ENERGY WASTAGE PROCESSES IN KETONE PHOTOCHEMISTRY

DAVID I. SCHUSTER

Department of Chemistry, New York University,
Washington Square, New York, NY 10003, USA

ABSTRACT

It is proposed that the quantum inefficiency typically observed on photochemical excitation of ketones in solution is usually due to reversion to the ground state of starting material from reaction intermediates, rather than to direct radiationless decay to the ground state from the spectroscopic singlet or triplet state. Examples are given from four areas of investigation utilizing a variety of flash and steady state photochemical techniques. (1) The deactivation of aromatic ketone triplets in benzene and substituted benzenes is shown to involve two mechanisms: formation of charge transfer and sigma diradical complexes. The choice of mechanism depends on the ionization and reduction potentials of the partners. (2) Self-quenching is found to be an important energy wastage mechanism for ketone n, π^* as well as π, π^* triplets. The process has implications in sensitization processes as well as in mechanisms of product formation. Numerous studies with Michler's ketone are described, including the possible observation of a triplet excimer. (3) The large inefficiency observed in the photochemistry of 4,4-disubstituted cyclohexenones is shown not to involve reversion to ground state from diradical intermediates. The photochemical rearrangements of a simple unconstrained chiral cyclohexenone are shown to be largely if not totally stereospecific, and stereochemically consistent with the predictions of orbital symmetry. It is proposed that the shape of excited and ground state potential surfaces is the source of the observed inefficiency. (4) The much smaller but nonetheless evident inefficiency observed in photoexcitation of cross-conjugated cyclohexadienones is attributed to reversion to ground state from zwitterions. The conclusion is based on variable temperature and zwitterion-trapping studies of photoexcited 4-methyl-4-trichloromethylcyclohexadienone.

INTRODUCTION

The quantum yield Φ of a photochemical reaction is a quantitative measure of the efficiency with which energy provided by light is made chemically useful. It measures the amount of material which has reacted and/or product which has formed relative to the number of light quanta absorbed by a particular compound. The quantity can depend on wavelength, temperature, concentration of reactants and even the intensity of the light beam. While quantum yields of 1.0 (i.e. 100 per cent efficient utilization of light energy) and even higher (e.g. chain reactions) are not uncommon, it is the more typical situation in the liquid phase for quantum yields to be significantly less than unity, representing an overall wastage of light energy. While this situation is not always amenable to correction, it is of theoretical if not practical significance (particularly at this historical juncture) to understand the nature of energy wastage in photochemistry.

The problem is unique to the chemistry of excited states. In ground state chemistry, one is principally concerned with the nature of energy barriers characteristic of various types of reactions. Using a statistical mechanical analysis, one can calculate the number of molecules that will react per unit time (i.e. that will surmount these barriers) given the height of each barrier, the concentration of the various molecular species, probability factors, and the thermal energy available to the molecules. Normally barriers are high relative to the thermally available energy of the reactants. In photochemistry, electronic excited states more often than not have sufficient energy to react, for example by cleavage of weak bonds or by reactions which have a small 'activation energy'†, such as inter- or intra-molecular hydrogen abstraction[1], and yet such reactions are rarely totally efficient. It is therefore of considerable interest to enquire into the chemical mechanisms of the non-reactions as well as the reactions of excited states, in order to better understand the manner in which energy derived from light is utilized chemically. Such studies have no direct counterpart in ground state chemistry.

The simplest kinetic analysis is given in *Scheme 1*, where we assume that a

$$K^{\circ} \xrightarrow{h\nu} K^{\star}$$

$$K^{\star} \xrightarrow{k_r} P$$

$$K^{\star} \xrightarrow{k_d} K^{\circ}$$

$$\Phi_P = k_r/(k_r + k_d)$$

$$\tau_{K^{\star}} = (k_r + k_d)^{-1}$$

Scheme 1

reactive excited state $K^{\star}$ (multiplicity undefined for the moment) formed with 100 per cent efficiency partitions between conversion to product P with a rate constant k_r and decay to ground state of starting material K° with rate constant k_d. The quantum efficiency Φ_p for product formation and the lifetime of $K^{\star}$ are then as given in *Scheme 1*, and are related by $\Phi_P = k_r \tau_{K^{\star}}$. It is common practice to experimentally evaluate such rate constants k_r and k_d assuming this kinetic scheme governs the situation, based on conventional measurements of quantum yields[3] and of excited state lifetimes either directly by flash techniques[4] or indirectly from quenching studies[5].

However, it is increasingly evident that the kinetics are usually more complicated for photochemical reactions of most organic molecules in solution, and especially in ketone photochemistry. One possibility is illustrated in *Scheme 2*, in which an intermediate I is formed with 100 per cent efficiency from $K^{\star}$ with a rate constant k_r, followed by partitioning of the intermediate between formation of product P (rate constant k_p) and decay to ground state K° (rate constant k_d). In this situation, the lifetime of the excited state

---

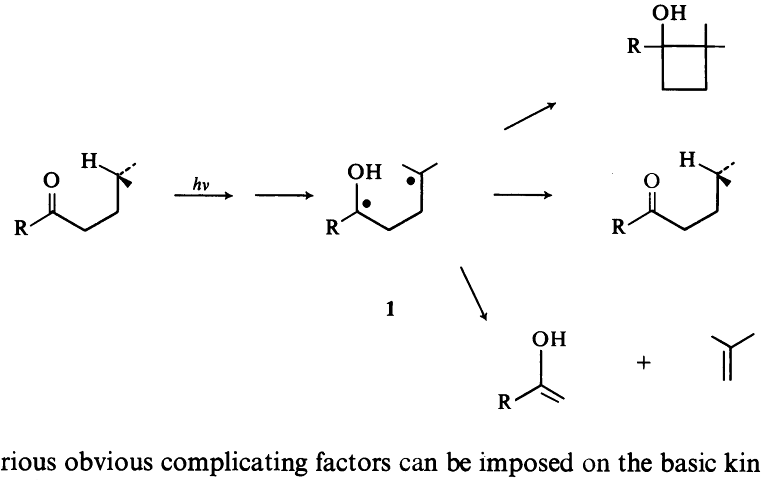
† There are obvious problems associated with the application of transition state theory to photochemical reactions[2]. The experimental quantity derived from the dependence of *rate constants* of excited state processes on temperature might be better termed simply the 'temperature coefficient'.

$$K^\circ \xrightarrow{h\nu} K^\star$$

$$K^\star \xrightarrow{k_r} I$$
$$I \xrightarrow{k_p} P$$
$$I \xrightarrow{k_d} K^\circ$$
$$\Phi_P = \Phi_I\, k_p/(k_p + k_d)$$
$$\tau_{K^\star} = (k_r)^{-1}$$

Scheme 2

$\tau_{K^\star}$ is determined solely by k_r ($\tau_{K^\star} = 1/k_r$) while Φ_p is determined by the partitioning ratio $k_p/(k_p + k_d)$. Accordingly, measurements of Φ_p and $\tau_{K^\star}$ give absolutely no information about the magnitudes of k_p or k_d, and additional experiments must be made to characterize the intermediate I and determine the partitioning ratio. The best known example of this kinetic situation is the Norrish Type II reaction of aliphatic and aromatic ketones. Wagner and others[6] have unequivocally demonstrated the intermediacy of 1,4-biradicals of type **1** which partition between cyclization to cyclobutanols, cleavage to give the typical Type II products and reverse H-transfer to regenerate starting material in its ground state. The reaction in the case of phenyl ketones occurs exclusively from triplet excited states, whose lifetime is determined exclusively by the rate constant k_r for intramolecular H-transfer[6].



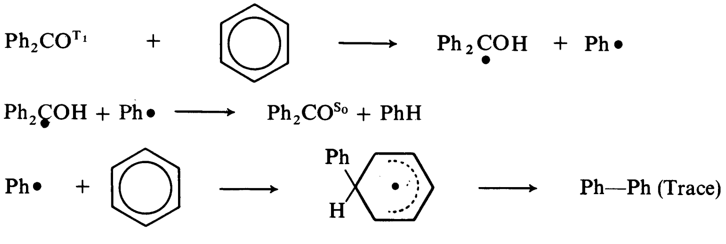
1

Various obvious complicating factors can be imposed on the basic kinetic outline in *Scheme 2*. For example, radiationless decay or light emission from the excited state can sometimes compete with formation of the intermediate I, in which case Φ_I is less than unity and $\tau_{K^\star}$ is less than $1/k_r$. As in the case of Type II reactions of dialkyl ketones, both singlet and triplet excited states can be reactive[6], with details of product formation (e.g. stereospecificity) dependent on multiplicity. Sometimes more than one reaction intermediate is involved in the reaction mechanism, each of which may partitition between reaction pathways in mechanistically significant ways. This appears to be the case in some reactions of cyclohexadienones, to be discussed later.

In the course of several completely independent studies of reaction mechanisms in ketone photochemistry in solution, we have been compelled by the experimental data to seriously consider a number of different types of energy wastage processes which will now be discussed. Most of these are probably of general occurrence in photochemistry, with subtle variations from system to system, although they by no means exhaust the possibilities. We have been forced to the conclusion that for ketones in solution energy wastage more often than not involves the reversible formation of discrete intermediates. The experimental evidence derives from the application of a variety of flash and steady state photochemical techniques to a number of systems. At least for the systems to be described, and perhaps throughout ketone photochemistry in solution, it appears that direct radiationless decay from spectroscopic (i.e. non-distorted) triplet states to the ground state is rarely an important kinetic process.

BENZOPHENONE AND RELATED KETONES IN BENZENE AND SUBSTITUTED BENZENES

The photochemistry of benzophenone has been extremely well studied[7]. Yet, when we began working in this area in 1969 there were some apparent inconsistencies in the literature that were mechanistically intriguing. Thus, although benzophenone (abbreviated B) was photochemically unreactive ($\Phi = 0 \pm 0.05$) in benzene compared to other solvents[8], benzophenone ketyl radical $Ph_2\dot{C}OH$ (abbreviated $BH^{\bullet}$) was reported[9] to be formed with $\Phi \sim 0.1$. The following scheme (*Scheme 3*) was proposed. The unprecedented reverse H-transfer from $BH\cdot$ to phenyl radicals $Ph\cdot$[9] is unusual given the very rapid rate of trapping of $Ph\cdot$ by benzene to give phenylcyclohexadienyl radicals[10], suggesting the possible operation of a cage process. Furthermore, H-abstraction from benzene by $^3B^\star$ is surprising considering the very low reactivity of benzene in such reactions even toward highly reactive radicals[11].



Scheme 3

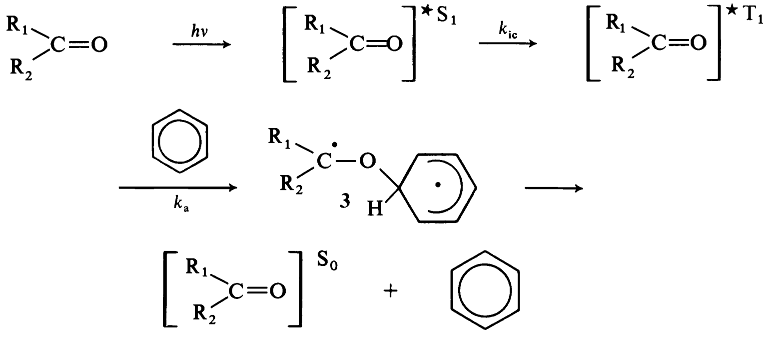
Even more interesting to us was the observation that the lifetime of $^3B^\star$ in benzene was 10 microseconds ($\pm 50\%$)[9], two orders of magnitude less than the triplet lifetime subsequently observed in fluorocarbon solvents at room temperature (0.7–1.0 ms)[12]. The observation of phosphorescence emission from $^3B^\star$ in fluorocarbon solvents at room temperature[12] ($\Phi_{phos} \sim 0.1$) was of the greatest significance, since it indicated the possibility of directly measuring triplet lifetimes in solutions under reaction conditions using luminescence techniques. Previously, in order to get triplet lifetimes in solution one had to resort to either (a) flash absorption studies which were frequently complicated by other absorbing transients[9, 13], (b) quenching experiments whose accuracy depends[5] on assumed values of k_q, or (c) extrapolations from phosphorescence measurements at low temperature in glasses. From values of Φ_{phos} and τ_{phos} for $^3B^\star$ in perfluoromethylcyclohexane[12] a radiationless decay constant k_d of $1.2 \times 10^3\ s^{-1}$ can be calculated, presumably a good approximation to this quantity in a truly inert solvent. Since the triplet decay rate in benzene is faster by two orders of magnitude, some additional interaction with the solvent must be occurring, which is ultimately unproductive as far as ketone disappearance is concerned. It was the nature of this interaction that we sought to elucidate.

While the discussion will centre around recent studies from our laboratory, it should be recognized that important contributions in this area have also been made in the last few years by Saltiel, Dedinas, Cohen, Steel and numerous others.

Reactive free radicals do not abstract hydrogen atoms from benzene, but rather add to the ring to form complexes of type **2**, as well documented from pulse radiolysis[14] as well as more conventional free radical investigations[11].

2

Taking our cue from a suggestion of Baum and Norman[15] concerning biacetyl photochemistry in phenylacetic acid, we suggested some time ago[16] that the primary interaction of $^3B^\star$ and other n, $\pi^\star$ ketone triplets in benzene was to form a sigma complex **3**. The main fate of this complex was to dissociate into benzene and the ketone in its ground state (*Scheme 4*), although other reaction modes were conceivable[16]. If k_a [benzene] is greater than the normal radiationless decay rate constant k_d, the net effect of benzene is to catalyse the decay of the ketone triplet to the ground state via **3**. This pathway for dissipation of electronic energy was proposed



Scheme 4

independently by Saltiel and his co-workers[17], who found support for the hypothetical process in the reversible addition of benzoyloxy radical ($PhCO_2^{\cdot}$) to benzene[18], and also in the interaction of n, π★ ketone triplets with alkenes which leads to concomitant deactivation and *cis–trans* isomerization according to a Schenck-type mechanism[19].

We sought experimental verification of the proposed scheme (*Scheme 4*) from a standard structure–reactivity correlation, between (a) the rate constants k_a for interaction of $^3B^{\star}$ and other ketone triplets with a series of substituted benzenes, and (b) parameters which reflect the electronic character and orientation of substituents on the benzene ring of the solvent. This approach requires determination of lifetimes of $^3B^{\star}$ and other triplets in solution in the various aromatics. In order to make meaningful comparisons of data in different solvents, it is obvious that the purity of materials is critical since adventitious quenchers could decrease lifetimes. Throughout our work we have gone to great pains to repeatedly purify materials by a variety of methods described in the original papers, using the empirical criterion that the 'best' quality of material for our purposes was that which afforded the longest experimental lifetimes. Previous studies[9] indicated that we should expect triplet lifetimes in the short microsecond or even submicrosecond time range in neat aromatic solvents. For such measurements, the conventional microsecond flash apparatus of the classic Porter design[20] is inadequate, and even modified units with flash decay times of a few microseconds[9,21] have a large error associated with triplet lifetimes of less than 10 μs. Accordingly, we turned to nanosecond flash techniques to accurately measure absolute triplet lifetimes in these systems.

Initial experiments were made in collaboration with Dr Michael Topp at the Royal Institution[22] and later at Bell Telephone Laboratories, utilizing the newly developed nanosecond laser flash method[22], and these results are given in *Table 1*, column 3. Subsequent experiments were made more conveniently using single photon counting[23]. This technique, usually used to measure fluorescence lifetimes, is ideal for measuring triplet lifetimes in the range 10^{-4} to 10^{-7} s as long as the triplet is at least weakly emissive in solution, which is fortunately the case with $^3B^{\star}$ in benzene and related solvents[12,24]. Our investigations at NYU have been made in collaboration with Professors Arthur Halpern[25] and Nicholas Geacintov[26], and the results are summarized in *Table 1*, column 4. Two different sets of apparatus have been used for this work. On a given unit, using different batches of purified materials, lifetimes are generally reproducible within ten per cent, although lifetimes measured most recently[26] are slightly shorter than those obtained initially[25]. Relative lifetimes, however, are largely unchanged.

A different approach uses the aromatics as quenchers of ketone triplets under conditions where the triplets are relatively long-lived. Fluorocarbons are not very satisfactory for such experiments because of their poor solvent properties and the highly variable purity of commercially supplied materials[12]. We have found that purified carbon tetrachloride[27], in which $^3B^{\star}$ has a lifetime of 120μs[26], is fine for such experiments, while Steel has utilized acetonitrile in related studies[1,24]. Using straightforward microsecond flash techniques[20] and monitoring the decay of either triplet absorption or emission, absolute rate constants for quenching were obtained from lifetimes as a

Table 1. Quenching of benzophenone triplets by substituted benzenes at room temperature

Aromatic[a]	Ionization potential[b], eV	$1/\tau, s^{-1}$ Laser flash photolysis[c]	Single photon counting[d]	k_a in CCl_4^e, $M^{-1} s^{-1}$ Triplet absorption	Triplet emission	$1/\tau, s^{-1}$, calcd[f]
C_6H_5Br	8.98	—	4.7×10^5	—	—	—
C_6H_5Cl	9.07	—	1.6×10^5	—	—	—
$1,4\text{-}C_6H_4F_2$	9.15	—	2.3×10^5	—	3.4×10^4	3.4×10^5
C_6H_6	9.25	1.0×10^5	1.07×10^5	0.8×10^4	2.4×10^4	2.6×10^5
C_6D_6	—	0.8×10^5	1.07×10^5	—	—	—
C_5H_5N	9.25	—	1.15×10^5	—	—	—
C_6H_5F	9.26	—	1.08×10^5	—	2.9×10^4	3.1×10^5
$1,3,5\text{-}C_6H_3F_3$	9.30	—	4.9×10^4	—	—	—
			$(8.0 \times 10^4)^g$	—	—	—
$1,2\text{-}C_6H_4F_2$	9.31	—	$2.8 \times 10^{5\,g}$	—	—	—
$1,2,4\text{-}C_6H_3F_3$	9.37	—	$3.5 \times 10^{5\,g}$	—	—	—
$1,2,4,5\text{-}C_6H_2F_4$	9.39	—	5.8×10^5	—	1.6×10^5	1.5×10^6
$(C_6H_5)_2CO$	9.45	—	$1.6 \times 10^{5\,h}$	—	3.3×10^5	—
$C_6H_5CF_3$	9.68	—	4.9×10^4	—	1.6×10^4	1.3×10^5
			$(7.5 \times 10^4)^g$			
C_6H_5CN	9.71	—	2.1×10^6	—	—	—
C_6HF_5	9.84	—	6.8×10^5	8.0×10^4	2.4×10^4	2.2×10^6
C_6F_6	9.97	1.4×10^6	1.6×10^6	3.5×10^5	3.5×10^5	2.8×10^6

[a] Purified as described in the original references.

[b] Photoionization values from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Hesson, K. Draxl and F. H. Field, 'Ionization potentials, appearance potentials and heats of formation of gaseous positive ions', US Department of Commerce, National Bureau of Standards (1969).

[c] Ref. 22. Aromatic is solvent.

[d] Ref. 25 except where indicated. Aromatic is solvent. Benzophenone concentration 3×10^{-3} *M*.

[e] Ref. 27. Benzophenone concentration 10^{-2} *M*.

[f] Lifetime in neat aromatic solvent calculated from data for quenching of emission and the density of the pure liquid.

[g] Ref. 26.

[h] Ref. 39.

function of concentration of the aromatic (equation 1)[27]. These values of k_a are given in the fifth and sixth columns of *Table 1*.

$$1/\tau = 1/\tau^\circ + k_a[\mathrm{Ar}] \tag{1}$$

From these values of k_a, lifetimes of $^3\mathrm{B}^\star$ in the neat aromatic can be calculated from the concentration of the aromatic in the neat liquid. Using the data from phosphorescence quenching, which are considered to be more accurate than absorption data since only triplet processes are being monitored, these extrapolated values are given in *Table 1*, last column. The excellent agreement between the calculated and experimental lifetimes in neat aromatic clearly shows that quenching of $^3\mathrm{B}^\star$ by the aromatic is almost entirely a bimolecular process even in the aromatic as solvent. Clearly, some kind of complex(es) must be formed on interaction of $^3\mathrm{B}^\star$ with the series of benzenes in *Table 1*, although attempts to observe complexes directly using nanosecond and microsecond flash techniques have thus far been unsuccessful. In all solvents except C_6F_6, a long-lived transient which decays by second order kinetics is observed. While this is most likely the ketyl radical BH$^\bullet$, we cannot exclude other assignments at this time. For example, the sigma complex **3** is expected to have an absorption spectrum similar to that of BH$^\bullet$ in the region 500–550 nm. In benzene, the absorption spectrum of this second transient is very similar to that of BH·[9, 13], although there are minor differences. Assuming it is BH·, we find that its quantum yield at 0.01 *M* B in benzene is 0.052[28]; a value of 0.022 has been recently determined by Dedinas[21].

From the data in *Table 1*, some conclusions as to the nature of the interaction of $^3\mathrm{B}^\star$ and benzenes can be deduced. Because of the current interest in exciplexes and charge transfer interactions in quenching processes[29], it is fashionable to construct plots of log k_q versus the ionization potential of the quencher and/or the quenchee. If charge transfer toward the carbonyl compound, symbolized by $(\mathrm{Ar}^+ \ldots \mathrm{B}^-)^\star$, is occurring to a significant degree in our systems, the relationship in equation 2 should be obeyed[30]. The first

$$\Delta G_c = -{}^3\Delta E_{0,0} + IP_D - E(\mathrm{A}^-/\mathrm{A}) + C \tag{2}$$

term on the right is the triplet excitation energy (E_T) of the ketone, the second is the ionization potential (*IP*) of the aromatic, and the third is the reduction potential of the ketone. Cohen and Guttenplan[30] have indeed shown that for seventeen potential electron donors, plots of log k_q versus IP_D give two straight lines of negative slope (*Figure 1*). One line includes a series of aliphatic amines, sulphides and ethers, while the line of steeper slope includes mainly aromatic amines, ethers and hydrocarbons, including benzene. The larger slope in the latter group was interpreted in terms of a higher degree of charge transfer to the carbonyl compound[30]. That benzene can function as an electron donor toward ketone triplets is supported by the much more rapid decay of triplets of α-trifluoroacetophenone versus acetophenone in benzene and alkylbenzenes[31], as well as by the very rapid quenching of decafluorobenzophenone (DFB) triplets by benzene ($k_q = 1.6 \times 10^8\, M^{-1}\, s^{-1}$)[32], which corresponds to a lifetime of only 0.5 ns for $^3\mathrm{DFB}^\star$ in benzene! Other recent data for a series of substituted benzophenones supports the

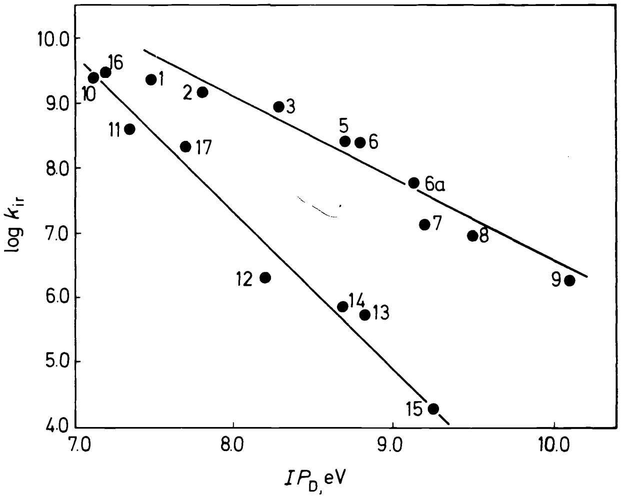


Figure 1. Relation of rate constant for quenching of benzophenone triplet to ionization potential of a series of aliphatic (top line) and aromatic (bottom line) donors. We thank Professor Cohen and the *Journal of the American Chemical Society* for permission to reproduce this figure from ref. 30.

charge-transfer concept in that quenching by benzene is enhanced by electron-withdrawal and diminished by electron donation in the benzophenone component[33].

Figure 2 is our previously-published[25] plot of the initial set of data from *Table 1* for quenching of $^3B^\star$ by benzenes with electron-withdrawing groups. While the plot of log k_q versus *IP* does not show a good linear correlation, there is an unmistakeable trend. The most efficient quenchers in this series were the benzenes with largest *IP*, which are also presumably those with the greatest electron affinity. This suggested the possibility that (partial) charge-transfer was occurring, but in the opposite sense from that normally observed, i.e. with the ketone triplet as donor and the substituted benzene as acceptor $(B^+ \ldots Ar^-)^\star$. The data for quenching of $^3B^\star$ by all the benzenes studied by Cohen and us, plotted versus *IP*, are shown in *Figure 3*. This plot leaves no doubt that at least two different quenching mechanisms are in operation, one which dominates for strong electron donors (e.g. $PhNR_2$, PhOR) and another which dominates for strong electron acceptors (e.g. C_6F_6). A similar curved plot would of course result if log k_q were plotted against Hammett's σ or related parameters.

Our initial data were subsequently analysed by Loutfy and Yip[34] along with analogous data for quenching of acetone triplets by a similar set of substituted benzenes. They showed that data for benzene, pyridine and monohalobenzenes neatly fit a correlation of log k_q versus *IP* (*Figure 4*), suggesting that these benzenes function as electron donors toward ketone triplets, as in Cohen's study[30]. The data for quenching by the polyfluorobenzenes and benzonitrile were shown to correlate with halfwave reduction potentials of the quenchers (*Figure 5*), which was taken as support for our earlier postulate[25] of reverse charge-transfer. However, our original[25] data for quench-

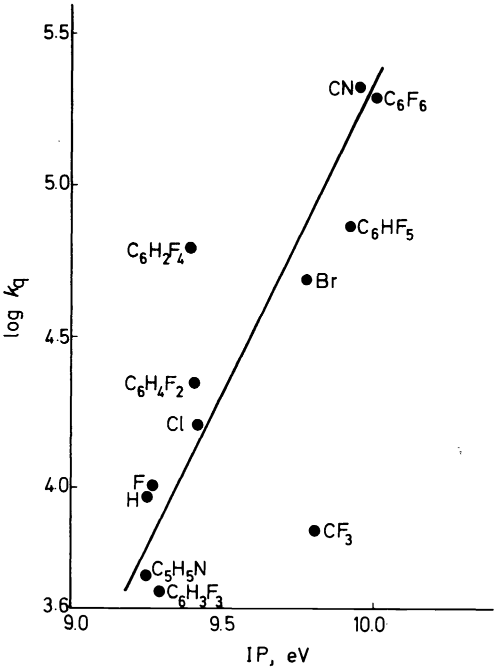


Figure 2. Plot of logarithms of rate constants for quenching of benzophenone triplet versus ionization potentials of a series of electron-deficient benzenes.

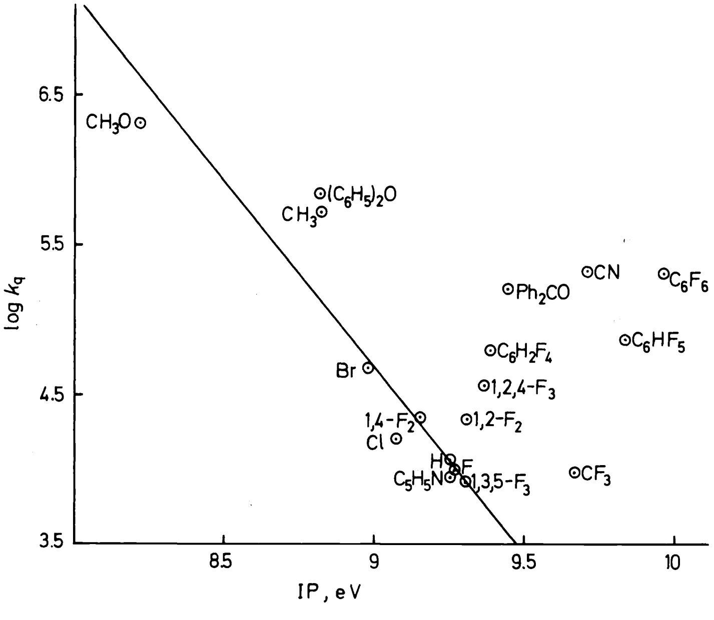


Figure 3. Quenching of benzophenone triplet by substituted benzenes. Plot of log k_q versus ionization potentials of the benzenes.

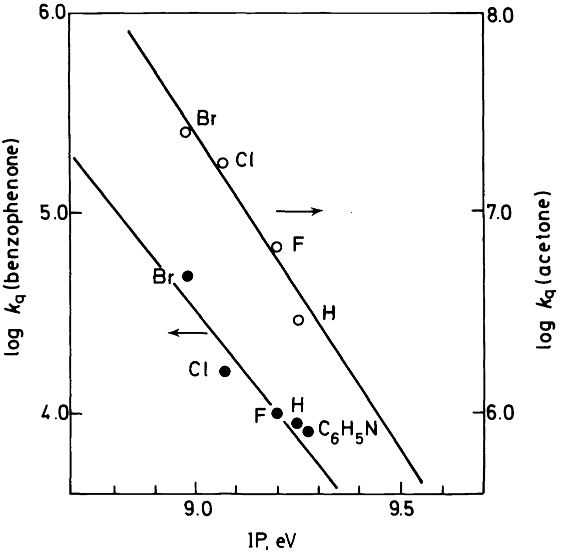


Figure 4. Rates of quenching of benzophenone and acetone triplets by some substituted benzenes. Correlation of log k_q and ionization potential. Reproduced by permission of the National Research Council of Canada from ref. 34.

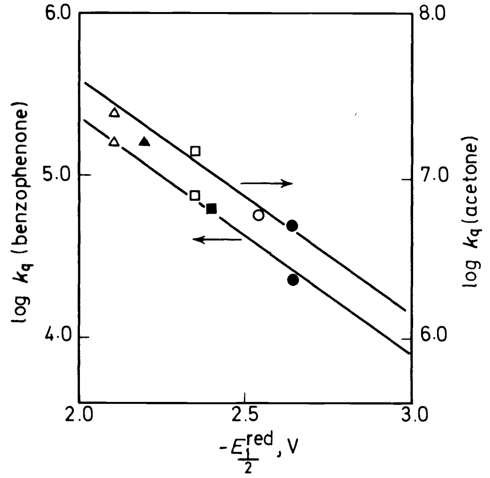
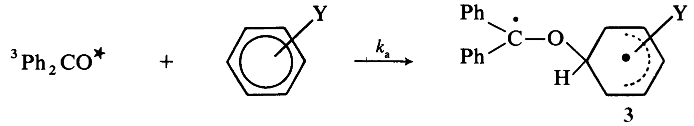


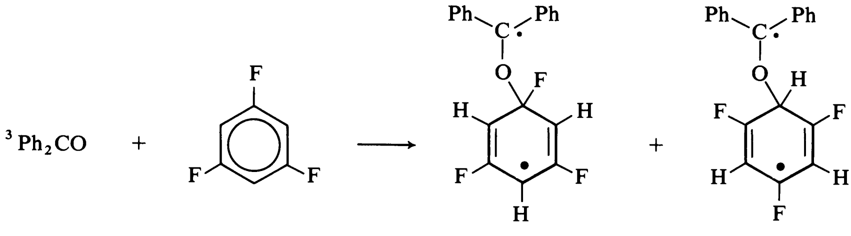
Figure 5. Rates of quenching of benzophenone and acetone triplets by benzenes with electron-withdrawing substituents. Correlation of log k_q and reduction potentials. Reproduced by permission of the National Research Council of Canada from ref. 34.

ing by $PhCF_3$ and 1,3,5-$C_6H_3F_3$, which show large unexplained deviations from the line in *Figure 2*[25], were neither included in the Loutfy–Yip plots nor mentioned in their text[34]. The failure of the data to be satisfactorily correlated by either ionization or reduction potentials convinced us that the reverse charge-transfer mechanism proposed for quenching of $^{3}B^{\star}$ by the group of polyfluorobenzenes, PhCN and $PhCF_3$, was incorrect. We now suggest that for aromatic quenchers whose *IP* is sufficiently large that complexes of the type $(Ar^+ \ldots B^-)^\star$ are energetically inaccessible, quenching occurs via formation of sigma diradical complexes **3**, as first postulated[18].



3

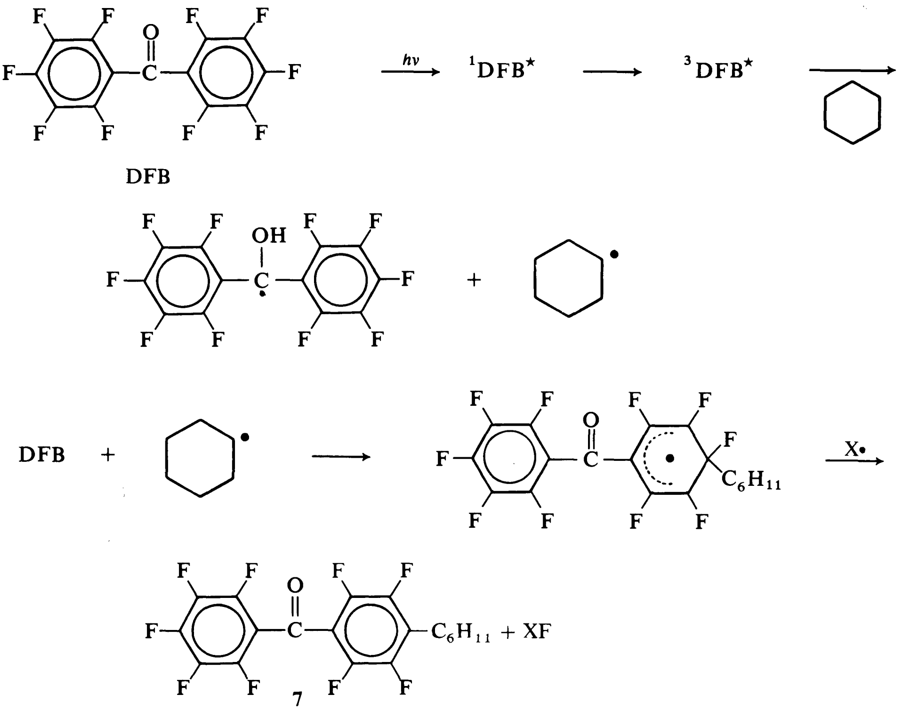
The stability of such complexes, and therefore the rate constants for their formation, should depend on the stabilization of the cyclohexadienyl radical moiety by substituents. This will be greatest for substituents located directly on the ring, and *ortho* or *para* to the site of substitution. Thus, little stabilization is provided by the CF_3 group, accounting for the low rate of quenching by $PhCF_3$. The low reactivity of 1,3,5-$C_6H_3F_3$ can be understood if $^3B^\star$ were to attack the ring preferentially at a fluorine-bearing carbon to give complex **4** as opposed to **5**; in **4**, the remaining fluorines are not in proper positions for stabilization of the cyclohexadienyl radical. Support for this



4 **5**

postulate comes from studies of radical reactions with fluorobenzenes which proceed by the usual addition–elimination route[35]. High reactivity of C_6F_6 compared to C_6H_6 is observed as well as a strong tendency in mono- and di-fluorobenzenes for reaction at a fluorine-bearing carbon, with eventual loss of fluorine[35]. A further illustration comes from the photolysis of decafluorobenzophenone in cyclohexane[32] which afforded high yields of *ortho*- and *para*-cyclohexylnonafluorobenzophenone (**6** and **7**), which are products of replacement of fluorine by cyclohexyl radicals, as shown in *Scheme 5*. This effect may arise from intrinsic properties of the C—F bond[36], as reflected also in the regiospecificity of cycloadditions to unsymmetrical fluoroolefins such as 1,1-difluoro-2,2-dichloroethylene[37] where initial bond formation occurs at the fluorine-bearing carbon.

Recent data from our laboratories tend to support this hypothesis. Thus, although 1,3,5- and 1,2,4-trifluorobenzene have nearly identical ionization (and probably also reduction) potentials, their rates of quenching of $^3B^\star$ are very different[26]. This was predicted, since in the 1,2,4-compound at least one fluorine is in a suitable stabilizing position in the diradical complex.



Scheme 5

From *Figure 3*, it appears that the predominant quenching mechanism for the 1,3,5-compound is charge-transfer, while the alternative mechanism operates for the 1,2,4-compound. We predict on this basis a relatively long lifetime for $^3B^\star$ in 1,3-$C_6H_4F_2$ compared to its 1,2- and 1,4-isomers, but unfortunately we have not been able to prepare the 1,3-compound in sufficient purity for meaningful lifetime measurements. Experiments using the three corresponding dicyanobenzenes are in progress.

Further support for these two quenching mechanisms comes from studies of other fluorine-substituted benzophenones. Triplet lifetimes by single-photon counting are given in *Table 2*. The rapid quenching by benzene of 4-trifluoromethylbenzophenone and decafluorobenzophenone (DFB) triplets compared to $^3B^\star$ is totally consistent with charge-transfer interactions of the type $(K^- \ldots\ldots Ar^+)^\star$.

In contrast, all three triplets have similar lifetimes in C_6F_6; for DFB, the triplet lifetime is three orders of magnitude *greater* than in benzene! Since the stability of diradical complexes of structure **3** should be only minimally affected by substituents on the benzophenone moiety, the observations are consistent with the suggestion that quenching of these triplets by C_6F_6 involves the formation of such complexes. One would be hard-pressed to rationalize these results by the reverse charge-transfer hypothesis, i.e. $(K^+ \ldots\ldots Ar^-)^\star$.

The quenching data require further elaboration as in *Scheme 6* in which

Table 2. Triplet lifetimes by single photon counting

Ketone	Solvent	
	Benzene	Hexafluorobenzene
Ph_2CO	10.0 μs[a]	0.6 μs[a]
$4\text{-}CF_3\text{-}Ph_2CO$	1.4 μs[b]	0.4 μs[b]
$(C_6F_5)_2CO$	0.5 ns[c]	0.21 μs[d]

[a] Ref. 25 [b] Ref. 41 [c] Ref. 32 [d] Ref. 26

$$^3K^\star + Ar \underset{k_{-\mathrm{dif}}}{\overset{k_{\mathrm{dif}}}{\rightleftharpoons}} \underset{\mathrm{I}}{^3K^\star\text{----}Ar} \xrightarrow{k_c} \underset{\mathrm{II}}{\text{complex}} \longrightarrow K^\circ + Ar^\circ$$

$$k_q = (k_{\mathrm{dif}}/k_{-\mathrm{dif}})k_c$$

Scheme 6

$^3K^\star$.... Ar represents some sort of collision complex or exciplex (I) which is in diffusional equilibrium with uncomplexed $^3K^\star$. This species then proceeds to the charge-transfer or diradical complex (II) which eventually collapses to ground state ketone. In this case, the rate constant for quenching k_q would be given by $(k_{\mathrm{dif}}/k_{-\mathrm{dif}})k_c$ and would reflect the stability of II through variations mainly in k_c. Note that $k_q (= k_a)$ is generally orders of magnitude less than diffusion controlled in these systems.

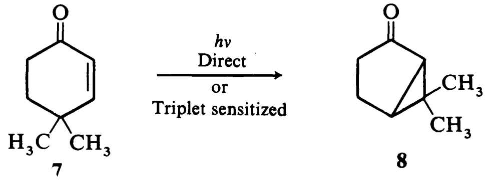
The temperature coefficient of the decay of $^3B^\star$ in benzene was determined from the temperature dependence of the triplet lifetime as measured by laser flash photolysis[28]. Preliminary data give a value of 1.3 ± 0.1 kcal/mole. Similar experiments in C_6F_6 provide a value of 5.8 ± 0.2 kcal/mole. The small value in benzene could be simply due to changes in solvent viscosity with temperature[1]. At least, this value rules out participation by equilibrium concentrations of $^1B^\star$ in the quenching of excited benzophenone by benzene at room temperature. If the singlet were involved, an 'activation energy' of at least 5 kcal/mole would be required[38].

We[28,39] and others[17,40] have further found that the decay of benzophenone and related triplets in benzene and substituted benzenes is accompanied by a very inefficient reaction to give benzpinacol and biaryls, $\Phi \leqslant 0.005$. This reaction decreases in efficiency in the solvents in *Table 1* as the lifetime of $^3B^\star$ decreases[28], indicating that the reaction does *not* occur *via* the intermediate formed in the quenching process. It now seems that H-abstraction from the aromatic ring (in benzene $k_{\mathrm{abs}} = 16\,M^{-1}\,s^{-1}$)[17,39], while energetically unfavourable, can compete (barely) with the deactivation mechanism.

In summary, we suggest that energy wastage on excitation of ketone triplets in aromatic solvents occurs by two mechanisms: (a) charge-transfer quenching, and (b) formation of a sigma diradical complex. Benzene has long been considered an inert solvent for photochemical reactions, and has probably been used more often than any other solvent in solution photochemistry. It should be recognized that the reactivity of ketone triplet states can be profoundly affected by benzene even though product formation involving benzene is extremely inefficient. Because of the duality of mechanisms available, almost all substituted benzenes are better quenchers of ketone triplets than benzene itself.

SELF-QUENCHING OF KETONE TRIPLETS

Following the pioneering research of the late Professor Förster[42], the quenching of excited singlet states by the ground state of the same compound with formation of singlet excimers has achieved prominence in photochemistry. Singlet excimers play a role in the photochemistry of many aromatic hydrocarbons and heterocycles, including substances of biochemical importance such as nucleotides and nucleic acids[43]. Until recently, however, very little attention had been paid to self-quenching effects in ketone photochemistry. Chapman and Wampfler[44] first pointed out that this could be a significant process on the basis of their observation that the efficiency of the triplet-sensitized conversion of 4,4-dimethylcyclohexenone **7** to the bicyclic ketone **8** was decreased as the sensitizer concentration increased. Plots of $\Phi_0/\Phi_{\text{sens}}$ versus [sens] were linear, and from the slopes of such plots approximate values of the rate constants k_{sq} for the interaction of $^3S^\star$ and S^0 could be obtained, making some reasonable assumptions. For four ketones, all of whose lowest triplet states have $^3\pi,\pi^\star$ configurations, values of k_{sq} ranged from 10^8 to 6×10^{10} M^{-1} s^{-1} [44]. The authors suggested the possibility that excimers might be generated by the interaction of $^3S^\star$ and S^0. No such effects were observed using typical $^3n,\pi^\star$ sensitizers such as benzophenone and acetophenone. Besides raising important questions relating to theory and mechanism, these results provided a warning about the indiscriminate use of triplet sensitizers.



Not long afterward, evidence was reported that the primary process on photoexcitation of Michler's ketone **9** in benzene involved a reaction between $^3MK^\star$ and MK^0 [45]. It was suggested that a complex was formed which might have charge-transfer character, and which partitioned between decay to two ground state molecules and hydrogen transfer to give radicals **10** and **11**. From quenching kinetics, the rate constant k_{sq} could be estimated as 1×10^9 M^{-1} s^{-1}.

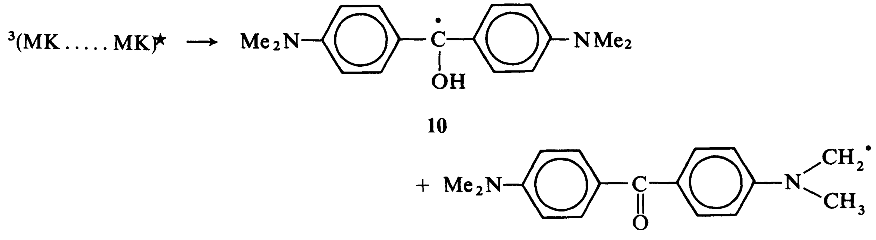
An analogous interaction between $^3MK^\star$ and benzophenone ground states, which could involve a triplet exciplex, was also discovered[46].

For other reasons, we had been interested for some time in the photochemistry of MK and had been measuring its triplet decay rates by flash technique in various solvents[41, 47]. We discovered at the same time the above

$$\mathrm{MK^0} \xrightarrow{h\nu} {}^1\mathrm{MK}^\star \longrightarrow {}^3\mathrm{MK}^\star$$

$${}^3\mathrm{MK}^\star + \mathrm{MK^0} \xrightarrow{k_{sq}} {}^3(\mathrm{MK}\ldots\ldots\mathrm{MK})^\star$$

$${}^3(\mathrm{MK}\ldots\ldots\mathrm{MK})^\star \longrightarrow 2\,\mathrm{MK^0}$$



10

11

reports appeared, that these rates were dependent on MK concentration and our data unequivocally required the inclusion of a self-quenching term in the decay kinetics.

$$1/\tau_{\mathrm{obs}} = 1/\tau^0 + k_{\mathrm{sq}}[\mathrm{MK^0}] \tag{3}$$

From our flash data, absolute values of k_{sq} could be obtained, and these are given in *Table 3* along with similar data for 2-acetonaphthone **12** and

Table 3. Self-quenching of ketone triplets

Ketone	Solvent	k_{sq}, $M^{-1}\,s^{-1}$
Michler's ketone (**9**)[a]	Benzene	$1.3 \pm 0.2 \times 10^8$
	Carbon tetrachloride	$7.6 \pm 0.9 \times 10^7$
	2-Propanol	$2.0 \pm 0.4 \times 10^7$
2-Acetonaphthone (**12**)[a]	Benzene	$2.5 \pm 0.3 \times 10^5$
	Carbon tetrachloride	$2.6 \pm 0.4 \times 10^5$
	Cyclohexane	$8.4 \pm 0.5 \times 10^5$
Benzophenone	Benzene	$1.6 \pm 0.2 \times 10^5$ [b]
		$4.3 \pm 0.1 \times 10^5$ [c]
	Carbon tetrachloride	$3.2 \pm 0.3 \times 10^5$ [b]
		2.2×10^5 [c]
	Water	1.0×10^8 [d]
	Vapour phase	5.0×10^7 [e]
Anthraquinone	Vapour phase	4.3×10^8 [e]
Thiobenzophenone	Cyclohexane	4.2×10^9 [f]
Michler's thione	Cyclohexane	2.9×10^9 [f]
Thioxanthone	Benzene	$2.3 \pm 0.5 \times 10^9$ [g]

[a] Ref. 47 [b] Ref. 28 [c] Ref. 48 [d] Ref. 49 [e] Ref. 50 [f] Ref. 51 [g] Ref. 52

benzophenone[28]. For MK and ketone **12**, whose lowest triplets have π,π★ or charge-transfer configurations, the observation of self-quenching was not surprising on the basis of Chapman's data[44]. However, we were initially surprised to see the same effect with purified benzophenone in a variety of media. Singer and co-workers have independently observed[48] self-quenching of benzophenone triplets in benzene and CCl_4, while the effect in aqueous solution is very large (perhaps because of the formation of aggregates) according to Ledger and Porter[49]. It is noteworthy that the magnitude of

k_{sq} for Ph_2CO, a typical n,π★ triplet, is not very different from that for **12**, a typical π,π★ triplet, in the two solvents (benzene and CCl_4) in which data for both triplets are now available. Hidden in the literature was a report several years ago[50] of self-quenching of delayed fluorescence in the vapour phase from benzophenone as well as anthraquinone, from which the values of k_{sq} in *Table 3* could be evaluated.

There are several implications of these observations. The first has to do with the efficiency of triplet-sensitized photochemical reactions. In the presence of an acceptor of triplet excitation, the lifetime of a sensitizer triplet is given by equation 4, where $1/\tau^0$ is the limiting decay rate of the sensitizer

$$1/\tau_{sens} = 1/\tau^0 + k_{sq}[S^0] + k_{et}[A^0] \tag{4}$$

$$\Phi_{ET} = k_{et}[A^0]\,\tau_{sens} \tag{5}$$

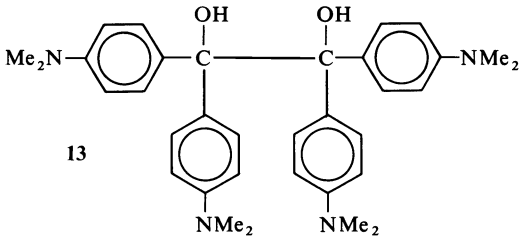
triplet at low sensitizer concentrations in the absence of the acceptor A, and k_{et} is the rate constant for transfer of triplet excitation. It is clear from equations 4 and 5 that the efficiency of energy transfer depends on the relative magnitudes of $1/\tau^0$, k_{et} and the concentrations of sensitizer S^0 and acceptor A^0. For all of these ketone sensitizers, whether their lowest triplets have n,π★ or π,π★ configurations, self-quenching may well compete with energy transfer even when the latter is nearly diffusion-controlled. This is especially true if the usual precautions are taken to ensure that the exciting light is absorbed by the sensitizer and not by the acceptor, i.e. that $[S^0] > [A^0]$[5]. In qualitative sensitization studies, it is not uncommon to use standard sensitizers such as benzophenone or acetophenone in quantities as large as solubility will allow, which will of course optimize self-quenching. Much effort is now being made in the use of modified aceto- and benzophenones as sensitizers of photobiological reactions in aqueous solution[53]; it may be that self-quenching is also very important in these systems. It has been customary to account for inefficiencies in triplet-sensitized reactions in terms of inefficient intersystem crossing of the sensitizer, reduced rate constants for energy transfer because of the relative triplet excitation energies of sensitizer and acceptor (i.e. $E_{TS} < E_{TA}$), and/or inefficient reaction modes of acceptor triplets[54]. While none of these factors can be neglected, one must also now consider sensitizer self-quenching, which in many cases may prove to be the dominant energy wastage process. In quantitative studies of triplet energy transfer, it is necessary to explicitly consider or determine the importance of sensitizer self-quenching, and many data already in the literature need to be reevaluated on this basis. For most systems, there will usually be an intermediate sensitizer concentration which gives optimum sensitization efficiency.

The question of greatest theoretical importance relates to the mechanism(s) of self-quenching of ketone triplet states. It has been suggested in several places that a triplet excimer might be formed on interaction of a triplet excited state of a ketone and its ground state[39, 44, 45, 47]. However, there are theoretical factors which suggest that triplet excimers should have very small binding energies compared with the corresponding singlet excimers[42], and attempts to observe triplet excimers by luminescence have largely been unsuccessful[42, 55]. It is suggested that 'effective excimer interaction in the triplet state is to be expected only if the charge transfer interaction is greater than in aromatic hydrocarbons like benzene and naphthalene[42]. The variations in k_{sq} in *Table 3* do not permit any firm conclusions. It certainly would be of interest to determine k_{sq} for a given ketone as a function of solvent polarity, but no such study has been reported thus far. We have approached the problem empirically, undaunted by the theoreticians, and have attempted to detect excimers using flash techniques in the case of Michler's ketone[41, 47]. We have not detected any changes in the shape of the absorption and emission spectra of MK in benzene and CCl_4 as a function of MK concentration. The only encouraging note is that a long-lived transient which decays by first-order kinetics in benzene and CCl_4 has been detected by absorption between 500 and 550 nm using the microsecond flash technique, with $k_d = 1.7 \times 10^3\ s^{-1}$ in benzene and $1.8 \times 10^2\ s^{-1}$ in CCl_4[47]. The decay rates are much slower than those of the triplet under these conditions (as measured by phosphorescence decay) and are distinguishable from the second order decays of radicals **10** and **11**. Whether this transient is an excimer or not is still undecided. A firm assignment awaits the completion of additional experiments.

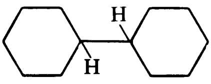
The final point is that the interaction of ketone triplets and their ground states may lead to new products. We have shown that benzophenone ground state is capable of donating a hydrogen atom to $^3B^\star$ to give $Ph_2\dot{C}OH$ and ultimately benzpinacol[28, 39]. Thus, plots of $(\Phi_{pinacol})^{-1}$ versus $[Ph_2CO]^{-1}$ are linear in benzene as well as CCl_4[28, 39, 56]. Mechanistically, the kinetic data are interpretable either in terms of partitioning of a triplet excimer between transfer of a hydrogen atom (minor process) and decay to two ground state molecules (major process), or in terms of competitive H-abstraction and decay without involving an excimer[39]. Studies with labelled benzophenone and labelled benzene are consistent with these mechanisms[28].

Implications as to product formation for self-quenching of MK are evident from earlier work[45], where reactions ascribable to the intermediate radicals **10** and **11** have been observed. There was an implication[45] that the formation of **10** and **11** from $^3MK^\star$ and MK^0, and the ability of solvents to trap these radicals and regenerate ground state MK, could explain the solvent effect on the photoreactivity of MK observed some time ago by Porter and Suppan[57]. They found that MK was photoreactive in cyclohexane but not in 2-propanol[57]. Inversion in the ordering of the two lowest triplet states (n, $\pi^\star$ and CT) in the two solvents was postulated, consistent with spectral data, with the unreactive $^3CT^\star$ state as the lowest triplet in 2-propanol. While the intermediacy of **10** and **11** could possibly account for the Porter–Suppan observations at moderate to high MK concentrations, it cannot explain the observations which were made[57] at 10^{-5} *M* MK since one can calculate using our value of k_{sq} that self-quenching will be relatively unimportant kinetically under these conditions.

Some recent results from our laboratory[41] help to clarify some points regarding the photochemistry of MK, as well as raise additional questions. First of all, it should be recognized that commercial deep-blue MK is quite impure, and repeated recrystallization affords nearly colourless crystals. It is this purified material which we have used in all of our work. Previous studies of MK[56–59] did not include isolation of products, so that it was never really established what the photochemistry of MK was when irradiated in dilute solutions. Part of the difficulty arises from the necessity of doing irradiations in very dilute solution ($\sim 10^{-5}\,M$) because of the efficient self-quenching[47] and the concomitant chemistry[4,5]. We have been able to establish that continued irradiation of MK in 2-propanol at 350 nm slowly gives Michler's pinacol **13**, isolated and identified by comparison directly with authentic material. At 254 nm in 2-propanol, surprisingly, MK disappears at a much more rapid rate to give pinacol **13**, which itself disappears on further photolysis. In cyclohexane, the reaction seems more complex. The only product which has been definitely identified is bicyclohexyl **14**, indicating H-abstraction from cyclohexane has occurred. Quantum yields for these processes have yet to be measured. We have, however, determined triplet yields for MK in a characteristic hydrocarbon solvent (benzene) and a polar solvent (2-propanol), by a standard triplet counting experiment. We use 1,3-cyclohexadiene (CHD) as quencher and monitor the yield of CHD dimers using gas–liquid chromatography from competitive irradiation at 366 nm of thoroughly degassed solutions of MK and benzophenone on an optical bench. We find that in benzene, Φ_{ST} for MK is 1.01 ± 0.08 in benzene (average of five runs), in agreement with Hammond and Lamola[60], but only 0.26 ± 0.04 in 2-propanol (average of three runs). This effect of solvent polarity on Φ_{ST} has precedent in the work of Cohen on *p*-aminobenzophenone (PAB). Thus, to some extent, reactivity variations of MK and PAB in different solvents are attributable simply to changes in Φ_{ST}. It is not yet possible to say whether this is sufficient to account for all of the observations. The cause of the peculiar (and to some extent contradictory) wavelength effects seen earlier[57–59] and now by us is still obscure. In any event, energy wastage in the photochemistry of MK involves at least two processes: (1) efficient self-quenching of the triplet, and (2) deactivation of the singlet in polar solvents.



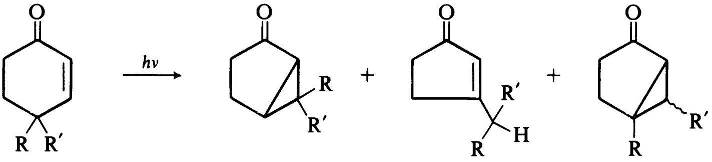
13



14

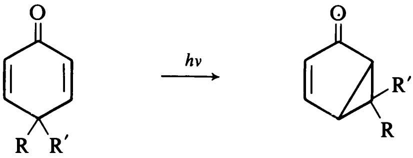
PHOTOCHEMICAL REARRANGEMENTS OF CYCLOHEXENONES

We now turn our attention to predominantly organic aspects of ketone photochemistry. Despite the superficial similarity of their photochemical transformations, the rearrangement of 4,4-disubstituted cyclohexenones **15** to ketones with structures **16**, **17** and **18** is a very inefficient process ($\Phi \sim 0.01$),



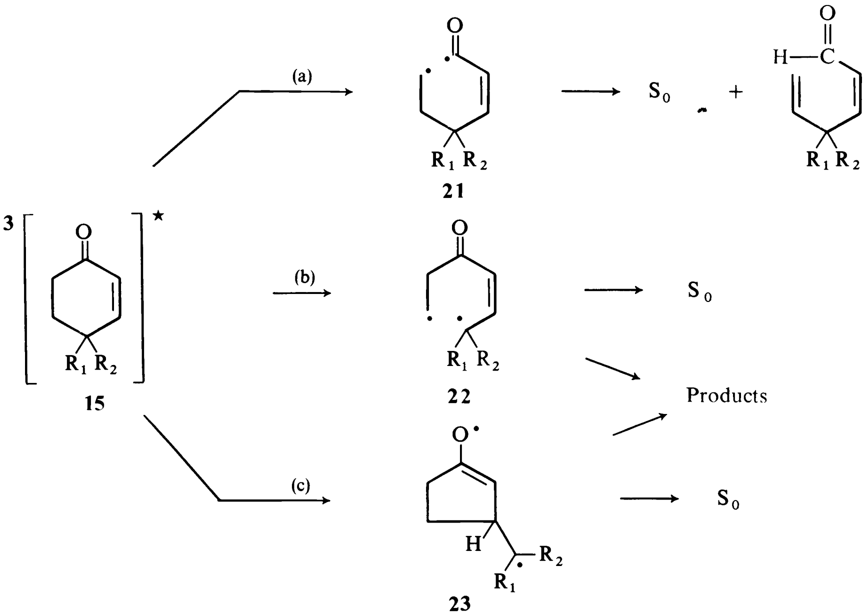
15 **16** **17** **18**

while the analogous rearrangement of 2,5-cyclohexadienones **19** to lumiketones **20** is normally very efficient ($\Phi = 0.7\text{–}1.0$)[63]. Alkyl substituents at C_3 or C_5 in **15** often destroy photochemical reactivity altogether[64]. The source of this inefficiency in the reactions of excited enones **15** has resisted elucidation[63].



19 **20**

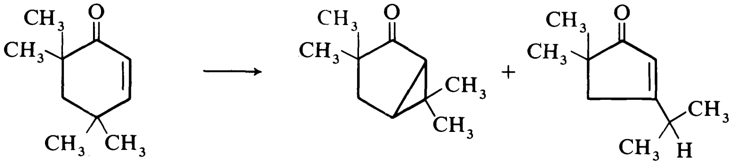
We suggested a few years ago[16] that this effect might be due to the formation from excited states of **15** of diradicals which could revert to enone ground state in competition with transformations to products. Specifically, we had in mind the types of diradicals shown in *Scheme* 7. Diradical **21** is



Scheme 7. Biradicals as source of energy wastage.

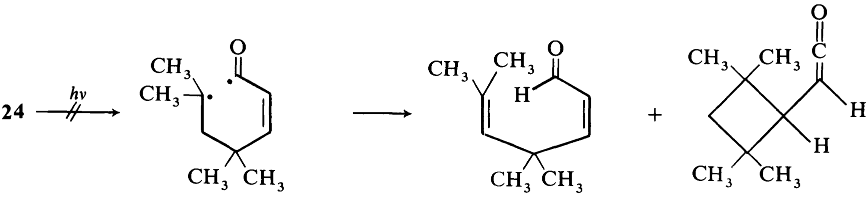
analogous to the amply documented diradicals formed by α-cleavage of electronically excited states (singlet and/or triplet) of saturated cyclic ketones[63] and 2-cyclopentenones[65]. Diradicals **22** and **23** are attractive intermediates in rationalizing the formation of products **16** and **17**. We have recently carried out investigations to specifically test for the intermediacy of such species[66–68].

To probe into the possibilities of α-cleavage, a system was chosen (**24**) in which the propensity for α-cleavage should be enhanced relative to the more typical reaction modes of enones **15** without substitution at C_6. Photolysis of 0.02 *M* solutions of **24** afforded the typical rearrangement



24 **25** **26**

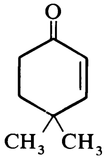
products **25** and **26** in four different solvents: benzene, *t*-butyl alcohol, methanol and 2-propanol[66]. Structures of products were unambiguously assigned from spectral data, independent synthesis and comparisons with properties of structurally related compounds previously studied in our laboratory[66]. In 2-propanol, additional products were formed which were apparently products of photoreduction of **24**, a known enone photoreaction in this solvent[63]. A search was made in all solvents for products derived from the hypothetical diradical **27**, in particular aldehyde **28** and products (e.g. esters) of ketene **29**. However, careful examination of vapour chromatograms and infra-red and nuclear magnetic resonance spectra of photolysates



27 **28** **29**

provided no evidence for the formation of such products, within the limits of detection by such techniques. We must conclude, therefore, that there is currently no basis for postulating the involvement of diradical **27** in the photochemistry of **24**. α-Cleavage does not appear to take place on excitation of **24** or any other cyclohexenone studied to date, to the best of our knowledge.

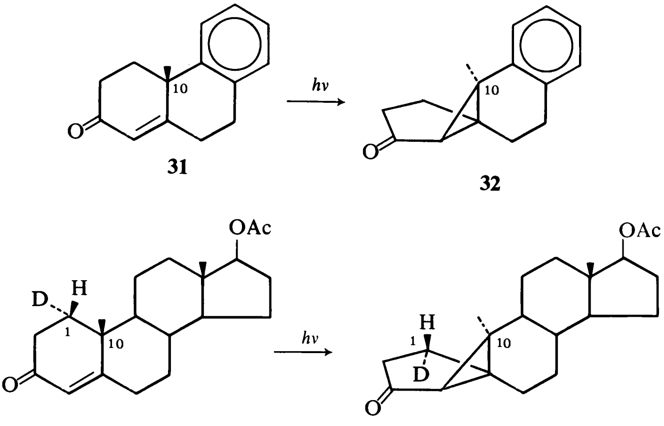
Sensitization and quenching experiments established that **25** and **26** are formed from the same triplet of **24**[66]. It is noteworthy that the quantum efficiency for disappearance of **24** in *t*-BuOH at $\lambda > 300$ nm was established as 0.013 by direct comparison with the enone **30** ($\Phi = 0.014$)[63, 69], although the

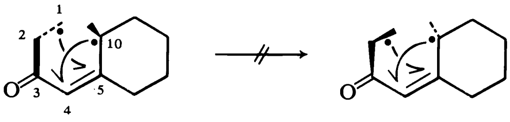


30

triplet state lifetime of **24** in *t*-BuOH (2.0×10^{-9} s) determined from quenching by naphthalene[66] is substantially less than the value for **30** ($1.9–2.6 \times 10^{-8}$ s) determined by Chapman *et al.*, from quenching experiments[63, 69]. This result indicates that α-substitution accelerates reaction as well as decay processes, suggesting that these are intimately related. We shall return to this point later.

Stereochemistry has been used to probe into the intermediacy of diradicals **22** and **23** in these systems. In prior studies, Chapman *et al.*[70], established that the photorearrangement of **31** to **32** proceeded with ⩾95 per cent retention of optical activity, while Schaffner and co-workers[71] used the deuterated ketone **33** to demonstrate that the rearrangement to **34** proceeded with complete retention of configuration at C_1. The configuration at C_{10} is necessarily inverted (see below). While these results rule out the intermediacy of planar achiral diradicals in these reactions, they do not require the operation of a concerted reaction mechanism nor do they rule out the intermediacy of non-planar diradicals of type **35**, as previously argued by us[16] and by Chapman[63]. Steric constraints operate in these fused polycyclic systems, according to molecular models, which make it unlikely that diradicals **35** formed by cleavage of the C_1—C_{10} bond would be planar. Racemization in the reactions of **31** and related steroidal enones requires rotation of the C_1–C_5 chain around the angular methyl group to give **36**, which would allow bond formation between C_1 and C_5 from the top face (as in **36**) as well as the bottom face (as in **35**) of the molecule. From examination of models, the rotations required in **35** → **36** appear to be energetically



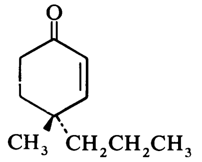


35 **36**

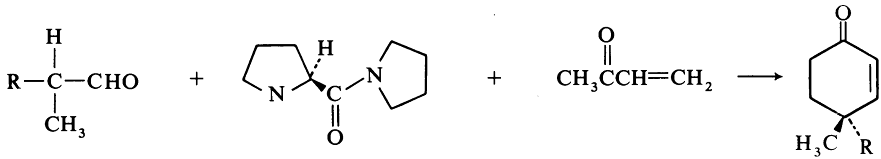
prohibitive, and would not compete with ring closure in **35** on the bottom face, accounting for the observed stereospecificity[70, 71]. Furthermore, because of the necessary *cis*-fusion of the cyclopropane ring to the five- and six-membered rings in **32** and **34**, these transformations are constrained to proceed with inversion of configuration at C_{10}.

To hopefully avoid such ambiguities and to gain further insight into the mechanism of these reactions, we have examined the photolysis of a simple

R – (+) 37



unconstrained chiral cyclohexenone, **37**[66, 67]. In the monocyclic system, for example, the lumiketone rearrangement can occur *a priori* with either retention or inversion of configuration at C_4, the only controlling factor being the reaction mechanism, in contrast with the factors which prejudice the course of reaction in the fused ring systems such as **31** and **33**. Compound **37** was prepared using the convenient asymmetric induction route described by Yamada and Otani[72] involving condensation of methyl vinyl ketone with the enamine of aldehyde **38** and L-proline pyrrolidide **39**. The optically



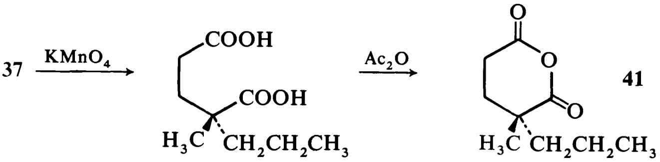
38 **39** **40**

active cyclohexenones **40** produced in this manner should all have preponderantly the same absolute stereochemistry at C_4, which is confirmed experimentally by circular dichroism[72]. The configuration as shown in structure **40** has been unambiguously confirmed independently for R = phenyl or isopropyl[72]. Thus, the absolute configuration of **37** (α_D + 4.60°) as synthesized in this manner can be safely assigned as ***R*** as shown. The optical purity of this sample was established as 10 ± 1 per cent using a chiral n.m.r. shift reagent†. While splitting of the nuclear resonance of the methyl

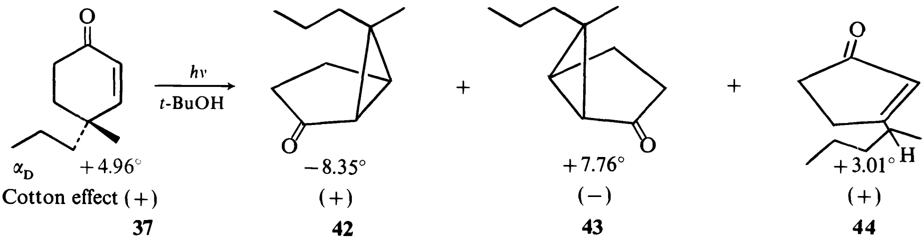
---

[†] Tris-[3-(heptafluoropropylhydroxymethylene)-d-camphorato] europium (III).

at C_4 in **37** could not be achieved in the presence of the shift reagent, it was achieved in anhydride **41** produced by oxidation of **37**.

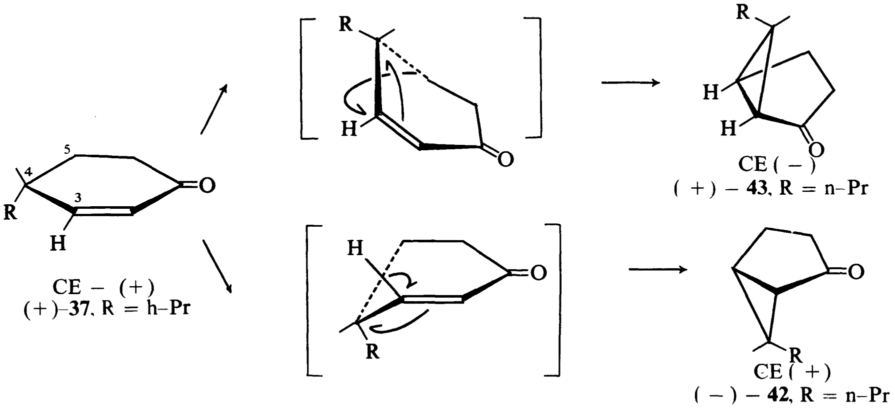


Photolysis of 37, α_D + 4.60°, in *t*-BuOH using 350 nm lamps for 325 hours gave 72 per cent conversion to products **42**, **43** and **44** (*Scheme 8*), which were isolated along with residual starting material by preparative gas–liquid chromatography[66, 67]. The structures of the products were established mainly by spectral data, while the relative stereochemistry of the two lumiketones **42** and **43** (i.e. exo-endo relationship of substituents at C_6) was assigned on the basis of (a) the relative effects of shift reagent on the n.m.r. chemical shifts of the substituents, and (b) n.m.r. spectra of benzylidene derivatives[66, 67]. All isolated materials were optically active, and had rotations as indicated in *Scheme 8*. The optical purities of **42** and **43** were found to be 10 ± 1 per cent on the basis of the splitting of the resonance of the C_6 methyls in the presence of the chiral shift reagent. Absolute configurations of the cyclopropyl ketone chromophores in **42** and **43** were assigned using circular dichroism from the signs of the long wavelength Cotton effects. The 'inverse octant rule'[73] successfully correlates such Cotton effects and known absolute configurations of a number of substituted bicyclo[3,1,0]-hexan-2-ones and related compounds. Since (−)-**42** and (+)-**43** show, respectively, positive and negative Cotton effects centred at 292 nm, these compounds have the absolute configurations shown in *Scheme 8*. Assignment of optical purity and absolute configuration to cyclopentenone **44** must await the completion of more elaborate experiments in progress[68]. The quantum yield for disappearance of racemic **37** in *t*-BuOH was found to be 0.010 at 350 nm, and it was demonstrated using standard sensitization and quenching techniques that the formation of **42**, **43**, and **44** in *t*-BuOH proceeds from a triplet excited state of **37** with a lifetime (from quenching data) of 6.8×10^{-9} s[66].



Scheme 8

It is clear from these data that no racemization of **37** is detectable after 325 hours of continuous irradiation, and that the lumiketones **42** and **43** are formed stereospecifically, within experimental error†. These results rule out the involvement of any diradical along the reaction coordinate which can undergo rotation around the former C_3—C_4 bond of **37**, since such rotation would lead to loss of stereospecificity in lumiketone formation. Referring to *Scheme 9*, it can be seen that the formation of (−)-**42** from (+)-37 involves movement of C_4 downward and bonding between C_3 and C_5 on the bottom face of the cyclohexenone ring (as drawn) with inversion of configuration at C_4, while the formation of (+)-**43** involves movement of C_4 upward and bonding between C_3 and C_5 on the top face of the cyclohexenone once again with inversion of configuration at C_4. In Woodward–Hoffmann terminology, the addition to the π-bond of **37** is antarafacial, and the addition to the C_4—C_5 σ-bond is also antarafacial (inversion at C_4 and retention at C_5[71]), so that the reaction can be described formally as



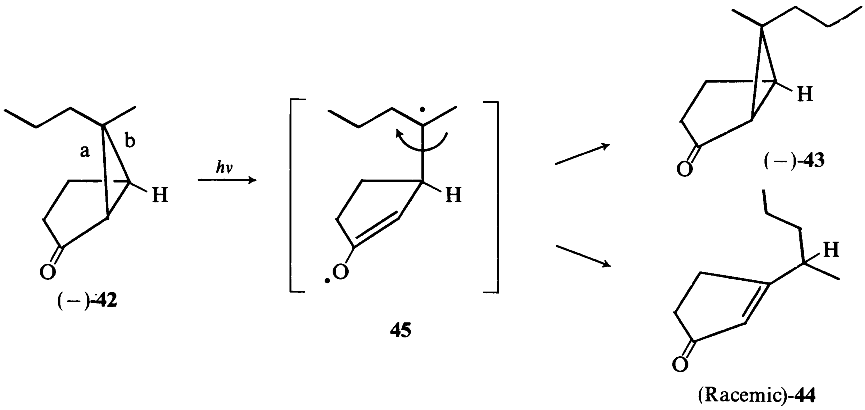
Scheme 9

a $_{\sigma}2_a + _{\pi}2_a$ cycloaddition[74]. This designation, however, should not obscure the fact that the carbonyl group is necessarily involved in the reaction, at least in the initial n → π★ absorption and subsequent intersystem crossing.

It has also been established that photolysis of (−)-**42** at 300 nm in *t*-BuOH gives (−)-**43** as well as racemic **44**. Thus, the photochemical epimerization does not alter the absolute configuration of the cyclopropyl ketone chromophore, and most likely takes place as in *Scheme 10* by cleavage of bond a in **42** and pivoting around bond b[75]. The diradical **45** which is an intermediate in the epimerization is thus specifically excluded from the pathway utilized in the formation of the lumiketones from enone **37**. In fact there is no experimental support for the involvement of diradicals at any stage in the photolysis of 37 or any other cyclohexenones, and it appears that the conversion of cyclohexenones to lumiketones is a totally concerted $_{\sigma}2_a + _{\pi}2_a$ process. The reaction follows the predictions of orbital symmetry although it originates from a triplet excited state of the enone[63–71]. Although we have not yet determined if the formation of cyclopentenone **44** is also totally

---

† The results of recent experiments on 37 and **40** (R = Ph) are more definitive in this respect[68].



Scheme 10

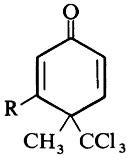
concerted, at least it cannot proceed entirely via diradicals such as **45** in which rotation around the C_3—C_4 bond competes with the 1,2-hydrogen shift. It may be that the ring contraction and hydrogen shift which give **44** also occur concertedly.

These investigations demonstrate that energy wastage in these systems cannot be ascribed to reversion to ground state of starting material from diradical intermediates. Rather, all the data are consistent with a very rapid relaxation of the spectroscopic enone triplet (i.e. with a geometry which corresponds to the minimum in the S_0 surface) by torsion around the carbon–carbon double bond[76, 77] to a twisted triplet, which then partitions between decay to the ground state potential surfaces of starting material (major pathway) and products (minor pathway). Following the approach of Michl[77], one would expect that these ground state surfaces have energy maxima in the region corresponding to the 'twisted π-bond biradicaloid', so that this geometry serves as the ideal point ('funnel') for crossing from the excited triplet state to the ground state surfaces. The partitioning ratio, and hence the reaction efficiency, should then depend critically on the exact shape of the S_0 and T_1 surfaces in this region, which could explain the otherwise mystifying effect of substituents on quantum efficiency in these systems[64].

PHOTOCHEMISTRY OF CROSS-CONJUGATED CYCLOHEXADIENONES

The complex photochemical rearrangements of cross-conjugated cyclohexadienones have intrigued organic photochemists for many years[63, 78]. One of the characteristics of these reactions is their high quantum efficiencies, usually between 0.5 and 0.9[63, 79], although they fall to about 0.2 for some 4-alkyldehydrotestosterones[79]. However, there is always some residual inefficiency, and it was of some interest to track down its source. Although there is ample documentation that these rearrangements arise from dienone triplet states formed with near 100 per cent efficiency[63, 80, 81], quenching of these triplets in solution by typical quenchers such as naphthalene or dienes is notoriously inefficient[81–83]. The most efficient quencher found by us thus far is 1,3-cyclohexadiene (CHD)[83]. If quenching by CHD is near diffusion controlled, which is far from certain, the dienone triplet lifetime appears to be on the order of 0.1–10 ns[80–83]. In order for radiationless decay directly from these triplets to the ground state to compete with reaction, rate constants k_d on the order of 10^7–$10^{10}\,s^{-1}$ would be required. Such magnitudes for k_d are unprecedented. It is more reasonable to postulate that the situation in *Scheme 2* obtains, that the triplet lifetime is determined only by the rate constant for formation of intermediates, and that return to ground state occurs generally from some later point along the reaction coordinate. We will now present some recent data to support this proposal.

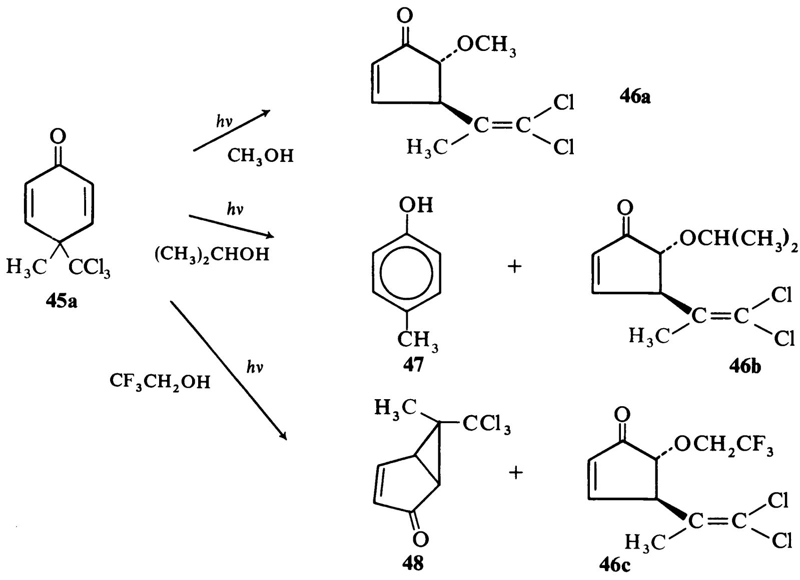
The study of the photochemistry of 4-methyl-4-trichloromethyl-2,5-cyclohexadienones **45** has proved to be extremely fruitful in the elucidation

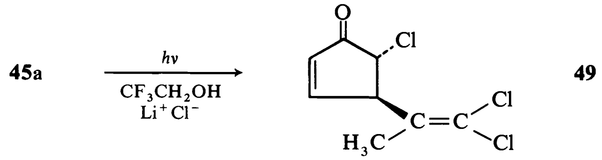


45a, R = H
45b, R = CH_3

of mechanisms of characteristic photochemical reactions of 2,5-cyclohexadienones[81, 85–87]. This is due to the unusual richness of the photochemistry of this system, and the sensitivity of this photochemistry to reaction conditions, which provides an ideal mechanistic probe. For example, the nature and distribution of products varies extensively with the choice of solvent[85–87]. Analytical problems are usually minimal in this system, since it is relatively simple to make qualitative as well as quantitative studies of products using gas–liquid chromatography. This was therefore an ideal system in which to investigate the source of energy wastage, and this phase of our studies in this area will now be summarized.

The relevant new data are as follows[88]: (a) In methanol, the dominant reaction of **45a** is the formation of the methyl ether **46a**. The quantum yield for this reaction decreases steadily as the temperature is raised in the range 0–64°C. (b) In 2-propanol, photolysis of **45a** gives predominantly *p*-cresol **47** and the ether **46b**. When the temperature is raised from 24°C to 61°C, the quantum yield for formation of **47** increases by a factor of 2.5 while that for **46b** decreases by a factor of 2.2. (c) When **45a** is irradiated in trifluoroethanol the main product is the lumiketone **48**, accompanied by minor amounts of the ether **46c**. Chloride salts are quenchers of both these reactions, as well as the formation in 2-propanol of the ether **46b** but not of *p*-cresol **47**[87]. Chloride quenching leads to the formation of compound **49** at the expense of the quenched products. The quantitative chloride quenching data establish that there is a common intermediate in the formation of ethers **46**, lumiketone **48** and the adduct **49**, and this intermediate has been suggested to be the long-postulated[78] zwitterion **50**[87]. When irradiations of **45a** in CF_3CH_2OH are carried out in the presence of 1.2*M* LiCl, the yield of the chloride adduct

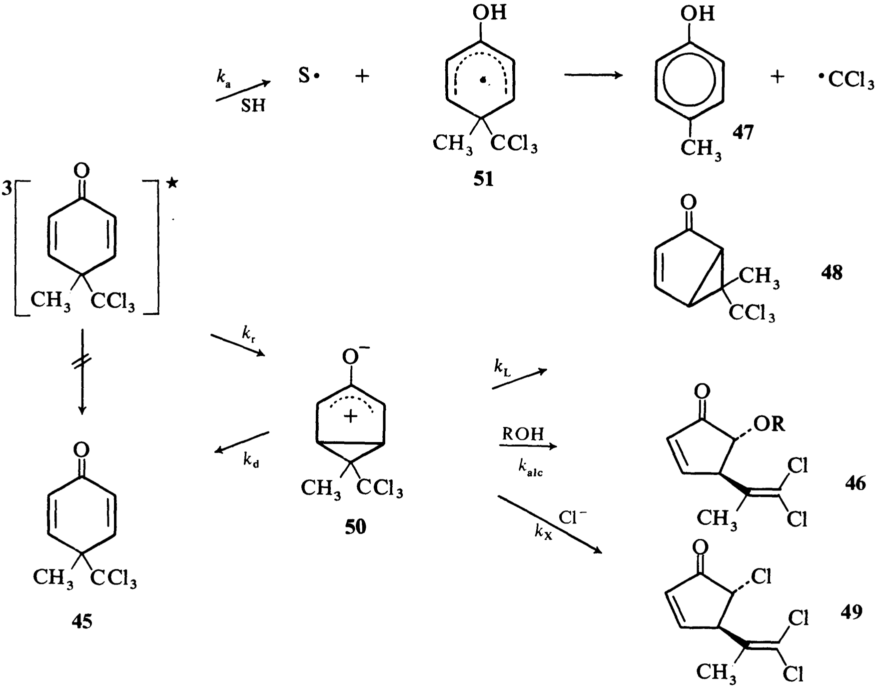




49 is much greater than the yield of lumiketone **48** formed in the absence of chloride. This enhancement is greater at 38° (factor of 2.4) than at 0°C (1.8)[88].

These observations can be understood on the basis of the mechanistic picture shown in *Scheme 11*, which is a slightly modified version of a mechanistic scheme presented by us some time ago[85]. There are two critical partitioning points in this scheme. The triplet state partititions between decay (with intersystem crossing) to zwitterion **50** and hydrogen abstraction from the solvent which leads to radical **51** and ultimately *p*-cresol **47**. The 'activation energy' for H-abstractions ought to be larger than that associated with decay to **50**, so that it was entirely expected that the efficiency of H-abstraction relative to zwitterion formation would increase as the temperature was raised. This is supported by some preliminary studies in ethyl ether at low temperatures: whereas *p*-cresol formation dominates almost completely in room temperature photolyses of **45a**[85], a large number of other products are formed when the irradiation is carried out at −70°C[88]. Contrary to the more typical situation in ground state chemistry, the photochemistry of **45** and other dienones[89] increases in complexity as the temperature is lowered.

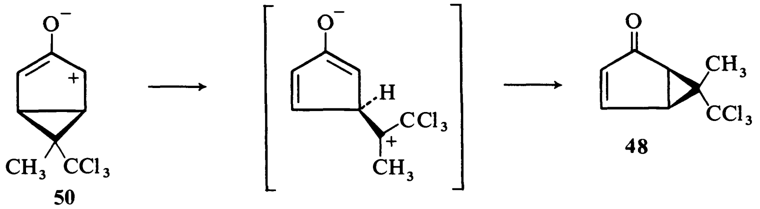
According to *Scheme 11*, we propose that the zwitterion **50** partitions between rearrangement to lumiketone **48**, reaction with nucleophiles (alcohols and chloride ion in this work) and decay to ground state dienone.



Scheme 11

The observations above are understandable if the decay mode gains most in importance as the temperature is raised. First, this would account for the reduction in yield of the normal zwitterion products as the temperature is raised. Secondly, if trapping by chloride ion can be considered 'zwitterion counting' analogous to the better known triplet counting[60], the data show that the zwitterion yield (at least in CF_3CH_2OH) is larger than is accounted for by product yield in the absence of Cl^-, and this discrepancy increases as the temperature is raised. The conversion of ground state zwitterion **50** to ground state dienone is a 'forbidden' process on the basis of orbital symmetry considerations[74]; Zimmerman and Swenton[84] have shown that the zwitterion correlates with a doubly excited state of the dienone. These arguments would suggest that if the reversion of zwitterion to dienone were to occur at all, it ought to have a substantial energy barrier. We suggest that it is in fact this process which accounts for all or most of the inefficiency observed on excitation of cyclohexadienones; that the ring opening of **50** to give **45a** does indeed have a high barrier, higher than that of any other reaction of **50**, and that therefore the extent of reversion from zwitterion to ground state dienone increases with temperature. We would predict on this basis that quantum yields for formation of zwitterion-derived products ought to decrease as the temperature is raised as a general feature of dienone photochemistry. It is too early to state whether or not this is in fact the case.

It should be pointed out that one of the unanticipated features of the photochemistry of **45** is that the zwitterion **50** is relatively long-lived compared to zwitterions from dienones with only alkyl or phenyl groups at C_4. Presumably the reason for this is that the rate of rearrangement of **50** to lumiketone **48** is retarded relative to other dienone–lumiketone rearrangement rates because the transition state for this [1,4]-sigmatropic shift, in which positive charge is localized to some extent at the bridging carbon atom, ought to be relatively destabilized by the CCl_3 group. This permits trapping of zwitterion **50** by nucleophiles, which is not observed with the zwitterions produced on irradiation of 4,4-diphenylcyclohexadienone or α-santonin[87]. It also suggests how to construct zwitterions that should be even longer-lived than **50**.



One complicating feature in this picture should be mentioned parenthetically. We have considerable evidence from quenching studies of dienone **45b** that, at least in this system, H-abstraction (leading to 3,4-dimethylphenol) and the lumiketone rearrangement arise from kinetically distinct triplet states[81]. The Stern–Volmer quenching slopes for these two reactions respond quite differently to changes in the concentration of starting dienone. Such effects have not been seen in the photochemistry of **45a**. Moreover, it is concluded tentatively that the lumiketone rearrangement arises in **45b** from a π,π★ triplet and not an n,π★ triplet[81], which is contrary to the conclusion reached in the case of **45a**[85], as well as the seminal mechanistic analysis of this reaction due to Zimmerman[78, 84, 90, 91]. The effect of temperature on the photochemistry of **45b** and other dienones may clear up some of these discrepancies[92]. Studies are also underway on some unusual effects of light intensity on the course of photoreactions of dienones **45a** and **45b** and related compounds[92].

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge my excellent collaborators in these investigations. They not only performed the experiments, but also provided me with general stimulation, frank criticism, and many suggestions for new and fruitful avenues of research. In alphabetical order, these are George Barile, Bob Brown, Jens Eriksen, Marc Goldstein, Atma Gupta, Kou-chang Liu, Vasanth Prabhu, Bruce Resnick, M. Santhanam and Tomas Weil. I am also indebted for criticism, advice and encouragement to numerous colleagues at New York University, and in particular to Professors Arthur Halpern and Nicholas Geacintov for their collaboration on the singlet photon counting studies. Finally, the support of the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, was essential to the execution of these investigations.

REFERENCES

[1] L. Giering, M. Berger and C. Steel, *J. Amer. Chem. Soc.* **96**, 953 (1974).

[2] G. S. Hammond, *Advanc. Photochem.* **7**, 373 (1969).

[3] J. G. Calvert and J. N. Pitts Jr, *Photochemistry*, p 795ff. Wiley: New York (1966).

[4] A. A. Lamola. ed., *Creation and Detection of the Excited State*, Marcel Dekker: New York (1971).

[5] A. A. Lamola, and N. J. Turro, *Energy Transfer and Organic Photochemistry*, Interscience: New York (1969).

[6] P. J. Wagner, *Accounts Chem. Res.* **4**, 168 (1971);
N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.* **91**, 7550, 7551 (1969).

[7] N. J. Turro, *Molecular Photochemistry*, Benjamin: New York (1965).

[8] A. Beckett and G. Porter, *Trans. Faraday Soc.* **59**, 2038 (1963).

[9] J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.* **85**, 528 (1963).

[10] D. F. De Tar, R. A. J. Long, J. Rendleman, J. Bradley and P. Duncan, *J. Amer. Chem. Soc.* **89**, 4051 (1967).

[11] C. Walling, *Free Radicals in Solution*, Wiley: New York (1957);
W. A. Pryor, *Free Radicals*, McGraw-Hill: New York (1966).

[12] C. A. Parker and T. A. Joyce, *Chem. Commun.* 749 (1968); *Trans. Faraday Soc.* **65**, 2823 (1969).

[13] G. Porter and F. Wilkinson, *Trans. Faraday Soc.* **57**, 1686 (1961);
T. S. Godfrey, J. W. Hilpern and G. Porter, *Chem. Phys. Letters*, **1**, 490 (1967).

[14] R. Wander, P. Neta and L. M. Dorfman, *J. Phys. Chem.* **72**, 2946 (1968);
P. Neta and L. M. Dorfman, *Advances in Chemistry Series, No. 81*, American Chemical Society: Washington, DC (1968);
M. C. Sauer and B. Ward, *J. Phys. Chem.* **71**, 3971 (1967), and other references cited in these papers.

[15] E. J. Baum and R. O. C. Norman, *J. Chem. Soc. B*, 227 (1968).

[16] D. I. Schuster and D. F. Brizzolara, *J. Amer. Chem. Soc.* **92**, 4357 (1970).

[17] J. Saltiel, H. C. Curtis and B. Jones, *Mol. Photochem.* **2**, 331 (1970).

[18] J. Saltiel and H. C. Curtis, *J. Amer. Chem. Soc.* **93**, 2056 (1971).

[19] N. C. Yang, J. L. Cohen and A. Shani, *J. Amer. Chem. Soc.* **90**, 3264 (1968);
J. Saltiel, K. R. Neuberger and M. Wrighton, *J. Amer. Chem. Soc.* **91**, 3658 (1969).

[20] G. Porter, in *Technique of Organic Chemistry*, Volume 8, second edition, A. Weissberger, ed., Interscience-Wiley: New York (1963).

[21] A. V. Buettner and J. Dedinas, *J. Phys. Chem.* **75**, 187 (1971).

[22] G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970);
D. I. Schuster, T. M. Weil and M. R. Topp, *Chem. Commun.* 1212 (1971).

[23] W. R. Ware, in Ref. 4;
A. M. Halpern and W. R. Ware, *J. Chem. Phys.* **54**, 1271 (1971).

[24] W. D. K. Clark, A. D. Litt and C. Steel, *Chem. Commun.* 1087 (1969);
J. Amer. Chem. Soc. **91**, 5413 (1969).

[25] D. I. Schuster, T. M. Weil and A. M. Halpern, *J. Amer. Chem. Soc.* **94**, 8248 (1972).

[26] D. I. Schuster and M. Santhanam, unpublished results, in collaboration with N. Geacintov.

[27] D. I. Schuster and T. M. Weil, *Mol. Photochem.* **4**, 447 (1972).

[28] T. H. Weil, *Ph.D. Dissertation*, New York University (1973).

[29] For leading references, see:
H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.* **67**, 791 (1963);
M. Ottolenghi, *Accounts Chem. Res.* **6**, 153 (1973);
R. A. Caldwell and L. Smith, *J. Amer. Chem. Soc.* **96**, 2994 (1974).

[30] J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.* **94**, 4040 (1972);
H. Knibbe, D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.* **73**, 839 (1969).

[31] P. J. Wagner and R. A. Leavitt, *J. Amer. Chem. Soc.* **95**, 3669 (1973);
92, 5806 (1970).

[32] J. Dedinas and T. H. Regan, *J. Phys. Chem.* **76**, 3926 (1972).

[33] G. Favaro, *Chem. Phys. Letters*, **21**, 401 (1973).

[34] R. O. Loutfy and R. W. Yip, *Canad. J. Chem.* **51**, 1881 (1973).

[35] P. A. Claret, G. H. Williams and J. Coulson, *J. Chem. Soc. (C)*, 341 (1968);
P. Lewis and G. H. Williams, *J. Chem. Soc. (B)*, 120 (1969);
P. H. Oldham and G. H. Williams, *J. Chem. Soc. (C)*, 1260 (1970);
P. H. Oldham, G. H. Williams and B. A. Wilson, *J. Chem. Soc. (B)*, 1346 (1970);
E. K. Fields and S. Meyerson, *J. Org. Chem.* **32**, 3114 (1967).

[36] W. A. Sheppard and C. M. Sharts, *Organic Fluorine Chemistry*, Benjamin: New York (1969).

[37] P. D. Bartlett and L. K. Montgomery, *J. Amer. Chem. Soc.* **86**, 628 (1964);
P. D. Bartlett, *Science*, **159**, 833 (1968).

[38] J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle and M. Wrighton, *J. Amer. Chem. Soc.* **92**, 410 (1970).

[39] D. I. Schuster and T. M. Weil, *J. Amer. Chem. Soc.* **95**, 4091 (1973).

[40] J. Dedinas, *J. Phys. Chem.* **75**, 181 (1971).

[41] D. I. Schuster and M. D. Goldstein, unpublished results.

[42] Th. Förster and K. Kasper, *Z. Phys. Chem.*, NF, **1**, 275 (1954).

[43] W. Klöpfer, Chapter 7 in *Organic Molecular Photophysics*, Volume I, J. B. Birks, ed., Wiley: London (1973).

[44] O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.* **91**, 5390 (1969).

[45] T. H. Koch and A. H. Jones, *J. Amer. Chem. Soc.* **92**, 7503 (1970).

[46] C. C. Wamser, G. S. Hammond, C. T. Chang and C. Baylor Jr, *J. Amer. Chem. Soc.* **92**, 6362 (1970).

[47] D. I. Schuster and M. D. Goldstein, *J. Amer. Chem. Soc.* **95**, 986 (1973).

[48] L. A. Singer, R. E. Brown and G. A. Davis, *J. Amer. Chem. Soc.* **95**, 8638 (1973);
L. A. Singer, R. E. Brown and J. Parks, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract ORGN 23.

[49] M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. I*, **3**, 539 (1972).

[50] N. A. Borisevich and V. V. Gruzinskii, *Proc. Acad. Sci. USSR*, **175**, 578 (1967).

[51] D. R. Kemp and P. de Mayo, *Chem. Commun.* 233 (1972).

[52] C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.* **94**, 655 (1972).

[53] See for example, A. A. Lamola, *Photochem. and Photobiol.* **8**, 601 (1968);
M. L. Meistrich, A. A. Lamola and E. Gabbay, *Photochem. and Photobiol.* **11**, 169 (1970).

[54] P. S. Engel and B. M. Monroe, *Advanc. Photochem.* **8**, 245 (1971).

[55] E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.* **92**, 705 (1970).

[56] D. I. Schuster and T. M. Weil, *Mol. Photochem.* **6**, 69 (1974).

[57] G. Porter and P. Suppan, *Trans. Faraday Soc.* **61**, 1664 (1965);
62, 3375 (1966);
G. Porter and P. Suppan, *Pure Appl. Chem.* **9**, 499 (1964).

[58] P. Suppan, *Ber. Bunsenges. Phys. Chem.* **72**, 321 (1968).

[59] C. Walling and M. Gibian, *J. Amer. Chem. Soc.* **87**, 3361 (1965);
E. J. Baum, J. K. S. Wan and J. N. Pitts Jr, *J. Amer. Chem. Soc.* **88**, 2652 (1966).

[60] A. A. Lamola and G. S. Hammond, *J. Phys. Chem.* **43**, 2129 (1965).

[61] D. Valentine, N. J. Turro and G. S. Hammond, *J. Amer. Chem. Soc.* **86**, 5202 (1964).

[62] S. G. Cohen, M. D. Saltzman and J. B. Guttenplan, *Tetrahedron Letters*, 4321 (1969);
See also J. B. Guttenplan and S. G. Cohen, *Tetrahedron Letters*, 2125 (1969).

[63] O. L. Chapman and D. S. Weiss, in *Organic Photochemistry*, Vol. III, O. L. Chapman, ed., Marcel Dekker: New York (1973).

[64] W. G. Dauben, G. W. Shaffer and N. D. Vietmeyer, *J. Org. Chem.* **33**, 4060 (1968).

[65] W. C. Agosta and A. B. Smith III, *J. Amer. Chem. Soc.* **93**, 5513 (1971);
W. C. Agosta and A. B. Smith III, *Tetrahedron Letters*, 4517 (1969);
P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.* **91**, 4437 (1969).

[66] B. M. Resnick, *Ph.D. Dissertation*, New York University (1974).

[67] D. I. Schuster and B. M. Resnick, *J. Amer. Chem. Soc.* **96**, 6223 (1974).

[68] D. I. Schuster and R. H. Brown, submitted for publication.

[69] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton and P. Fitton, *Tetrahedron Letters*, 2049 (1963);
G. Wampfler, *Ph.D. Dissertation*, Iowa State University (1970).

[70] O. L. Chapman, J. B. Sieja and W. J. Welstead Jr, *J. Amer. Chem. Soc.* **88**, 161 (1966).

[71] D. Bellus, D. R. Kearns and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

[72] S. Yamada and G. Otani, *Tetrahedron Letters*, 4237 (1969);
S. Yamada, private communication of unpublished results.

[73] C. Djerassi, W. Klyne, T. Norin, G. Ohloff and E. Klein, *Tetrahedron*, **21**, 1631 (1965);
G. Snatzke, *J. Chem. Soc.* 5002 (1965).
[74] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie GmbH-Academic Press Inc.: New York (1970), especially pp 89ff.
[75] H. E. Zimmerman, K. G. Hancock and G. C. Licke, *J. Amer. Chem. Soc.* **90**, 4892 (1968).
[76] P. J. Wagner and D. J. Bucheck. *J. Amer. Chem. Soc.* **91**, 5090 (1969).
[77] J. Michl, *Mol. Photochem.* **4**, 243, 257 (1972).
[78] For reviews of the literature and primary references, see:
(a) H. E. Zimmerman, *Advanc. Photochem.* **1**, 183 (1963);
(b) O. L. Chapman, *Advanc. Photochem.* **1**, 323 (1963);
(c) K. Schaffner, *Advanc. Photochem.* **4**, 81 (1966);
(d) P. J. Kropp, in *Organic Photochemistry*, Vol. I, O. L. Chapman, ed., Marcel Dekker: New York (1967).
[79] D. I. Schuster and W. C. Barringer, *J. Amer. Chem. Soc.* **93**, 731 (1971);
D. I. Schuster and W. V. Curran, *J. Org. Chem.* **35**, 4192 (1970).
[80] D. I. Schuster and A. C. Fabian, *Tetrahedron Letters*, 1301 (1968).
[81] D. I. Schuster and K. V. Prabhu, *J. Amer. Chem. Soc.* **96**, 3511 (1974).
[82] D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran and D. H. Sussman, *J. Amer. Chem. Soc.* **90**, 5027 (1968).
[83] D. I. Schuster and N. K. Lau, *Mol. Photochem.* **1**, 415 (1969).
[84] H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.* **89**, 906 (1967).
[85] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.* **90**, 5145 (1968);
D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.* **90**, 5137 (1968).
[86] D. I. Schuster and V. Y. Abraitys, *Chem. Commun.* 419 (1969).
[87] D. I. Schuster and K. Liu, *J. Amer. Chem. Soc.* **93**, 6711 (1971).
[88] D. I. Schuster and K. Liu, unpublished results;
K. Liu, *Ph.D. Dissertation*, New York University (1973).
[89] O. L. Chapman, J. C. Clardy, T. L. McDowell and H. E. Wright, *J. Amer. Chem. Soc.* **95**, 5086 (1973);
O. L. Chapman, private communication of unpublished results.
[90] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.* **84**, 4527 (1962).
[91] See also M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.* **85**, 3029 (1963);
G. Marsh, D. R. Kearns and M. Fisch, *J. Amer. Chem. Soc.* **92**, 2252 (1970).
[92] D. I. Schuster, G. C. Barile and K. Liu, submitted for publication.