Topics in Current Chemistry

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66

Triplet States III

P. J. Wagner
Excited Triplet Organic Carbonyl Compounds

H. Dürr · B. Ruge
Triplet States from Azo Compounds

H. Dürr · H. Kober
Triplet States from Azides

G. Fischer
Line Broadening in Large Molecules

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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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Chemistry of Excited Triplet Organic Carbonyl Compounds

Professor Peter J. Wagner

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I. Introduction

Anyone who has ever taught organic chemistry realizes how important and varied are the reactions of carbonyl compounds. It is not surprising that studies of carbonyl compounds, particularly ketones, have played a very large role in the development of synthetic and mechanistic photochemistry. Not only do ketones and aldehydes absorb light in the convenient near ultraviolet, they can be prepared with seemingly infinite structural variations and they undergo a wide variety of synthetically useful photoreactions. The wide variety of *measurable* chemical and physical reactions undergone by excited ketones has allowed extensive correlations of structure with reactivity, such that the photochemistry of the carbonyl group is understood far better than that of any other functional group.

The photochemistry of acid derivatives is not well understood. Since these compounds absorb in the far ultraviolet and rarely react with great quantum efficiency, they have not been studied at all systematically. Consequently, this review will emphasize aldehyde and especially ketone photochemistry. So much is known about carbonyl photochemistry and so much is added each year (*e. g.*, over 200 pages in the Chemical Society's 1973 survey of photochemistry [1)]), that this review had to be limited to but a few aspects of carbonyl photochemistry. Although the main kinds of carbonyl photoreactions have been adequately reviewed often [2)], several important generalizations have resulted from the past few years' work. This review will attempt to summarize these new generalizations which may not yet be familiar to the entire chemical community. Several unresolved problems will also be outlined.

The dynamics of photochemical reactions are generally considered from a statistical viewpoint. Once a molecule is electronically excited by absorption of a photon, it can undergo several competing physical decay reactions. The most important of these are:

internal conversion to lower excited states;

intersystem crossing between singlet and triplet manifolds;

emmision of light (fluorescence or phosphorescence);

radiationless decay to the ground state; and

energy transfer to another chromophore.

Any chemical reaction of a particular excited state must compete with these physical decay modes. For a photoreaction to occur at all efficiently, some excited state of the reactant must undergo an irreversible chemical reaction at a rate comparably fast to those of the physical decay reactions. Knowledge of rate constants is much more important in photochemistry than it is in ground state chemistry because excited states, unlike ground states, do not sit around patiently waiting for someone or something to make them react. A general understanding of the photoreactions of the carbonyl group demands a good understanding of the nature of the different possible carbonyl excited states and how the rates of the various chemical and physical reactions of these excited states vary with structure.

The quantum yield of a photoreaction represents the probability that light absorption will produce that reaction. Not only does the quantum yield measure the efficiency of a photoreaction, it is the only kinetic parameter which can be measured under steady state conditions, since photoreactions generally follow zero order kinetics. For a triplet reaction, the quantum yield can be dissected into three separate probabilities, any or all of which can be less than unity [3].

$$\Phi_R = \phi_{isc} \cdot \phi_R \cdot P_P \tag{1}$$

$$\Phi_R = k_{isc}\,\tau_S \cdot k_r\,\tau_T \cdot P_P \tag{2}$$

The intersystem crossing yield ϕ_{isc} is the fraction of singlets which cross over to the lower energy triplet instead of reacting themselves, fluorescing, or otherwise decaying. This quantity can usually be measured independently by using the compound to photosensitize some well known triplet reaction of another compound, such as the phosphorescence of biacetyl [4] or the *cis-trans* isomerization of an olefin [5]. The only requirement is that the triplet of the sensitizer be long-lived enough to transfer energy to practicable concentrations of the acceptor. The rate constant k_{isc} for intersystem crossing is large ($>10^8$ sec^{-1}) for all ketones, so that they often form triplets in high yield. For this reason, many phenyl ketones are among the most popular photosensitizing agents. With aliphatic ketones, fluorescence, intersystem crossing, and chemical reaction are often competitive reactions of the lowest excited singlet so that study of these compounds has provided a wealth of information about differences in reactivity between singlets and triplets.

The probability ϕ_R that an excited state will react is defined according to its rate parameters simply as $k_r\tau$, where k_r is the rate constant for the reaction and τ is the kinetic lifetime of the excited state (τ_T for the triplet), determined by the rates of *all* reactions undergone by that state. The unimolecular physical reactions of excited triplets are spin-forbidden and therefore relatively slow, so that chemical reactions are often highly efficient ($k_r\tau_T \approx 1$).

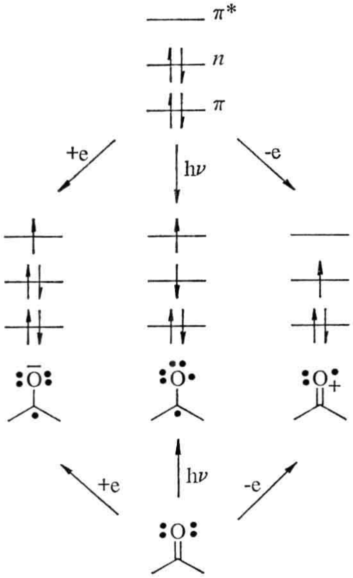
Despite high probabilities for triplet formation and for triplet reaction, many overall photoreactions proceed in low quantum efficiency. In the absence of competing chemical reactions, the factor most often responsible for low quantum yields is the revertibility [3] of primary triplet reactions. Metastable intermediates such as radicals, biradicals, and charge transfer complexes (either excited or ground state) are the usual photoproducts from excited triplet reactions. These intermediates generally can revert to ground state reactant, thus providing a chemical path for "radiationless decay", as well as proceed to stable products. Hence, the factor P_p is necessary to describe the probability that the intermediate will form product.

There is one physical reaction of triplets which is not slow. Bimolecular exothermic energy transfer proceeds at rates which approach those of diffusion control [6]. It is thus possible to selectively quench out the triplet photoreactions of a given compound by adding a compound which has a lower triplet excitation energy but which does not itself absorb significantly at the wavelength being used. Conjugated dienes have been most often employed to quench aliphatic ketones. 1,3-Pentadiene is very useful because it is a relatively poor quencher of excited singlets [7] and it undergoes easily measurable geometric isomerization [5]. Its only serious drawback is that it is a good radical scavenger. 2,5-dimethyl-2,4-hexadiene does not suffer from this drawback but is a rather efficient singlet quencher 7). With phenyl ketones polynuclear aromatics such as naphthalene can be employed. Actually, aromatics such as biphenyl and naphthalene can be used to quench even aliphatic ketone triplet state photochemistry. Even though these aromatics have much higher extinction coefficients than the ketones at all wavelengths, they transfer their singlet excitation to the ketones 8). With the yellow α-diketones, aromatics such as anthracene and pyrene are good triplet quenchers. Molecular oxygen quenches most excited triplets; even the small concentrations normally present in air-equilibrated solutions are sufficient to quench triplets which do not react within one μsec. Lamola's review on energy transfer 6) tabulates the triplet energies of many readily available potential quenchers.

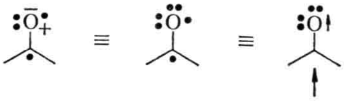
The efficiency of quenching is proportional to the rate constant for energy transfer, k_q, and the lifetime τ of the excited triplet being quenched. Since k_q values are so close to being diffusion controlled, quenching studies provide a simple method for measuring triplet lifetimes.

There are two distinct types of electronic excitation which occur in carbonyl compounds and which produce excited states with quite different physical and chemical properties. In aliphatic ketones and aldehydes, the weak absorption with λ_{max} at 280—300 nm represents an $n \rightarrow \pi^*$ transition, in which a nonbonding electron on oxygen is promoted into a π^* orbital. The resulting excited state resembles a diradical both in its physical and chemical properties. In particular, the chemical reactions of triplet n,π^* states parallel those of alkoxy radicals 2,9), almost as if the electron in the antibonding orbital does not affect the electron left on oxygen.

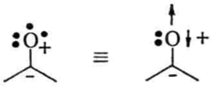
It is perhaps valuable to compare electronic excitation with one-electron redox processes. For example, an $n \rightarrow \pi^*$ excitation is equivalent to oxidizing the n-orbital and reducing the π-system. The predominant valence bond structure of the



radical anion has an odd electron on the carbon and a negative charge on oxygen; that of the radical cation has the odd electron and the positive charge both on oxygen; combining the two gives the diradical. Inasmuch as an electron in the π^* orbital results in a partial negative charge on carbon, the n,π^* state has another



resonance form which emphasizes that the oxygen atom as well as its n orbital is electron-deficient, while the carbon is somewhat electron-rich. It has been noted



by several authors that n,π^* singlet carbonyls demonstrate marked nucleophilicity at carbon, whereas n,π^* triplets behave more like diradicals. This difference is probably due to the necessity for electrons with parallel spin to get as far apart as possible, such that the zwitterionic resonance form is destabilized in the triplet but not in the singlet.

In conjugated ketones, the $n \rightarrow \pi^*$ transition occurs at lower energy, with $\lambda_{\max}$ occuring at 325 nm for typical phenyl ketones. In terms of triplet energies, those of aliphatic ketones are usually taken to lie in the 76—80 kcal/mole range. A more precise figure is not obtainable because the phosphorescence of aliphatic ketones shows no vibrational structure so that a 0—0 band energy is not assignable. Aldehydes presumably have lower n,π^* triplet energies, since that of formaldehyde is 72 kcal/mole [10]. The n,π^* E_T values of phenyl alkyl ketones lie around 72 kcal [11]. while that of benzophenone lies at 68 kcal [12]. The n,π^* triplets of conjugated enones also lie 70—72 kcal above their ground states [13].

Although the $\pi \rightarrow \pi^*$ transitions of aliphatic ketones occur at very high energy, those of conjugated ketones lie much lower. In particular, phenyl ketones have π,π^* triplets which lie less than 75 kcal above the ground state [14], while enones have π,π^* triplets which lie within a few kcal either way of their n,π^* triplets [13]. Substituents on the benzene ring of phenyl ketones or on the double bond of enones independently stabilize or destabilize the n,π^* and π,π^* transitions, so that such substituents usually determine which of the two triplets is lower in energy. The polarity of the solvent also affects relative triplet energy levels, with π,π^* triplets being stabilized in hydrogen-bonding and high dielectric solvents [14]. When an acyl group is attached to any aromatic ring bigger than benzene, the lowest triplet of the compound is basically a perturbed π,π^* triplet of the aromatic.

The excited state behavior of a compound usually depends largely on the nature of its lowest triplet. In compounds where the two triplets are energetically proximate, they can equilibrate thermally before decaying and they may also mix with each other. How much these two phenomena affect chemical reactivity is still the subject of active research and speculation. The latest thinking is that mixing is not significant unless the two "pure" triplets would be within 0.5 kcal

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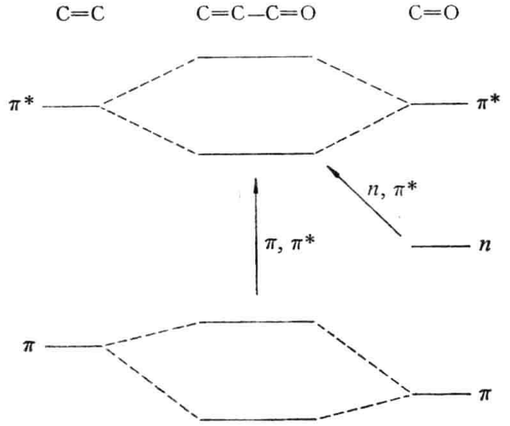
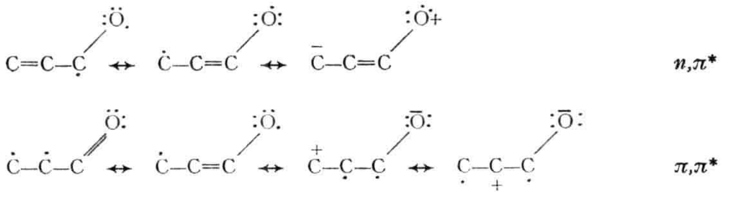
of being isoenergetic [15]. Consequently, it is usually fairly safe to think of these triplets in terms of a simple m.o. model. An orbital diagram and commonly accepted valence structures are presented below for the n,π^* and π,π^* states of a simple enone. The π,π^* triplet is more nucleophilic than electron-deficient at oxygen and may have diradical character. Inasmuch as the chemical reactions of such states reflect the electronic distribution of the reactant, quite different chemical reactivity is expected and observed for n,π^* and π,π^* triplets.



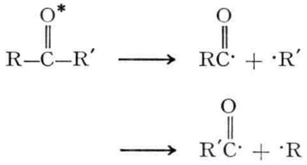


II. Primary Photoreactions

The photochemistry of alkanones has been reviewed recently [2c]. It would appear that rate constants for the physical decay processes of both singlets and triplets vary only slightly among a wide collection of structurally varied acyclic, cyclic, and polycyclic alkanones. Consequently, relative triplet yields are determined primarily by relative rates of excited singlet chemical reactions. As in most triplet reactions, overall quantum yields are usually determined primarily by the partitioning of metastable primary photoproducts.

All of the photoreactions of aliphatic carbonyl compounds result from just four primary reactions of n,π^* states. More complicated carbonyl compounds can undergo various rearrangement reactions and reactions characteristic of π,π^* states but also undergo the four basic carbonyl reactions. A brief summary of these reaction types is presented in this section; the remainder of this review is devoted to a critical summary of how structure affects the rates and efficiencies of these basic reactions. Since each of the primary photoreactions produces another reaction intermediate, the chemistry of both the excited states and the intermediates must be understood if quantum efficiencies are to be predictable.

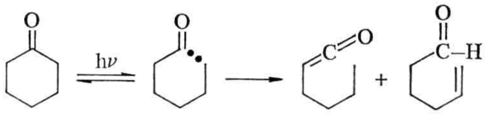
A. α-Cleavage is the common unimolecular, intrachromophoric radical-producing reaction of the excited carbonyl group and is closely analogous to the *β*-cleavage of alkoxy radicals [16]. Acyclic compounds yield a pair of radicals



$$R-\overset{O^*}{\overset{\|}{C}}-R' \longrightarrow R\overset{O}{\overset{\|}{C}}\cdot + \cdot R'$$

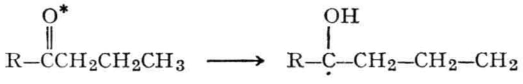
$$\longrightarrow R'\overset{O}{\overset{\|}{C}}\cdot + \cdot R$$

which can either react in the initial solvent cage or diffuse apart and initiate typical radical reactions. Cyclic compounds yield diradicals which can either recouple or disproportionate to yield stable products.



B. Hydrogen Atom Abstraction is the other alkoxy-radical-like reaction of triplet *n,π** carbonyls. The substrate can be another molecule, in which case a pair of radicals is formed; or an accessible hydrogen in the same molecule, in which case a diradical is formed.

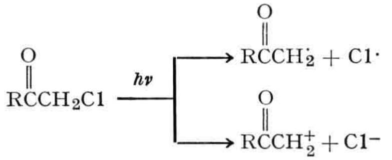
$$R_2C{=}O^* + S{-}H \longrightarrow R_2{-}\dot{C}{-}OH + S^{\cdot}$$



$$R-\overset{O^*}{\overset{\|}{C}}CH_2CH_2CH_3 \longrightarrow R-\overset{OH}{\overset{|}{\underset{\cdot}{C}}}-CH_2-CH_2-CH_2$$

C. Charge Transfer Complexation. The one-electron oxidation and reduction potentials of excited triplets are lower than those of the ground state by the triplet excitation energy E_T. Therefore, excited triplets (and all excited states) are very prone to get involved in charge transfer and electron transfer processes. Charge transfer complexation seems to account for most bimolecular chemical reactions of ketone triplets which are not initiated by hydrogen abstraction. There is as yet no hard evidence whether the CT complexes so formed are still electronically excited (exciplexes) or whether they represent some high energy ground state configuration, but exciplexes certainly are likely intermediates. Depending on the nature of the substrate, the complex can proceed to products by various chemical paths; but reverse electron transfer always operates to quench a significant fraction of the complexes.

D. β-Cleavage. Ketones substituted with heteroatoms on an α-carbon, including α-halo, α-tosyl and α-aminoketones, undergo photoinduced loss of that substituent either as a radical or as an anion [17].



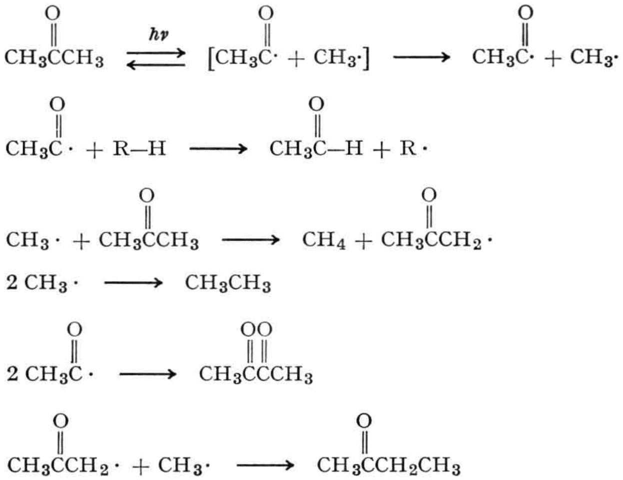
$$R\overset{O}{\overset{\|}{C}}CH_2Cl \xrightarrow{h\nu} \begin{cases} R\overset{O}{\overset{\|}{C}}\dot{C}H_2 + Cl\cdot \\ R\overset{O}{\overset{\|}{C}}CH_2^+ + Cl^- \end{cases}$$

III. α-Cleavage

A. Acyclic Aliphatic Ketones

The photolysis of ketones into radicals is called Norrish type I cleavage. The efficiency of this cleavage depends strongly on the ketone's structure and on the medium.

The simplest ketone, acetone, has remained one of the hardest to understand. It photofragments efficiently in the gas phase with unit quantum yield above 100 °C [18]. In inert solvents, however, it fragments so inefficiently [19] as to require CIDNP techniques to be detected [20]; even then, only in water is CIDNP readily detected for the products expected from cleavage. (In solvents with labile C—H bonds, acetone is photoreduced [21]).



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \overset{h\nu}{\rightleftarrows} [CH_3\overset{O}{\overset{\|}{C}}\cdot + CH_3\cdot] \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\cdot + CH_3\cdot$$

$$CH_3\overset{O}{\overset{\|}{C}}\cdot + R{-}H \longrightarrow CH_3\overset{O}{\overset{\|}{C}}{-}H + R\cdot$$

$$CH_3\cdot + CH_3\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow CH_4 + CH_3\overset{O}{\overset{\|}{C}}CH_2\cdot$$

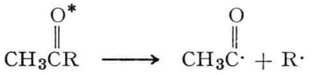
$$2\,CH_3\cdot \longrightarrow CH_3CH_3$$

$$2\,CH_3\overset{O}{\overset{\|}{C}}\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CH_3$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_2\cdot + CH_3\cdot \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

Unlike acetone, diethyl ketone cleaves well even in cumene [22]. 2-Pentanone triplet undergoes considerable α-cleavage in competition with rapid intramolecular hydrogen abstraction, as judged by the buildup of an efficient triplet quencher [23]. Biacetyl is the only likely candidate for that quencher and is the major product of α-cleavage of methyl ketones at temperatures low enough that decarbonylation of the acetyl radical is slow. Isopropyl, *tert*-butyl, and benzyl ketones all cleave quite efficiently and various reports have appeared on the CIDNP spectra of products derived from the radicals [24].

The rate constant for triplet α-cleavage depends strongly on the stability of the radical produced, as judged by both intramolecular competition and by measured triplet lifetimes. An order of magnitude comparison of rate constants can be estimated for cleavage of progressively more stable radicals R· as follows: CH_3, 10^3—10^4 sec^{-1}; CH_3CH_2, $\sim 10^6$—10^7 sec^{-1}; $(CH_3)_2CH$, $\sim 10^8$ sec^{-1}; $C(CH_3)_3$; 2×10^9 sec^{-1}; $PhCH_2$, 10^{10} sec^{-1}. The last two are measured [25,26]; the second would explain the above-mentioned behavior of 2- and 3-pentanone.

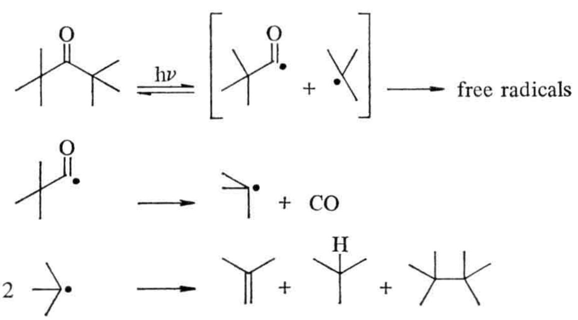


$$CH_3\overset{O^*}{\overset{\|}{C}}R \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\cdot + R\cdot$$

The values for methyl and isopropyl have not been even indirectly measured. They were chosen by analogy to the known relative rates of β-cleavage of alkoxy radicals [27]. The number so chosen for methyl explains the inefficient cleavage of acetone in solution. Although this rate is large enough to compete with quenching by unreactive solvents, it is not large enough to compete with quenching by product biacetyl. By the time 10^{-6}M biacetyl is produced (0.001% conversion for 0.1 M acetone), the reaction is half-quenched by product, since k_q is on the order of $10^{10}M^{-1}$ sec^{-1} in most common solvents [6]. Although quenching by product has long been recognized as an *a priori* possibility in all photoreactions, it is a serious complication surprisingly rarely.

It is noteworthy that the excited singlets of *t*-butyl ketones undergo α-cleavage only 1/100 as fast as their triplets [25], despite their 5 kcal greater energy. This fact has been a real puzzle for some time and remains so today. Turro suggested that the triplet ketone can correlate with a repulsive triplet of the radical pair [28,29]. Salem has recently applied simple symmetry considerations to this photocleavage reaction [29] and concluded that the singlet radical pair with the same symmetry as the n,π^* ketone singlet is a high energy state, whereas the n,π^* triplet can indeed pass smoothly to the lowest energy triplet radical pair either by mixing with an upper triplet or by losing all symmetry by cleaving in a non-coplanar fashion. Other calculations [30] and some experiments [31] suggest that the latter is the case.

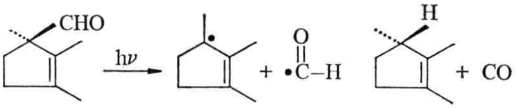
Decarbonylation regularly accompanies α-cleavage reactions at higher temperatures in the gas phase but occurs at room temperature in solution only if the acyl radical can form a very stable alkyl radical (tert-alkyl, benzyl). For example, di-*tert*-butyl ketone photofragments with a total quantum yield of 0.7 in solution [25]. Cage recombination invariably cuts the efficiency of type I cleavage in solution. In terms of the general kinetic scheme, P_p is less than unity.



If decarbonylation of the acyl radical is slow, aldehydes and diketones are formed.

B. Aldehydes

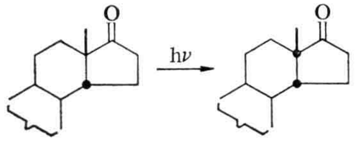
Photoreactions of aldehydes have a strong tendency to become messy if radicals are produced, because of the high reactivity of aldehydic hydrogens in abstraction reactions. β,γ-unsaturated aldehydes undergo a highly stereospecific decarbonylation, which probably takes place from the excited singlet [32].

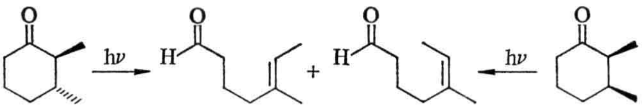


C. Cyclic Ketones

α-Cleavage of a cyclic ketone necessarily produces a diradical. It is now well accepted that the photorearrangement of cycloalkanones to ω-unsaturated aldehydes and to ketenes proceeds via such diradicals. It has not always been adequately appreciated that a diradical mechanism had to be a possibility for this rearrangement given that excited ketones cleave into radicals. The only way the rearrangement could be primarily or exclusively a concerted process would be if that process were much faster than the homolytic cleavage.

The evidence for diradicals in cycloalkanone photochemistry is widespread. Proton [33], fluorine [34], and ^{13}C-CIDNP [35] spectra have been recorded for products and reactant ketone. This evidence indicates that a diradical is at least partially involved in the rearrangement as well as in the well-known photoepimerization of certain keto-steroids [36]. Such loss of stereochemistry is usually associated with the presence of an sp^2-hybridized intermediate. Here a diradical is the obvious choice. The identical product distribution from both *cis* and *trans*-2,3-dimethylcyclohexanone is a more subtle indication that there is an intermediate involved in the rearrangement which loses its configurational integrity at carbon 2 [37].

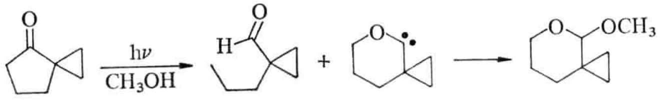


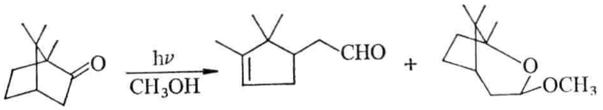


The kinetics of these rearrangements demand an intermediate. Triplet lifetimes depend strongly on α-substitution [38,39] in line with what would be expected for relative stabilities of the alkyl-half of the diradical. 3- and 4-Substituents have only small effects on rates of triplet decay. Most important, there is no correlation between quantum yield and triplet state reactivity [38], symptomatic behavior for photoreactions in which an intermediate reverts to starting material.

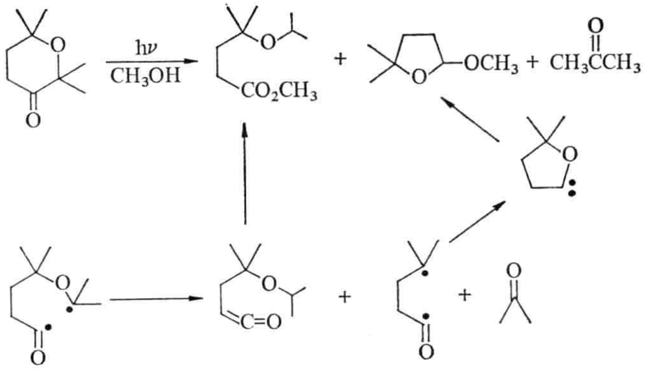
Relative rates of α-cleavage to yield primary : secondary : tertiary : benzylic alkyl radical sites are 1:30:300:1000, just as with the α-cleavage of acyclic ketone triplets into radicals. For the cyclohexanones, the absolute rates are very similar to these for α-cleavage of acyclic ketones, as befits a similar mechanism. The rate for 2-phenylcyclohexanone is considerably larger than first reported [38], more in line with the behavior of dibenzyl ketone [26]. Cyclopentanones cleave ten times faster than the corresponding cyclohexanones, presumably manifesting the release of ring strain. It is noteworthy that excited singlet lifetimes *increase* with α-substitution [39]. The rearrangements of the cyclic ketones are therefore predominantly triplet reactions, although the fact that part of the cleavage of α,α-dialkylcyclohexanones is inquenchable [40] indicates some singlet α-cleavage. In this respect, it is worth mention that application of Kaptein's rule to the CIDNP spectra of Norrish type I cleavage reactions [24] suggests the intermediacy of triplets. Since this conclusion is derived only from the sign of polarization, it is impossible to rule out partial (<50%) singlet participation.

Most of the remaining uncertainties in cycloalkanone photochemistry are concerned with the behavior of the diradical intermediate. Its major reactions include recoupling and disproportionation in two senses to yield ketene or unsaturated aldehyde. A few strained cyclopentanones also partially recyclize to oxycarbenes [41].





1,4-Acyl, alkyl diradicals also apparently close to oxacarbenes. This statement derives from the most rational mechanism for the observed photoproducts of the 3-oxacyclohexanone below [42].



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