulated to proceed from vibronic states

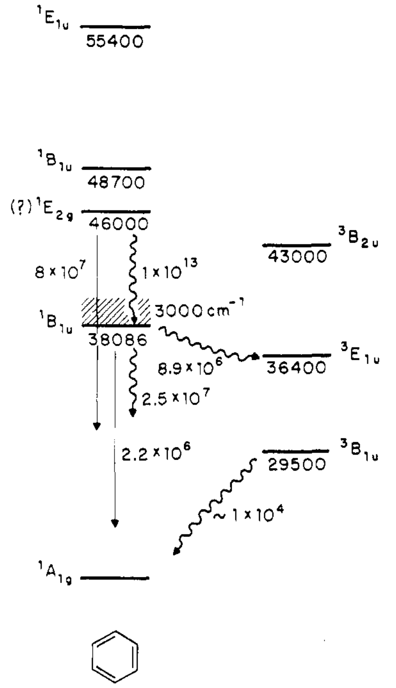


**Figure 7.** Spectroscopic data for benzene. Energies are in cm$^{-1}$.

populated by absorption on a timescale short relative to vibrational relaxation to thermally equilibrated $S_1$.[76] In this mechanism the asymmetric nuclear motions which destroy the forbiddeness of the $^1A_{1g} \rightarrow {}^1B_{2u}$ transition are postulated to be promoters of the valence bond isomerism leading to photochemical rate constants competitive in rate with fast decay processes ($>10^{11}$ in solution). This interpretation requires the postulate that the photochemical rate constant is independent of what one might expect to be differing degrees of excitation of this vibrational mode, since there is no wavelength dependence for the quantum yield in solution.

In the second, and more popular explanation,[71] deactivation to the thermally equilibrated $S_1$ state is presumed to precede photochemistry in solution, but to compete in the gas phase to account for the differing wavelength dependence in the two phases. However, the photochemical process requires activation which may be achieved thermally in solution since the fluorescence and intersystem crossing rate constants are slow enough ($<10^7$ s$^{-1}$)[77] to accommodate competition from activated processes with barriers of not more than several kcal/mol. The photochemical process leading to benzvalene may be associated with the well-known thermally activated internal conversion of $S_1$ benzene. In fact, barriers calculated for benzvalene production ($\sim$7 kcal/mol, $A$ factor $\sim10^{12}$ s$^{-1}$),[78] appear comparable to those obtained for internal conversion through a combination of fluorescence and intersystem crossing measurements (8 kcal)[79] and wavelength dependence of fluorescence (3200 cm$^{-1}$).[80] Partitioning to photochemical products or benzene ground state may then occur from the states resulting from such activated radiationless conversion. The latter process is required since the limiting quantum yields for isomerization account for only a fraction of the total quantum yield of activated radiationless conversion.[81]

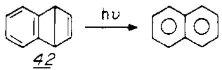
The circumstances described for photochemical reaction from the $S_1$ state of benzene, in which a thermal barrier must be surmounted, appear to be a general case in which wavelength dependence only shows up when vibrational relaxation rate constants are slowed down by going from solution to the gas phase. However, we shall encounter other examples in which wavelength effects are apparent even in condensed phases, and these are presumably the result of smaller barriers or, more correctly, larger ratios of $E_{\text{available}}/E_{\text{activation}}$ in these systems.

**TABLE IV. Quantum Yields of Photoprocesses in Benzene Vapor**[c]

| | 253 nm | 248 nm | 242 nm | 237 nm |
|---|---|---|---|---|
| Benzvalene[a] | 0.016 | 0.022 | 0.024 | 0.037 |
| Benzene-butene photoadduct[a] | 0.01 | 0.008 | 0.006 | 0.003 |
| Fluorescence[b] | 0.18 | 0.10 | 0 | 0 |
| Triplets[b] | 0.6 | 0.6 | small | |

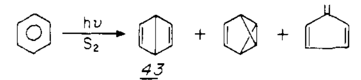
[a] In 1 atm of *cis*-but-2-ene, 25 Torr of benzene. [b] Alkenes cause little or no quenching of benzene fluorescence unless they bear substitutents which confer marked donor or acceptor character relative to benzene. [c] Table adopted from L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **90**, 3291 (1968).

This situation appears to obtain, for example, in the adiabatic photochemical conversion of Dewar naphthalene to naphthalene studied by Michl, Yang, and co-workers.[82] A clear wavelength dependence of the observed quantum yield of product formation, manifested in increasing luminescence intensity from the product with increasing reactant excitation energy, is observed in the photolysis of **42.**



42

Excitation in the $S_2$ and $S_3$ bands of liquid benzene leads to a different photochemical result. Dewar benzene (**43**), as well as benzvalene and fulvene, is formed in significant amounts.[83] Selective irradiation in the $S_2$ band at 206 nm also yields Dewar benzene (**43**).[84] In dilute solution, or in the presence of triplet quenchers, yields of all three isomers are increased, presumably as a result of decreasing amount of triplet benzene catalyzed decomposition. Earlier work of Braun et al.,[38] in which $\Phi_{\text{isc}}$ and $\Phi_{S_n} \rightarrow \Phi_1$ were measured after excitation to $S_2$ and $S_3$ indicated that some process or processes must compete with intersystem crossing to $T_1$ or internal conversion to $S_1$ under these conditions. However, the quantum yield discrepancy is much higher than can be accounted for by the isolated yields of photochemical products (0.6 vs. $\sim$0.05).[85] As in the case of benzvalene from the $S_1$ state, it seems unlikely that the photochemical product could return to benzene ground state during the deactivation, or by a subsequent transformation. The rate constant for decay of the $S_2$ state has been estimated to be 9.9 $\times$ $10^{12}$ s$^{-1}$ in fluid solution by Birks et al.[86] These workers have attributed the overall decay to two processes, one of which proceeds by the way of the deactivation channel accessible to vibrationally excited $S_1$, which we have previously noted to be associated with formation of benzvalene, and a second channel which may be the "normal" $S_2 \rightarrow S_1$ internal conversion. Benzvalene may also be formed directly from $S_2$. It does seem clear that it is not arising from a thermalized $S_1$ state since its formation via $S_2$ excitation is not subject to a thermal barrier as has been observed in its production via $S_1$ excitation.[71] It is not obvious how Dewar benzene formation fits into the overall decay picture. It may constitute a third channel proceeding at a somewhat slower rate since the overall quantum yields are low, or it may be one eventual outcome of the two decay channels proposed. Although quenching experiments seem to rule out $T_1$ as a photochemical precursor to Dewar benzene,[84] the available experimental results could still be compatible with a short-lived $T_n$ state populated via $S_2$. In the gas phase, only fulvene and hexadienynes are obtained. This suggests that the less stable Dewar benzene and benzvalene do not survive long enough to be deactivated to their ground states.

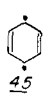


43

(14)

In summary, then, it appears that some process or processes which lead to isomerization may compete with return to ground state benzene from the photoexcited $S_2$ state. The internal conversion process itself may lead to nuclear configurations which are predisposed to close to the valence-bond isomers (i.e., nonplanar prebenzvalene **44** or pre(Dewar benzene) biradicals **45**). If not, it is required that the photochemical reaction occur with a rate constant of $\geq 10^{11}\ s^{-1}$ to be competitive with other decay processes from $S_2$. Bryce-Smith has rationalized the production of benzvalene from $S_1$ and Dewar benzene from $S_2$ using orbital symmetry arguments.[71]


44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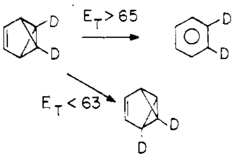
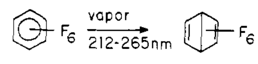
It is interesting in this connection that benzvalene also shows energy-dependent photochemistry in the triplet manifold.[88] Triplet sensitizers of energies greater than 65 kcal lead to predominant rearrangement to benzene, while those with energies between 53 and 65 kcal/mol give predominantly degenerate rearrangement with deuterium scrambling. This behavior has been interpreted as implying the intermediacy of two different benzvalene triplet states: a high-energy triplet $T_2$ which is converted to benzene $T_1$ and a low-energy $T_1$ which undergoes degenerate rearrangement. This assignment must be considered somewhat tentative until the singlet and triplet energies of benzvalene have been determined.



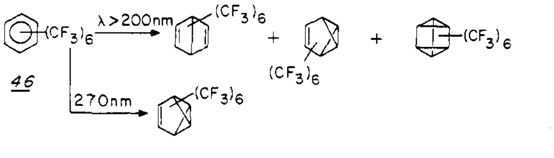
(15)

Various substituted benzenes have also been proposed to undergo reaction from higher excited states. In the vapor phase at moderate bath gas pressures, hexafluorobenzene can be converted to hexafluoro(Dewar benzene) upon excitation at 212-265 nm.[89] Arguments for reaction from $S_2$ based primarily on the observed wavelength dependence, and correlated with the fluorescence studies of Phillips,[90] have been presented by Haller[89] and Bryce-Smith[71] and will not be detailed here. The surprising feature of this reaction, however, is that in cyclohexane solution no Dewar isomer is isolated. Rather, solvent incorporation products and hexafluorobenzene dimers and oligomers are obtained.[89] This is somewhat surprising since it has been shown that increasing bath gas pressures (up to 100 Torr) lead to increasing yields of hexafluoro(Dewar benzene) in the vapor-phase photolysis. It is also in contrast to the results with benzene itself, in which Dewar benzene may be isolated in solution, but appears not to survive in the gas-phase photolysis. The failure to obtain isomerization in solution has been explained by suggesting increased rates of internal conversion and intersystem crossing in solution, and trapping of intermediate biradicals to account for the observed products. Since the onset of the $S_2$ level in this molecule is not well defined, the differentiation between $S_2$ reactions and vibrationally excited $S_1$ is somewhat difficult. The latter mechanism seems a plausible alternative and perhaps is better able to account for the change in behavior in passing from the gas phase to solution.



(16)

Two other substituted systems show benzene-like wavelength effects. Perfluorohexamethylbenzene (**46**) can be converted photochemically into the corresponding Dewar benzene, benzvalene, and prismane isomers.[91] The reactant shows two absorption bands ($\lambda_{max}$ 283, 212 nm) in solution. Excitation into $S_1$ leads strictly to benzvalene, while excitation into $S_2$ leads to all three isomers. In the latter case, perfluorohexamethylbenzvalene and the corresponding Dewar benzene isomer appear to be primary products while the prismane derivative results from a secondary reaction of benzvalene. No quantitative study on this system has been carried out but its congruence with benzene is notable. Similarly, perfluoropentaethylpyridine (**47**) may be converted to the corresponding Dewar isomer at long wavelengths, while at short wavelengths the prismane is obtained.[92] In this case, however, the wavelength dependence is misleading, as the prismane derivative is a product of the secondary photolysis of the Dewar pyridine, which absorbs only weakly at longer wavelengths.



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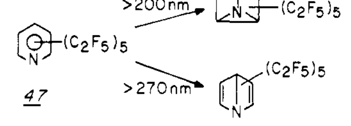

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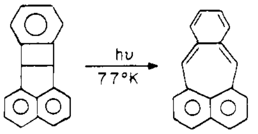
(18)

The isomerization of *o*-xylene to *m*- and *p*-xylene from the $S_1$ state has been studied as a function of both temperature and wavelength in vapor and solution phases. In solution, the temperature dependence of this process has been used to estimate an activation energy of approximately 10 kcal/mol.[93] Furthermore, it appears that this barrier cannot be surmounted by additional activation supplied via excitation to upper levels of the $S_1$ state since excitation at 275 or 248 nm led to identical quantum yields.[94] In the gas phase, however, chemical reaction apparently can compete with relaxation within $S_1$. Noyes and Harter have reported increasing quantum yields as the excitation wavelength was decreased from 275 to approximately 240 nm.[95]

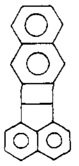
## 2. Pleiadene Family

It was first proposed in 1970, that compound **48** rearranges to pleiadene (**49**) after population of an upper triplet state by biphotonic excitation in rigid glasses at 77 K.[96] This work was subsequently elaborated upon, with the demonstration that derivatives **50, 51,** and **52** showed similar behavior,[97] and other workers reported the conversion of **53** to **54**.[98] With all of these molecules solution irradiation at room temperature or at low temperature leads to no reaction, and for compound **53** it has been shown that triplet sensitization in solution is similarly ineffective.[99] This is in contrast to other benzocyclobutene[100] and cyclobutene[101] systems (**55, 56**) for which reaction was shown to proceed via $S_1$ or $T_1$.



48 49

(19)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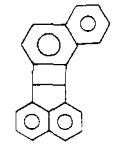
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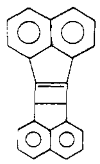
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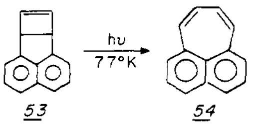

53 54

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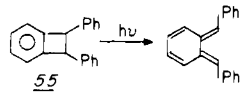

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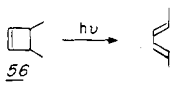


56 (22)

Experimental results on **48** are described in the most detail,[97] but compounds **50–53** seem to behave at least qualitatively similarly. Thus, reaction was achieved only in matrices at 77 K using UV and visible radiation sources simultaneously in a biphotonic process, or with a single UV source in a monophotonic process, at wavelenghts much shorter than that required to populate $S_1$ ($v = 0$).[102] In the two-photon excitation experiments the product yield is maximized when the visible source is tuned to wavelengths appropriate for known naphthalene $T_1 \rightarrow T_n$ absorption maxima (~400–415 nm). Since the absorption and luminescence properties of **48** are similar to naphthalene itself, this implies a triplet–triplet absorption of the second photon.

The proposed mechanism in the two-source experiments is UV absorption followed by relaxation to a long-lived $T_1$ state (3.3 s for **53** at 77 K),[99] then triplet–triplet absorption of the visible photon to populate some higher triplet state $T_n$, from which steps leading to chemical reaction occur. For compound **48** Michl et al. have proposed that $n = 7$.[96] In the single source experiments higher singlet states are apparently populated by direct excitation using a monochromatic, short-wavelength source. Excitation at 214 nm is apparently sufficiently energetic to populate any one of 11 singlet states of comparable or lower energy.[103] The results on this system may be summarized as follows.

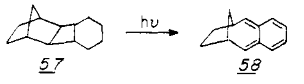
(1) Some barrier to chemical reaction from $S_1$ and $T_1$ exists.

(2) This barrier must be sufficiently high that reaction cannot compete with fluorescence or intersystem crossing from $S_1$ at room temperature ($\tau_{fl}$ of **53** = $3.3 \times 10^{-8}$ s, $E_a \lesssim 8$ kcal/mol).

(3) The barrier can be surmounted or circumvented by excitation to higher states when the rate constants for return to equilibrated $S_1$ or $T_1$ state are impeded by the low temperature and high rigidity of the matrix structure.

Again, as in the earlier work on the isomerization of benzene and xylenes, barriers to chemical reaction from the lowest excited states in some systems but not in structurally related ones. Both Bryce-Smith and Michl have used orbital and state correlation diagrams to explain these results.

Recently Miller, Kolc, and Michl[104] reported yet another compound which undergoes a photochemical ring opening only in matrices at 77 K, thus possibly from a higher triplet state. For example, **57** is photostable at room temperature in solution whereas irradiation at 77 K in 3-methylpentane resulted in production of **58.**



57 58 (23)

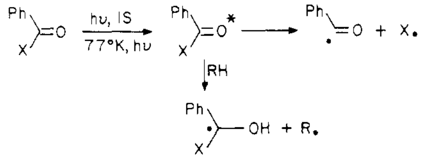
The work of Michl seems to be a specific example of a general two-photon process for aromatic molecules in matrices at low temperature although the chemical result is usually photoionization or photodissociation rather than isomerization. Since our interest here is primarily in reactions of organic chemical interest, this literature will not be surveyed. However, it is noteworthy that photoionization has also been observed in fluid solution, although in these cases ground state complexation is often implicated. The reader is referred to ref 105 for a discussion and leading references.

## C. Carbonyl Compounds

Both the spectroscopy and photochemistry of the carbonyl chromophore have been studied in great detail. Carbonyl compounds in general posses a low-lying $n\pi^*$ singlet ($S_1$), but the nature of the low-lying triplet ($T_1$) seems to be dependent on solvent and substituent. The energy gap between $T_1$ and $T_2$ ($n\pi^*$ and $\pi\pi^*$) is usually small and the intersystem crossing ($S_1 \rightarrow T_1$) is normally very efficient. In spite of a large number of studies, there are not too many reactions which show real wavelength dependence. In this section we discuss these few wavelength-dependent photochemical reactions of dialkyl, aralkyl, and diaryl ketones.

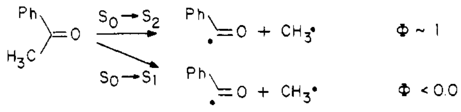
One of the early aromatic aldehydes thought to undergo photoreaction (reduction, dimerization, and cycloaddition) from $T_2$ ($n,\pi^*$) is 9-anthraldehyde,[106–111] but it was subsequently demonstrated by Suppan[112,113] that these reactions, in fact, take place from $S_1$ and $T_1$ and are independent of wavelengths of excitation.

Recently, it has been reported that benzaldehyde, acetophenone, and benzophenone undergo wavelength-dependent photochemistry both in a solid matrix[114] and in the vapor phase,[115] but no wavelength-dependent photochemistry of these molecules in solution has been reported. It appears as though both in the vapor phase and a solid matrix the reactions originate from higher triplets. Benzaldehyde, acetophenone, and benzophenone upon irradiation into the $S_1$ band in a glass at 77 K (methanol, ethanol, or EPA matrix) were found to undergo intersystem crossing efficiently to give $T_1$ which did not react at 77 K, but irradiation of these triplets ($T_1$) with another intense light source gave radicals derived from an $\alpha$-cleavage process as detected by their EPR spectra. Therefore, it appears as though $\alpha$-cleavage occurs from either a vibrationally excited $T_1$ or a higher triplet ($T_n$) produced by T–T absorption. This observation is similar to that of pleiadenes which are known to react in a glassy matrix from their higher triplet.[95–99] (see eq 24).



(24)

Similarly, irradiation of acetophenone in its $S_1$ band in the vapor phase gave products due to $\alpha$-cleavage very inefficiently ($\Phi < 0.01$), but $S_0 \rightarrow S_2$, $S_3$ excitation gave ethane derived from $\alpha$-cleavage very efficiently ($\Phi \sim 1.0$).[115] It is suggested that the reaction occurs from a vibrationally hot $T_1$ based on further experimental observations which will not be discussed here. Likewise, benzaldehyde gave benzene (suggested to be intramolecular) only upon irradiation into the $S_2$ band, again suggesting that the reaction originates from a higher or hot triplet state. These two observations have interesting implications since the conventional $\alpha$-cleavage for carbonyl compounds from their $T_1$ state is estimated to have activation energies of ~10 kcal/mol in solution.



(25)

It has been shown (section II.A) that when two electronic states are close in energy, thermal equilibrium may exist between these two states and emission can occur from the higher state if it can compete with depopulation rate of the lower states. Reactions could similarly arise from higher states under the above conditions and this phenomenon is, in fact, observed in $p$-methoxyacetophenones. Spectroscopic investigations have established that $n\pi^*$ and $\pi\pi^*$ triplets of methyl- and methoxy-substituted acetophenones lie within a few kcal of each other and the lowest state is $\pi\pi^*$ triplet.[116] Wagner[117] has measured the internal hydrogen abstraction rate constants for phenyl alkyl

**TABLE V. Photoelimination of Select Phenyl Ketones and *p*-Anisyl Ketones**[a]

A. Phenyl Ketones ($PhCOCH_2CH_2R$)

| R | $\Phi_{II}$[b] | $k_q\tau$, $M^{-1}$ [c] | $10^7 k_r^n$ $s^{-1}$ [d] | Rel $k_r$ |
|---|---|---|---|---|
| (PI) $CH_3$ | 0.36 | 660 | 0.8 | (1) |
| (P2) $CH_2CH_3$ | 0.33 | 40 | 12.5 | 16 (1) |
| (P3) $CH(CH_3)_2$ | 0.25 | 11 | 45.0 | 60 |
| (P4) $CH_2CH_2CO_2CH_3$ | 0.64 | 125 | 4.0 | 0.32 |
| (P5) $CH_2CH_2CN$ | 0.46 | 500 | 1.0 | 0.08 |

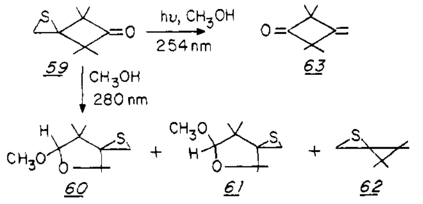
B. *p*-Anisyl Ketones ($CH_3OC_6H_5COCH_2CH_2R$)

| R | $\Phi$[e] | $k_q\ \tau$, $M^{-1}$ | $k_\tau$, $10^4$ $s^{-1}$ | $k_d^\tau$ $s^{-1}$ | Rel $k_\tau$ |
|---|---|---|---|---|---|
| (AI) $CH_3$ | 0.04 | 3550 | 0.056 | 1.4 | (1) |
| (A2) $CH_2CH_3$ | 0.26 | 2300 | 0.56 | 1.6 | 10 (1) |
| (A3) $CH(CH_3)_2$ | 0.67 | 1100 | 3.0 | 1.5 | 51 |
| (A4) $CH_2CH_2CO_2Me$ | 0.14 | 2500 | 0.28 | 1.7 | 0.50 |
| (A5) $CH_2CH_2CN$ | 0.015 | 2700 | 0.03 | 1.8 | 0.06 |

[a] 0.10 M ketone solutions irradiated at 3130 Å to 5% conversion. [b] Quantum yield of acetophenone formation in benzene. [c] Slope of Stern–Volmer quenching plot; all averages of duplicate runs. [d] $k_r^n = 1/\tau$, $k_q$ assumed to equal $5 \times 10^9$: W. D. Clark, A. D. Litt, and C. Steel, *J. Am. Chem. Soc.*, **91**, 5413 (1969); G. Porter and M. R. Topp, *Proc. R. Soc. London, Ser. A*, 315, 163 (1970). [e] Maximum quantum yield of ketone reaction; see P. J. Wagner and H. N. Schott, *J. Am. Chem. Soc.*, **91**, 5383 (1969).

ketones [known to have $T_1$ ($n\pi^*$)] and *p*-anisyl ketones [$T_1 = \pi\pi^*$]. These are shown in Table V. Comparison of ketones $P_1$, $P_2$, and $P_3$ and $A_1$, $A_2$, and $A_3$ indicates that the selectivity of the two carbonyl triplets towards primary, secondary, and tertiary C–H bonds is almost identical. Comparison of ketones $A_2$, $A_4$, and $A_5$ with $P_2$, $P_4$, and $P_5$ is even more revealing. All have secondary C–H bonds at the $\gamma$ position. Electron-withdrawing groups at the $\delta$ position deactivate the electrophilic $n\pi^*$ triplet of the benzoyl group. They have an identical effect on the triplet state reactivity of the anisoyl group. Wagner suggests that it would be extremely unlikely for the $n\pi^*$ triplet, which must have a relatively electron-rich oxygen atom, to be subject to the same inductive effects as the electrophilic $n\pi^*$ state. Consequently, most of the hydrogen abstraction in *p*-anisyl ketones probably occurs from a level above the lowest level of the $\pi\pi^*$ state, an upper level that is mostly $n\pi^*$ in character.[117]

Cyclobutanones are known to undergo wavelength-dependent photochemistry in the vapor phase and the reactive state is shown to be the vibrationally hot $S_1(n\pi^*)$,[119] but there is no report of their wavelength dependence in solution.[120] A related compound **59** is reported to undergo the anticipated ring expansion to the cyclic acetals **60** and **61** upon irradiation into the $n\pi^*$ ($S_1$) band.[120] On the other hand, upon irradiation at shorter wavelengths (254 nm), **59** gives predominantly **63**. The origin of this wavelength effect is thought to be the selective excitation of C–S ($n\pi^*$, $S_2$) upon irradiation through quartz (254 nm). Such dual chromophoric systems constitute a special case of higher excited state reactions, in which the electronic factor in the internal conversion is small due to poor spatial overlap. Another compound having –C–S– bond and carbonyl chromophores which shows a wavelength effect is **64**,[121] Irradiation of **64** into its charge-transfer band yields exclusively **65** whereas irradiation into the $n\pi^*$ band gives nearly equal amounts of **65**, **66**, and **67**; however, neither of these two cases (**64** and **59**) has been studied in detail. Similar wavelength effects in bichromophoric systems are discussed in a later section (section III.E).



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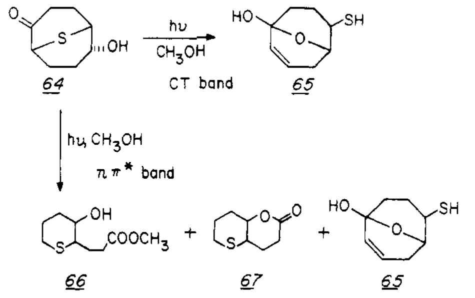

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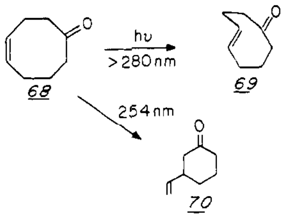
Crandall[122] has reported that 4-cyclooctenone (**68**) undergoes wavelength-dependent chemistry, but the origin of the wavelength effect has not been clearly established. Irradiation of **68** through Pyrex (>280 nm) gave **69**, the geometric isomer, whereas irradiation through quartz (254 nm) gave cyclohexanone **70**. Neither **69** nor **70** seems to come from the triplet state as acetone sensitization failed to produce these products.



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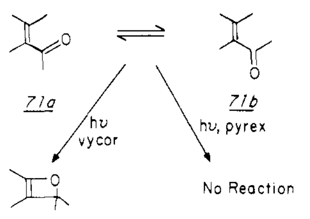
## D. $\alpha,\beta$-Unsaturated Ketones

In opposition to the saturated ketones, $\alpha,\beta$-unsaturated ketones have been shown to undergo wavelength-dependent photochemical reactions in a number of specific cases. These will be reviewed in this section. In general both alicyclic and acyclic $\alpha,\beta$-unsaturated ketones show a long-wavelength absorption which is $n\pi^*$ in nature, and a closer lying $\pi\pi^*$ state.[123] Among these $\alpha,\beta$-unsaturated ketones only a few rigid cyclic compounds have been shown to emit, and then only phosphorescence is observed. The nature of the low lying triplets as well as singlets in these cases depends on substituent and solvent; the energy gap between these low-lying states ($S_1$ and $S_2$ or $T_1$ and $T_2$) is normally small.

$\alpha,\beta$-Unsaturated ketones undergo both unimolecular and bimolecular processes from the lowest states. In addition, reactions dependent on the wavelength of excitation have often been observed. These wavelength-dependent reactions are thought to be derived from the $S_2$ state in most cases. In spite of a large number of examples showing wavelength-dependent behavior, no single mechanism seems to explain all the results for the $\alpha,\beta$-unsaturated ketones as a group.

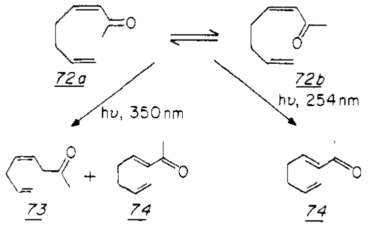
### *1. Intramolecular Reactions*

One of the common $n\pi^*$ reactions among ketones is the addition of the carbonyl group to double bonds to give oxetanes.[124] There exists a case in which this addition has been shown to be wavelength dependent. Irradiation of 3,4-dimethylpent-3-en-2-one in hexane solution through a Pyrex filter gave no observable reaction after 35 h.[125] However, irradiation through a Vycor filter gave the expected oxetane.[126] No detailed study has been done to identify the reactive state. The wavelength dependence in this reaction could arise from a difference in absorption properties of the conformers **71a** and **71b**. The required conformer for the reaction, **71a**, may absorb at shorter wavelengths compared to **71b**. The results may also be accommodated by the postulate that the reaction which originates from the $T_1$ ($n\pi^*$) may be reached more efficiently from $S_2$ than from $S_1$.



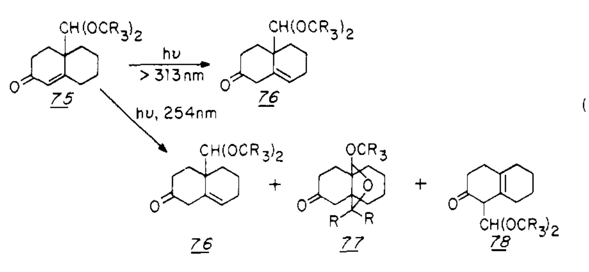
(29)

Similar to the above observation, the $\alpha,\beta$-unsaturated ketone **72** also shows wavelength dependence.[127] Irradiation of **72** at 350 nm gave **73** and $\beta,\gamma$-unsaturated ketone **74**. On the other hand, irradiation at 254 nm gave only **73** and no deconjugation was observed. Both benzophenone and acetophenone failed to sensitize the deconjugation reaction. Similarly, naphthalene and piperylene did not quench the formation of **74**. These observations are taken to implicate the $S_1$ ($n\pi^*$) state as the reactive state for deconjugation reactions. The absence of formation of **74** upon short-wavelength irradiation is taken to indicate that $S_2$ to $S_1$ internal conversion does not compete with the other processes which consume the $S_2$ ($\pi\pi^*$) state, including reaction to **73**. However, the above experimental observations can be explained without involving a higher state ($S_2$) as the reactive state as follows. The formation of **74** could occur only from the conformer **72b** whereas **73** could arise from either conformers **72a** or **72b**. Therefore, excitation of **72a** would be expected to give only **73** whereas **72b** would give both **73** and **74**. The irradiation at 350 nm excites predominantly **72b** whereas at 254 nm only **72a** is excited.



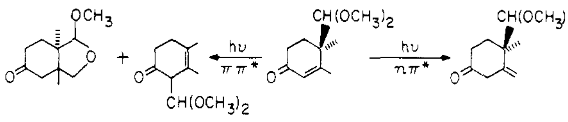
(30)

Cyclic $\alpha,\beta$-unsaturated ketones also show wavelength-dependent photochemical reactions.[128] Because of the structural constraints on the chromophore, complications due to conformational freedom are reduced. The enone **75**, upon irradiation into $n\pi^*$ band, (>313 nm) gave **76**, in which double bond migration has occurred to yield the $\beta,\gamma$-unsaturated isomer. On selective excitation into the $\pi\pi^*$ band (254 nm) new reactions were observed.[129] The specific reactions induced upon $\pi\pi^*$ excitation are the $\gamma$–$\alpha$ shift to give **78** and hydrogen abstraction followed by cyclization to give **77**. The reactive state in these cases is suggested to be either a thermally equilibrated $S_2$ state or a state derived from $S_2$.

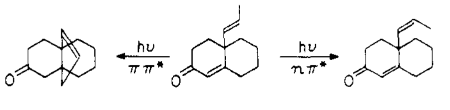


(31)

The above selective transformation has been observed with a wide variety of enones as illustrated with a few examples shown in eq 32–35.[130–133] The mechanistic details will not be discussed here and only the conclusions are mentioned. The hydrogen abstraction followed by cyclization to give **77** is an *intramolecular* reaction[134] and the hydrogen transfer takes place to the *α-carbon* rather than to carbonyl oxygen. Similarly, the 1,3($\gamma\rightarrow\alpha$)-dimethoxymethyl shift to give **78** is *intramolecular* in nature and the primary photochemical step is the cleavage of the $\gamma$-C–C– bond.[135]



(32)



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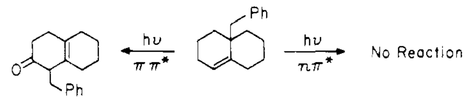

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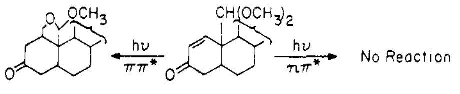
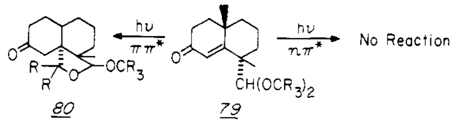


(35)

The reactive state in these cases has not been clearly identified. However, a similar transformation of **79** → **80** has been studied in detail.[130]



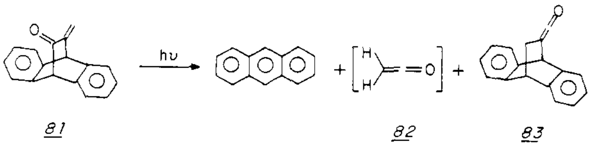
(36)

The poor quantum yield ($<10^{-3}$) for the formation of **80** from **79** upon irradiation into the $S_1$ band, in contrast to the higher quantum yield (0.02) upon irradiation into $S_2$ band, suggests that the reactive state is not $S_1$. Efficient intersystem crossing from $S_1$ is demonstrated by the ability of **79** to sensitize the dimerization of 1,3-cyclohexadiene. This suggests further that, upon irradiation in the $S_1$ band, both $S_1$ and $T_1$ state are available for **79** but do not undergo transformation to **80**. Therefore, it is concluded that the reactive state is either $S_2$ or a state derived from $S_2$, for the formation of **80** from **79**. Similar reasoning suggests that the $\gamma\rightarrow\alpha$ shift process also arises from $S_2$ rather than $S_1$ or $T_1$. In any case more quantitative studies need to be done before any firm conclusions with respect to the reactive state in these reactions can be reached.

Even though the above two processes, (a) hydrogen abstraction by the $\alpha$ carbon and, (b) $\gamma$-bond cleavage, are established to be sufficiently general with a variety of enones, no clear explanation for their ability to compete with internal conversion from $S_2 \rightarrow S_1$ ($T_2 \rightarrow T_1$) has been offered. The internal conversion from $S_2 \rightarrow S_1$ or $T_2 \rightarrow T_1$, as discussed earlier (section I), is controlled by both an electronic factor and a vibrational factor. Since the energy gap between the two states ($S_2$ and $S_1$) is expected to be small, the Franck–Condon factor may not be the rate-limiting factor for the slow internal conversion as in the case of azulene. Rather since the two states involved, $S_2$ and $S_1$, are $\pi\pi^*$ and $n\pi^*$, respectively, their different symmetry may lead to poor overlap of the electronic wave functions and therefore give rise to poor internal conversion.

In addition to the above relatively well-studied wavelength-dependent unimolecular photochemistry of enones, there are a large number of reactions which are not general for $\alpha,\beta$-unsaturated ketones as a class, but which involve that chromophore and show significant wavelength effects.

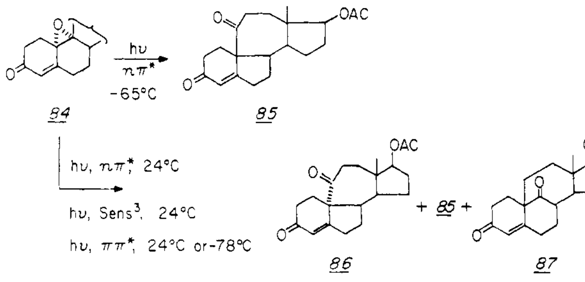
The $\alpha,\beta$-unsaturated ketone **81** upon irradiation undergoes fragmentation to give anthracene and **82** and rearrangement to give **83**.[136] The ratio of fragmentation to rearrangement was found to be wavelength dependent. It has been suggested that the $n\pi^*$ and $\pi\pi^*$ triplets are of similar energy with cleavage



(37)

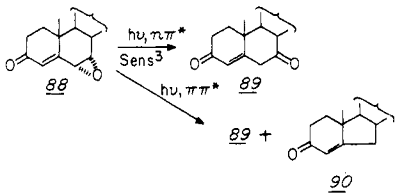
occurring primarily from $\pi\pi^*$ and rearrangement from an $n\pi^*$ state.

$\alpha,\beta$-Unsaturated $\gamma$–$\delta$-epoxy ketones also show wavelength-dependent photochemical reactions. For example, irradiation of **84** in ethanol at −65 °C into the $n\pi^*$ band gave the rearranged enedione **85** as the only product.[137] But irradiation into $\pi\pi^*$ band at −78 °C gave a mixture of **85, 86,** and **87.** The same product mixture was also obtained upon irradiation into the $n\pi^*$ band at room temperature. The absence of formation of **86** and **87** upon $n\pi^*$ excitation at −65 °C seems to imply the presence of a thermal barrier for their formation from $S_1$ of **84.** Both acetophenone and Michler's ketone sensitize the formation of **85, 86,** and **87** at room temperature. Therefore, probably it is the triplet $T_1$ that is responsible for their formation. The difference in product composition between $S_1$ and $S_2$ irradiation at low temperature (−78 °C) suggests that some of the $n\pi^*$ singlet energy may become available as thermal energy to overcome the barrier. Therefore, it appears as though the reaction or, more probably, intersystem crossing originates from a vibrationally hot $S_1$ ($S_2 \rightarrow T_1$ or $S_2 \rightarrow S_1^{**} \rightarrow T_1$).



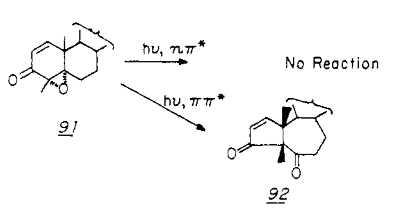
(38)

Irradiation of **88** into the $S_1$ band (>310 nm) gives **89** as the only product whereas $S_2$ band irradiation (254 nm) gives a new product **90** along with **89.**[138] The origin of **89** is known to be $T_1(n\pi^*)$. Acetophenone sensitizes the formation of **89** and not **90.** Therefore, neither $S_1$ nor $T_1$ seems to initiate the formation of **90.** Then, the new product **90** is suggested to arise from $S_2$ or a state derived from $S_2$.



(39)

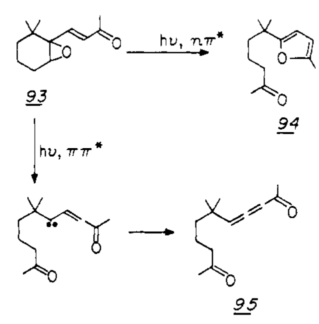
Upon irradiation in the long-wavelength $n\pi^*$ absorption band, **91** remained unchanged and the expected rearrangement to **92** occurred only when **91** was excited to the second singlet ($\pi\pi^*$) state with 254-nm light.[139]



(40)

Similarly, irradiation of *trans*-$\beta$-ionone epoxide **93** into the $n\pi^*$ band ($S_1$) gives the furyl ketone **94** whereas irradiation into the $\pi\pi^*$ band ($S_2$) gives the allene **95.**[140]

A few bicyclo[3.1.0]hexenones also have been demonstrated to show wavelength-dependent photochemistry. For example, **96** on irradiation through Pyrex gave a single product, but upon irradiation with 253-nm light source gave a mixture of **97** and **98.**[141] A clear explanation for the effects of differing wavelengths on these reactions, however, is not available.



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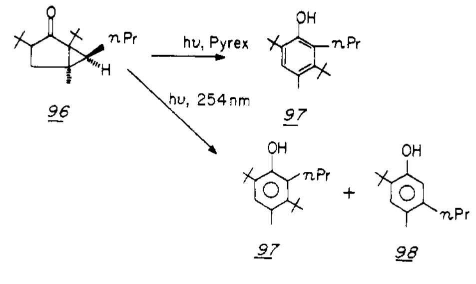
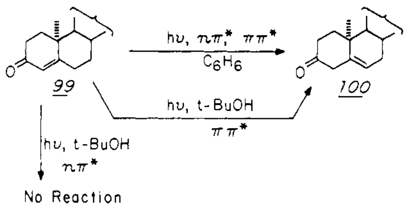


(42)

## 2. Intermolecular Reactions

One of the most common $n\pi^*$ ($T_1$) reactions among $\alpha,\beta$-unsaturated ketones, intermolecular H abstraction followed by double bond migration to the $\beta,\gamma$-unsaturated isomer, also show wavelength dependence in a few cases. The $\alpha,\beta$-unsaturated ketone **99** upon irradiation in the $S_1$ band ($n\pi^*$) in *tert*-butyl alcohol did not give any products, but on irradiation in the $S_2$ band ($\pi\pi^*$) gave **100** by intermolecular hydrogen abstraction.[142] The intermolecular nature of the reaction is shown by irradiating in *t*-BuOD wherein deuterium was found to be incorporated in the C-4 position. In contrast to the wavelength dependence in *t*-BuOD, irradiation in benzene gave **99,** independent of the wavelength of irradiation. The above results are taken to imply that the reaction in *tert*-butyl alcohol is initiated either in the $S_2$ ($\pi\pi^*$) state or in a high vibrational level of the $S_0$ or $T_{\pi\pi^*}$ state. It is possible for the following reasons that the reaction may not originate from a higher state ($S_2$).

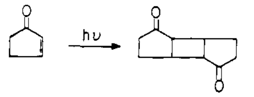


(43)

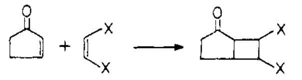
The reaction is thought to be intermolecular in nature and under the condition of irradiation (~$10^{-2}$ M), assuming the rate constant for hydrogen abstraction as $10^9$ (diffusion limit), the lifetime of the reactive state would be ~$10^{-7}$ s which is two orders of magnitude longer than the longest lived higher excited state on record (unless there is a large inefficiency after the primary photochemical step). Also the wavelength independence in benzene is unexpected if in *tert*-butyl alcohol reaction occurs from a higher excited state. The experimental observations may be accommodated by the reactive state being $T_1$ ($n\pi^*$) in both butanol and benzene. The explanation requires that $T_1$ be reached efficiently from $S_1$ in benzene but inefficiently in *tert*-butyl alcohol. This could have resulted from a solvent effect on the energy levels of $S_1$, $S_2$, $T_1$, and $T_2$. Then, $S_2$ irradiation produces $T_1$ ($n\pi^*$), the reactive state, in *tert*-butyl alcohol efficiently by isc from a higher state.[143]

The above suggestion of a higher state during intermolecular reaction of enones is not unprecedented. A higher triplet ($T_2$) was formerly thought to be involved in the dimerization and cycloaddition of cyclopentenones and cyclohexenones.[144] But careful study has demonstrated that $T_1$ is the reactive state, not $T_2$.[145] A discussion of this system serves to illustrate the importance of careful study when one considers higher states during bimolecular reaction.

Irradiation of cyclopentenone gives dimers and, in the presence of olefins, gives cycloadducts in addition to dimers. These reactions have been studied carefully and the conclusion that $T_2$ is the reactive state was reached based on the following observations:[144]



(44)



(45)

(i) The triplet energy (lowest) of cyclopentenone was estimated to be ~61 kcal/mol based on sensitization of stilbene isomerization by cyclopentenone.

(ii) The isc efficiency was estimated to be unity by the Hammond and Lamola method. Therefore, it is expected that upon direct irradiation the lowest triplet (~61 kcal/mol) must be reached efficiently.

(iii) On the other hand, the dimerization or cycloaddition could be sensitized only by acetophenone or xanthone (73 kcal/mol) but not by benzophenone, thus suggesting that the triplet populated by benzophenone (the lowest triplet, ~61 kcal/mol) is inefficient in producing dimers. In fact, benzophenone's triplet state is quenched by enones as shown by phosphorescence quenching at 77 K. In addition, the photoreduction of benzophenone by 2-propanol was quenched by cyclopentenone at room temperature. Thus quenching of benzophenone triplet by cyclopentenone is demonstrated by both chemical and physical studies. Therefore, it was concluded that the triplet populated by acetophenone is the reactive state, and the one populated by benzophenone does not undergo dimerization.

The above conclusion was shown to be erroneous by the following experimental observations.[145]

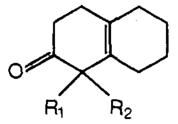
(i) Even though neither cyclopentenone nor cyclohexenone showed emission, several steroidal enones were found to show phosphorescence. Based on 0–0 band overlap of emission and absorption, the triplet energies were estimated to be in the range of 71–74 kcal/mol. Estimates of the triplet energies in these compounds by the stilbene isomerization method yielded values in the range of 61 kcal/mol, similar to cyclohexenone and cyclopentenone. The large discrepancy suggests that the estimated triplet energies are in error.

(ii) The phosphorescence of benzophenone was quenched by cyclopentenone at room temperature, not at the diffusional limit, but at $6 \times 10^5\ M^{-1}\ s^{-1}$. This slow rate would be unusual for thermoneutral or exothermic energy transfer and further suggests that the triplet energy of cyclopentenone may be higher than 61 kcal. Therefore, acetophenone probably sensitizes $T_1$ while benzophenone give $T_1$ inefficiently or not at all.

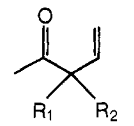
## E. β,γ-Unsaturated Ketones

β,γ-Unsaturated ketones formally contain two separate chromophores, the carbonyl group and the alkene group.[146] When these two groupings are *not in the same plane* they are coupled, the intensity of the nπ* band of the carbonyl group being 10–100 times larger than that of an isolated carbonyl group. This intensity enhancement of the nπ* band can be the result either of its mixing with a $\pi_{cc}\pi_{co}{}^*$ charge transfer band or by a direct mixing with the $\pi_{cc}\pi_{cc}{}^*$ transition. The triplet state of β-γ-unsaturated ketones also shows special spectroscopic properties. From phosphorescence studies at 77 K it has been shown that the lowest triplets have a ππ* configuration with energies from 68 to 74 kcal/mol. Also the lowest excited singlet (nπ*) show broad structureless fluorescence.

**TABLE VI.**[a] **$\Phi_f{}^{rel}$ and $\tau_f$ Values of Select β,γ-Enones 101–106**[b]



**101**, $R_1=R_2=H$
**102**, $R_1=CH_3$; $R_2=H$
**103**, $R_1=R_2=CH_3$

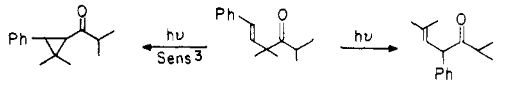


**104**, $R_1=R_2=H$
**105**, $R_1=CH_3$; $R_2=H$
**106**, $R_1=R_2=CH_3$

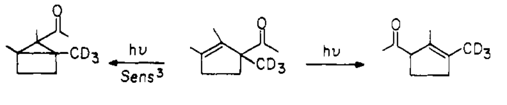
| | **101** | **102** | **103** | **104** | **105** | **106** |
|---|---|---|---|---|---|---|
| $\tau_f$, ns[c] | 1.8 | 2.6 | 4.0 | 1.9 | 2.2 | 2.6 |
| $\Phi_f{}^{rel}$ [d] | 1.0 | 1.3 | 1.7 | 1.0 | 1.3 | 1.8 |

[a] Table adopted from J. C. Alton, M. Shen, and J. J. Snyder, *J. Am. Chem. Soc.*, **98**, 5023 (1976). [b] Approximately 0.1 M solutions in spectral grade hexane or heptane. [b] Fluorescence lifetimes measured by the single photon counting technique. Absolute error ±15%. [c] Quantum yields of fluorescence measured relative to 1 for 1–3 and relative to 4 for 4–6. $\lambda_{ex}$ 310 nm. Error ±10%.

In general, β,γ-unsaturated ketones undergo 1,3-acyl shifts upon direct irradiation.[146] Triplet sensitization results in a 1,2-acyl shift and cis–trans isomerization as illustrated by eq 46–48. The 1,2-shift and cis–trans isomerizations which are not commonly observed on direct irradiation are believed to occur from the $T_1$ (ππ*) state. On the other hand, the widely accepted belief that the 1,3-acyl shift comes from the (nπ*) $S_1$ state has recently been questioned. The state responsible for this reaction is suggested to be the $T_2$ (nπ*) state.[147]



(46)



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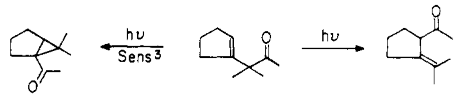
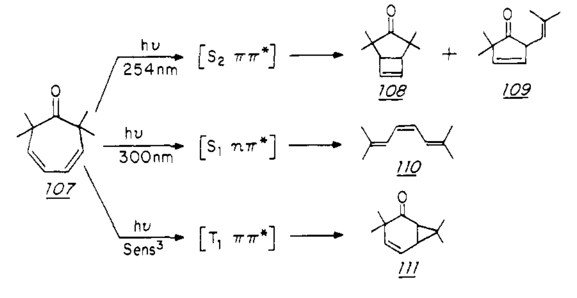


(48)

Doubt about $S_1$ being the reactive state in 1,3-acyl shift is cast by (i) *the observation of fluorescence from both β,γ-enones* which are reactive and β,γ-enones which are unreactive toward the 1,3-acyl shift; (ii) the fact that 1,3-acyl shifts are often unable to compete with intermolecular γ-hydrogen abstraction from the β,γ-enone $n\pi^{*1}$ state; and (iii) reports that the use of the high-energy sensitizer, acetone, sometimes results in sensitized, albeit inefficient, 1,3-acyl shift reactions of alkyl β,γ-unsaturated ketones. The quantum yield of fluorescence ($\Phi_{fl}$) as well as the lifetime ($\tau_{fl}$) of the β,γ ketones **101–106** were measured. As is seen in Table VI, as methyl groups replace hydrogens both $\Phi_{fl}$ and $\tau_{fl}$ increase slightly. This is inconsistent with the $S_1$ (nπ*) state being responsible for 1,3-acyl shift since the reactivity toward [1,3] acyl shift also increases as methyls replace hydrogen.[148] It appears as though the fluorescence yield and lifetime are not coupled to the efficiency with which the ketone undergoes an acyl shift. Therefore, it is proposed that $T_2$ (nπ*) is the reactive state involved in the 1,3-acyl shift (at least in some cases).

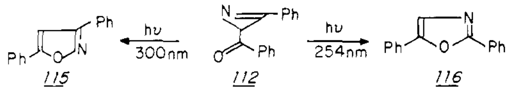
If the 1,3-acyl shift is occurring from $T_2$, then β,γ enones, which on direct irradiation yield a 1,3-acyl shift but no $T_1$ photoproducts, must undergo reaction from $T_2$ at a rate much faster than the rate of internal conversion from $T_2$ (nπ*) to $T_1$(ππ*). This seems conceivable, however, given that (i) β,γ-enone (nπ*) $T_2$ states should be very reactive toward α-cleavage[149]; and (ii) internal conversion from a (nπ*) $T_2$ to a (ππ*) $T_1$ state in β,γ-enones may be slower than normal $T_2$ to $T_1$ internal conversion to the extent that the two states are localized on different nonconjugated chromophores.

INDO model calculations suggest that $S_1$ excitation is largely localized on the CO group and $S_2$ excitation on the "diene" group in the case of **107.**[150] In agreement with this $S_1$ (300 nm) and $S_2$ (254 nm) irradiation gave different products characteristic of these chromophores. Irradiation into the $S_1$ band gave **110** and **111** whereas $S_2$ irradiation gave **108** and **109** in addition to **110** and **111.** Since triplet sensitization gives only **111,** the products **108** and **109** must originate from a state different from $S_1$ or $T_1$. This reactive state is suggested to be $S_2$. Once again it is worth mentioning that the slow internal conversion from $S_2$ to $S_1$ probably results from the localization of excitation energy on the noninteracting chromophores.



(49)

Wavelength effects observed in azirines **112–114** have similarities to the $\beta,\gamma$-unsaturated ketones discussed above.[151] The lack of interaction between the two chromophores, azirines (C=N) and carbonyl (C=O), is suggested by their absorption spectra. Examination of the absorption spectra of several model compounds reveals that the spectrum of **112,** for example, approximately matches the sum of the spectra of the separate benzoyl- and phenylazirine chromophores, both in their band maxima and extinction coefficients. The lowest singlet ($S_1$) and triplet ($T_1$) are thought to be localized in the carbonyl group based on emission spectra.



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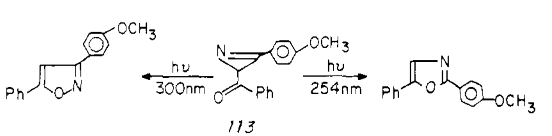
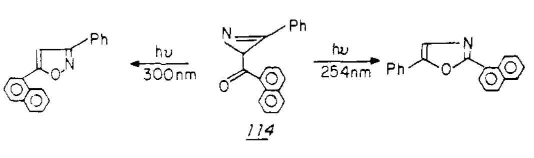
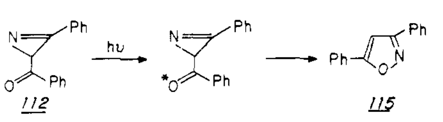


(51)

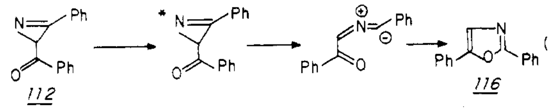


(52)

A discussion of one of these azirines (**112**) serves to illustrate the nature of the reactive states involved in their transformation to oxazole and isoxazoles. Irradiation of **112** (>300 nm) gives mainly isoxazole **115,** whereas irradiation into the $S_2$ band (254 nm) gives only oxazole **116.**[151] Triplet sensitization of **112** results in the formation of only isoxazole. Therefore, the isoxazole **115** observed upon $S_1$ irradiation probably results from isc to the $T_1$ state. Consistent with this assignment, the formation of **115** may be explained on the basis of the known chemistry of carbonyl group.[124] On the other hand, oxazole **116** formed upon $S_2$-band irradiation must arise either from the $S_2$ state or a state derived from it ($T_n$). Based on the absorption spectra, the $S_2$ state is thought to be localized on azirine moiety. The formation of **116** from **112** can readily be explained based on the known photochemistry of the keto azirine chromophore.[152] Therefore, the observed wavelength dependence in these systems appears to be due to selective excitation of the two noninteracting chromophores.



(53a)



(53b)

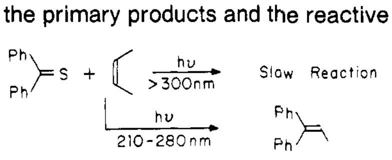
## F. Thiones

All thiocarbonyl compounds show a long-wavelength absorption band which has been attributed to an $n\pi^*$ transition.[153] With saturated substances this occurs near 500 nm; with conjugation this shifts closer to 600 nm. In addition, on the long-wavelength side of this band there may be a smaller absorption band which has been attributed to an $S_0 \rightarrow T_1$ transition. At shorter wavelengths thiones show high-intensity bands, and it seems likely that this is due to a $\pi\pi^*$ absorption. In the case of aliphatic thiones there is another band overlapping at somewhat higher energy, which may be $n \rightarrow \sigma^*$. The energy separation between $S_1$ and $S_2$ levels is in the range of 40–50 kcal/mol, comparable to that of azulene. For example, thiobenzophenone's $S_1$ and $S_2$ are assigned to be at 40 and ~ 85 kcal/mol, respectively, and those of adamantanethione at 56 and 95 kcal/mol. This large energy gap coupled with the difference in electronic state symmetry ($n\pi^*$, $\pi\pi^*$) (eq 1) of the two levels should make radiative and radiationless decay from $S_2$ level slow. The decay from $S_2$ through the triplet manifold is not well understood as only the energies of the lowest triplet states are known. As was discussed earlier (section II.A), a few of the thiones do emit from $S_2$.[23-25] Of these xanthione and aralkylthiones are particularly important as they also undergo chemical reactions from the higher excited states. In this section we discuss these reactions occurring from higher states of thiones.

### *1. Intermolecular Reactions*

#### a. Cycloaddition

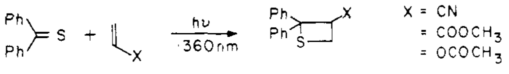
Bimolecular reactions from higher excited states are expected to be rather rare, since the lifetimes of these states would ordinarily be shorter than diffusion rates. However, thiones provide a clear example of intermolecular reactions originating from $S_2$. Both aromatic and aliphatic thiones undergo cycloaddition to olefins upon irradiation in either the $S_1$ or $S_2$ band. Kaiser and Wulfers were the first to recognize the wavelength dependence of the addition of thiobenzophenone to *cis*-butene but failed to identify both the primary products and the reactive state.[154]



(54)

Confirmation of the wavelength dependence of the addition of thiobenzophenone to electron-poor olefins was obtained by several workers,[155,156] and a quantitative study designed to identify the reactive state in these reactions was carried out by de Mayo and co-workers.[157] They concluded that the reactive state is $S_2$.

Thiobenzophenone gave thietanes in high yield upon irradiation in the $S_2$ band in presence of electron-poor olefins. In contrast to this, $S_1$ irradiation yielded no isolable products.[155,156] The addition following $S_2$ irradiation is stereospecific as demonstrated in the case of 1,2-dicyano- or 1,2-dichloroethylene.



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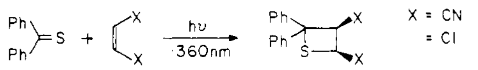
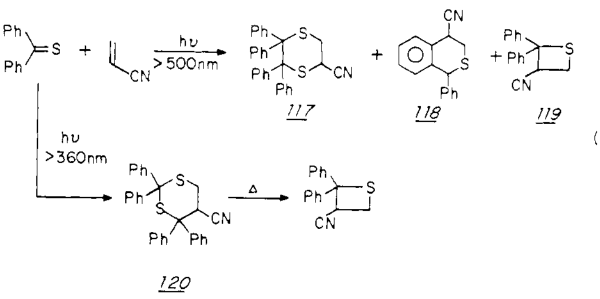


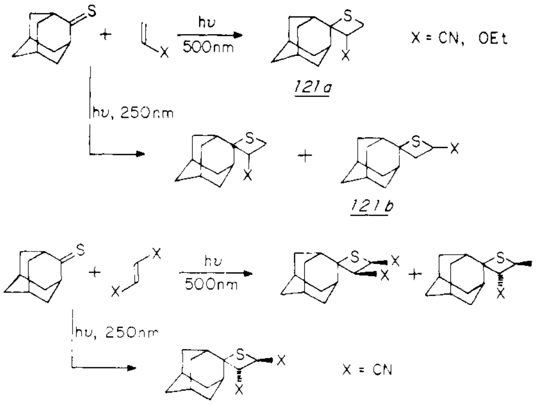
(56)

The thiobenzophenone-acrylonitrile system has been studied in detail and the addition is known to occur from $S_2$ of thiobenzophenone.[157] Evidence for reaction directly from $S_2$ is as follows. Irradiation at $S_1$ (>500 nm) gave three products, **117, 118,** and **119,** all in low quantum yield (~$10^{-3}$).[158] $S_2$ irradiation gave the same thietane **119** obtained on $S_1$ irradiation but via a 1,3-dithiane intermediate and in relatively high quantum yield (~0.05). The formation of **118** upon $S_1$ irradiation is quenched by cyclooctatetraene, thus suggesting $T_1$ as the reactive state. So far neither emission nor reaction from $S_1$ of thiobenzophenone has been observed. Therefore, even though no measurement of the intersystem crossing efficiency ($S_1 \rightarrow T_1$) has been made, there is a fair possibility that $S_1$ efficiently crosses over to $T_1$. Thietane **119** formation upon $S_2$ irradiation is quenched by biacetyl ($E_{S_1}$ = 64; $E_{T_1}$ = 57 kcal/mol), giving a linear Stern-Volmer plot. The lifetime of the state being quenched is calculated to be ~$5 \times 10^{-11}$ s, assuming a diffusional quenching by biacetyl. This quenching suggests that the reactive state is not $S_1$ or $T_1$ as both have lower energies than those of biacetyl. Furthermore, since $T_1$ gives **117** and **118** in addition to **119,** the reactive state during $S_2$ irradiation is not $T_1$ derived from $S_2$. The observed short lifetime ($10^{-11}$ s) and the quenching by biacetyl (singlet quenching of $S_2$) suggests that $S_2$ may be the reactive state. It must be borne in mind that these quenching results do not rule out the possibility of a higher triplet derived from $S_2$ (>57 kcal/mol) as the reactive state.



(57)

Similar to aromatic thiones, aliphatic thiones also undergo cycloaddition to both electron-deficient and electron-rich olefins upon $S_1$ or $S_2$ band irradiation. Adamantanethione has been studied in detail, and the results clearly show that $S_2$ and $T_1$ are the reactive states upon $S_2$ and $S_1$ irradiation, respectively.[159,160]



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(59)

The thietane formation upon $S_1$ irradiation is nonstereospecific but regiospecific for the olefins *trans*-1,2-dicyanoethylene, ethyl vinyl ether, and acrylonitrile,[159] but the addition via $S_2$ irradiation is found to be stereospecific and nonregiospecific.[160] The quantum yields (Φ) of product formation were measured, and there is a large difference in Φ between $S_1$ and $S_2$ irradiation as shown in Table VII. The large difference in Φ of product formation (Table VII) and the difference in nature of addition (stereo and regiospecificity) between $S_1$ and $S_2$ irradiation clearly suggest that the reactive states are not the same during these two irradiations.

**TABLE VII. Comparison of $\Phi^a$ at 500 and 250 nm.$^d$ Dimerization and Cycloaddition of Adamantanethione**

| Reaction | $\Phi_{500}{}^b$ | $\Phi_{250}{}^c$ |
|---|---|---|
| Dimerization<br>[A] = 0.2 M | $1.5 \times 10^{-4}$ | 0.22 |
| Cycloaddition to acrylonitrile<br>[A] = 0.2 M<br>[O] = 1.5 M | $2.3 \times 10^{-4}$ | 0.017 |
| Cycloaddition to ethyl vinyl ether<br>[A] = 0.1 M<br>[O] = 2.0 M | $9.0 \times 10^{-4}$ | 0.019 |

[a] Error ±10%. [b] Solvent: benzene. [c] Solvent: cyclohexane. [d] Table adopted from A. H. Lawrence, C. C. Liao, P. de Mayo, and V. Ramamurthy, *J. Am. Chem. Soc.*, **98,** 3572 (1976).

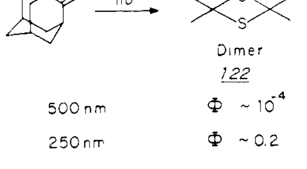
**TABLE VIII. Sensitized Photocycloaddition of Adamantane Thione to Acrylonitrile$^a$**

| Sensitizer | Product |
|---|---|
| β-Acetonaphthone$^b$ (λ 305 ± 4 nm) | Dimer + **121a** |
| Michler's ketone$^{c,e}$ (λ 362 ± 4 nm) | Dimer + **121a** |
| Triphenylene$^b$ (λ 306 ± 4 nm) | Dimer + **121a** |
| *p*-Methoxyacetophenone$^{b,e}$ (λ 334 ± 4 nm) | Dimer + **121a** |
| Acetone$^d$ (λ 306 ± 4 nm) | Dimer + **121a** |

[a] Cyclohexane solvent. Table adapted from A. H. Lawrence, C. C. Kial, P. de Mayo, and V. Ramamurthy, *J. Am. Chem. Soc.*, **98,** 3572 (1976). [b] [A] = 0.01 M; [Sens] = 0.01 M; [O] = 1.5 M. [c] [A] = 0.01 M; [Sens] = 0.001 M; [O] = 1.5 M. [d] [A] = 0.01 M; [Sens] = 1.0 M; [O] = 1.5 M. [e] Prolonged irradiation resulted in the formation of 6.

The addition to olefins upon $S_1$ irradiation is quenched by 9-methylanthracene ($E_T$ = 41.9 kcal/mol), cyclooctatetraene ($E_T$ < 40), and alloocimene ($E_T$ = 47). The same thietanes **121** are formed upon triplet sensitization (Michler's ketone, 2-acetonaphthone, and triphenylene) with about the same quantum yields as upon $S_1$ irradiation. These results suggest that the reactive state is $T_1$ upon $S_1$ irradiation, and Φ of intersystem crossing is close to unity. Acrylonitrile, one of the olefins used for addition, has a triplet energy in the range of 60–70 kcal/mol, but it failed to undergo triplet-sensitized dimerization during $S_2$ irradiation. This suggested that there is not a quenchable triplet between 79 and 95 kcal/mol. Several triplet sensitizers employed in the range 60–80 kcal/mol failed to produce the same thietanes formed upon $S_2$ irradiation, instead giving the thietanes derived from $T_1$ as shown in Table VIII. This suggests that there is no reactive triplet in the range 55–80 kcal/mol. The above evidence taken together suggests the reactive state to be $S_2$ upon excitation at 250 nm, and this is quenched by 1,1′-azoisobutane by efficient singlet energy transfer ($E_{S_1}$ < 68 kcal/mol). The lifetime of the state being quenched ($S_2$) is calculated to be ~$10^{-10}$ s based on quenching data. The reaction rate constants toward acrylonitrile and ethyl vinyl ether are estimated to be $5 \times 10^9$ and $4 \times 10^8$ $M^{-1}$ $s^{-1}$, respectively.

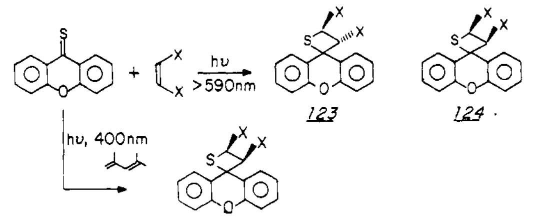
Adamantanethione is also found to dimerize to give 1,3-dithiane **122** upon $S_1$ and $S_2$ irradiation. Based on similar experiments to those already described for olefin addition, the reactive states are assigned to be $T_1$ and $S_2$.



(60)

Similar to these thiones, xanthione also undergoes stereospecific addition to maleic and fumaric esters upon $S_2$ irradiation to give thietanes **123** and **124.**[161] The stereospecificity of addition is demonstrated by selective quenching of $T_1$ by a diene as $T_1$ also gave thietanes but in a nonstereospecific manner.

A general reaction which does not proceed upon $S_1$ irradiation is the addition to the nitrile function.[162] This occurs only on $S_2$ irradiation with aromatic, aliphatic and aralkyl thiones as in eq 62a-3. Although wavelength dependence has been noted, it is not clear whether it is due to reaction from higher excited state or due to efficient intersystem crossing from a higher state to $T_1$. No detailed study has yet been reported.



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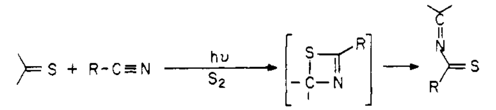
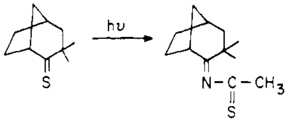
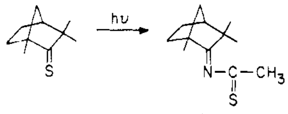


(62a)



(62b)



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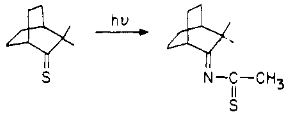

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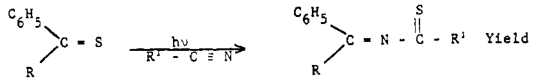


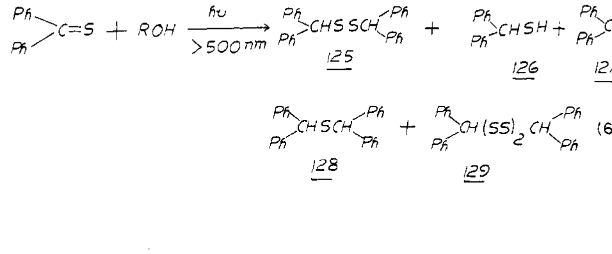
$$C_6H_5(R)C=S \xrightarrow[R^1-C\equiv N]{h\nu} C_6H_5(R)C=N-C(=S)-R^1 \quad \text{Yield} \qquad (62e)$$

| | | |
|---|---|---|
| a) $R = -C(CH_3)_2-CH_2-CH_3$ | ; $R^1 = -CH_3$ | (88%) |
| b) $R =$ " | ; $R^1 = -CH(CH_3)(CH_2-CH_3)$ | (64%) |
| c) $R = -C(CH_3)_2-CH_2-CH_3$ | ; $R^1 = CH_3$ | (10%) |
| d) $R = -C(CH_3)_2-(CH_2)_2-C(CH_3)_3$ | ; $R^1 = CH_3$ | (77%) |
| e) $R = -C_6H_5$ | ; $R^1 = CH_3$ | (33%) |

## b. Hydrogen Abstraction

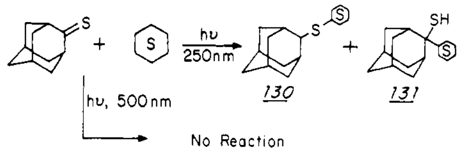
The wavelength-dependent intermolecular hydrogen abstraction by thiones was recognized as early as 1962 by Oster, Citarel, and Goodman in the case of thiobenzophenone.[163] Since then several studies have been made, and the results indicate that the reactive state may not be $S_1$ or $T_1$ upon $S_2$ irradiation.

Thiobenzophenone, upon irradiation in the $S_1$ band, in ethanol gave **125** to **129.**[164,165] The same products were obtained in 2-propanol and other alcohols as shown below, but thiobenzophenone was found to be inert in cyclohexane or diphenylmethane upon $S_1$ irradiation. Irradiation into the $S_2$ band in all the above alcohols gave the same product mixture but at an accelerated rate. Surprisingly, even in cyclohexane, thiobenzophenone underwent photoreduction upon $S_2$ irradiation (note it was inert during $S_1$ irradiation). The difference in reactivity of thiobenzophenone upon $S_1$ and $S_2$ irradiation probably suggests that the reactive states may be different in the two cases, but no clear experiments have been done to indicate the reactive state during $S_2$ irradiation. Based on reports that the $\Phi_{isc}$ is close to unity for thiobenzophenone, the reactive state may be $T_1$ upon $S_1$ irradiation and a higher state, either $S_2$ or $T_n$, upon $S_2$ irradiation.



(63)

Adamantanethione has been studied in greater detail than any other thione with respect to photoreduction.[159,160] Irradiation (>500 nm) of adamantanethione in cyclohexane was found to give only 1,3-dithiane. In contrast, irradiation into the $S_2$ band (250 nm) gave two products, **130** and **131** in a very clean reaction, in addition to 1,3-dithiane. A kinetic investigation was done on this reaction and the reactive state was found to be $S_2$ with a lifetime of ~$10^{-10}$ s. The investigation is very similar to the cycloaddition of acrylonitrile or ethyl vinyl ether to adamantanethione.

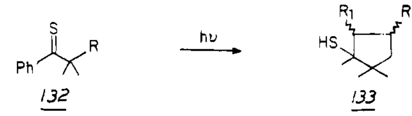


(64)

### 2. Intramolecular Abstraction

Thiones undergo both intermolecular and intramolecular hydrogen abstraction from higher excited states. The intramolecular abstraction by aralkyl thiones has been well studied and the reactive state has been identifed as $S_2$.

Aralkyl thiones **132a–k,** upon irradiation into the $S_2$ band, gave the corresponding cyclopentylthiols.[166] These products can be considered to result from δ-hydrogen abstraction by the "thione". These reactions do not occur upon $S_1$ irradiation. A kinetic investigation was done on **132c.** The quantum yield of product formation **133c** upon $S_2$ irradiation was found to be 0.032 (313 nm, benzene). In contrast to $S_2$ irradiation, the Φ of disappearance of **132c** at 572 nm irradiation was less than $10^{-5}$ indicating that $S_1$ is not responsible for the formation of **133c.** The reaction upon $S_2$ irradiation cannot be quenched by piperylene ($E_T$ ~ 58 kcal), suggesting that the reactive state may not be a quenchable triplet above ≃58 kcal/mol. The δ-hydrogen abstraction cannot be sensitized by benzophenone, β-acetonaphthone, or other sensitizers. This clearly suggests that the reactive state is not a triplet below 69 kcal/mol, including $T_1$. The formation of **133c** is quenched by biacetyl and the lifetime of the state being quenched is estimated to be ~$1.7 \times 10^{-10}$ s, in fair agreement with the lifetime measured by fluorescence decay of $S_2$ emission ($4 \times 10^{-10}$ s). Therefore the reactive state must be $S_2$ which can be quenched by biacetyl by singlet energy transfer.

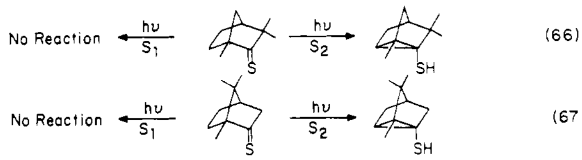


(65)

**132a**, $R = -(CH_2)_2CH_3$
**b**, $R = -(CH_2)_3CH_3$
**c**, $R = -CH_2CH(CH_3)_2$
**d**, $R = -(CH_2)_{10}CH_3$
**e**, $R = -(CH_2)_3C_6H_5$
**f**, $R = -(CH_2)_3OCH_3$
**g**, $R = -CH_2CH(CH_3)(CH_2CH_3)$
**i**, $R = -CH_2CH_3$
**j**, $R = -(CH_2)_2C(CH_3)_3$
**k**, $R = -(CH_2)_2CH(CH_3)(CH_2CH_3)$

**133a**, $R_1 = R_2 = H$
**b**, $R_1 = CH_3$; $R_2 = H$
**c**, $R_1 = H$; $R_2 = CH_3$
**d**, $R_1 = -(CH_2)_7CH_3$; $R_2 = H$
**e**, $R_1 = C_6H_5$; $R_2 = H$
**f**, $R_1 = OCH_3$; $R_2 = H$
**g**, $R_1 = H$; $R_2 = CH_2CH_3$
**h**, $R_1 = R_2 = CH_3$

There is another class of intramolecular hydrogen abstraction in alicyclic thiones which shows wavelength dependence.[167] Thiocamphor and thiofenchone, upon irradiation into the $S_2$ band, undergo $\beta$-hydrogen abstraction to give tricyclic thiols. This reaction does not go when these species are irradiated in the $S_1$ band. A detailed study to locate the reactive state has not yet been reported.



(66)

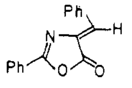
(67)

The results presented here clearly establish the fact that the higher electronic states of thiones are long lived (~$10^{-10}$ s) and both intermolecular and intramolecular reactions can compete with relaxation to lower excited states.[168]

## G. Miscellaneous Reactions

### 1. Lactones

Many lactones have been observed to undergo wavelength-dependent photochemical reactions, and in specific cases, both competition between reaction and internal conversion of higher excited states, and competition between reaction and vibrational relaxation within a given electronic state have been postulated. In a series of papers, Ullman and co-workers[169] have investigated the photochemistry of the oxazolone **134** and its counterparts **135** and **136**. The photochemistry observed consisted of two processes, cis–trans isomerization about the exocyclic double bond and hydrogen abstraction from solvent, leading in the case of **134** to **137**. All three compounds showed substantial changes in the ratio of isomerization/abstraction with changes of irradiating wavelength and, while the wavelength effects were not identical for the three systems, the mechanistic conclusions were similar. These conclusions may be summarized as follows:



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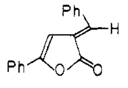

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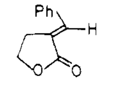

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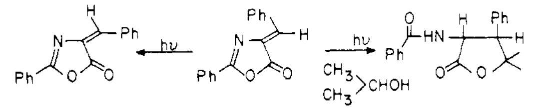


134 137

(68)

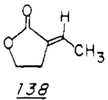
(1) Hydrogen abstraction occurs from a long-lived (~$10^{-4}$ s) $T_2$ state ($n,\pi^*$)

(2) Geometric isomerization occurs from $T_1$ ($\pi,\pi^*$) state.

(3) These states may be differentially populated, either with appropriate triplet sensitizers or by direct excitation at the appropriate $\lambda$. For **136**, irradiation at 313 nm produces only $T_1$ products while 254-nm radiation leads to $T_2$-derived products. Therefore, in the direct irradiation experiments, one must also conclude that $S_n \rightarrow S_1$ is slower than $S_n \rightarrow T_2$.

It is the long lifetime of the hydrogen-abstracting state which is the most unusual feature of these data. Using the oxygen perturbation method of Evans,[170] Ullman and co-workers have assigned the $T_1$ energy in **134** as 43 kcal/mol. Furthermore, from the failure of perylene to quench the hydrogen abstraction, and the cut-off value in sensitizer energy for selective excitation of the geometric isomerization the energy of $T_2$ in **134** may be estimated to be ~58 kcal/mol. This energy gap is not exceptionally large, and one might expect internal conversion rate constants, everything else being equal, of ~$10^{11}$ $s^{-1}$ as Birks has suggested for $S_2 \rightarrow S_1$ conversions with similar gaps in aromatic hydrocarbons.[171] Nonetheless, if the sensitization experiments are dominated by singlet energy transfer through emission–reabsorption, as has been suggested,[172] then the experimental data would also appear to be consistent with a mechanism involving reaction only from the lowest states in each manifold, cis–trans isomerization from $S_1$, and hydrogen abstraction from $T_1$. This would not require an exceedingly long-lived upper excited state and would also seem to be more consistent with the lack of quenching of isomerization by $O_2$.

Wavelength effects have also been observed in similar compounds by other workers, but, in general, the mechanisms have not been as thoroughly investigated as in the above examples. Thus, lactone **138** has been shown to undergo both isomerization and abstraction with wavelength-dependent relative yields and a $T_2$ state has been proposed as the precursor to hydrogen abstraction.[173] Similarly, **139** has been shown to undergo cis–trans isomerization followed by intramolecular acylation to produce coumarin **140**.[1] Again the wavelength effects and lifetimes were adduced to be consistent with the original proposal of a long-lived $T_2$ state in the acylation reaction. Carboxylate anions **141** and **142** were irradiated and found to show wavelength dependence specific for the substitution pattern.[175] The unsubstituted or methyl-substituted cinnamates **142a–c** gave the most distinct wavelength dependence, showing predominant hydrogen abstraction with $\lambda$ >280 nm, but predominant lactonization with $\lambda$ 254 nm.



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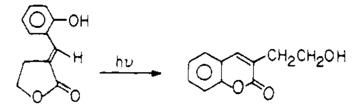

139 140

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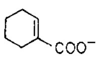
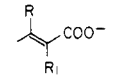


141



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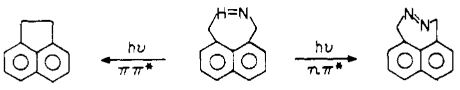
**a**, R = R′ = H
**b**, R = $CH_3$; R′ = H
**c**, R = H; R′ = $CH_3$
**d**, R = $C_6H_5$; R′ = $C_6H_5$
**e**, R = H; R′ = $C_6H_5$

Finally, a number of years ago, Simonaitis and Pitts[176] reported that the parent $\gamma$-butyrolactone (**143**) and two methyl-substituted derivatives gave products characteristic of cleavage of both the $\alpha$ C–C and C–O bonds after photochemical excitation in solution, and that the ratio of these products changed with excitation wavelength. At 254 nm the ratio of quantum yields $\Phi_{C-C}/\Phi_{C-O}$ from **143** was ~3.8, while at 238 nm it decreased to ~1.9. Since both of these wavelengths lie within the $S_1$ band, and since the lifetime of the dissociating state ($S_1$) was determined to be $<10^{-10}$ s by quenching experiments, the authors proposed competitive cleavage and vibrational relaxation (est $k = 10^{11}$–$10^{12}$ s) from upper vibronic levels of the lowest singlet excited state. Subsequently, numerous other studies have shown that such competition is, in fact, feasible, and that these estimated rate constants for vibrational relaxation of large molecules in solution are approximately correct.[177] An interesting extension of this type of experiment might be to attempt to determine whether specific vibronic levels lead to specific preferences for one mode of cleavage or whether the wavelength dependence can be rationalized with a statistical model in which the vibrational component of the vibronic energy is randomized on the timescale of chemical reaction in solution.

### *2. Azo Compounds*

Azo compounds in general possess well-separated $n\pi^*$ and $\pi\pi^*$ bands. In spite of the large energy gap, authenticated examples of higher state reactivity in azo compounds are few. A variety of azobenzenes and derivatives are suggested to undergo geometric isomerization from upper triplet states.[178] Recently 1,1′-azonaphthalene and phenylazo-1-naphthalene were shown to undergo geometric isomerization from higher triplets.[179] An interesting example of wavelength-dependent reaction is that of **144.** Irradiation of **144** into the $n\pi^*$ band gives rise to isomerization whereas $\pi\pi^*$ irradiation gives rise to nitrogen extrusion.[180]



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