Radiationless Decay in the Aromatic Ketones as Studied By Opto-Acoustic Spectroscopy

M. B. Robin* and N. A. Kuebler

Contribution from the Bell Laboratories, Murray Hill, New Jersey 07974. *Received November 21, 1974*

Abstract: A comparison of the opto-acoustic spectra of acetophenone and benzaldehyde clearly reflects different modes of relaxation. In acetophenone, excitation into S_1 relaxes radiationlessly to the ground state at a rate of 1.2×10^3 sec^{-1}, whereas excitations into S_2 and S_3 yield even slower heats due to initial decomposition into free radicals which recombine slowly at such low concentrations. These decompositions can be repressed by adding a high pressure of a second gas. In benzaldehyde, the S_1 state is photochemically active, but this can be repressed by again adding a high pressure of a second gas. Unlike acetophenone, the overall relaxation rate in the S_2 state of benzaldehyde is rapid, because the products of the photochemistry are closed shell molecules which do not react further. The S_3 state of benzaldehyde does relax slowly, even in the presence of an excess of a second gas, and it is concluded that S_3 initially decays rapidly ($>3 \times 10^9$ sec^{-1}) to yield radicals which then recombine slowly.

The aromatic ketones have become the classic molecules for luminescence and photochemical studies. When combined with low and high resolution optical absorption work, these studies constitute an almost complete step-by-step accounting of the fate of the molecule once it leaves the ground state. In general, what is missing is a measure of the relaxations which lead to heat rather than to light or photoproducts. The present work offers information on these radiationless processes as measured by opto-acoustic spectroscopy.

In this technique, pulses of light which are absorbed by the gas of interest are converted to heat in those molecules preferring radiationless decay, and the resultant pressure waves are sensed using a microphone and phase-sensitive amplification. The apparatus is described more fully in ref 1-3. All of the ketones studied here were purified by gas-phase chromatography immediately before use.

Whatever heat is generated by the relaxation and finally sensed by the microphone is obviously the end result of a large number of successive rovibronic relaxations, the details of which are completely lost to us. What we do measure is the relative amounts of heat released upon irradiation at each point in the spectrum, and more interestingly, the phase angle between the light pulses and the pressure pulses, shifted by $\pi/2$. This latter is intimately related to the *overall* rate of radiationless relaxation, which we find to vary dramatically throughout the spectra of some compounds, but not to vary at all in others.[4] The problem then, is how to interpret these changes of rate with wavelength, and how to integrate this knowledge into the broader framework derived from other types of spectroscopic experiments.

Returning briefly to the molecules of concern to this study, an aspect of the aromatic ketones of great interest is the near degeneracy of the (n,π^*) and (π,π^*) (^3L_b) triplet states and the effects of this on the luminescence and radiationless relaxation rates. Thus in certain ring-substituted ketones $^3(n,\pi^*)$ is below $^3(\pi,\pi^*)$ and a phosphorescence lifetime of ca. 10 msec results, whereas methylation of this ketone may place $^3(\pi,\pi^*)$ below $^3(n,\pi^*)$, in which case the phosphorescence lifetime increases to ca. 1 sec.[5] Presumably, in the latter case, the competing $T_1 \rightsquigarrow S_0$ radiationless transition has also become ca. 10^2 slower since the phosphorescence quantum yield remains high. Note, however, that in the case of the aromatic ketones, the radiative lifetime data are for the molecule in a cold, condensed phase whereas we will study the vapor at room temperature. Furthermore, recent microwave-optical double-resonance work shows that the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ vibronic levels are mixed appreciably in the aromatic ketones.[6]

Acetophenone

We consider the acetophenone molecule first because more is known about it, and so the interpretation of its opto-acoustic spectrum may be simpler. In hydrocarbon matrices and in fluid solution, excitation of acetophenone in its $^1(n,\pi^*)$ band (centered at 3230 Å, Figure 1) is followed by rapid intersystem crossing to the (π,π^*) triplet (^3L_b) with unit quantum yield,[5,7] and there then follows an internal conversion from $^3(\pi,\pi^*)$ to $^3(n,\pi^*)$.[6] From this lowest triplet level (T_1) there is observed a phosphorescence of high quantum yield ($\varphi_p \sim 0.5$) and a radiative lifetime of a few milliseconds.[5] Since the quantum yield is given by $\varphi_p = k_r/(k_r + k_{nr})$, where k_r and k_{nr} are the radiative and nonradiative rate constants, respectively, it is clear that $k_r \sim k_{nr}$, and that heat from this band will appear at a rate of ca. 10^3 sec^{-1}. Self-quenching and/or quenching at the walls could make it appear more rapidly than this, with a concomitant shortening of the phosphorescence lifetime.

As seen from Figure 1, the heat resulting from $S_0 \rightarrow S_1$ excitation has a near-constant phase angle from 3500 to 2940 Å, at which point there is an abrupt change. The constancy of the phase angle in this region shows that excitation to each of the vibronic components of the S_1 band is rapidly relaxed to a common level (T_1) which then relaxes slowly to the ground state. More likely, the heat signal here is the vector sum of a rapid but low-amplitude heat coming from vibrational relaxation within both the S_1 and the T_1,T_2 manifolds, and a slow but large-amplitude heat coming from the $T_1 \rightsquigarrow S_0$ relaxation. The phase angle in the $n \rightarrow \pi^*$ region is about 27° larger than that for the most rapid relaxation in biacetyl under the same conditions,[3] and this corresponds roughly to $k_{nr} \sim 1.2 \times 10^3$ sec^{-1} in acetophenone. Burger and Steel also have measured the unimolecular rate for the radiationless relaxation of T_1 in gaseous acetophenone and found 0.53×10^3 sec^{-1},[8] whereas Hunter reports a value of $k_{nr} = 1.47 \times 10^2$ sec^{-1} for acetophenone in an ethanol-ethyl ether glass at 77°K,[9] and Yang and Dusenbery[10] report 1.59×10^6 sec^{-1} in a benzene/2-propanol mixture at room temperature.

The constancy of the thermal phase angle in the $n \rightarrow \pi^*$ region of acetophenone is in accord with Griffin's comment[11] that the phosphorescence decay rate in a glassy ma-

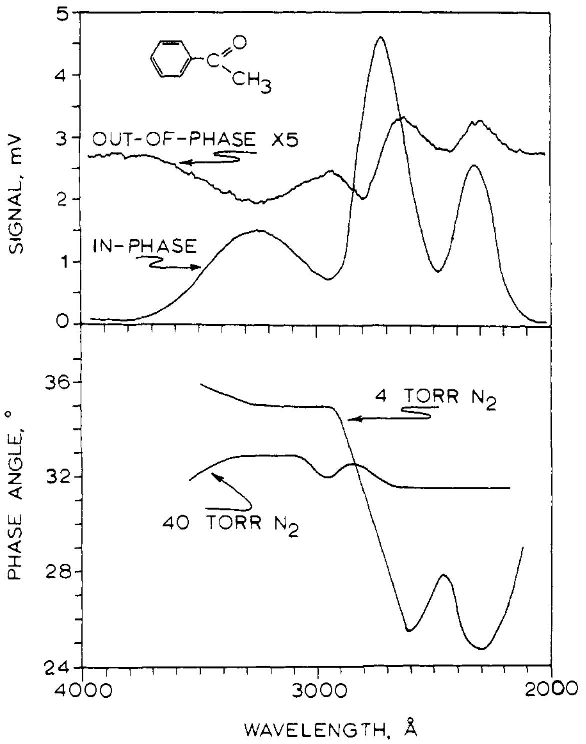


Figure 1. (Upper) The in-phase and out-of-phase opto-acoustic spectra of acetophenone vapor (0.24 Torr) plus 5 Torr of helium, at 100 Hz. (Lower) Phase angle plots measured for acetophenone vapor (0.24 Torr) mixed with 4 Torr and 40 Torr of N_2, at 100 Hz. The curve measured at 40 Torr of N_2 pressure has been displaced downward by 60°.

trix is independent of the excitation wavelength, though strongly nonexponential.

The sharp break of phase angle at 2940 Å signals the onset of heat release from the second singlet of acetophenone, the $\pi \rightarrow \pi^*$ transition corresponding to the 2600 Å band of benzene. Note that its phase angle corresponds to a heating rate even slower than that for excitation into S_1. The progressive drop of the null phase angle from 2940 to 2640 Å possibly results from the overlap of S_2 with the short-wavelength tail of S_1, which is of progressively smaller amplitude in this region.

The S_2 excited state of acetophenone has the $^1(\pi,\pi^*)$ configuration and, according to the rules elucidated by El-Sayed,[12] should intersystem cross rapidly to the lowest triplet $^3(n,\pi^*)$. Indeed, Shimada and Goodman[13] have recorded the phosphorescence excitation spectrum of acetophenone in a glassy matrix down to 2500 Å, showing that T_1 is accessible from S_2 and S_3 as well as from S_1. However, no quantum yield data are available for excitation in the S_2,S_3 regions and so one cannot comment on the $S_2,S_3 \rightsquigarrow T_1$ rates, nor can one rule out the possibility that S_2,S_3 relax to S_1, which then relaxes to T_2,T_1. According to Setser et al.,[14] metastable nitrogen can also excite acetophenone, lifting it to a triplet state in the vicinity of 2000 Å, which eventually relaxes to T_1 and phosphoresces.

Returning to the opto-acoustic result, one might argue that in spite of the advantageous spin-orbit matrix element between S_2 and T_1, the overall heating rate is slow due either to poor Franck-Condon overlap or to a low density of levels in the region close to the S_2 origin. A more likely explanation is that the absorption of light into S_2 of acetophenone leads to the production of free radicals at low concentrations due to our low light flux, and that the subsequent reactions of these species to yield further heat proceed only slowly. Such a mechanism is expected only under conditions of low collision frequency, because at higher pressures, the excited molecules may be relaxed before they can undergo photochemistry. Indeed, in the presence of 40 Torr of nitrogen, Figure 1, it is seen that the slow heat beginning at 2940 Å is almost totally repressed. At 40 Torr of pressure, the collision rate is 5×10^8 sec^{-1}, which must be more rapid than the initial photodecomposition step. A similar effect is observed with added oxygen, but this may be due to a chemical reaction rather than a physical relaxation. The near constancy of the phase angle at high nitrogen pressures implies that the S_2 and S_3 higher states of acetophenone when quenched in large part revert to T_1 and then undergo slow $T_1 \rightsquigarrow S_0$ relaxation. One must argue then that the low-pressure photodecomposition following $S_0 \rightarrow S_2$ excitation in the gas phase is quenched in a glassy matrix, thereby allowing eventual T_1 excitation and phosphorescence.

Prior to the work of Burger and Steel, the photodecomposition of acetophenone had not been studied in any detail. Duncan and Trotman-Dickenson[15] report that illumination in the gas phase at unspecified wavelengths leads to phenyl radicals, with the yield of products decreasing with increasing pressure. Working in fluid and glassy hydrocarbon solutions, Sowden and Davidson report quantum yields for the production of benzene as 0.1–1 in fluid solution, but no sign of photochemistry in the same solution when frozen at 77°.[16] In their latest work on this system, Burger and Steel[8] report that photochemistry in the S_1 band of acetophenone is insignificant, but that excitation into S_2 leads to the production of C_6H_5CO and CH_3 radicals with quantum yields approaching 1 at low pressures. Our interpretation of the opto-acoustic spectrum of acetophenone is consistent with these observations.

In our earlier opto-acoustic work on benzene,[3] the $\pi \rightarrow \pi^*$ band at 2600 Å was found to relax heterogeneously; i.e., from the origin at 2600 to 2450 Å, the heat was "slow" ($k_{nr} = \sim 10^6$ sec^{-1}), but at this point the heating rate increased considerably. Apparently the same process is active in the corresponding band of acetophenone, for at 2640 Å, the heat begins again to accelerate, mirroring the change in benzene.

The increased rate of heating in the S_2 band is short lived, for at 2490 Å, S_3 begins its absorption and the heat flow then slows to about the middle of this band (2310 Å), at which point the rate increases again. Note that below 2600 Å, the rates of heating are generally slow in spite of a small rise at 2310 Å, and these rates are increased noticeably (Figure 1) when a second gas is added; this behavior suggests that a large part of the heat in this region is the result of a slow recombination of free radicals, or possibly the result of the relaxation of a long-lived geometric isomer.

The breaks in the rates of heat evolution at 2640, 2490, and 2310 Å in acetophenone could result from many circumstances, prime among them being unsuspected levels at these wavelengths (singlets or triplets[19]) or the surmounting of energy barriers to photochemistry at these wavelengths. It is also possible that the barriers are not energetic, but involve overlap factors instead. Whatever the explanation, it is remarkable that the slow $S_1 \rightsquigarrow T_2 \rightsquigarrow T_1 \rightsquigarrow S_0$ path is the most rapid heat-producing sequence in the molecule, with all of the higher ones being slower than 1×10^3 sec^{-1}. Of course, there may be a very rapid component to the heat at each of the wavelengths studied, but since it can only add vectorially to the other slow components, and an overall slow heat is measured, the fast heat component, if present at all, must have a small amplitude.

The behavior of the rate of heating in acetophenone stands in direct contrast to its behavior in the diazabenzenes,[4] where the heat from (n,π^*) excitation is slow but invariably speeds up in the (π,π^*) region. However, in the

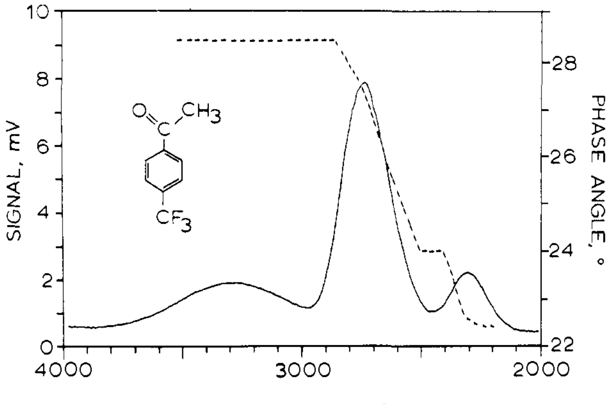


Figure 2. The opto-acoustic spectrum (full line) and phase angle plot (dashed line) for *p*-trifluoromethylacetophenone in the gas phase (0.12 Torr), with the addition of 10 Torr of helium, at 100 Hz.

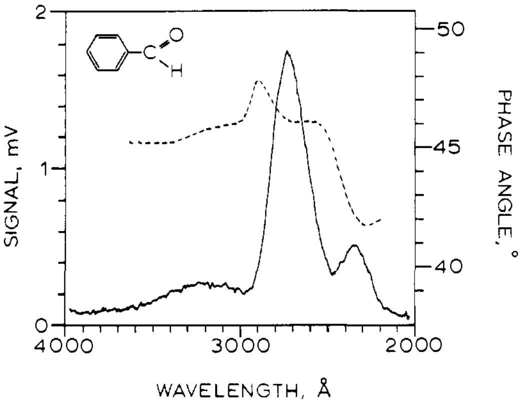


Figure 3. The opto-acoustic spectrum (full line) and phase angle plot (dashed line) for benzaldehyde in the gas phase (0.2 Torr), with 200 Torr of N_2 added, at 100 Hz.

case of the diazabenzenes, relaxation by photodecomposition is unimportant, whereas in the higher states of acetophenone, it is of the greatest importance at low pressures.

The phase angles in Figure 1 were measured in the presence of 4 Torr of N_2 gas. Since similar spectra were observed for He as the second gas, the possible vibrational excitation of the N_2 gas and its slow relaxation ($\tau = 1.6 \times 10^{-1}$ sec at 476°K) is seen not to be a factor. However, on replacing N_2 with O_2, (4 Torr) the null phase angles in the $n \rightarrow \pi^*$ region increase dramatically indicating a much faster heat, and the change of 10° from fastest to slowest in N_2 decreases to only 2° in O_2. We are seeing here the quenching of the excited states by O_2 at a rate far faster than that achieved by N_2, showing that either the radicals are immediately scavenged by oxygen and/or any triplet states in the relaxation chain are relaxed rapidly by oxygen.

The opto-acoustic spectrum of *p*-trifluoromethylacetophenone resembles that of acetophenone in several ways. In this compound, the phase angle across the $n \rightarrow \pi^*$ transition is constant, Figure 2, and remains so up to 2860 Å, from which point it decreases then by ca. 5°. Note that 2860 Å is far beyond the absorption threshold to S_2, which is more likely ca. 3050 Å. Thus excitation into S_2 near the origin relaxes at the same rate as excitation into S_1, presumably due to a slow step common to them both ($T_1 \rightsquigarrow S_0$). Apparently at 2860 Å, the barrier to photochemistry is surmounted, and radicals are formed which recombine only slowly. There is a momentary halt to the decrease (2500–2400 Å) but then absorption into S_3 commences, and the rate of heat release then becomes even slower. The monotonic drop in overall heating rate across the spectrum of *p*-trifluoromethylacetophenone may be due to an increasing quantum yield of slow photochemistry with decreasing wavelengths, or to a gradual change in the predominant mode of dissociation. A photochemical study would settle this point. It is clear from these experiments that free-radical photochemistry will commence from any point in S_2 in acetophenone, but only beyond 2860 Å in *p*-trifluoromethylacetophenone.

Addition of the *p*-trifluoromethyl group to acetophenone results in the inversion of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ levels, and as mentioned above, it is expected that this will make the relaxation from $^3(\pi,\pi^*)$ to S_0 very slow indeed. However, the present measurements do not show this slowing of the rate. Most likely, such long relaxation times require very large vessels in order to avoid relaxation at the walls, and this requirement is not met in our experiments.

Benzaldehyde

Photochemistry is much more obvious in the case of benzaldehyde, for a polymeric film is found to form on the opto-acoustic windows as soon as one scans into the $n \rightarrow \pi^*$ region. This could be avoided by adding either 200 Torr of He or 200 Torr of N_2 to 0.2 Torr of the benzaldehyde vapor. Though this allows one to take a spectrum free of window contamination, it obviously does so by quenching some photochemistry which otherwise is inherent to the excited states of benzaldehyde. This point should be borne in mind during the following discussion.

As in acetophenone, the heat resulting from $n \rightarrow \pi^*$ excitation in benzaldehyde has a rather constant phase angle, Figure 3, with the exception that a noticeable break in phase is observed at 3400 Å, corresponding to a slight increase in the rate of heating. This increase becomes even faster at 3000 Å, and rises to a peak at 2900 Å, receding to the lower rate at 2800 Å and beyond. Interestingly, 3000 Å is the wavelength at which a higher triplet state was found by Berger et al.[18] to intervene, with a rapid deactivation of the S_2 state as deduced from the photochemical yields of benzene and CO. Presumably, this higher triplet relaxes without passing through T_1, and is ineffective as an S_2 relaxation channel beyond 2800 Å. The relaxation rate then remains constant from 2800 to 2500 Å, at which point it slows precipitously as the $S_0 \rightarrow S_3(\pi,\pi^*)$ band is penetrated. This slowing must be due to a primary photochemical step which is going on at a far faster rate than the collision frequency (ca. 3×10^9 sec^{-1}), to yield radicals which then recombine slowly due to their low concentrations.

Several differences in the behaviors of acetophenone and benzaldehyde are clear from the present study: (i) the (n,π^*) state of benzaldehyde undergoes photochemistry far more readily than does that of acetophenone; (ii) in the S_2 region, benzaldehyde decomposes to yield closed shell molecules, whereas acetophenone decomposes to yield free radicals; (iii) in the S_3 region, a second gas quenches free radical photochemistry in acetophenone, but apparently not in benzaldehyde.

References and Notes

(1) W. R. Harshbarger and M. B. Robin, *Acc. Chem. Res.*, **6**, 329 (1973).
(2) W. R. Harshbarger and M. B. Robin, *Chem. Phys. Lett.*, **21**, 462 (1973).
(3) K. Kaya, W. R. Harshbarger, and M. B. Robin, *J. Chem. Phys.*, **60**, 4231 (1974).
(4) K. Kaya, C. L. Chatelain, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, **97**, 2153 (1975).
(5) A. A. Lamola, *J. Chem. Phys.* **47**, 4810 (1967).
(6) T. H. Cheng and N. Hirota, *Mol. Phys.*, **27**, 281 (1974).
(7) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(8) M. Burger and C. Steel, *J. Am. Chem. Soc.*, preceding paper in this issue.

(9) T. F. Hunter, *Trans. Faraday Soc.*, **66**, 300 (1970).
(10) N. C. Yang and R. Dusenbery, *J. Am. Chem. Soc.*, **90**, 5899 (1968).
(11) R. N. Griffin, *Photochem. Photobiol.*, **7**, 175 (1968).
(12) M. A. El-Sayed, *Acc. Chem. Res.*, **1**, 8 (1968).
(13) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965).
(14) D. D. Stedman, J. A. Meyer, and D. W. Setser, *J. Am. Chem. Soc.*, **90**, 6856 (1968).
(15) F. J. Duncan and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4672 (1962).
(16) R. G. Sowden and N. Davidson, *J. Am. Chem. Soc.*, **78**, 1291 (1956).
(17) J. B. Birks, private communication.
(18) M. Berger, I. L. Goldblatt, and C. Steel, *J. Am. Chem. Soc.*, **95**, 1717 (1973).
(19) In benzene, at least, this argument would not apply, since the rate of S_1 relaxation in the fast region ($k_{nr} \sim 10^{11}$ sec^{-1}) is too fast for an intersystem crossing.[17]

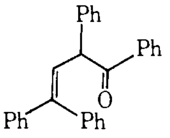
Systematic Structural Modifications in the Photochemistry of β,γ-Unsaturated Ketones. II. Acyclic Olefins and Acetylenes

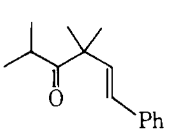
Mary A. Schexnayder and Paul S. Engel*

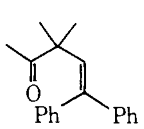
Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001.
Received January 25, 1975

Abstract: The photochemical reactions of six acyclic β,γ-unsaturated ketones have been investigated. Direct irradiation of those with a simple olefin (**11**, **15**, **16**) leads to an α-cleavage, cyclobutanol, or oxetane, with the quantum yield of ketone disappearance decreasing when the olefin is more heavily alkylated. Although β,γ-acetylenic ketone **12** also exhibits α-cleavage, an overwhelming preference for turning around of the allylic moiety is found in ketone **14**, in which the two modes of cleavage are allowed to compete. Ten unsaturated C_{10} hydrocarbons have been determined from irradiation of **14**. Photolysis of bis-β,γ-unsaturated ketone **13** gives turnaround ketone **24** and a mixture of three C_{10} hydrocarbons, probably via the very short-lived acyl radical **33**. **11**, **12**, and **16** show no products on triplet photosensitizaton, but **15** exhibits olefin cis-trans isomerization. The triplet state of **13** and **14** undergoes intramolecular [2 + 2] cycloaddition, followed by ring opening in the case of **14**. Two new simple carboxylic acids have been prepared during the course of the work: 2,2-dimethylbutynoic acid (**36**) and 2,2,3,4-tetramethylpent-3-enoic acid (**51**).

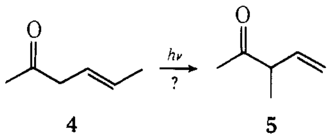
The photochemistry of β,γ-unsaturated ketones (β,γ-UK's) has become an actively researched area in recent years, particularly in regard to the oxadi-π-methane (ODPM) rearrangement.[1] Although most of the compounds which have been examined to date are cyclic, the ODPM rearrangement was actually discovered[2] in an open chain compound (**1**). Like compound **1**, many of the other acyclic cases contained an aromatic ring conjugated with either the carbonyl group or double bond.[3-6] No pattern in photochemical behavior is apparent on examining the limited data available; for example, triplet sensitization[3] of **2** gives ODPM rearrangement but **3** does not.[4]


1

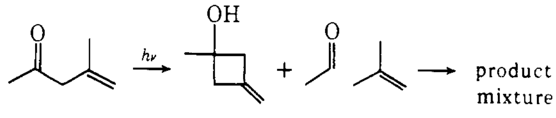

2


3

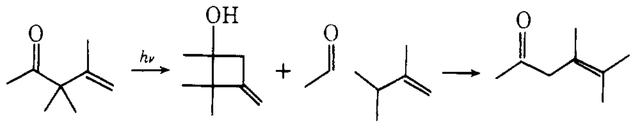
We have been interested in compounds with no conjugating substituents, an area in which published work is also scarce. In 1964 Morrison[7] reported that direct irradiation of **4** gave olefin trans-cis isomerization plus products from acetyl and 2-butenyl radicals; however, no mention was made of the expected **5**. More recent work[8] on **4** showed that olefin isomerization could also be sensitized by triplet acetone. Direct irradiation of compounds **6**[9] and **8**[10] gave products of α-cleavage and γ-hydrogen abstraction. Although these three cases are the only simple, acyclic β,γ-UK's which have been studied, they do show the other principal reactions known for this class of compounds as a whole.



4 5



6 7



8 9 10
+
others

The purpose of the present study was twofold: to elucidate the factors which govern the competition between the various pathways, and to examine the effect of a second unsaturated group on the photochemistry. We were also concerned with the α-cleavage process and the fate of the radicals produced. Two reactions which are new to the acyclic series have been found in the course of this work: intramolecular triplet [2 + 2] cycloaddition of bis-β,γ-UK's, and oxetane formation from simple, electron-rich β,γ-UK's.

Results

Acetone Sensitization. As mentioned in a preliminary report,[11] irradiation of 3,3-dimethyl-4-penten-2-one (**11**) in acetone did not produce the ODPM product **17** (cf. Scheme 1). **11** was not inert, however, because cis-trans isomerization of the double bond could be demonstrated when a deuterium atom was substituted for one terminal olefinic pro-