

SELECTED ASPECTS OF PHOTOCHEMISTRY

I Photochemistry of Carbonyl Compounds

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1 Introduction

The photochemistry of organic molecules has been extensively studied and can be described systematically. Just as the ground state of compounds with a particular functional group undergoes characteristic (thermal) reactions, so a particular electronically excited state of the compounds undergoes characteristic, though different, reactions. The difference between thermal and photochemical reactions arises because of the different electron distributions in ground and excited states and because of the extra energy of the excited state. Observable photochemical reactions usually have fast primary steps with low activation energies, whereas other reactions may be obscured by rapid physical decay of the excited state.

This review is a survey of the major reaction types in the photochemistry of compounds containing the carbonyl (C=O) group. Photochemical reactions of unsaturated carbonyl compounds which involve mainly the unsaturated linkage are omitted (*e.g.* cyclobutane-forming cycloaddition and dimerization, and *cis-trans* isomerization), the large group of reactions involving rearrangement of cyclic enones and dienones is described only briefly, and the value of carbonyl compounds as triplet energy-transfer agents in bringing about photochemical change in other systems is also omitted. Otherwise an attempt is made to present a balanced outline of the current state of knowledge.

The mechanistic detail of some reaction types has been elucidated, and this is dealt with where appropriate. Many photochemical reactions are of preparative value and lead to systems not as readily accessible by thermal routes. These are not indicated in the text, but surveys of synthetically useful photochemical reactions have been published.¹

2 Excited States of Carbonyl Compounds

The ultraviolet and vacuum ultraviolet absorption spectra of saturated aliphatic

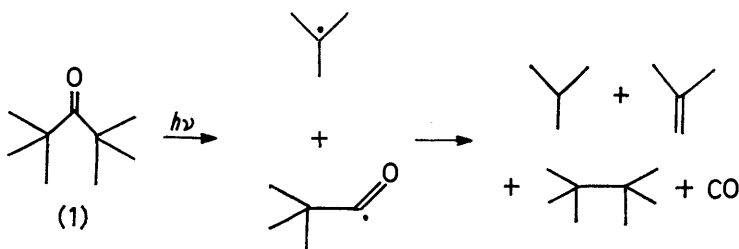
¹ (a) A. Schönberg, 'Preparative Organic Photochemistry,' Springer-Verlag, Berlin, 2nd edition, 1968; (b) P. G. Sammes, *Quart. Rev.*, 1970, 24, 37.

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ketones show four main bands centred around 280, 195, 170, and 155 nm. The first of these corresponds to an $n \rightarrow \pi^*$ transition, and the last to a $\pi \rightarrow \pi^*$ transition, but the assignment of the others is not certain.² The wavelengths of radiation most frequently employed in photochemical reactions are well above 200 nm, and the most readily accessible excited states of aliphatic ketones are the $n\pi^*$ singlet and triplet states. These are the states responsible for much of the photochemistry of carbonyl compounds. Even when a higher energy excited state is populated initially by use of shorter wavelength radiation, internal decay to the lowest energy excited state is usually more rapid than chemical reaction from the higher state. The situation is different for conjugated, unsaturated carbonyl compounds, which have readily accessible $n\pi^*$ and $\pi\pi^*$ states. The $n\pi^*$ states are not always the lower in energy, and the chemistry is different for the two types of excited state because they differ widely in electron distribution.

3 α -Cleavage

In gas-phase photochemistry of saturated carbonyl compounds the electronic excitation energy of the carbonyl group generally becomes localized as vibrational energy in the weaker of the bonds adjacent to the carbonyl group, and cleavage of this bond occurs to give two radical fragments. Cleavage of the C(=O)—C(α) bond in this manner is often referred to as the Norrish Type 1 process. The secondary reactions of the radicals follow the normal pattern of fragmentation, combination or disproportionation, or radical substitution. Di-*t*-butyl ketone (1) gives the major products shown.³ Loss of carbon monoxide from aldehydes,



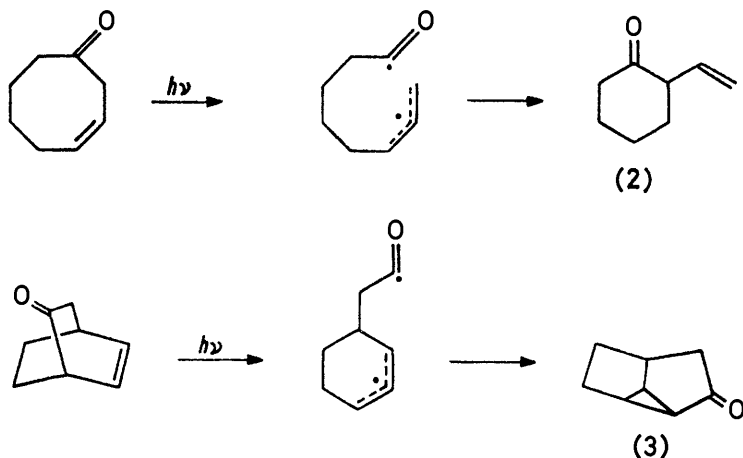
in contrast to other compounds, occurs with retention of configuration at the α -carbon.

In solution these processes are less important, particularly for ketones, because α -cleavage occurs most readily from upper vibrational levels of the electronically excited state. In solution vibrational deactivation is rapid, and alternative primary or secondary processes compete effectively. Systems with a particularly weak α -bond (in which the radical fragments are stabilized) undergo α -cleavage followed by loss of carbon monoxide as a major photo-

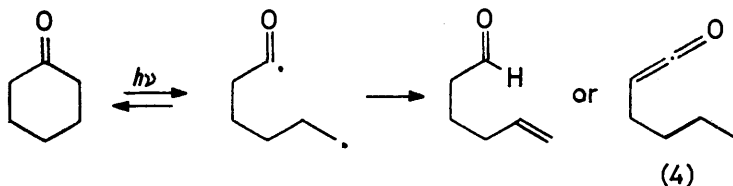
² H. Ito, Y. Nogata, S. Matsuzaki, and A. Kuboyama, *Bull. Chem. Soc. Japan*, 1969, **42**, 2453.

³ J. W. Kraus and J. G. Calvert, *J. Amer. Chem. Soc.*, 1957, **79**, 5921.

chemical process even in solution at room temperature. Such systems include acyl chlorides, alkyl t-butyl ketones, and benzyl or $\beta\gamma$ -unsaturated ketones [see (7) and (8)]. Cyclic $\beta\gamma$ -unsaturated ketones can alternatively undergo a 1,3-acyl shift (2),⁴ or form a cyclopropane derivative (3). Both processes can be formulated with initial α -cleavage, but in some systems the processes appear to be concerted.⁵



Cyclic ketones and cyclic esters (lactones) on photolysis undergo α -cleavage to give a biradical which can react further by recombination to give starting material or its epimer, or by loss of carbon monoxide or carbon dioxide to give hydrocarbon products (an important mechanism in the gas phase). Alternatively, intramolecular hydrogen transfer can occur to either radical centre from the position adjacent to the other radical centre. The products from cyclohexanone are hex-5-enal and n-butylketen (4).



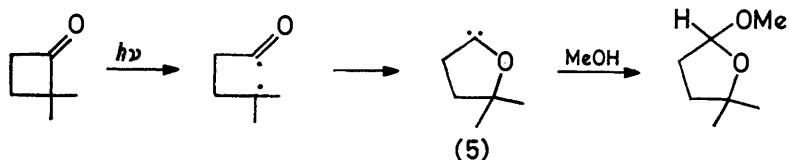
These reactions are most important for five- and six-membered cyclic carbonyl compounds, that is those for which the hydrogen transfer involves a five- or six-membered cyclic transition state. The competition between enal and keten

⁴ L. A. Paquette and R. F. Eizember, *J. Amer. Chem. Soc.*, 1967, **89**, 6205.

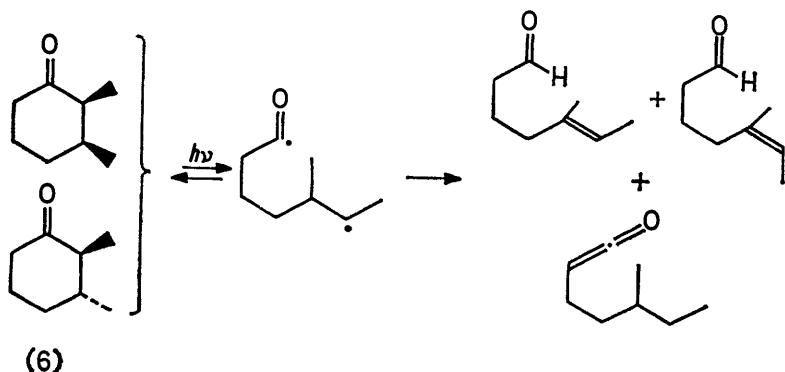
⁵ R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, 1971, **93**, 3963.

formation in cyclic ketones is governed by ring size and substitution pattern.⁶

When the hydrogen-transfer reactions are inhibited in cyclic compounds by ring size or other steric factors, another secondary route becomes prominent in which ring closure of the biradical with formation of a C—O bond occurs. The oxacarbene (5) formed initially is trapped as an adduct with added nucleophile. Cyclobutanones are compounds for which this is a major process.⁷



The mechanism of the α -cleavage process has been extensively studied. The primary step occurs from both singlet and triplet excited states of acyclic ketones, but mainly from the triplet excited state of cyclic ketones.⁸ There is good evidence that a biradical is a true intermediate in the photoreactions of cyclic ketones, and the nature of this evidence can be illustrated by reference to 2,3-dimethylcyclohexanone (6): (a) both *cis*- and *trans*-isomers of (6) undergo photoepimerization to the other isomer; (b) each isomer gives rise to the same product ratios; (c) the kinetics of product formation and ketone disappearance are in accord with a scheme involving a biradical intermediate.⁹ Further evidence is provided by a study of deuterium-labelled cyclohexanones.¹⁰



The intermediacy of radicals in the photochemistry of acyclic ketones is demonstrated by the formation of cross-product (9) in the statistically expected

⁶ J. D. Coyle, *J. Chem. Soc. (B)*, 1971, 1736.

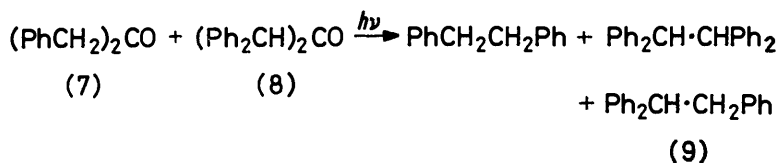
⁷ P. Yates, *Pure Appl. Chem.*, 1968, 16, 93.

⁸ J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, 21, 499.

⁹ J. A. Barltrop and J. D. Coyle, *Chem. Comm.*, 1969, 1081.

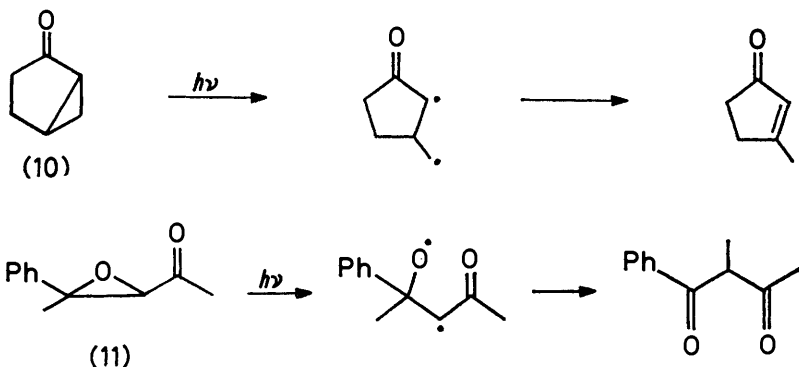
¹⁰ W. C. Agosta and W. L. Schreiber, *J. Amer. Chem. Soc.*, 1971, 93, 3947.

proportion when a mixture of ketones (7) and (8) is irradiated in solution. Similar results are obtained with esters.



4 β -Cleavage

In the electronic excited states of compounds with a relatively weak $\text{C}_\alpha\text{—C}_\beta$ bond the electronic energy may be dissipated by homolytic cleavage of this bond. Cyclopropyl ketones such as (10) and $\alpha\beta$ -epoxyketones¹¹ such as (11) provide examples of this behaviour.



There is evidence from the u.v. absorption spectra of interaction between the carbonyl group and the cyclopropane ring in conjugated cyclopropyl ketones. The $n\rightarrow\pi^*$ absorption band is shifted to longer wavelength and is increased in intensity as compared with the band for saturated ketones. This interaction presumably provides the mechanism by which energy is transferred from the carbonyl group to the $\text{C}_\alpha\text{—C}_\beta$ bond.

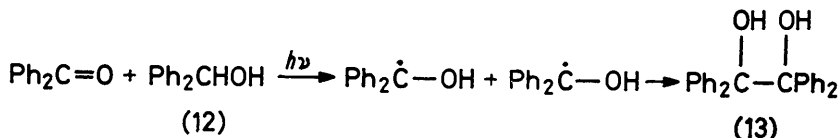
5 Photoreduction

Photoreduction of carbonyl compounds in the presence of molecules with readily abstracted hydrogen atoms is one of the best known photochemical reactions. Irradiation of benzophenone in the presence of benzhydrol (12), for example, leads efficiently to benzpinacol (13), a reaction useful as a standard in determining quantum yields. Aromatic ketones undergo intersystem crossing from the excited singlet to the triplet state so rapidly that photoreduction is observed

¹¹ A. Padwa, *Accounts Chem. Res.*, 1971, 4, 48.

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only from the triplet state. The $n\pi^*$ triplet state of benzophenone causes homolytic cleavage of the weakest bond to hydrogen in benzhydrol, and benzpinacol is formed by dimerization of the resulting ketyl radicals.



The reactivity of the carbonyl triplet towards hydrogen abstraction falls with increasing strength of the bond being broken, and because the triplet state has a greater chance of being deactivated by other pathways, the efficiency of photoreduction is low in solvents with strong bonds such as water or benzene.

As already mentioned, conjugated aromatic ketones have both low-lying $n\pi^*$ and $\pi\pi^*$ triplet states. On a simple valence-bond interpretation, $n \rightarrow \pi^*$ excitation of a carbonyl compound removes electron density from the carbonyl oxygen atom and the oxygen has electrophilic, free-radical character. In fact, there are noticeable similarities in the selectivity of triplet benzophenone and tert-butoxyl radicals, $\text{Me}_3\text{C}-\dot{\text{O}}$, towards intermolecular hydrogen abstraction from C—H bonds.¹² $\pi \rightarrow \pi^*$ Carbonyl excitation does not greatly reduce the electron density at the carbonyl oxygen atom, and so the $\pi\pi^*$ triplet state abstracts hydrogen very much less readily.

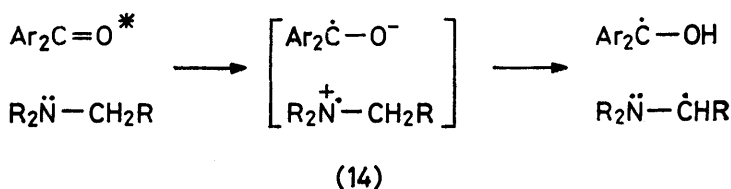
For simple aromatic ketones, such as benzophenone, the $n\pi^*$ triplet state is of lower energy than the $\pi\pi^*$ triplet state, and photoreduction is efficient in the presence of a good hydrogen donor. There are two factors which can invert this order of triplet states and make photoreduction much less efficient: they are (a) electron-donating substituents on the ketone, and (b) highly polar solvents.¹³ As an example of (a), increasing methyl-substitution on the aromatic ring of a phenyl alkyl ketone such as acetophenone (PhCOMe) decreases the efficiency of photoreduction. Evidence for the $n\pi^*$ or $\pi\pi^*$ nature of the lowest triplet can often be gained from a study of the phosphorescence spectrum and triplet lifetime of the molecule.

An electron-transfer mechanism has been proposed for the photoreduction of aromatic ketones in the presence of aliphatic or aromatic amines,¹⁴ or sulphides. An electron is rapidly transferred from the amine to the $n\pi^*$ triplet of the ketone to give an excited charge-transfer complex [e.g. (14)]. The subsequent transfer of the amine α -hydrogen as a proton completes the formation of the radical pair. Alternatively, the complex can undergo reverse electron transfer to give ground-state ketone and amine, which serves as a route for quenching the triplet excited ketone.

¹² C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 1965, **87**, 3361.

¹³ G. Porter and P. Suppan, *Trans. Faraday Soc.*, 1965, **61**, 1664.

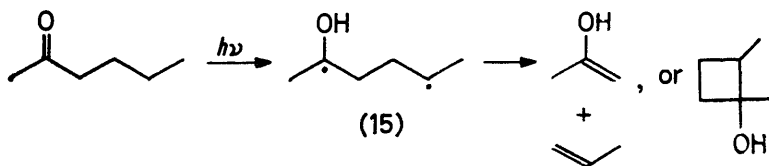
¹⁴ S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, 1968, **90**, 165.



Evidence for this electron transfer and quenching mechanism is that even amines without abstractable hydrogen, if they are of low ionization potential, can quench the photoreduction of benzophenone in benzhydrol.¹⁵

6 Intramolecular γ -Hydrogen Transfer

Photolysis of a carbonyl compound with a hydrogen atom in the γ -position can give, in addition to α -cleavage products, other products which are explained in terms of intramolecular hydrogen abstraction by the excited carbonyl group from the γ -position.¹⁶ The products are typically a shorter-chain carbonyl compound (formed initially as the enol tautomer) and an alkene, and also a cyclobutanol. The former reaction, involving cleavage of the $\text{C}_\alpha-\text{C}_\beta$ bond is often referred to as the Norrish Type 2 process. A biradical species, such as (15) from hexan-2-one, can be envisaged as a common intermediate for both the cleavage and cyclization reactions.



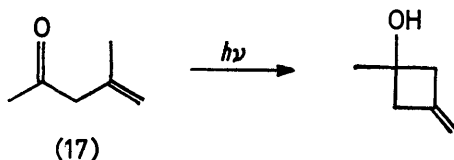
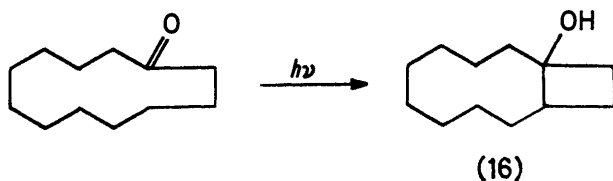
Cyclization is often the minor reaction pathway, but for certain systems cyclization is very efficient. In these there are either conformational factors facilitating formation of a four-membered ring or energetic factors inhibiting cleavage of the $\text{C}_\alpha-\text{C}_\beta$ bond. Such systems are cyclododecanone which gives about 75% of bicyclo[8,2,0]dodecan-1-ols (16), isomesityl oxide (17), α -diketones, and 11- or 20-oxo-steroids.

This is one of the most intensively studied of photochemical reactions from a mechanistic angle. Both singlet and triplet excited states of aliphatic ketones and aldehydes undergo the reaction. There is no reason to expect a great difference in reactivity between $n\pi^*$ singlet and triplet excited states for a given compound if the mechanism is the same for each state, since the energy and electron distribution in the two states are similar.¹⁷ In addition, the rate constant for

¹⁵ R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1969, 1098.

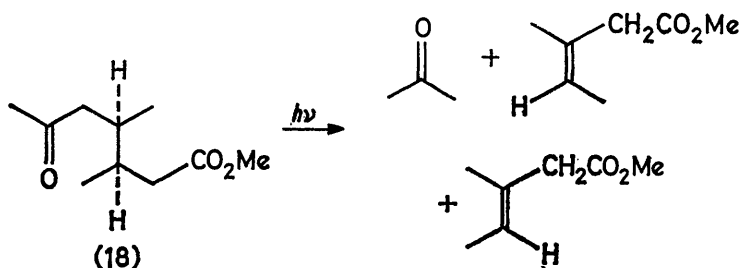
¹⁶ P. J. Wagner, *Accounts Chem. Res.*, 1971, 4, 168.

¹⁷ G. Porter in 'Reactivity of the Photoexcited Organic Molecule,' Interscience, New York, 1967.



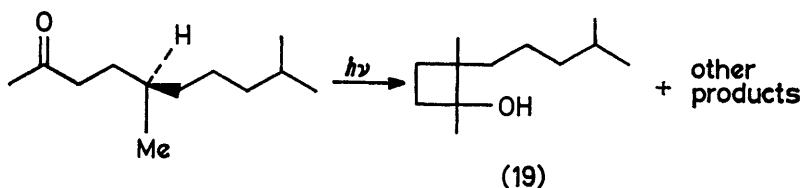
singlet reaction is often comparable to that for intersystem crossing, and the quantum *efficiency* of singlet reaction is reasonably high. The relative amounts of singlet and triplet reaction depend on the particular compound studied, since rate constants for hydrogen abstraction are sensitive to structure, particularly to the strength of the C—H bond broken, whereas the rate constants for intersystem crossing are not similarly sensitive. The efficiency of singlet reaction increases in a series of similar compounds as the C—H bond in the γ -position becomes progressively weaker, but reliable mechanistic interpretation is based on actual rate constants rather than on quantum yields, which are ratios of rate constants.¹⁸

The elimination reaction may be concerted or may proceed through a discrete biradical intermediate. For the *threo*- and *erythro*-isomers of (18), that part of the photoelimination which occurs from the singlet excited state is stereospecific whereas that from the triplet excited state is not.¹⁹ This suggests that the triplet reaction is non-concerted, but the singlet reaction is either a concerted process or proceeds through a very short-lived biradical for which a cleavage reaction is much faster than bond rotation. The same considerations apply to the photocyclization reaction, but studies on this are less extensive. There is some retention of optical activity in the cyclobutanols (19) derived from (5*R*)-5,9-dimethyl-decan-2-one, which suggests a degree of concertedness.

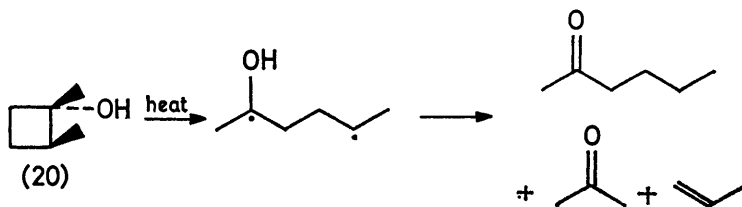


¹⁸ N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, 1969, 91, 7551.

¹⁹ L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *J. Amer. Chem. Soc.*, 1971, 93, 1984.



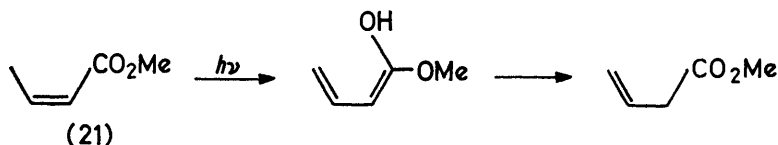
That a discrete biradical may be involved is supported by a study of the pyrolysis of 1,2-dimethylcyclobutanol (20),²⁰ which gives hexan-2-one as well as acetone, propene, and other products.



Aromatic ketones such as valerophenone ($\text{PhCOCH}_2\text{CH}_2\text{CH}_2\text{Me}$) differ from their aliphatic counterparts in that the rate constant for intersystem crossing is higher, and the efficiency of singlet reaction is negligibly low. Photoelimination and photocyclization occur solely from the triplet state.¹⁶ For many aromatic ketones the $n\pi^*$ and $\pi\pi^*$ triplet states are similar in energy, and when the $n\pi^*$ triplet is lower, photochemical reaction occurs with high efficiency, but when the $\pi\pi^*$ triplet is lower the efficiency of reaction is markedly reduced. This underlines the difference in the electronic nature of the two types of excited state and the consequent difference in reactivity.

Aromatic esters such as *n*-propyl benzoate ($\text{PhCO}_2\text{CH}_2\text{CH}_2\text{Me}$) undergo an analogous photoelimination reaction with low efficiency to give aromatic carboxylic acid and alkene. The inefficiency is caused by reversibility in the reaction sequence rather than by inefficiency in the primary chemical processes, which involve both singlet and triplet $\pi\pi^*$ excited states of the ester.²¹

Isomerization of certain $\alpha\beta$ -unsaturated carbonyl compounds to the $\beta\gamma$ -compounds is formally similar to the photoelimination described for saturated compounds, and again an enol is formed initially, for instance with methyl *cis*-but-2-enoate (21).²²



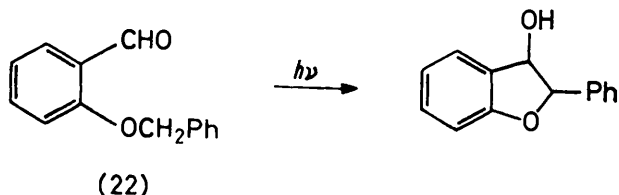
²⁰ E. D. Feit, *Tetrahedron Letters*, 1970, 1485.

²¹ J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. (B)*, 1971, 251.

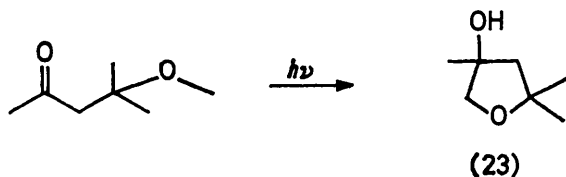
²² J. A. Barltrop and J. Wills, *Tetrahedron Letters*, 1968, 4987.

7 Other Intramolecular Hydrogen Transfers

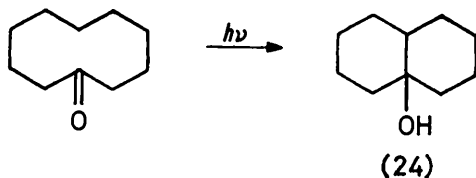
Systems without a hydrogen atom in the γ -position often give products by abstraction from another position, as with *o*-benzoyloxybenzaldehyde (22).²³



When competition can occur, the most favourable cyclic transition-state in photochemical (as in thermal) hydrogen abstraction is six-membered unless exceptional factors outweigh this preference in determining the relative rate constants for abstraction from various positions. One such factor is the bond strength at the site of abstraction, and 4-methoxy-4-methylpentan-2-one gives the tetrahydrofuran (23) as a photolysis product.²⁴ Abstraction of a hydrogen atom adjacent to an oxygen atom occurs in preference to a methyl hydrogen from the γ -position because of the weaker C—H bond involved in the former pathway.



A second factor influencing rate constants is conformational preference, and with cyclodecanone this plays an important part in the formation of (24) as major photolysis product²⁵ by abstraction from C-6. Cyclodecanone behaves 'normally', and as seen earlier gives bicyclo[8,2,0]dodecan-1-ol (16).



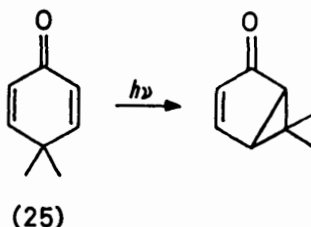
²³ S. P. Pappas and J. E. Blackwell, *Tetrahedron Letters*, 1966, 1171.

²⁴ D. J. Coyle, R. V. Peterson, and J. Hecklen, *J. Amer. Chem. Soc.*, 1964, **86**, 3850.

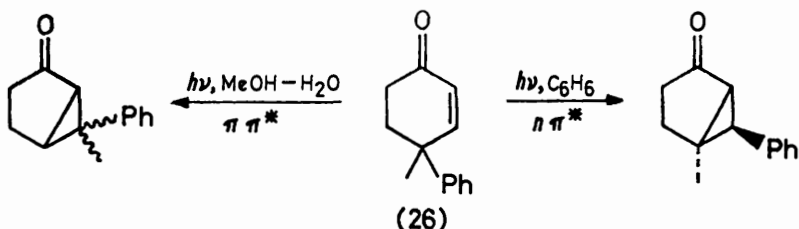
²⁵ M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, 1958, 302.

8 Molecular Rearrangements

The photorearrangements of cyclohexadienones and cyclohexenones have been the subjects of extensive research,²⁶ and an outline of the major reactions is given here. Cross-conjugated dienones, such as 4,4-dimethylcyclohexa-2,5-dienone (25), undergo an efficient rearrangement on photolysis to give bicyclic enones. There has been much discussion about the detailed reaction mechanism, and whether any intermediates involved have radical or polar ('zwitterionic') character. It seems agreed that rearrangement is a fast, triplet $n\pi^*$ reaction.



Conjugated cyclohexenones undergo a similar photorearrangement to give bicyclic ketones, but this reaction occurs less efficiently, apparently through a $\pi\pi^*$ triplet state. 4-Aryl-cyclohexenones can in addition undergo a rearrangement with aryl migration, *via* the $n\pi^*$ triplet. The polarity of the solvent alters the relative levels of the $n\pi^*$ and $\pi\pi^*$ triplet states, and thus controls the major products formed, as illustrated for 4-methyl-4-phenylcyclohex-2-enone (26).²⁷

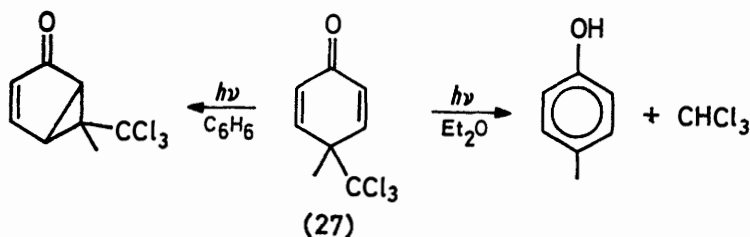


The $n\pi^*$ state of those cyclohexa-2,5-dienones with a good radical leaving group at C-4 may abstract hydrogen from a good hydrogen-donor solvent such as ether. The resulting radical can then break down to give a substituted phenol, as for the dienone (27).

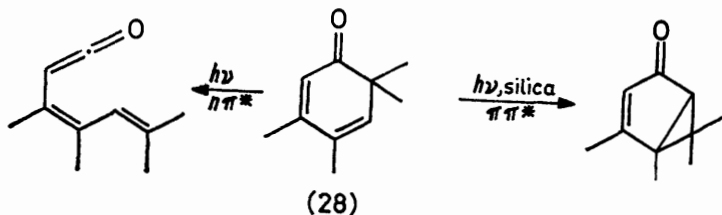
Cyclohexa-2,4-dienones afford different products according to the nature of the lowest excited state. The dienone (28) gives a ring-opened keten in normal solvents, when the lowest singlet state is $n\pi^*$. In the presence of silica gel, the

²⁶ For reviews, see (a) P. J. Kropp in 'Organic Photochemistry,' ed. O. L. Chapman, Dekker, New York, 1967, vol. 1, p. 1; (b) K. Schaffner, *Adv. Photochem.*, 1966, 4, 81.

²⁷ W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Amer. Chem. Soc.*, 1971, 93, 3674.

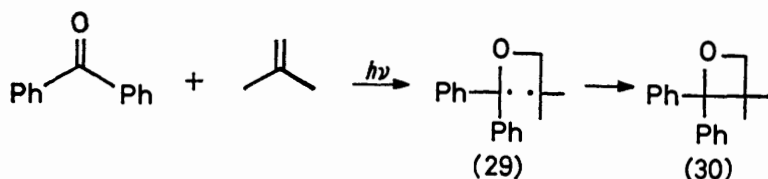


lowest state is $\pi\pi^*$ and the photorearrangement product is a bicyclic enone.²⁸



9 Photocycloaddition

Photolysis of carbonyl compounds in the presence of olefins generally leads to photocycloaddition products. Thus, benzophenone and isobutene give mainly (93%) the oxetan (30).²⁹



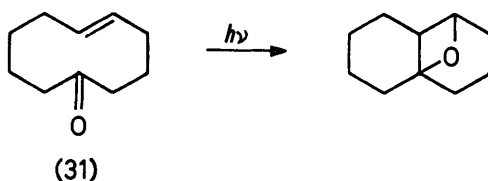
Only those carbonyl compounds with lowest triplet $n\pi^*$ states give oxetans efficiently; this parallels the efficiency for γ -hydrogen abstraction mentioned earlier. The electron-deficient oxygen atom of the carbonyl $n\pi^*$ state attacks the olefin to produce a biradical. Unsymmetrical olefins can produce more than one oxetan, but the major product has been rationalized as arising from the most stable biradical intermediate [e.g. (30) from (29)].³⁰

Addition may be intramolecular when the carbonyl and olefinic groups can attain a suitable geometry, as in the transannular reaction of *trans*-cyclodec-5-enone (31).

²⁸ J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, 1968, 90, 5296.

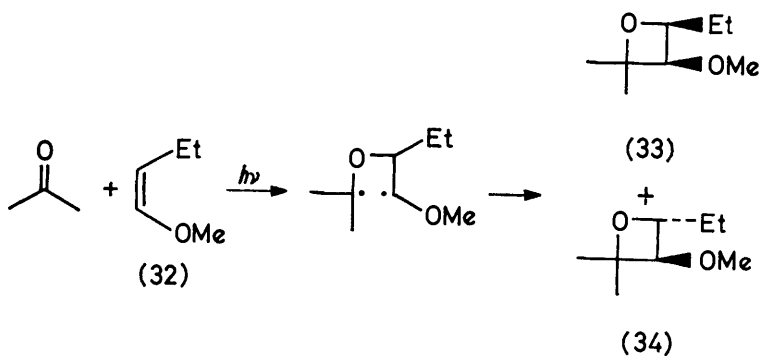
²⁹ For a review, see D. R. Arnold, *Adv. Photochem.*, 1968, 6, 301.

³⁰ G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, 1954, 76, 4327.



If carbonyl singlet and triplet states are of similar reactivity in photocycloaddition, the observed multiplicity of the reactive excited state depends on the relative rates of other competing processes available to the excited states of the carbonyl compound, such as intersystem crossing or triplet energy transfer.

Aliphatic carbonyl compounds react photochemically with electron-rich olefins through both singlet and triplet states. The singlet reaction largely retains the stereochemistry of the original olefin, and occurs by a concerted or very short-lived biradical pathway. The triplet mechanism involves biradical intermediates with sufficient lifetime for bond rotations to occur before ring-closure: acetone triplets react with *trans*- or *cis*-1-methoxy-1-butene (32) producing a 1:1 mixture of oxetans (33) and (34).³¹

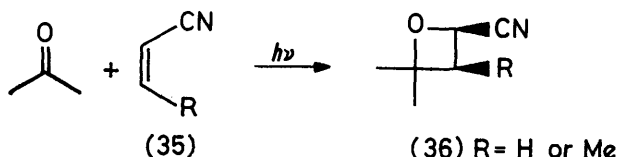


For aromatic carbonyl compounds, intersystem crossing occurs so rapidly that photocycloaddition is observed only from the triplet state.

Another mechanism of photocycloaddition is possible with electron-deficient olefins. Attack by the $n\pi^*$ carbonyl oxygen atom on the olefin is unfavourable because of the lowered electron-density at the double bond. However, electron transfer can occur from the singlet excited carbonyl compound to the electron-deficient olefin, giving an excited singlet complex. This complex may revert to reactants, or react to give oxetan. The addition is highly stereospecific; acetone and *cis*-crotononitrile (35; R = Me) give entirely the *cis*-oxetan (36; R = Me).³²

³¹ N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 1970, **92**, 320.

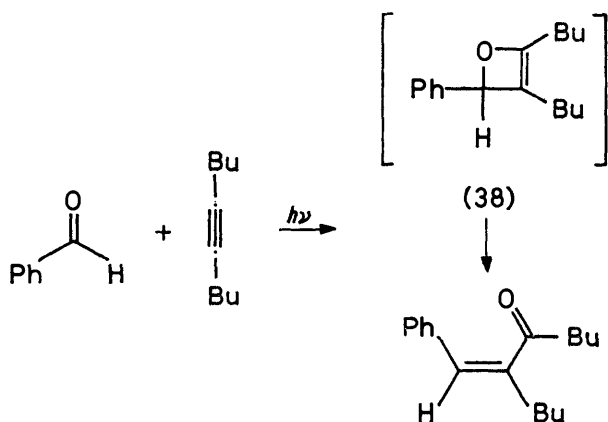
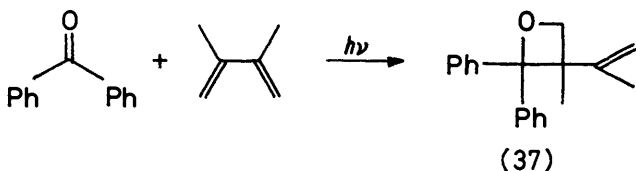
³² N. J. Turro, C. Lee, N. Schore, J. Barltrop, and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1971, **93**, 3079.



Another facet of this different mechanism of oxetan formation is that the product no longer has the orientation expected from a 'most stable biradical' mechanism: acetone and acrylonitrile (35; R=H) produce (36; R=H) as the only oxetan product. The observed orientation of addition is rationalized by a perturbational molecular orbital calculation on the *concerted* approach of the reactants.

When the triplet excitation energy of the olefin is below that of the carbonyl compound, triplet energy transfer from carbonyl to olefin is rapid. It then becomes possible to observe effective competition between energy transfer and photocycloaddition. Thus, benzophenone triplets add to a conjugated diene to give oxetan [e.g. (37) from 2,3-dimethylbuta-1,3-diene], and triplet energy transfer competes effectively.³³

Aliphatic ketones also undergo photocycloaddition to conjugated dienes.³⁴



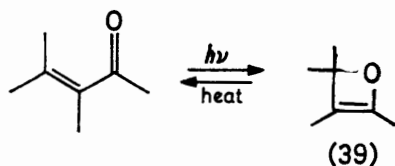
³³ J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, 1971, **93**, 4794.

³⁴ J. A. Barltrop and H. A. J. Carless, *Chem. Comm.*, 1970, 1637.

Reaction is apparently stereospecific and occurs from the ketone singlet excited state.

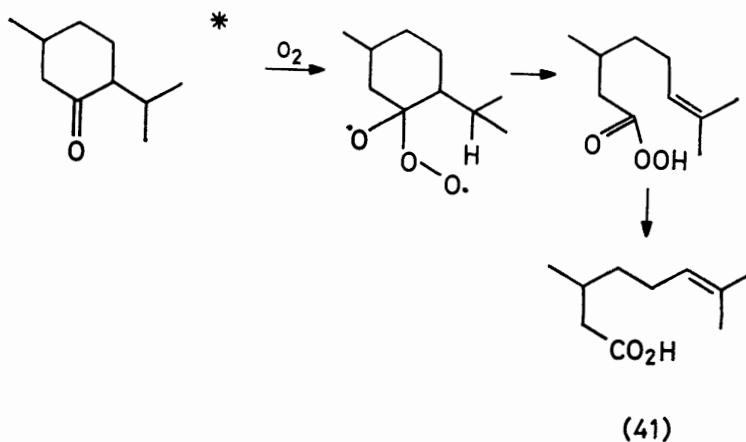
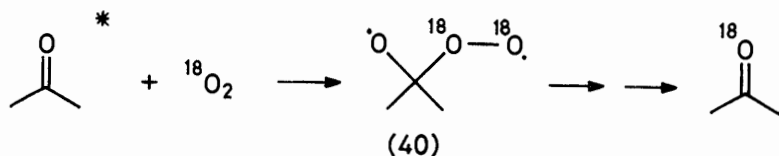
Carbonyl compounds undergo photocycloaddition to alkynes, to give oxetens such as (38), but usually the isolated products are the $\alpha\beta$ -unsaturated carbonyl compounds arising from thermal isomerization of the oxeten.

Oxetens such as (39) may also be formed by an intramolecular photoaddition of $\alpha\beta$ -unsaturated ketones.³⁵ The product regresses thermally to starting material—an observation which may help to explain the apparent photoinertness of certain acyclic $\alpha\beta$ -unsaturated ketones.



10 Photo-oxidation

The excited states of aliphatic ketones are reactive towards molecular oxygen, and acetone undergoes efficient isotope exchange³⁶ on irradiation with $^{18}\text{O}_2$. An adduct (40) is proposed as intermediate.



³⁵ L. E. Friedrich and G. B. Schuster, *J. Amer. Chem. Soc.*, 1969, 91, 7204.

³⁶ R. Srinivasan, *Adv. Photochem.*, 1963, 1, 83.

I. Photochemistry of Carbonyl Compounds

On irradiation in oxygen-saturated solutions, cyclic ketones are oxidized to unsaturated acids or keto-acids. Menthone, for instance, yields acid (41), possibly by the mechanism shown.³⁷

These reactions, unlike photoreduction reactions of ketones, have not yet been extensively investigated.

³⁷ G. Quinkert, *Pure Appl. Chem.*, 1964, 9, 607.