Photochemistry of Carboxylic Acid Derivatives

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I. Introduction

The photochemical reactions of organic compounds containing a carbonyl (C=O) group have been extensively investigated over the last 20 years or so. General reviews and books on organic photochemistry have justifiably chosen most of their examples from work on the more widely studied aldehyde and ketone compounds rather than carboxylic acids and their derivatives, and this review is intended to provide a balance by concentrating on the latter compounds. The photochemistry of acid derivatives is of interest in its own right, and the presentation here also brings out the similarities and differences between photoreactions of these compounds on the one hand and of aldehydes and ketones on the other. A recent book on the detailed photochemistry of heterocyclic systems[1] includes some of the compound types described here (for example, lactones and cyclic imides), but there is no wide-ranging review of the subject area.

The primary literature dealing with the photochemistry of carboxylic acid derivatives is very large, and this review does not make reference to all of it. Within the scope of the review are all photochemical reactions of compounds containing the C=O unit attached directly to a heteroatom group, except where the acid group is a "trivial" substituent, neither absorbing the radiation nor playing a significant part in the mechanism. The intention is to give a balanced accouht with a wide range of examples built into a mechanistic descriptive framework. Where a choice of example needed to be made, reference is often to more recently published work, not because newer necessarily equals better, but because the later publication normally contains all the relevant older references, whereas the reverse is obviously not true.

II. Excited States

The first electronically excited states (singlet and triplet) of carboxylic acids and their derivatives are higher in energy than are the lowest excited states of aldehydes or ketones, and the reason can be seen by considering a simple orbital interaction diagram (Figure 1). The doubly occupied nonbonding orbital on the saturated heteroatom adjacent to the carbonyl group interacts with the π-symmetry orbitals of the C=O group, and in particular the carbonyl π^* orbital is raised in energy. This means that the $n \rightarrow \pi^*$ transition in the acid derivative is of higher energy than the corresponding transition in the unperturbed carbonyl compound.

In the literature there are quite a number of ultraviolet absorption data for carboxylic acids and their derivatives. In general, the data indicate that aliphatic acids, esters, and amides exhibit an absorption maximum at fairly short wavelength (λ_{max} <220 nm) which is of low intensity ($\epsilon < 100$ L mol^{-1} cm^{-1}) and undergoes a blue shift in polar solvents. This behavior is typical of $n \rightarrow \pi^*$ carbonyl transitions, and it points to the lowest singlet excited states being (n,π^*) in character. In the vacuum ultraviolet region there is a more intense band, with λ_{max} ~160 nm ($\epsilon \sim$ 2500–4000). A recent detailed study[2] of the absorption spectra of aliphatic carboxylic acids (monomeric and dimeric) and esters gives average values for λ_{max} of 206 nm (average $\epsilon \sim 70$) for acids in acetonitrile solvent, and of 213 nm ($\epsilon \sim 75$) for ethyl alkanoates in hexane. This $n \rightarrow \pi^*$ band is at shorter wavelength in a more polar solvent, and for esters the band disappears in the presence of mineral acid because the carbonyl oxygen is protonated. With neat liquid samples a very weak band is seen at much longer wavelength (272 nm (ϵ <0.05) for acids, 276 nm ($\epsilon \sim 0.05$) for esters) which can be attributed to singlet → triplet transitions. Amides and γ- or δ-lactams show a similar $n \rightarrow \pi^*$ singlet → singlet absorption band at short wavelength (λ_{max} <210 nm), but for α-lactams there appears to be less interaction between the carbonyl group and the nitrogen atom, since the absorption maximum[3] is at much longer wavelength (250 nm in hexane, 235 nm in alcohol). Acid derivatives containing the larger heteroatoms (Cl, Br, S) have ultraviolet absorption bands at longer wavelength [e.g., for acetyl chloride[4] λ_{max} 259, 266 nm (ϵ 46); for acetyl bromide[4] λ_{max} 273 nm (ϵ 56); for ethyl thiolacetate[5] λ_{max} 231.5 nm ($\epsilon \sim 5000$)], and this indicates that the interaction between Cl, Br, or S and the C=O group is smaller than that between N or O and the C=O group.

Luminescence from simple aliphatic acids, esters, or amides is very weak, but a study[6] of emission from other amides such as α-oxoamides led to the conclusion that for simple amides the nonemissive lowest triplet state is (π,π^*) with an energy of about

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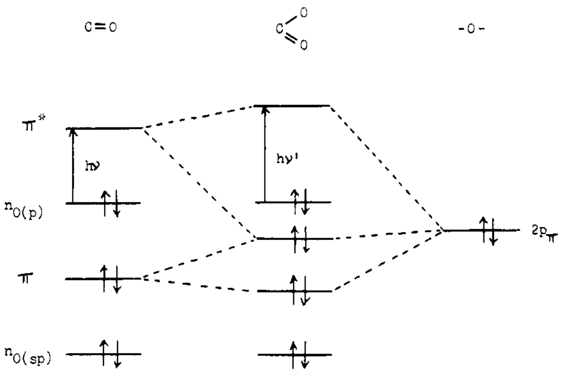


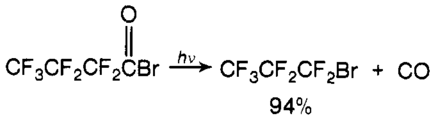
Figure 1. Orbital interaction diagram for a carboxylic acid derivative.

103–110 kcal mol^{-1}. Aromatic carboxylic acid derivatives fluoresce and phosphoresce more strongly, and both singlet and triplet emitting states are (π,π^*) in electronic character. Typical data[7] are: for alkyl benzoates at 77 K, the triplet energy is ~78 kcal mol^{-1} and the phosphorescent lifetime ~2.5 s; for alkyl benzamides at 77 K, E_T is ~78 kcal mol^{-1} and τ_p is ~1.6 s; fluorescence is weak ($\phi_f < 0.1$) for benzoates and very weak ($\phi_f < 0.01$) for benzamides. With phthalimides[8] the evidence points to the existence of a low-lying, nonfluorescent (n,π^*) singlet state.

The general pattern which emerges is that saturated carboxylic acids, esters, or amides have lowest excited states that are S_1 (n,π^*) and T_1 (π,π^*), whereas for aromatic compounds Ar–C(=O)–X both S_1 and T_1 are (π,π^*) in nature.

III. α-Cleavage

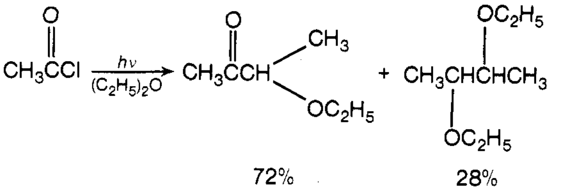
Cleavage of a bond α to an (n,π^*) excited carbonyl group is one of the most typical processes in the photochemistry of aldehydes and ketones, and the same process is widely encountered in the photochemistry of acid derivatives. The choice of which α-bond cleaves (carbon–carbon or carbon–heteroatom) varies from one type of acid derivative to another, and in a few classes of reaction the fragmentation of one of the radicals produced by α-cleavage (e.g., by loss of carbon monoxide) leads to products whose chemical composition does not provide an answer to the question of the sequence of bond cleavages. In general the α-bond with the lower homolytic bond strength is expected to break first. With acyl halides there is usually little doubt that the (O=)C—Hal bond breaks in preference to the (O=)C—C bond except for acyl fluorides, in which there is the relatively strong C—F bond. The overall product formation may not be helpful in identifying the sequence of cleavage if the reaction is one of decarbonylation (eq 1),[9] but in some instances the radical has been detected, as with the orange-red benzoyl radical (Ph$\dot{C}$=O) obtained[10] by low-temperature (−190 °C) photolysis of benzoyl bromide. In other cases the acyl radical reacts prior to decarbonylation, and in a good hydrogen-donating solvent such as ether the major products in the photolysis of acetyl chloride[11] are formed from the acetyl radical (eq 2). An exception to the generalization concerning carbon–halogen bond cleavage is with oxalyl chloride[12] from which products are formed by initial carbon–carbon bond cleavage (eq 3), although oxalyl bromide undergoes carbon–bromine homolysis to give eventually molecular bromine and carbon monoxide. The difference can be accounted for in terms of the relative strengths of the C–Cl, C–C, and C–Br bonds in these compounds.



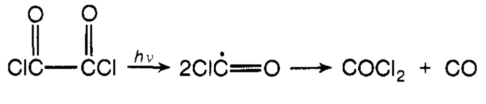
$$CF_3CF_2CF_2\overset{O}{\overset{\|}{C}}Br \xrightarrow{h\nu} CF_3CF_2CF_2Br + CO$$

(1)

94%



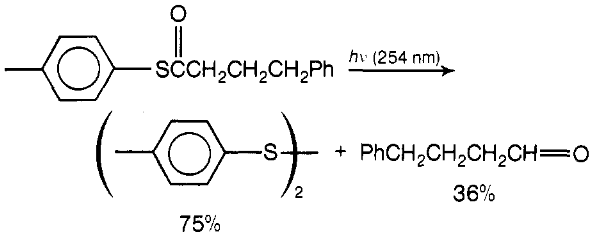
(2)



$$Cl\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}Cl \xrightarrow{h\nu} 2Cl\dot{C}{=}O \longrightarrow COCl_2 + CO$$

(3)

Thiolesters provide another example of compounds where homolytic carbon–heteroatom α-bond fission is the predominant primary process in the photochemical reactions. The major products are usually[13] an aldehyde formed by hydrogen abstraction of the acyl radical and a disulfide formed by combination of two thiyl radicals (eq 4). There is very little sign of reactions corresponding to the Norrish type 2 photoelimination (see section VI.B) or the photo-Fries reaction (see section III.A) of the corresponding oxygen compounds (esters). The ready generation of acyl radicals by photolysis of a thiolester can be employed[14] in synthetic procedures involving intramolecular radical cyclization (eq 5).



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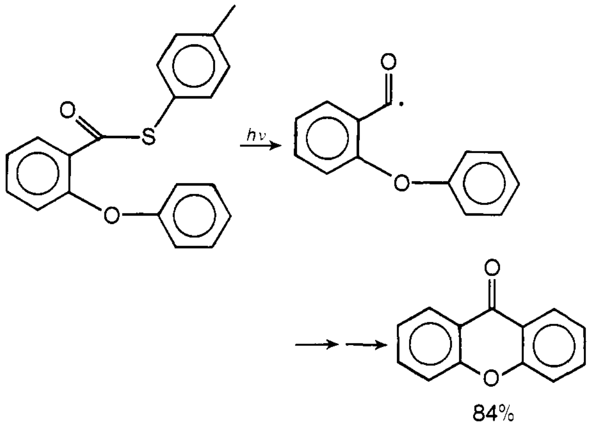
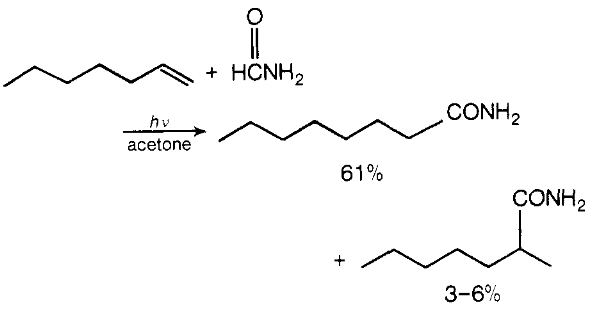


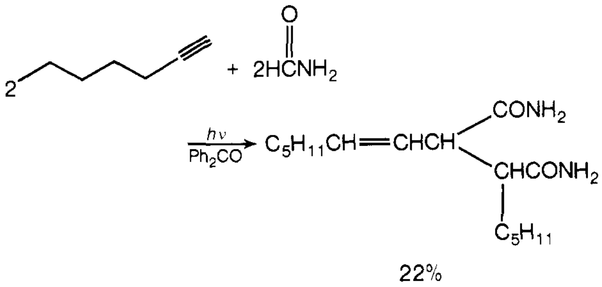
(5)

Formate esters and formamides undergo homolytic (O=)-C—H bond cleavage on irradiation. Carbon monoxide is a major product[15] in the photolysis of formates in the liquid phase, and a radical trapping and ESR study[16] indicates that the radical O=$\dot{C}$OR is formed. A competitive reaction to give R· by cleavage of the β oxygen-carbon bond (see section IV.A) is important if the radical is stabilized, as it is when R = *tert*-butyl. In a similar ESR study[17] the radical O=$\dot{C}NH_2$ has been detected in the low-temperature (77 K) photolysis of formamide. This particular α-cleavage process has been employed in the synthesis of more complex amides from formamide.[18] In the absence of added reagent, irradiation of formamide gives oxamide, $(H_2NCO)_2$. When a terminal alkene is present, anti-Markownikoff addition occurs to give an unbranched carboxamide (eq 6); nonterminal alkenes give mixtures of the two possible 1:1 products. With a terminal alkyne a 2:2 addition product[19] predominates (eq 7), whereas a nonterminal alkyne gives 1:2 products (eq 8). In neither case is it possible to isolate substantial amounts of the (intermediate?) 1:1 adducts. Aromatic hydrocarbons are also attached by the formamido radical, leading overall to substitution products.

The formamide reactions can be brought about by direct irradiation or by using a sensitizer such as acetone. In the presence of the ketone sensitizer it is likely that energy transfer does



(6)



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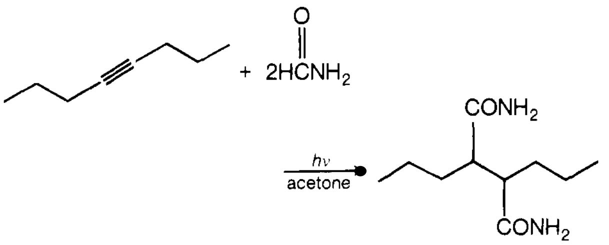


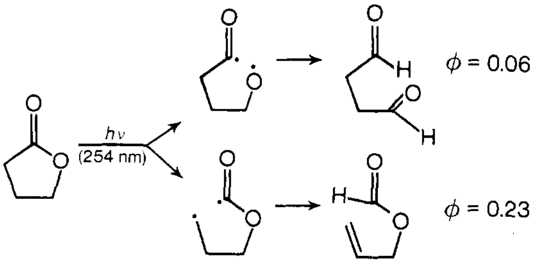
(8)

not occur, but rather the excited sensitizer abstracts a hydrogen atom from formamide to produce the $O{=}\dot{C}{-}NH_2$ radical.

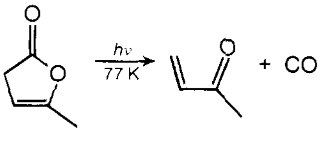
A. Esters

Esters and lactones can undergo α-cleavage of the (O═)C—O bond or the C—C(═O) bond on irradiation, or alternatively β-cleavage of the O—C bond (which often leads to decarboxylation; see section IV.A). The balance between α- and β-fission depends on a number of factors related to the relative bond strengths, and stabilization of a particular radical can have a major influence. Thus benzyl esters normally undergo β-cleavage to give benzyl radicals or ions, whereas phenyl esters or enol esters undergo preferential α-cleavage to give resonance-stabilized alkoxyl radicals. With simple alkyl esters (including formates[16]) carbon–carbon α-cleavage is the major primary process, and $O{=}\dot{C}{-}OR$ radicals are detected in flash photolysis experiments.[20]

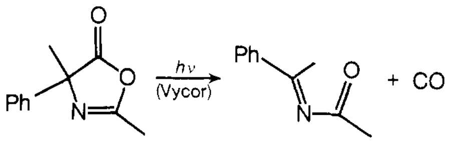
Saturated lactones such as γ-butyrolactone or its alkyl-substituted analogues undergo α-cleavage on either side of the carbonyl group[21] to give an unsaturated formate or a dialdehyde (eq 9). In each case homolytic bond fission is followed by hydrogen atom transfer to give the observed product, and the processes resemble the corresponding reactions of cyclic ketones which give unsaturated aldehydes on photolysis. A related enol lactone[22] gives a decarbonylated α-cleavage product (eq 10), which can be observed spectroscopically in a low-temperature irradiation. A structurally similar substituted Δ^2-oxazolin-5-one behaves in the same way (eq 11), although the corresponding 2-trifluoromethyloxazolinone liberates carbon dioxide in a process initiated by oxygen–carbon β-cleavage,[23] presumably because of the radical-stabilizing influence of the CF_3 group.



(9)

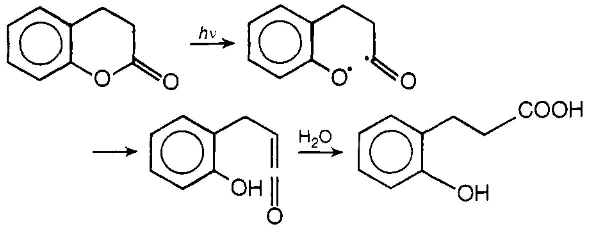


(10)



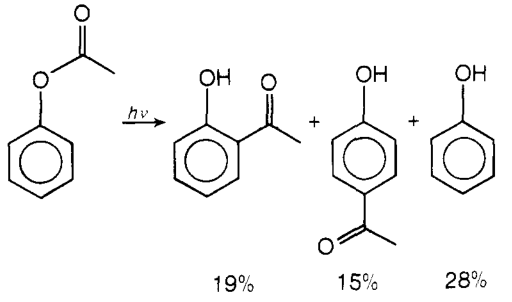
(11)

Dihydrocoumarin,[24] a lactone in which the saturated oxygen is linked directly to an aromatic ring, undergoes unambiguous (O═)C—O cleavage followed by hydrogen transfer to give a ketene (observed by infrared spectroscopy at low temperature) which subsequently reacts with water (eq 12) or another nucleophile in an overall photosolvolysis reaction.



(12)

The most characteristic photoreaction of phenyl esters is the photo-Fries rearrangement, in which *o*- and *p*-acylphenols are formed together with some of the parent phenol (eq 13). The photochemical reaction differs from the thermal (ionic) Fries reaction in that rearrangement or elimination of alkyl groups is much less frequently encountered in the photo-Fries process, ortho chlorine and some other ortho substituents can be dis-



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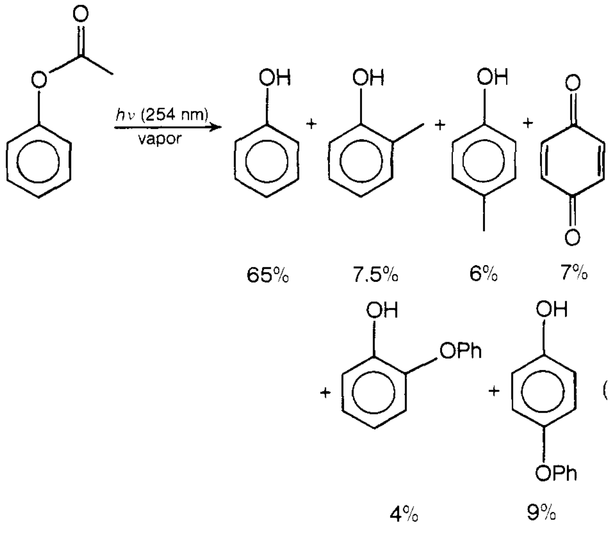
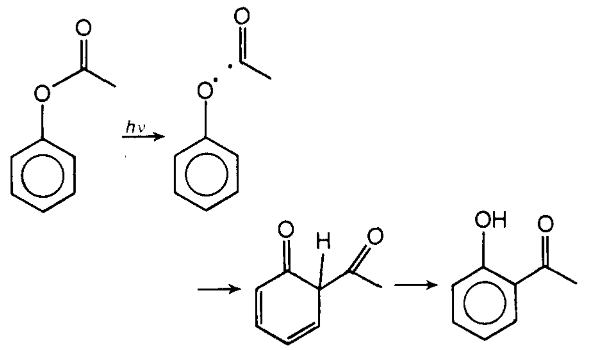


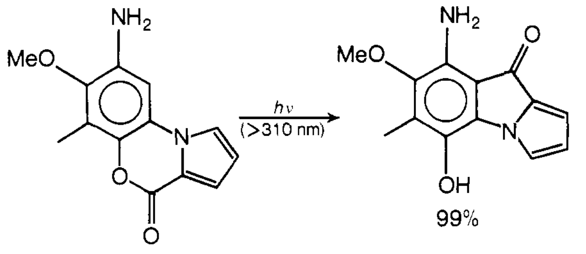
(14)



(15)

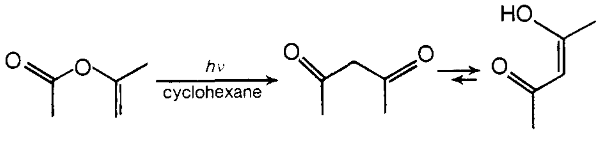
placed, and decarboxylation is occasionally a major side reaction. There have been a number of good reviews of this process,[25] and more recent results have supported the view that the reaction is an intramolecular process proceeding by way of homolytic α-cleavage in the singlet excited state, followed by in-cage recombination of the radicals. Phenoxyl radicals that escape from the solvent cage abstract hydrogen to form phenol, and in the vapor-phase photolysis of phenyl acetate[26] the major product is phenol and no photo-Fries rearrangement products are detected (eq 14). This is in keeping with a situation where there is no significant cage effect. CIDNP studies[27] of the photolysis of *p*-tolyl *p*-chlorobenzoate are compatible with a singlet caged-radical-pair mechanism, and flash photolysis studies[28] of phenyl acetate have led to the detection of phenoxyl radicals and a 2,4-cyclohexadienone intermediate (eq 15).

In a few instances a meta photo-Fries rearrangement has been observed where the molecular structure is such as to prevent ortho and para substitution and to promote meta substitution. Such an example is seen (eq 16) in the efficient photochemical rearrangement of a suitably substituted phenol lactone.[29]



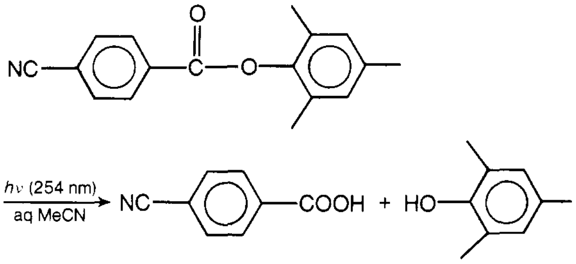
(16)

Vinyl esters[25] undergo a rearrangement which is very similar to the photo-Fries reaction, and the product is a β-diketone (eq 17). If the β-diketone is not largely enolized under the reaction conditions, further photoreaction occurs, and the β-ketoaldehydes ($RCOCH_2CH{=}O$) formed from simple vinyl esters ($RCOOCH{=}CH_2$) undergo efficient secondary photodecarbonylation. On the other hand, when the product β-diketone *is* largely enolized it acts as an efficient internal filter and also as a quencher for the photoreaction, and the extent of chemical conversion is limited.



(17)

Benzyl esters undergo photohydrolysis by a β-cleavage mechanism (see section IV.A), but aryl esters such as mesityl *p*-cyanobenzoate (which is incapable of undergoing an ortho or para photo-Fries reaction) also undergo photohydrolysis (eq 18). The reaction occurs through both the singlet and triplet (π,π^*) excited states, and the proposed mechanism[30] involves attack by water on the carbonyl carbon of the excited state, followed by heterolytic cleavage of the α bond. In methanol the product is methyl *p*-cyanobenzoate.

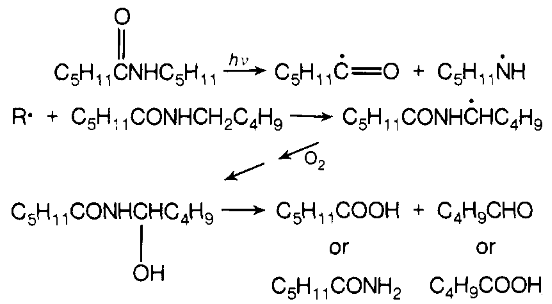


(18)

$\phi = 0.10$, ~90%

B. Amides

Like esters, amides undergo a wide variety of α-cleavage reactions on irradiation. Saturated acyclic or cyclic amides or imides give radical-derived products, although with systems such as *N*-hexylhexanamide ($C_5H_{11}CONHC_6H_{13}$) a rather complex mixture of products is formed[31] by reaction with the solvent. There is very little (<3%) product formation which might be attributed to a Norrish type 2 photoelimination process (see section VI.B). The photooxidation of amides is a reaction of significance in the photodegradation of natural or synthetic polyamides, and it is thought[32] to involve homolytic carbon–nitrogen α-cleavage in the light of results from carbon-14 labeling studies. The photolytic cleavage provides radicals which subsequently abstract the hydrogen atom on the carbon adjacent to the amide nitrogen (eq 19).



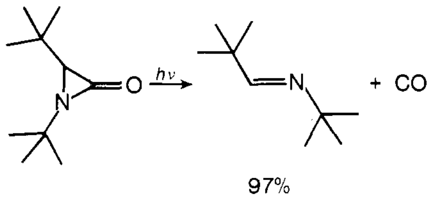
$$C_5H_{11}\overset{O}{\overset{\|}{C}}NHC_5H_{11} \xrightarrow{h\nu} C_5H_{11}\dot{C}{=}O + C_5H_{11}\dot{N}H$$

$$R\cdot + C_5H_{11}CONHCH_2C_4H_9 \longrightarrow C_5H_{11}CONH\dot{C}HC_4H_9 \xrightarrow{O_2}$$

$$\underset{\displaystyle OH}{C_5H_{11}CONHCHC_4H_9} \longrightarrow \begin{matrix} C_5H_{11}COOH & + & C_4H_9CHO \\ \text{or} & & \text{or} \\ C_5H_{11}CONH_2 & & C_4H_9COOH \end{matrix}$$

(19)

It is not possible to tell which α-bond breaks first in those photoreactions of amides which lead to decarbonylation. This occurs (eq 20) for α-lactams[3] (no carbon monoxide is produced by heating these α-lactams) and for some saturated cyclic imides (eq 21).[33] In other cases a distinction can be made. Thus



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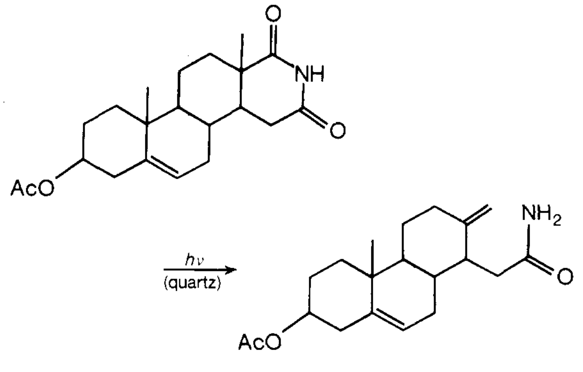

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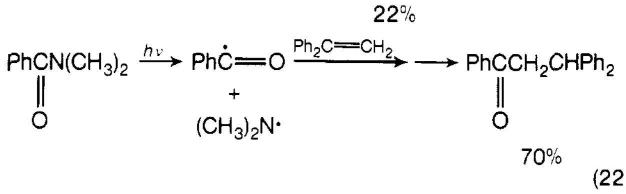
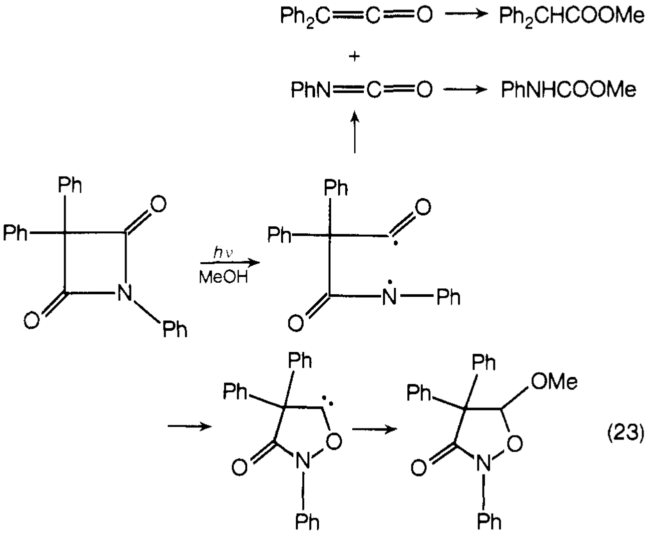


(22)

(O=)C—N cleavage takes place when *N,N*-dimethylbenzamide is irradiated[34] in the presence of 1,1-diphenylethylene, and the isolated adduct is derived from the benzoyl radical (eq 22).

A similar cleavage accounts[35] for the ring-expansion products formed from azetidinediones in alcohol (eq 23), a reaction in which the four-membered cyclic imide behaves like the related cyclobutanones or cyclobutanediones. An interesting α-cleavage and ring-contraction reaction is reported[36] on irradiation of cyclic saturated hydrazides (eq 24), though it is suggested that bonding of the carbonyl carbon atom to the β-nitrogen atom promotes the reaction and precedes α-cleavage.



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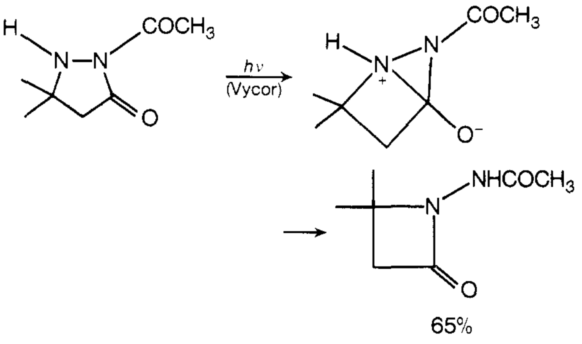
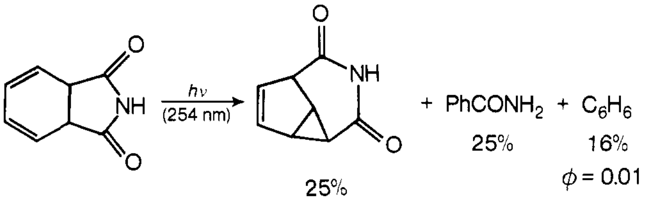


(24)

Cleavage of the other α-bond, (O=)C—C, can occur in amides or imides, and the methyl radical has been detected[17] by ESR spectroscopy in the photolysis of acetamide (CH_3CONH_2). In a different context, carbon–carbon α-cleavage must occur at some stage in the process by which 1,2-dihydrophthalimide undergoes a singlet state rearrangement[37] with a 1,2-shift to give a tricyclic imide (eq 25). The reaction bears a formal resemblance to the oxa-di-π-methane rearrangement of β,γ-unsaturated ketones, and a bond to the β-carbon may be formed before the α-bond breaks. The other major products of this reaction, however, probably do arise by initial cleavage of the carbon–carbon α bond. β-Lactams provide a nice example of the balance between the two modes of α-cleavage in amides,[38] since some β-lactams give imine and ketene by photocleavage (eq 26) and some give alkene and isocyanate (eq 27). The reaction seems to proceed by way of a singlet excited state, although thermal cleavage can also give rise to alkene and isocyanate.



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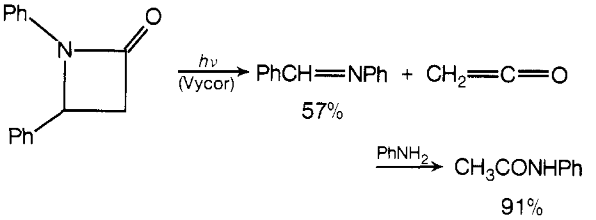

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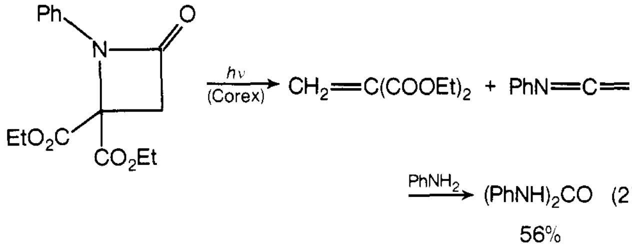
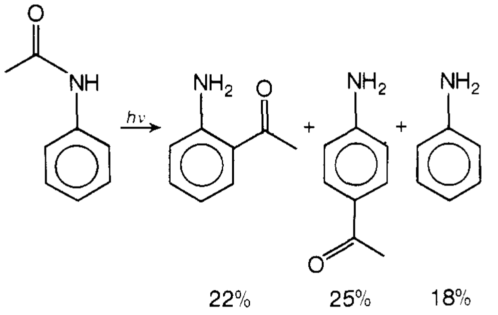


(27)

N-Acylanilines undergo a photochemical rearrangement which parallels the photo-Fries rearrangement of phenyl esters, and typically[39] acetanilide gives *o*- and *p*-acetylaniline and aniline itself (eq 28). The reaction is thought to occur, like the photo-Fries reaction, by a cage-radical-pair mechanism, and in one study[40] a small amount of substituted hydrazine was obtained (eq 29) as a result of the combination of two amino radicals which escape from the solvent cage.



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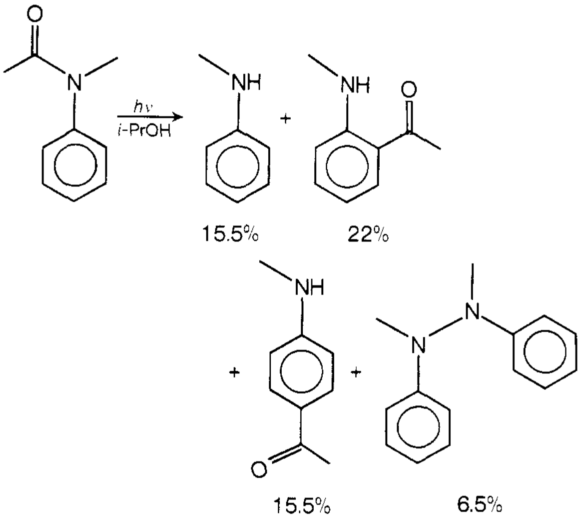
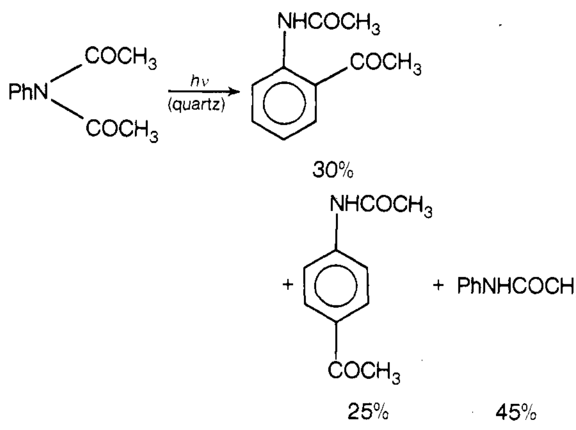
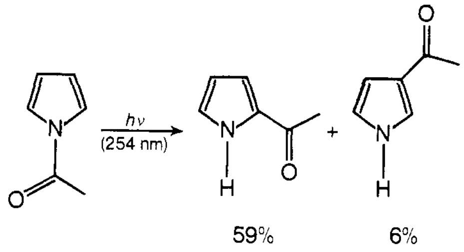


(29)

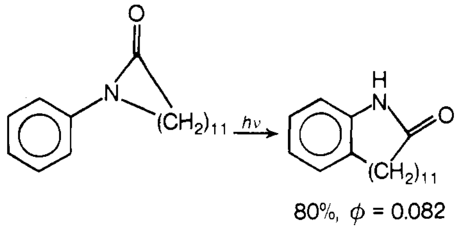
A variety of systems can take part in the process, including imides (eq 30),[41] *N*-acylpyrroles (eq 31),[42] and *N*-phenyl lactams (eq 32).[43] If the ortho position is blocked, the para rearrangement still occurs, and *N*-aryl lactams in this situation can give rise to para-bridged products (eq 33).[44]



(30)



(31)



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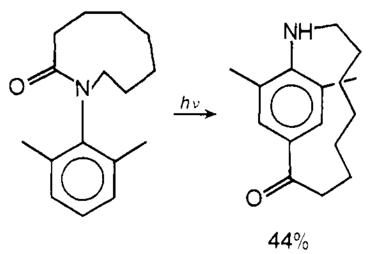
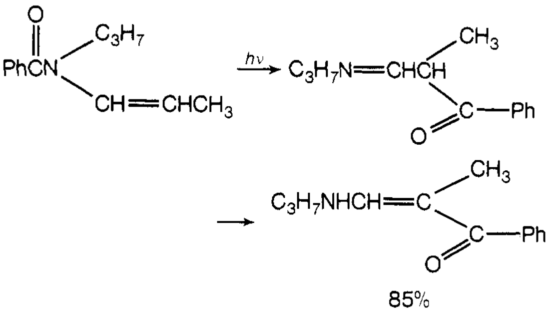
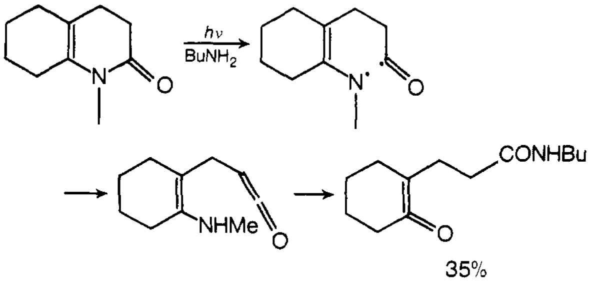


(33)

Enamides, like acylanilines, undergo a 1,3-shift[45] on irradiation (eq 34), and the first-formed product tautomerizes to give an enamino ketone. Some less flexible enamides undergo α-cleavage without acyl migration; instead hydrogen transfer gives a ketene which can be trapped[46] by added nucleophile (eq 35).



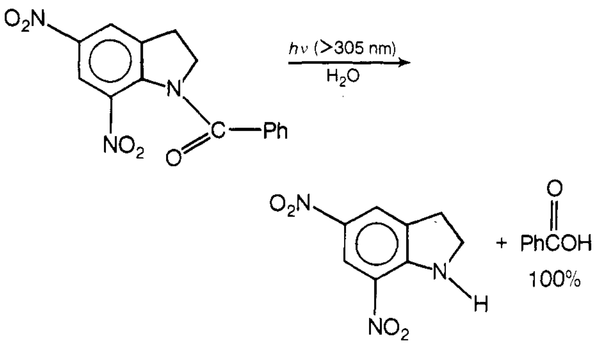
(34)



(35)

In this the enamide reaction resembles that of dihydrocoumarin (see eq 12). Finally, many enamides and acylanilines are also capable of taking part in photocyclization processes (see section V.A.). As an example, irradiation of benzanilide gives phenanthridone (see eq 88) as well as *o*- and *p*-benzoylanilines and aniline.

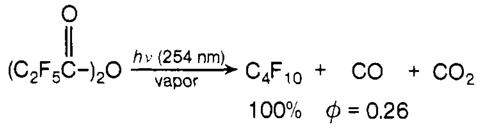
A heterolytic carbon-nitrogen α-cleavage mechanism has been postulated[47] to account for the efficient photohydrolysis of certain nitroaromatic substituted amides (eq 36). Whatever the details of the mechanism, the nitro group must play some part in it, because compounds lacking the NO_2 group in the ortho position do not undergo the reaction. These nitroaromatic amine derivatives may provide a useful photolabile protecting group for carboxylic acids.



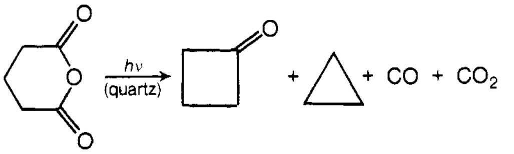
(36)

C. Anhydrides and Acids

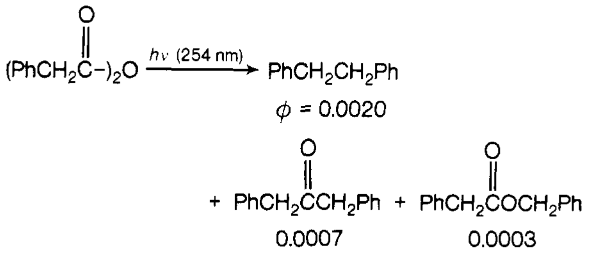
Irradiation of acid anhydrides leads to products by loss of carbon dioxide, loss of carbon monoxide, or loss of both, and reactions have been reported involving either direct irradiation or triplet mercury $Hg(^3P_0)$ sensitization. Perfluoroacyl anhydrides give rise[48] to perfluoroalkanes (eq 37), while glutaric anhydride on irradiation in the liquid phase[49] gives cyclobutanone as well as cyclopropane (eq 38). Phenylacetic anhydride gives[50] some dibenzyl ketone and benzyl phenylacetate as well as 1,2-diphenylethane (eq 39). The products do not indicate whether the initial cleavage involves the (O=)C—O or the (O=)C—C bond, nor does the fact that the phenylacetic compounds react much more efficiently than the 3-phenylpropanoic or 4-phenylbutanoic analogues, since the efficiency may reflect the competition between recombination and decarboxylation of the first-formed radicals rather than competition between two different initial cleavage steps. It has been suggested that loss of carbon monoxide to form the ester may take place by a different (polar) mechanism in the light of considerations of expected rate constants for decarbonylation and decarboxylation of radicals.



$$(C_2F_5\overset{\overset{\displaystyle O}{\|}}{C}\text{-})_2O \xrightarrow[\text{vapor}]{h\nu\ (254\ nm)} \underset{100\%}{C_4F_{10}} + \underset{\phi = 0.26}{CO} + CO_2 \qquad (37)$$

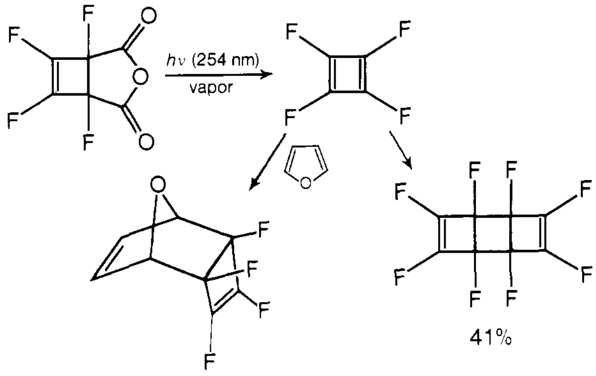


(38)



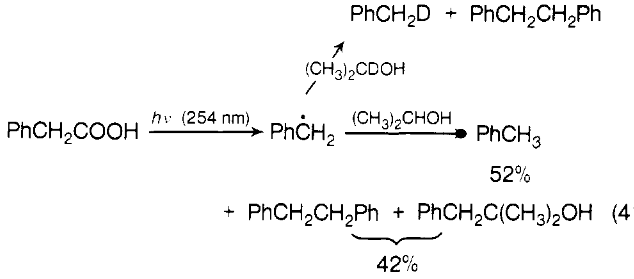
$$(PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{-})_2O \xrightarrow{h\nu\ (254\ nm)} \underset{\phi = 0.0020}{PhCH_2CH_2Ph} + \underset{0.0007}{PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2Ph} + \underset{0.0003}{PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_2Ph} \qquad (39)$$

Anhydrides, like β-lactones (see section IV.A), have been employed as photochemical precursors to reactive species such as substituted cyclobutadienes (eq 40)[51] or cyclobutadiene itself.



(40)

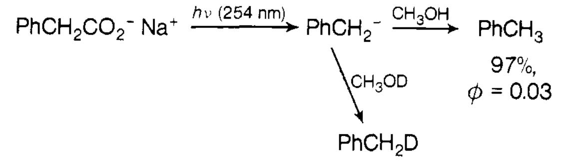
The photodecarboxylation of carboxylic acids and their salts has been the subject of a number of studies. The mechanism of reaction for phenylacetic acid on direct irradiation[52] involves a singlet excited state which undergoes cleavage of the α bond (O=)C—C to give the benzyl radical and then products derived from this radical (eq 41). In the presence of $(CH_3)_2CDOH$ the toluene produced contains one deuterium atom, which is in keeping with a radical pathway for the reaction. The reaction of the corresponding sodium salt gives largely the benzyl anion and thence toluene by protonation (eq 42); very little 1,2-diphenylethane is formed. In this case the presence of CH_3OD is required to produce deuterated toluene, supporting the operation of an ionic mechanism.



$$\mathrm{PhCH_2COOH} \xrightarrow{h\nu\ (254\ \mathrm{nm})} \mathrm{Ph\dot{C}H_2} \xrightarrow{\mathrm{(CH_3)_2CHOH}} \underset{52\%}{\mathrm{PhCH_3}}$$

$$\mathrm{Ph\dot{C}H_2} \xrightarrow{\mathrm{(CH_3)_2CDOH}} \mathrm{PhCH_2D} + \mathrm{PhCH_2CH_2Ph}$$

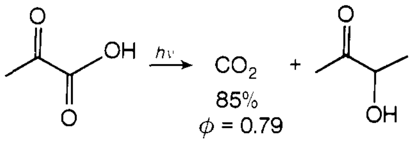
$$+ \underbrace{\mathrm{PhCH_2CH_2Ph} + \mathrm{PhCH_2C(CH_3)_2OH}}_{42\%} \qquad (41)$$



$$\mathrm{PhCH_2CO_2^-\,Na^+} \xrightarrow{h\nu\ (254\ \mathrm{nm})} \mathrm{PhCH_2^-} \xrightarrow{\mathrm{CH_3OH}} \underset{97\%,\ \phi = 0.03}{\mathrm{PhCH_3}} \qquad (42)$$

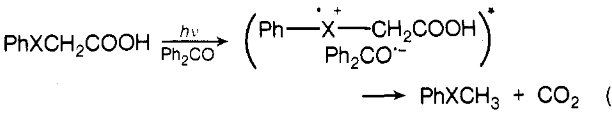
$$\mathrm{PhCH_2^-} \xrightarrow{\mathrm{CH_3OD}} \mathrm{PhCH_2D}$$

Many carboxylic acids undergo photochemical decarboxylation, and flash photolysis studies[20] of acetic and malonic acids provide evidence for the formation of $O{=}\dot{C}{-}OH$ radicals in the major primary process, so that homolytic (O=)C—C α-cleavage seems to be the primary process in the excited state. Pyruvic acid decomposes[53] to give acetoin and carbon dioxide (eq 43), although phenylglyoxylic acid (PhCOCOOH) gives benzaldehyde (60%) and CO_2. Sodium pyruvate is much more photostable, and the quantum yield for decarboxylation is less than 0.04.



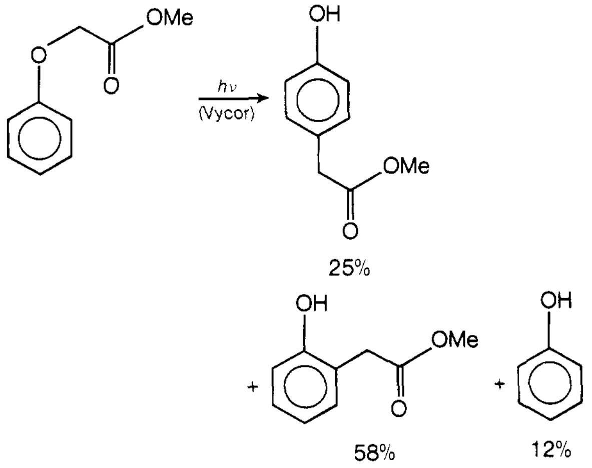
(43)

The sensitized photodecomposition of phenoxyacetic acid, phenylthioacetic acid, and N-phenylglycine proceeds by way of an exciplex[54] between the ketone (sensitizer) as acceptor and the substituted acetic acid as donor (eq 44). Support for this mechanism comes from the correlation between the rate constant for sensitizer-acid interaction and the ionization potentials of model compounds ($PhXCH_3$) related to the acids, and also from ESR and CIDNP studies,[55] which additionally point to the intermediacy of $PhX\dot{C}H_2$ radicals. The interest in these reactions lies partly in the need for an understanding of the photodegradation of related chlorophenoxyacetic acids used in herbicides.



$$\mathrm{PhXCH_2COOH} \xrightarrow[\mathrm{Ph_2CO}]{h\nu} \begin{pmatrix} \mathrm{Ph{-}\overset{\cdot\,+}{X}{-}CH_2COOH} \\ \mathrm{Ph_2CO^{\cdot -}} \end{pmatrix}^{*} \longrightarrow \mathrm{PhXCH_3} + \mathrm{CO_2} \qquad (44)$$

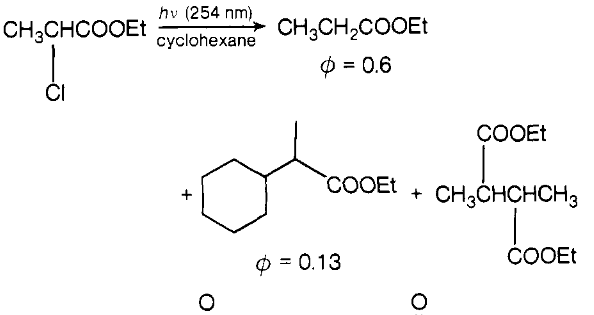
The methyl ester of phenoxyacetic acid undergoes photorearrangement[56] to methyl o- and p-hydroxyphenylacetates (eq 45). This is another process which resembles the photo-Fries reaction, although in this compound the reaction involves cleavage of a bond β to the ester carbonyl group.



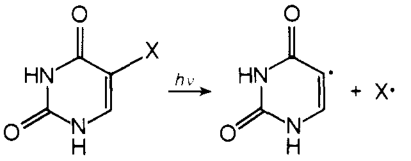
(45)

IV. β-Cleavage

There is a wide variety of photochemical reactions of acid derivatives in which electronic excitation results in initial cleavage of one of the bonds β to the C=O group. Usually the bond concerned is weaker than a normal C—C bond, and part of this effect is provided by stabilization of the resulting radicals or ions. For one fragment ($\dot{C}$—C(=O)- or -(O=)C—$\dot{X}$) the C=O group provides resonance stabilization, and often the other fragment exhibits conjugative stabilization through an aryl or other group. For example, α-halo esters undergo efficient cleavage of the carbon-halogen bond on irradiation. The process is generally a homolytic one,[57] and the products are those of subsequent radical reactions (eq 46). In the presence of added iodine, irradiation of ethyl chloroacetate or bromoacetate produces ethyl iodoacetate by trapping of the intermediate radical. The same type of cleavage occurs with 5-halouracils,[58] and this is a convenient source of the corresponding organic radical (eq 47, X = Cl, Br, I, but not F).



(46)

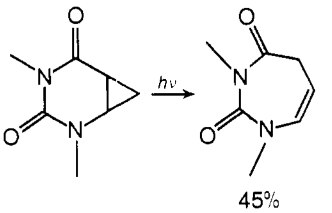


(47)

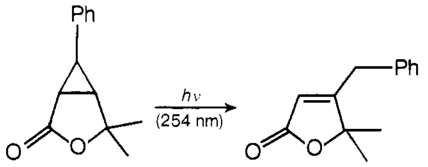
When the halogen is further removed from the carbonyl group, as it is with ethyl 3-chloropropanoate ($ClCH_2CH_2COOEt$) or ethyl 4-chlorobutanoate ($ClCH_2CH_2CH_2COOEt$), carbon–halogen bond cleavage does not occur. Reaction is much slower, and α-cleavage products predominate. There is evidence from the ultraviolet absorption spectra that an α-halogen interacts with the C=O group (the $n \rightarrow \pi^*$ absorption band is more intense, broader and at longer wavelength than that for esters without the halogen), whereas a β- or γ-halogen does not interact. This means that a formal mechanism is available for energy redistribution from the carbonyl group to the carbon–halogen bond.

A heterolytic β-cleavage mechanism of some kind may operate in the photoreactions of α-halo acids in aqueous solution, and the measurement of accurate quantum yields ($\phi_{254} = 0.34$) for the photohydrolysis of chloroacetic acid to give hydroxyacetic (glycollic) acid was achieved several decades ago.[59]

Cyclopropyl conjugated amides and related compounds offer the possibility of β-cleavage of a relatively weak carbon–carbon bond of the three-membered ring, and in the example shown (eq 48) a ring-expanded product is formed from a bicyclic pyrimidine derivative.[60] The reaction is similar to the corresponding process of bicyclo[4.1.0]heptan-2-ones, where one of the photoproducts is a cyclohept-3-enone. Cleavage of an "external" cyclopropane bond occurs in the process by which[61] a lactone with a bicyclo[3.1.0]hexane framework gives rise to an unsaturated γ-lactone (eq 49).

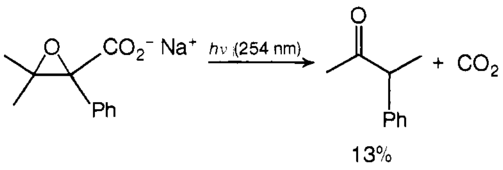


(48)

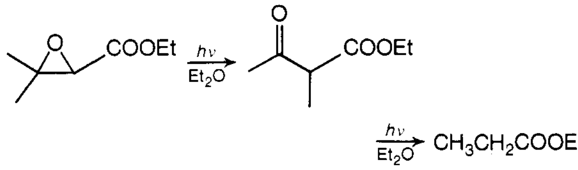


(49)

Oxiranyl conjugated esters and carboxylate salts (glycidates) are open to β-cleavage in a similar way, and it is β carbon–oxygen cleavage which is responsible for the photoreactions in which migration of a methyl group occurs, either with decarboxylation (eq 50) in the case of the salts,[62] or without it (eq 51) for the esters.[63] The ester reaction (eq 51) can be quenched by triplet quenchers, and it may well involve homolytic C–O cleavage. However, the reaction of the salts (eq 50) may involve heterolytic cleavage, and heterolytic γ oxygen–carbon bond cleavage seems to be responsible for the reactions both of β-phenylglycidate salts (eq 52) where no migration takes place,[62] and of some glycidate esters in methanol (eq 53) where the solvent is incorporated in a nonquenchable process.[64] In the latter reaction, protonation of the oxirane oxygen may play a key role, since no product is formed in the presence of sodium carbonate.



(50)



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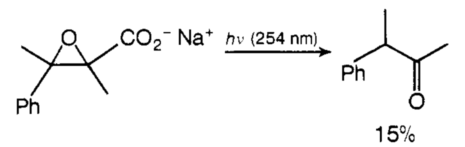
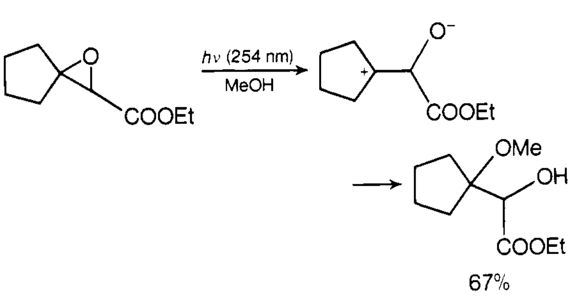
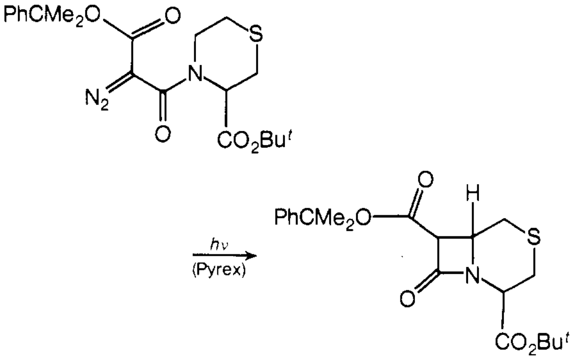


(52)

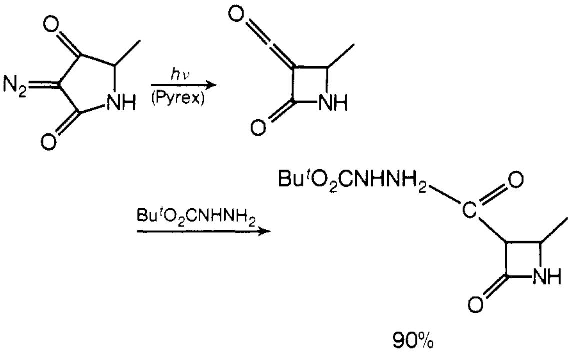


(53)

The photolysis of α-diazoamides has opened up two routes to β-lactams which have been employed in preparing synthetic penicillin and cephalosporin analogues.[65] The first route relies on β-cleavage to form a carbene which inserts into a C–H bond adjacent to the amide nitrogen (eq 54). The second route involves similar β-cleavage, but with migration and ring contraction to give the β-lactam (eq 55) in a photolytic Wolff rearrangement.



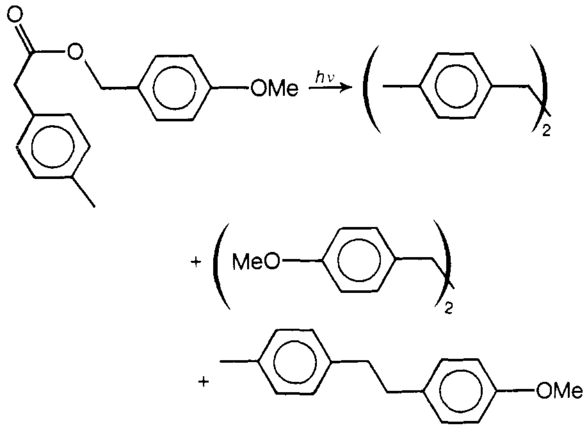
(54)



(55)

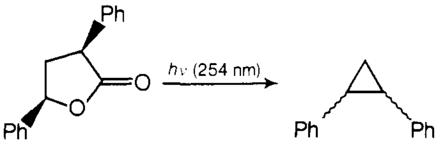
A. Esters

The majority of reported β-cleavage reactions involve bond rupture on the other side of the C=O group, that is, adjacent to the saturated heteroatom of the acid derivative. The most intensively studied group of processes involve cleavage of the (O=)C—O-/-C bond of an ester in systems where the resulting carbon radical is stabilized, usually by conjugation. At first sight the most straightforward reactions appear to be those of benzyl or related esters of α-arylcarboxylic acids. For example, p-methoxybenzyl p-methylphenylacetate undergoes photochemical decarboxylation[66] to give a mixture of hydrocarbons in high yield (eq 56). The reaction involves the ester triplet state, which undergoes homolytic cleavage (the β carbon–oxygen bond breaks first), and the hydrocarbons are formed in ratios near to those expected on the basis of random combination of separated free radicals. In a similar way, 2,4-diphenyl-γ-butyrolactone



(56)

99%, ϕ ~0.2, q ratio 1:1:2.5

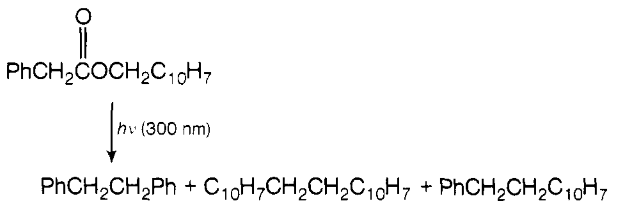


(57)

or trans 51%, ϕ ~ 0.02

gives 1,2-diphenylcyclopropane (eq 57), and the same mixture of cyclopropane stereoisomers is formed from either cis or trans lactone.[66]

The situation is more complex than is at first apparent. Some esters, such as α- or β-naphthylmethyl phenylacetates, give a mixture of hydrocarbons (eq 58) which consists mainly (>80%) of the unsymmetrical compound.[67] In this case the reaction cannot be quenched by triplet quenchers, and it is possible that a solvent cage effect is operating with the majority of radicals combining within the cage. The temperature and the viscosity of the solvent affect the extent of in-cage reaction.

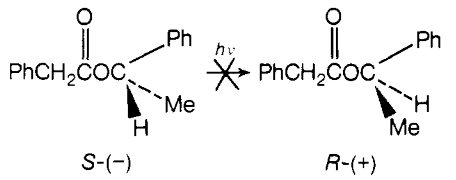


$$PhCH_2\overset{O}{\overset{\|}{C}}OCH_2C_{10}H_7 \xrightarrow{h\nu\ (300\ nm)} PhCH_2CH_2Ph + C_{10}H_7CH_2CH_2C_{10}H_7 + PhCH_2CH_2C_{10}H_7$$

ratio 1:1:10

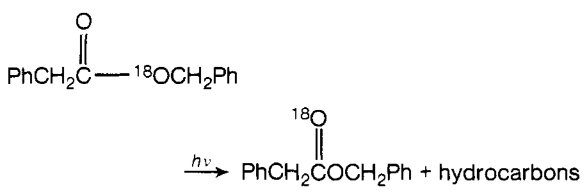
(58)

Studies have recently been reported of the processes by which some of the radicals revert to the starting ester. Optically active 1-phenylethyl phenylacetate[68] does not undergo racemization on irradiation (eq 59), but oxygen-18 labeled benzyl phenylacetate does undergo oxygen scrambling (eq 60). Similar results are obtained for 1-phenylethyl benzoates.[69] In contrast, 2,4-diphenyl-γ-butyrolactones show[68] neither cis–trans isomerization nor oxygen scrambling on irradiation (eq 61). It seems that reversal of the β oxygen-carbon bond cleavage step does not occur (or it is so rapid that radical inversion cannot compete) and that a different mechanism operates for the oxygen scrambling. A concerted 1,3-shift with retention of configuration at the migrating atom is proposed to account for the scrambling, and such a shift would not be available for the γ-lactones because of geometrical constraints.



(59)

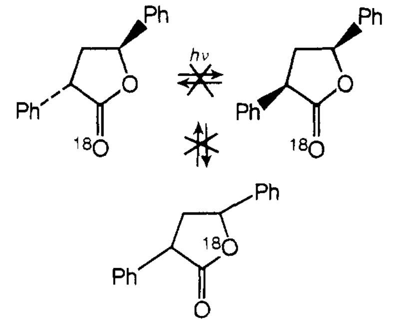
S-(−) R-(+)



$$PhCH_2\overset{O}{\overset{\|}{C}}{-}{}^{18}OCH_2Ph \xrightarrow{h\nu} PhCH_2\overset{{}^{18}O}{\overset{\|}{C}}OCH_2Ph + \text{hydrocarbons}$$

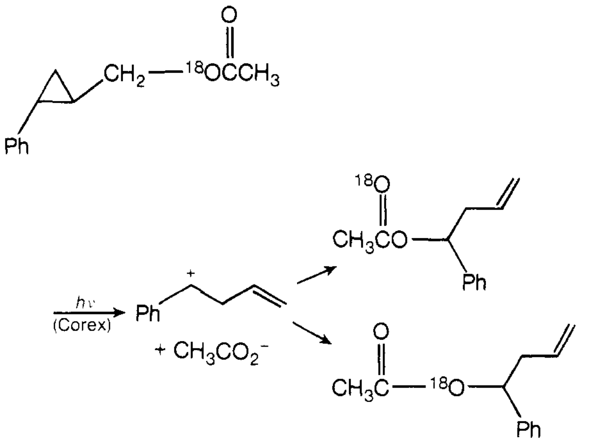
(60)

ϕ = 0.02



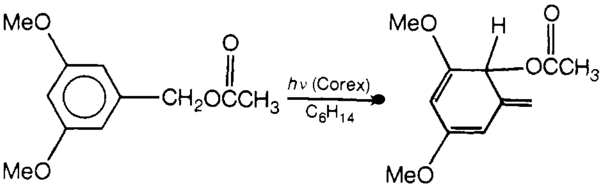
(61)

Oxygen scrambling in the photorearrangement of cyclopropylmethyl acetates occurs[70] by a nonconcerted route in which heterolytic β-cleavage seems to be the most likely first step (eq 62).



(62)

Some benzyl esters give rearrangement products which have not lost carbon dioxide. One of these is 3,5-dimethoxybenzyl acetate which gives,[71] in addition to products of homolytic decarboxylation, an ortho-rearranged product (eq 63) reminiscent of the first-formed cyclohexadienone in the photo-Fries rearrangement (see section III.A). Although benzyl benzoates are reported[69] to undergo some photodecarboxylation, benzyl benzoate itself gives rise[72] to a mixture of *o*- and *p*-benzyl-

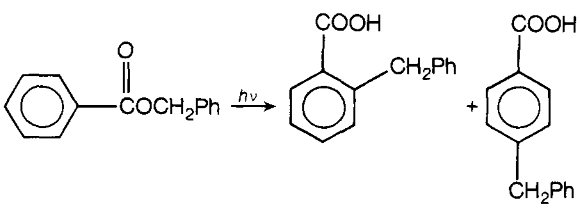


17%

$$+ ArCH_3 + ArCH_2CH_3 + ArCH_2CH_2Ar + ArCH_2C_6H_{13} \quad (63)$$

6% 47% 9.5% 17%

($Ar = 3,5\text{-}(MeO)_2C_6H_3$)

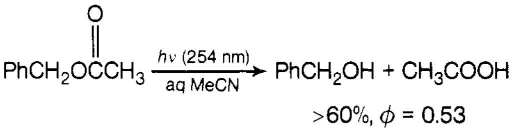


(64)

37% 29%

benzoic acids in reasonable yield (eq 64), and this is in keeping with the greater reluctance of benzoyloxy radicals than of phenylacetyloxy radicals to lose carbon dioxide.

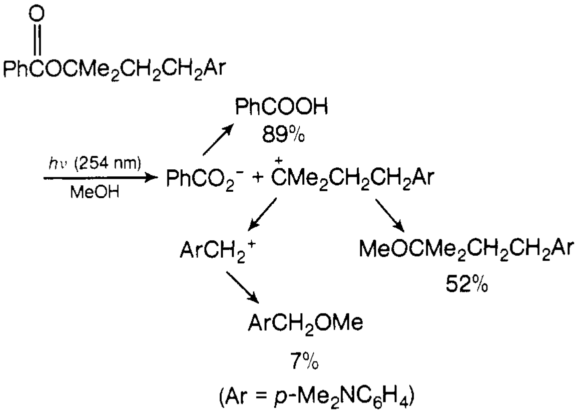
The photochemistry of benzyl esters also includes examples of heterolytic oxygen–carbon bond cleavage, as in the photohydrolysis of benzyl acetate[73] and other esters in aqueous acetonitrile (eq 65) or of 3,5-dimethoxybenzyl acetate[74] in aqueous dioxane (cf. the photorearrangement (eq 63) of the latter ester in nonpolar solvent). The benzyl acetate hydrolysis is thought to involve heterolytic cleavage from the excited singlet state to give ions, as is the other hydrolysis, although with 3,5-dimethoxybenzyl acetate there is also a small amount of accompanying homolytic cleavage. The fact[74] that optically active $ArCHDOCOCH_3$ is partially racemized during the reaction and that labeled $ArCH_2OC(={}^{18}O)CH_3$ undergoes partial oxygen scrambling suggests that the photochemical heterolytic cleavage may proceed by way of an ion-pair mechanism. (Note that aryl esters undergo photohydrolysis by an α-cleavage mechanism; see section III.A.)



$$\mathrm{PhCH_2O\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[\text{aq MeCN}]{h\nu\ (254\ nm)} PhCH_2OH + CH_3COOH} \qquad (65)$$

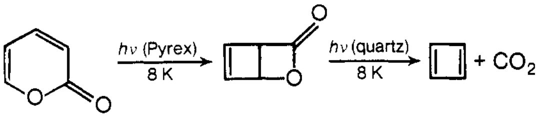
$$>60\%,\ \phi = 0.53$$

Benzoic acid is also the product of the Norrish type 2 photoelimination of alkyl benzoates, which is initiated by intramolecular hydrogen abstraction (see section VI.B), but for certain alkyl benzoates with an electron donor substituent on the alkyl chain[75] irradiation in methanol gives ether products (eq 66) which are indicative of a heterolytic β-cleavage mechanism. The corresponding ethers are not formed from "normal" alkyl benzoates, and electron transfer from the donor group to the benzoate group is the most likely intervening process in the alternative reaction pathway.



(66)

The photochemical β-cleavage reactions of esters have been put to synthetic use in a number of ways. Unstable species can be generated, and the most extensively reported[76] of these processes is the matrix formation of cyclobutadiene from the bicyclic β-lactone which itself is formed by photochemical electrocyclic ring closure of α-pyrone (eq 67). The results of deuterium labeling and carbon-13 labeling studies, and the effect on the infrared spectrum of cyclobutadiene of proximate molecules such as CO_2 in the matrix, have all been discussed in attempts to establish the nature of cyclobutadiene. Photochemical decarboxylation has also been employed in such syntheses as that[77] of [2.2]paracyclophane (eq 68).



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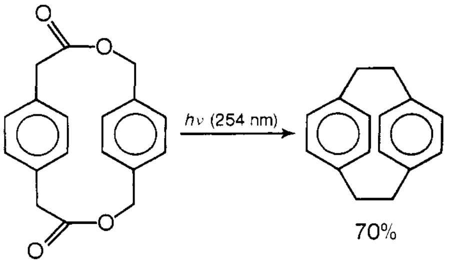
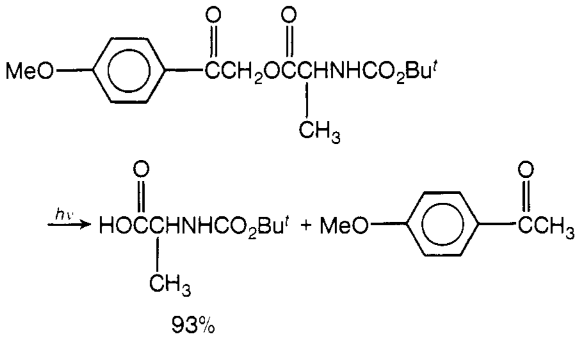


(68)

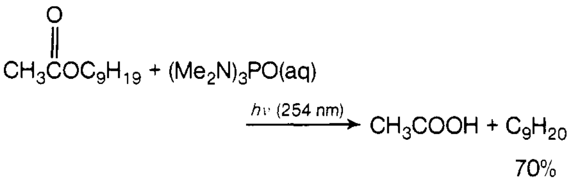
A number of ester systems have been proposed as protecting groups which can be removed photochemically, especially for peptide synthesis. As an illustration of the basic process, butyloxycarbonyl-L-alanine can be regenerated[78] from its *p*-methoxyphenacyl ester in good yield on irradiation (eq 69).



(69)

Homolytic β-cleavage followed by hydrogen abstraction accounts for the products, and there is little tendency for the acyloxy radical to decarboxylate in this system, although decarboxylation does occur from the benzyl ester of *N,N*-dialkylglycines.[79]

As a final example of ester photochemistry where β-cleavage occurs, aqueous hexamethylphosphoric triamide (HMPT) causes photoreduction of esters[80] with the production of alkane from the alcohol part of the ester (eq 70), and this has been used to reduce steroidal alcohols to the corresponding hydrocarbons. The other product is the carboxylic acid, but although β-cleavage seems to have occurred as judged from the products, the mechanism is not known with certainty. One possibility is that electron transfer to the ester takes place first, and that after protonation an alkyl radical is formed which abstracts a hydrogen atom to give the alkane.

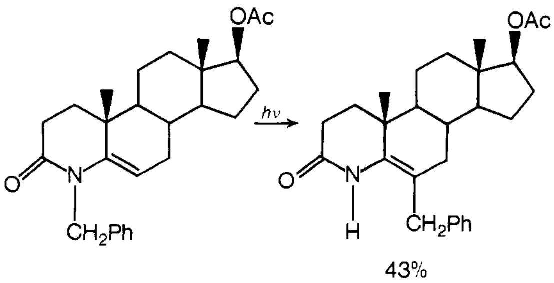


$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}OC_9H_{19} + (Me_2N)_3PO(aq) \xrightarrow{h\nu\ (254\ nm)} CH_3COOH + C_9H_{20}} \qquad (70)$$

$$70\%$$

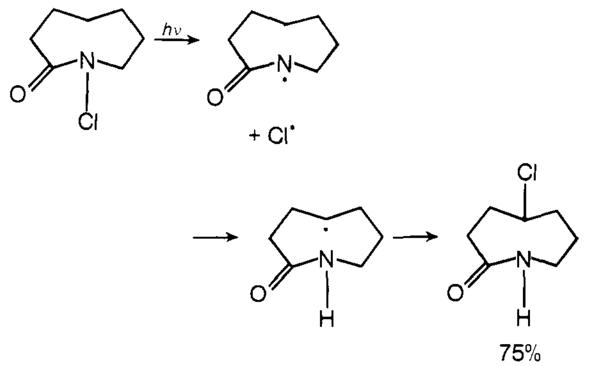
B. Nitrogen Derivatives

N-Benzylamides can also undergo cleavage of the β nitrogen–carbon bond, although the literature is not as extensive as that for benzyl esters. The benzyl migration in an enamido compound (eq 71) probably involves a reaction of this type,[81] followed by recombination and proton transfer.



(71)

The remaining major groups of compound for which photochemical β-cleavage occurs are those where the relevant bond is between two heteroatoms, i.e., those of the general type (O═)C—X—Y. Acyl hypohalites (RCOOHal) are a good source of acyloxy radicals on irradiation because of homolytic oxygen–halogen bond cleavage; these radicals readily decarboxylate. *N*-Halo amides and imides undergo nitrogen–halogen bond cleavage in the excited state, and for *N*-bromosuccinimide this can be the primary step in the use of the compound for allylic or similar bromination.[82] The major process for many *N*-halo amides or lactams of alkylcarboxylic acids (or for *N*-halo acyclic imides) involves intramolecular hydrogen abstraction after the initial bond cleavage, and subsequent formation of a *C*-halo amide (eq 72)[83] or of the γ-iminolactone formed from it by ring closure (eq 73).[84] Where a choice is possible there is a preference[85] for abstraction by the nitrogen radical from the *N*-alkyl part of the molecule rather than from the acyl group (eq 74). This report[85] also brings out the free radical chain nature of the reaction since quantum yields of up to 131 are reported for systems of this type.



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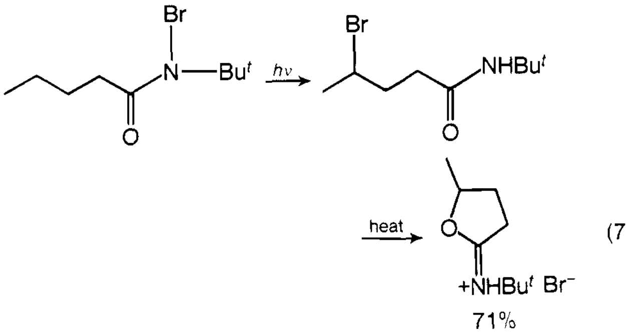

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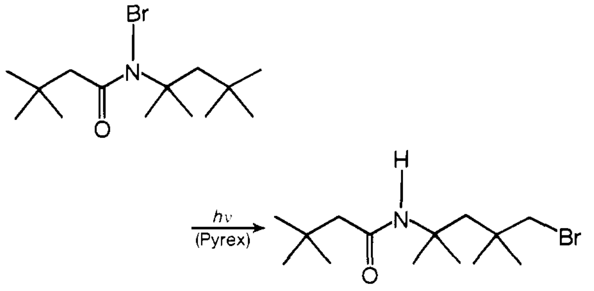
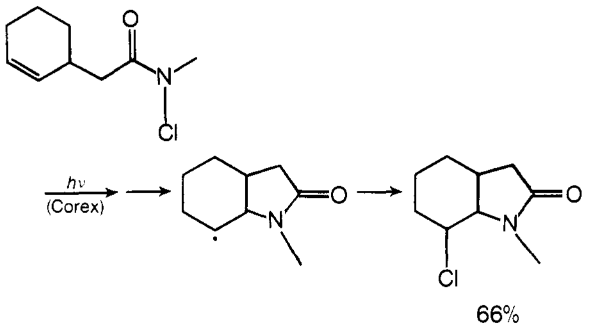


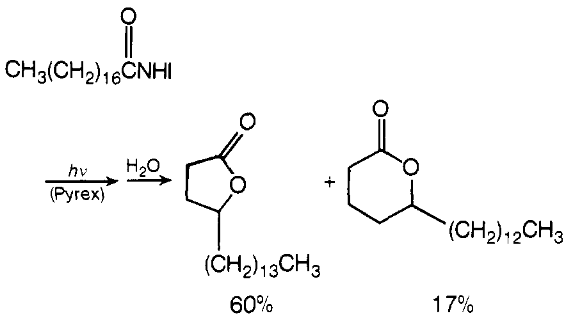
(74)

Further support for the radical nature of the process comes from the loss of optical activity[86] at the site of hydrogen abstraction as a result of reverse hydrogen transfer, and from the ease of intramolecular trapping by an alkene double bond to give[87] a cyclized product (eq 75). For *N*-iodostearamide[86] the preference for the position of hydrogen abstraction is not as strong as in some other systems, and the δ-lactone is formed as well as the major γ-lactone after hydrolysis (eq 76).

β-Cleavage of a nitrogen–nitrogen bond occurs on irradiation of *N*-nitrosoamides, hydrazides, and acyl azides. *N*-Nitrosoamides behave in a very similar way to *N*-halo amides: in short-chain compounds the *N*-nitroso group appears as nitrous oxide (eq 77) after hydrogen abstraction by the NO unit.[88] In longer chain compounds a *C*-oximino amide results from intramolecular hydrogen abstraction by the first-formed nitrogen radical (eq 78), with the normal preference for a six-membered transition state in the abstraction step.



(75)



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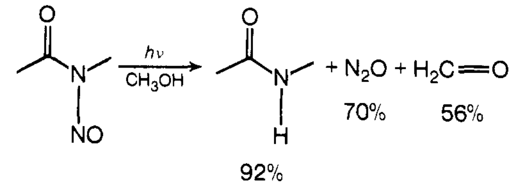

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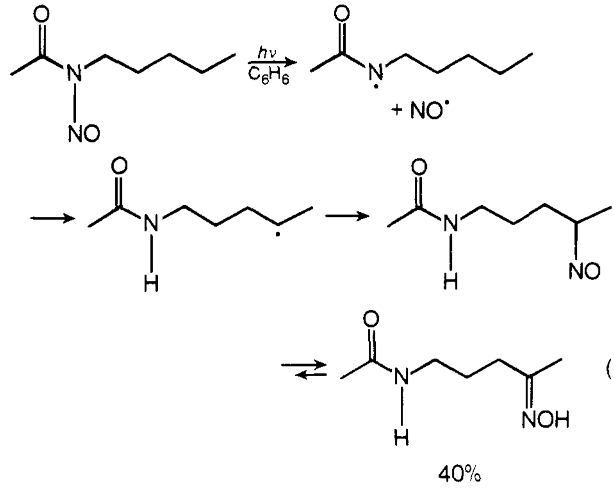
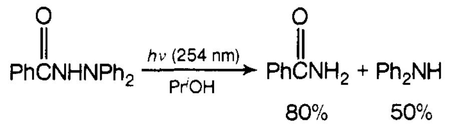


(78)

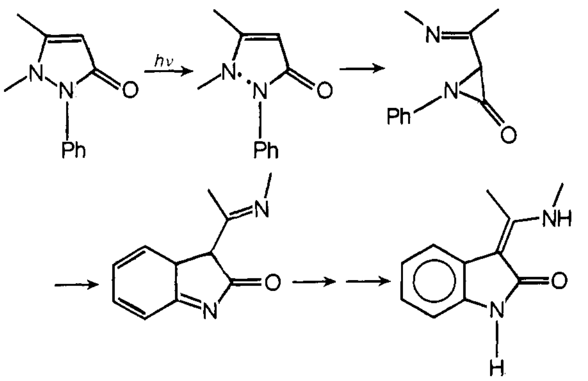
Hydrazides undergo photochemical nitrogen–nitrogen bond cleavage with the formation[89] of amide and amine in the presence of a hydrogen-donating solvent (eq 79), although when the



$$\mathrm{Ph\overset{O}{\overset{\|}{C}}NHNPh_2} \xrightarrow[\mathrm{Pr^iOH}]{h\nu\ (254\ \mathrm{nm})} \underset{80\%}{\mathrm{Ph\overset{O}{\overset{\|}{C}}NH_2}} + \underset{50\%}{\mathrm{Ph_2NH}} \qquad (79)$$

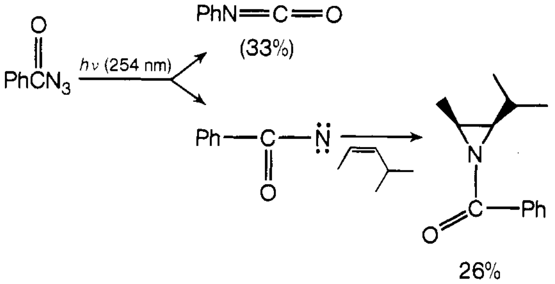
amine radical fragment is less effectively stabilized, as with $\mathrm{PhCONHNMe_2}$, a small amount of (O═)C—N α-cleavage also takes place.[90] Nitrogen–nitrogen β-cleavage is responsible for the photochemical isomerization[91] of Phenazone (Antipyrine) which eventually leads to a substituted indolinone (eq 80).

Benzoyl azide undergoes two competing photochemical processes.[92] Phenyl isocyanate is formed in a reaction which is independent of solvent or added reagent, and benzoylnitrene is produced in a different process and can be trapped in a highly

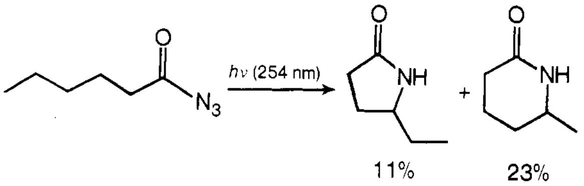


(80)

stereoselective reaction with added alkene (eq 81). The Curtius rearrangement product (isocyanate) is formed in lower yields than in the thermal process. Azides of aliphatic carboxylic acids give the acylnitrene on photolysis,[93] which goes on to yield γ- and δ-lactams by intramolecular insertion into C–H bonds (eq 82), with a preference for insertion into the δ C–H bond.

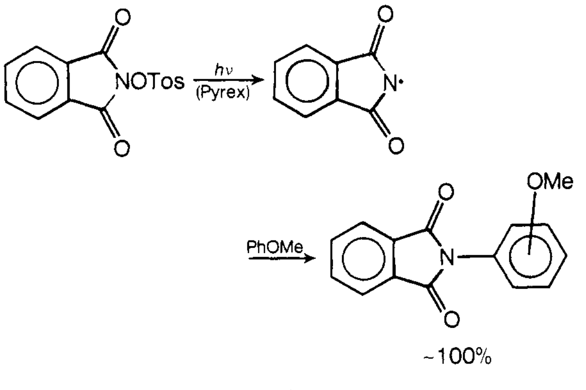


(81)



(82)

Acyloxy or sulfonyloxy amides and related compounds contain a relatively weak β nitrogen–oxygen bond which can undergo homolytic cleavage in the excited state. *N*-Tosyloxyphthalimide, for instance, is a good source of phthalimido radicals,[94] which in aromatic solvents can lead to *N*-arylphthalimides in good yield (eq 83). Similar homolytic N–O bond cleavage is probably responsible for the apparent Norrish type 2 photoelimination of *N*-alkoxy-2-pyridones (see eq 121) and for the triplet-sensitized ring transposition[95] of benzisoxazolinones (eq 84).



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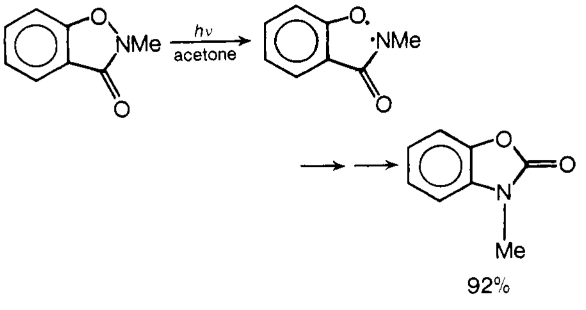
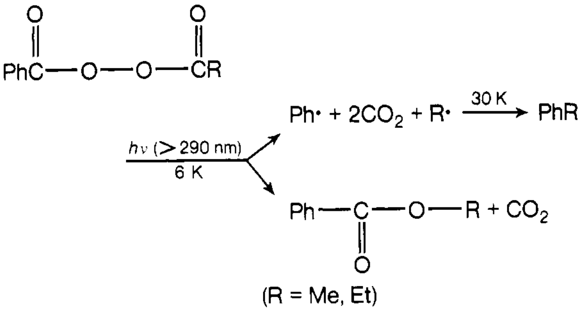


(84)

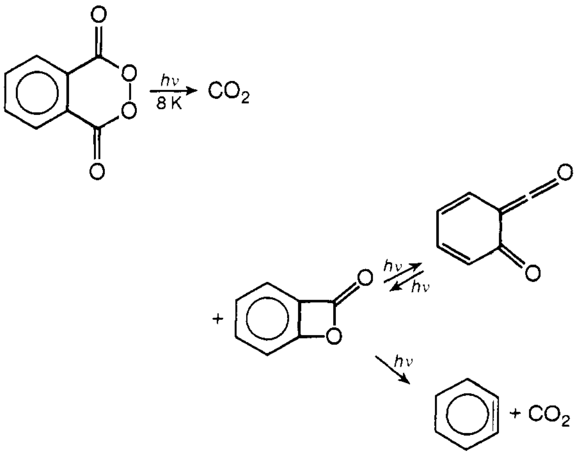
C. Acyl Peroxides

Our final examples of photochemical β-cleavage assisted by the relatively low bond strengths of heteroatom–heteroatom bonds involve the oxygen–oxygen linkage of peroxy compounds, particularly of acyl peroxides. Matrix photolysis[96] of acyl benzoyl peroxides gives rise to phenyl and alkyl radicals, and also to some ester (eq 85). Warming the matrix to 30 K allows combination of the radicals to give alkyl aromatic.

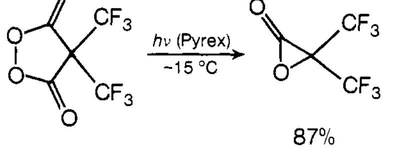


(85)

The formation of benzoate ester is in accord with the greater ease of decarboxylation of acetyloxy (or propanoyloxy) radical than of benzoyloxy radical, though it is not clear at which point the divergence of reaction pathway takes place for the benzoyloxy fragment, some to give phenyl radical and some to give ester. Cyclic acyl peroxides can be employed to generate strained species such as[97] benzyne or an intermediate benzo-β-lactone from phthaloyl peroxide (eq 86). The reaction to give benzyne can be triplet sensitized, but on direct irradiation the reaction is wavelength dependent because of the four different photochemical preocesses in the scheme. In a similar reaction at much higher temperature (−15 °C) an α-lactone can be generated[98] from a malonyl peroxide (eq 87). In each case oxygen–oxygen bond cleavage and monodecarboxylation account for the ring-contraction step.



(86)

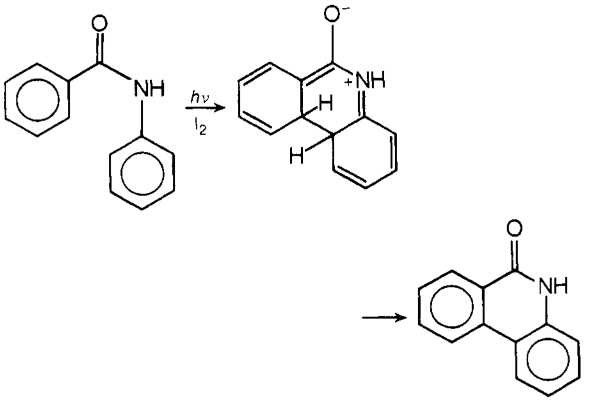


(87)

V. Cyclization

A. Aryl Amides and Enamides

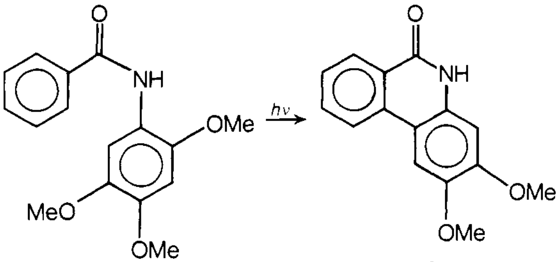
The photocyclization of acid derivatives, especially of amides, to give heterocyclic systems has been widely studied, and the opening up of new or improved routes to pharmaceutically interesting compounds has been a major objective.[99] A number of mechanistically distinct processes have been employed. One group of reactions involves a stilbene → phenanthrene type of photocyclization, as in the reaction[100] of benzanilide (eq 88) or related amides with different aryl groups. It is generally assumed that a dihydro intermediate is formed which is readily oxidized, in this instance by the added iodine.



47%

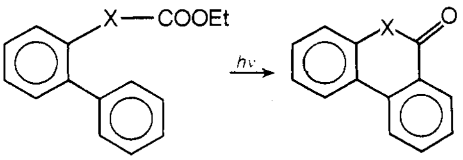
(88)

The "photo-anilide" rearrangement (see section III.B) is in competition with this cyclization process, and *o*- and *p*-benzoylanilines are formed. A nonoxidative version of the cyclization reaction is available when an *o*-methoxy group or other suitable substituent[101] is present in the aromatic ring (eq 89). The initial cyclization product readily undergoes elimination of methanol. The two aryl groups need not be separated by the amide linkage, and the biphenyl–urethane or –carbonate systems[102] give cyclized products on irradiation (eq 90), in each case with elimination of ethanol in an overall nonoxidative reaction.



55%

(89)



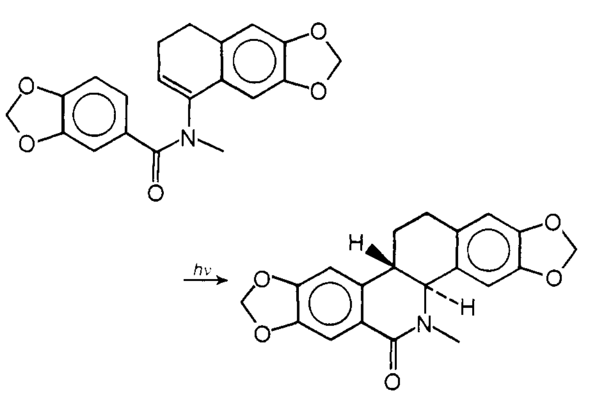
85%

(X =O; NH)

(90)

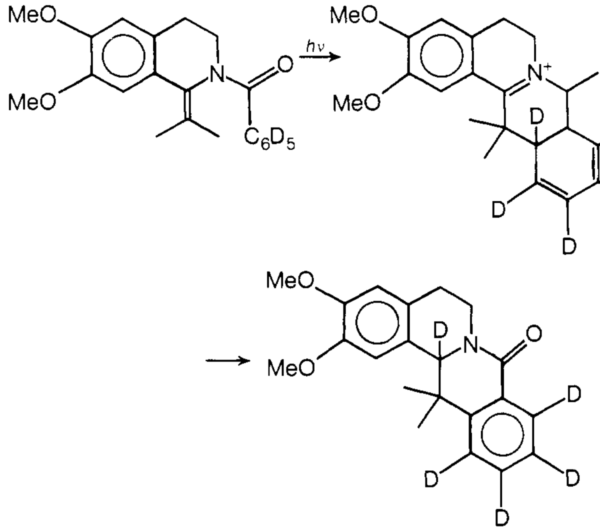
A related process occurs with aryl enamides, except that in the absence of an oxidizing agent the major product arises[103] by a formal 1,5-hydrogen shift in the intermediate (eq 91). The nature of the shift has been demonstrated[104] by deuterium-labeling studies (eq 92).

The presence of added iodine in these reactions causes dehydrogenation, but a better (higher yield) route to the dehydrogenated product involves the use of an *o*-methoxy substituent in the substrate (or *o*-F, -OAc, -SMe, $-NO_2$).[101] Cyclization occurs predominantly at the methoxy-bearing position, and elimination of methanol completes the reaction (eq 93).

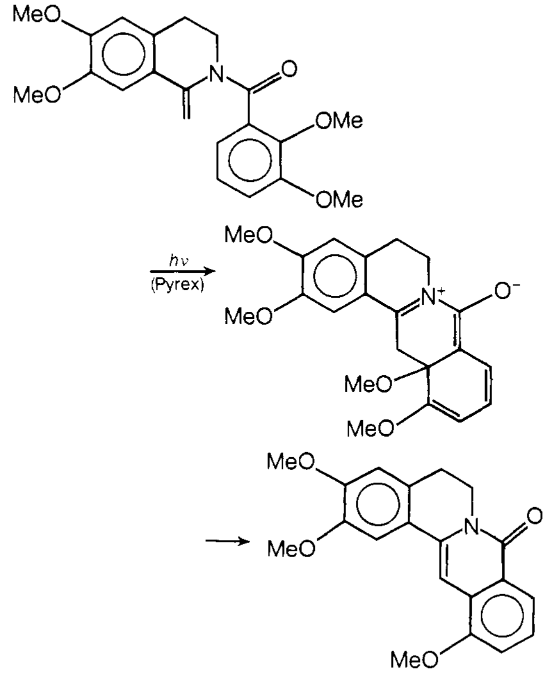


52%

(91)



(92)

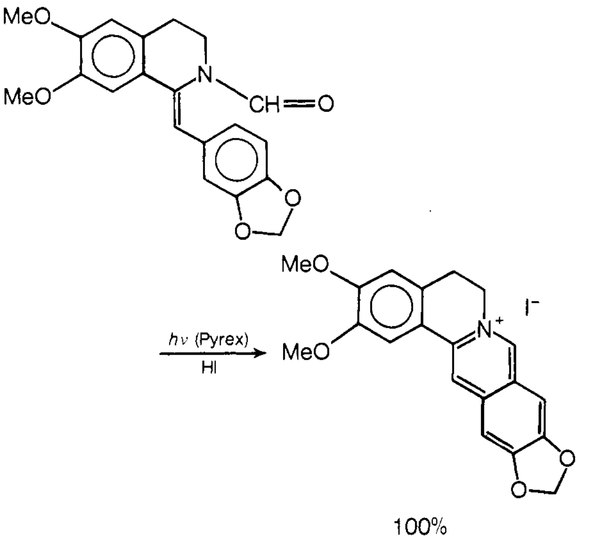


85%

(93)

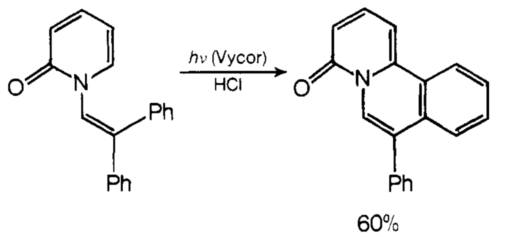
A nonoxidative cyclization is also involved in the synthesis of protoberberine-related systems by irradiating[105] enamides in which the participating aryl group is attached to the alkene rather than to the carbonyl group (eq 94). A hydrogen shift and dehydration (probably acid-promoted) are required to yield the observed product. It is interesting that the chemical yield is quantitative despite the possibility of *Z*/*E* isomerization of the enamide and the fact that the other isomer could undergo photocyclization to a phenanthrene system, as is observed with the related *N*-ethoxycarbonyl compound.

N-(Diphenylvinyl)-2-pyridone photocyclizes under acid conditions[106] in a typical stilbene-like process (eq 95). This may

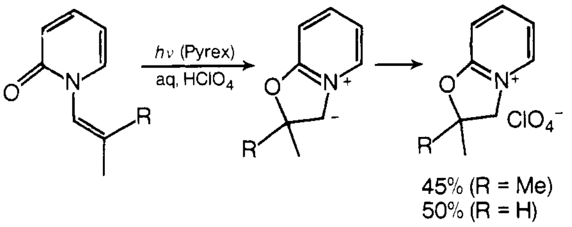


(94)

occur by way of the protonated hydroxypyridinium species, although if this is so it is surprising that cyclization does not occur to the hydroxyl-bearing position (see eq 93). When this reaction is unavailable, as it is with some other *N*-alkenyl-2-pyridones, a completely different process occurs and the product incorporates the amide oxygen in the new ring (eq 96); a stabilized ylide intermediate is proposed.[107]



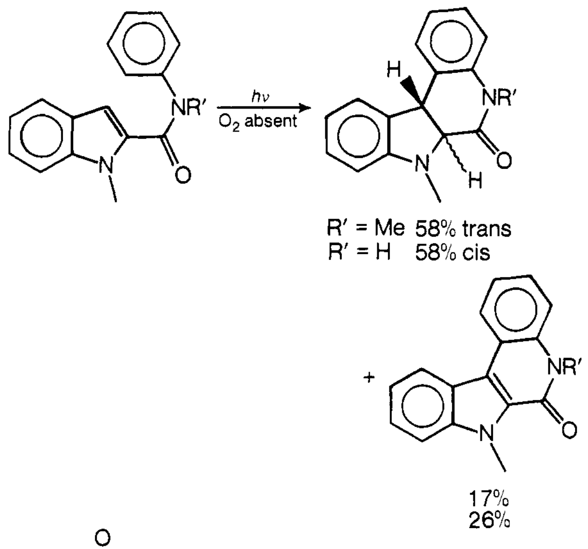
(95)



(96)

N-Aryl amides of α,β-unsaturated carboxylic acids can take part in photocyclizations of the stilbene type, although the products isolated are usually not oxidized unless iodine is added. A study[108] of *N*-phenylindole-2-carboxamides suggests that when the amide is secondary (eq 97, R′ = H) the hydrogen-shifted dihydro product has a cis ring junction because proton shifts are involved, whereas when the amide is tertiary (eq 97, R′ = Me) the ring junction is trans because a 1,5-hydrogen shift occurs. Support for these ideas comes from deuterium-labeling studies: when the solvent is labeled (D_2O), the cis product incorporates deuterium, but the trans does not, whereas when the *N*-phenyl group is labeled (C_6D_5), the trans product incorporates deuterium but the cis does not. These results confirm an earlier suggestion[109] based on stereoisomer ratios obtained from *N*-phenylcyclohexene-1-carboxamides (eq 98).

The early report[100] of the photocyclization of benzanilide to phenanthridone also indicated that the same product can be obtained from a benzanilide substituted by iodine in the ortho position of either aromatic ring (eq 99). The reaction of these compounds almost certainly involves homolytic carbon–iodine bond fission in the first step. Such a process is typical of the photoreactions of aryl iodides or bromides, and support for it comes from the large amounts of products isolated in which iodine has been replaced by phenyl from the solvent.



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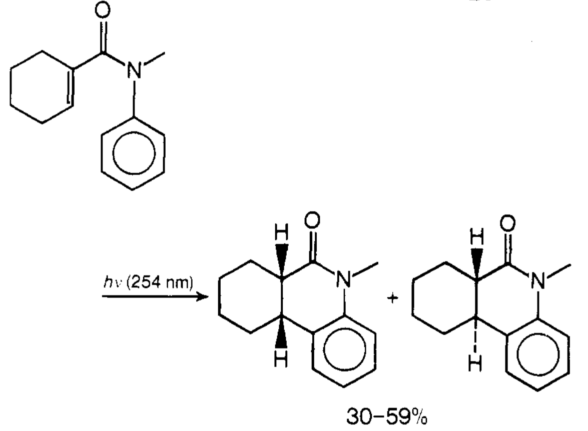
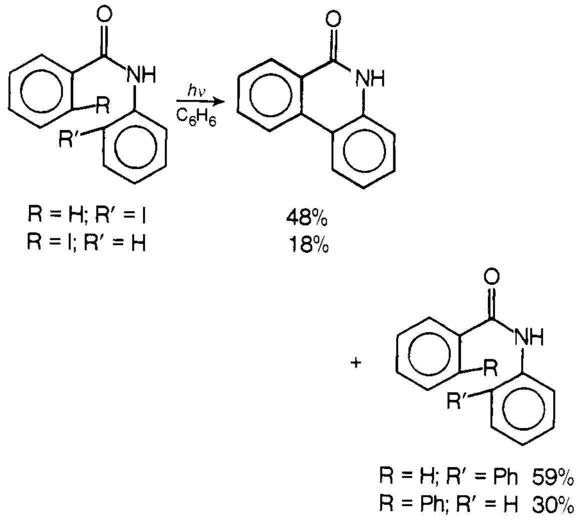
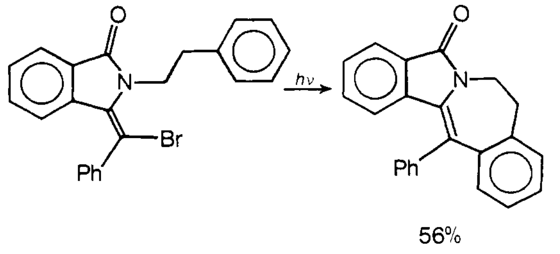


(98)

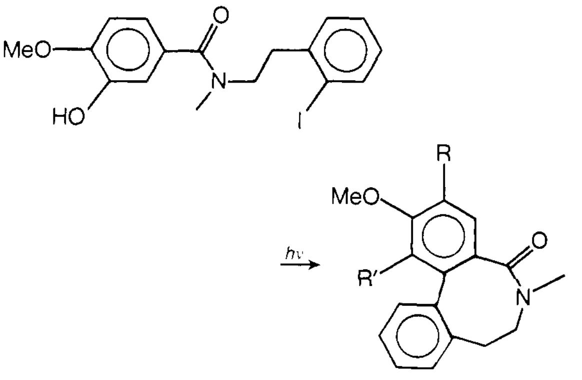


(99)

Related processes have been reported leading via homolytic aryl or vinyl carbon–halogen bond fission to new five-membered,[110] six-membered,[111] seven-membered (eq 100),[112] or eight-membered (eq 101)[113] nitrogen heterocycles. A similar reaction occurs also in the photocyclization of *N*-iodobi-



(100)



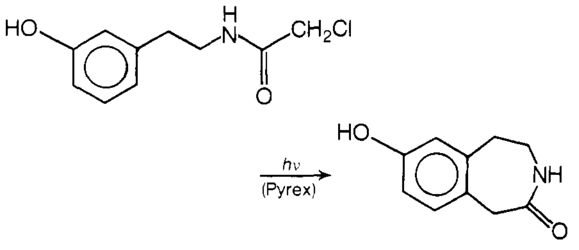
(101)

R = OH; R′ = H 37%
R = H; R′ = OH 15%

phenyl-2-carboxamides,[114] where the initial step is the homolytic cleavage of the β nitrogen–iodine bond (see section IV.B).

B. Chloroacetamides

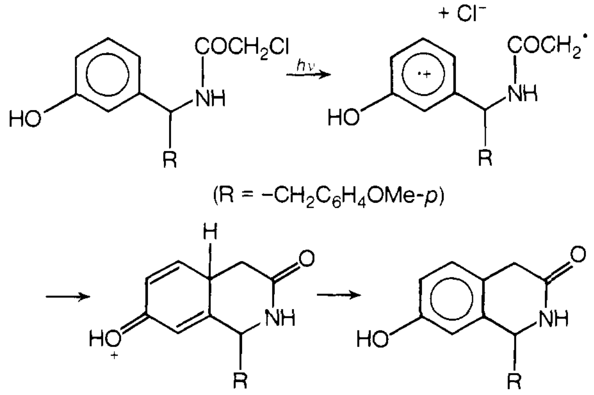
A third major group of compounds which provide a photochemical route to nitrogen heterocycles are 2-chloroacetamides. A typical example[115] of this cyclization (the Witkop cyclization) is the formation of a benzazepinone from the chloroacetyl derivative of *m*-tyramine (eq 102).



(102)

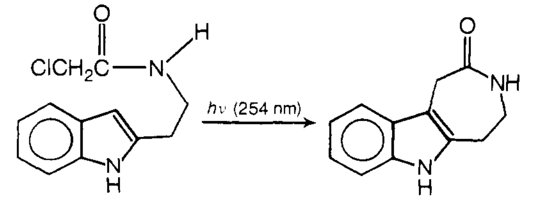
70%

For efficient reaction the aromatic ring must contain a hydroxyl group meta to the chloroacetyl-carrying substituent, and cyclization then occurs to a position para to the OH. The need for this substituent pattern can be appreciated in the light of the suggested mechanism: cleavage of the carbon–chlorine bond β to the carbonyl group is assisted by electron transfer from the aromatic part of the molecule. The β cleavage is related to that of α-halo esters (see eq 46). This is followed by cyclization to form a protonated dienone species which readily aromatizes.



(103)

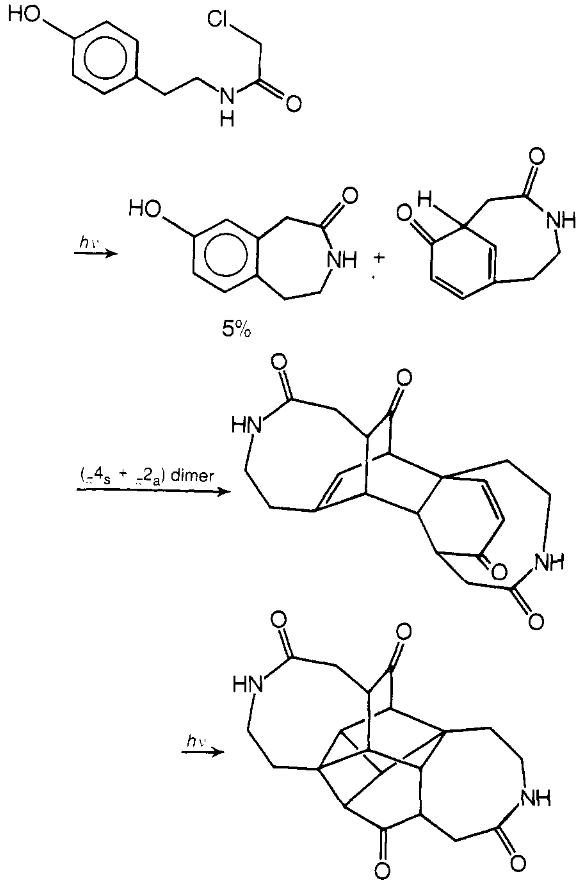
49%



(104)

The reaction[116] of a benzylamine derivative to give an isoquinolone (eq 103) illustrates the sequence. The position of cyclization can be on a nonbenzenoid position, as with[117] the reaction of 2-substituted indole derivatives (eq 104).

With substituents other than a *m*-hydroxyl group in the benzene ring, the yield of this type of product is often low, and alternative modes of ring closure are observed which give nonaromatic products. With tyramine derivatives a cyclohexa-2,4-dienone is proposed[118] as the intermediate which gives rise to the major product (eq 105). If *o*- and *p*-methoxy substituents are present,[119] one of the methyl groups is lost in the reaction sequence (eq 106).



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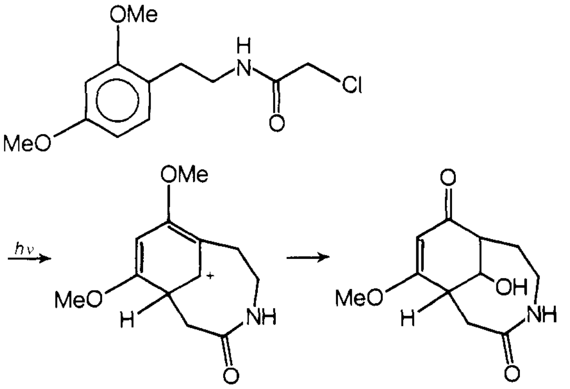
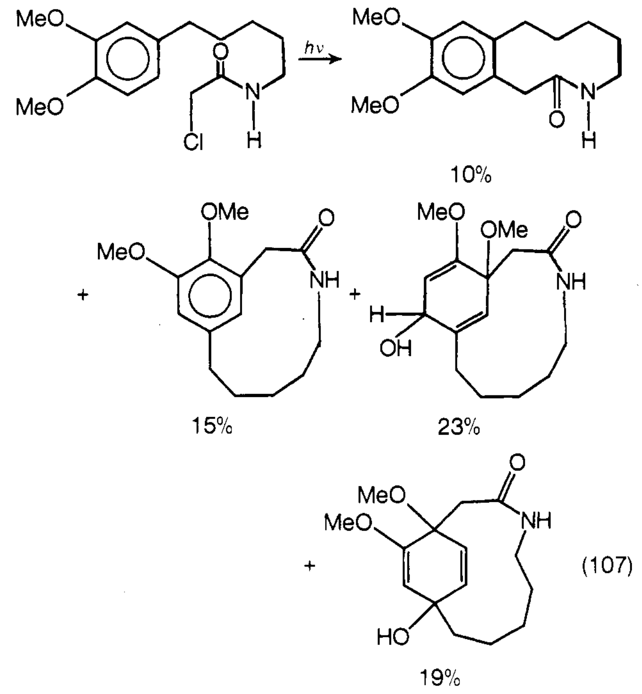


(106)

26%

The alkyl chain linking the amide nitrogen to the aromatic ring can be lengthened. When it is five methylene units long (eq 107) a new ten-membered ring is formed[120] in one of the products. Support for the positively charged intermediates comes from the nature of the products in this reaction.

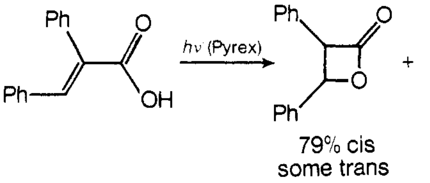
Cyclization to an unsubstituted position leads to an aromatic product by proton loss, whereas cyclization to a methoxy-bearing



(107)

position leads to attack by water to give a nonaromatic product with an extra OH group.

An interesting photocyclization of α,β-unsaturated esters and amides has been reported[121] in which a β-lactone (eq 108) or β-lactam (eq 109) is formed. The reaction is general for compounds with at least one phenyl substituent on the double bond. It is suggested that the mechanism is related to that of electrocyclic reactions, though it is also possible that it is related to the photochemical addition of water to the double bond of α,β-unsaturated acid derivatives (see section VI.D).



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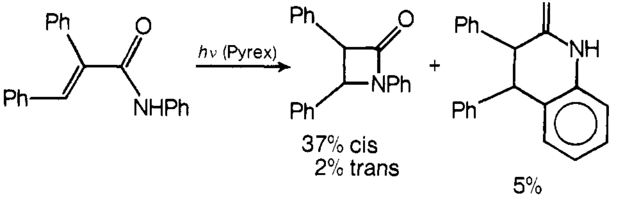


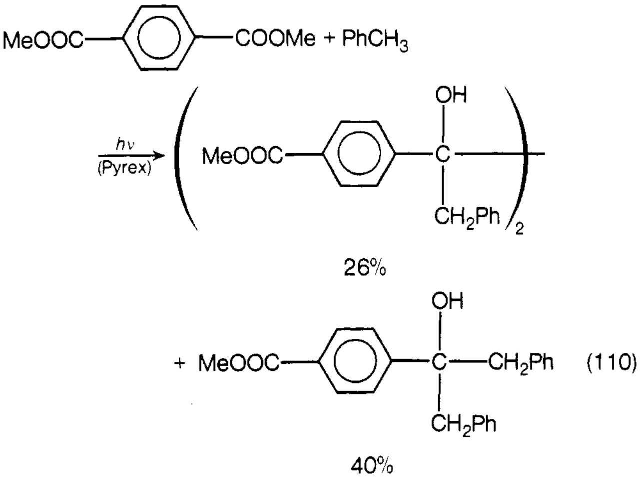
(109)

VI. Hydrogen Abstraction

Abstraction of a hydrogen atom by the oxygen of an (n,π^*) excited state of a carbonyl group is one of the processes that features extensively in ketone and aldehyde photochemistry. Formally analogous reactions can also be achieved with lowest excited states that are (π,π^*) in electronic character if the hydrogen donor contains an electron-donating group close to the site of abstraction; the abstraction process then occurs by a sequence of electron transfer followed by proton transfer. Carboxylic acid derivatives also undergo photoreactions which involve transfer of hydrogen to the oxygen atom of the excited carbonyl group.

A. Photoreduction

Intermolecular photoreduction of acid derivatives is not extensively documented. Esters of aromatic acids substituted in the ring with electron-withdrawing groups are photoreduced[122] by such hydrogen donors as toluene to give alcohols and pinacols in which the toluene group is incorporated (eq 110). Cumene is a better hydrogen donor, and the pinacol is derived from the ester moiety only (eq 111). It is likely that a charge-transfer interaction occurs between the ester and the hydrogen donor, particularly since aliphatic hydrocarbons such as cyclohexane are ineffective as reducing agents.



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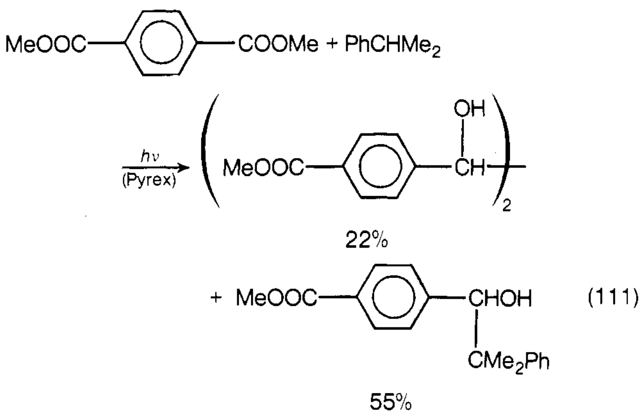
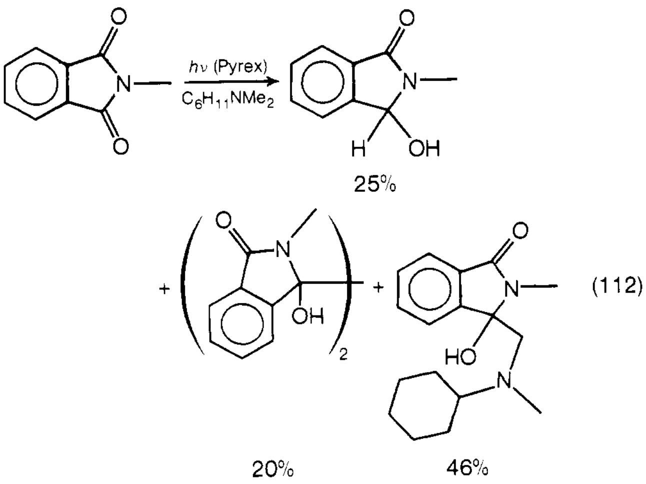


(111)

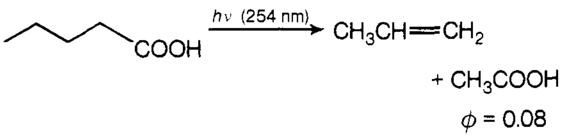
Phthalimides can be photoreduced by alkylbenzenes, amines, ethers, alkenes or alcohols.[123] With amines a variety of products is formed (eq 112), but with most other types of hydrogen donor the major product by far is the 1:1 adduct of the imide and the donor molecule. The lowest excited states of phthalimides may be (n,π^*) in nature,[8] and if this is correct there is a striking parallel between enones (O=C—C=C, π,π^*) and enediones (O=C—C=C—C=O, n,π^*) on the one hand, and amides (O=C—N, π,π^*) and imides (O=C—N—C=O, n,π^*) on the other.



(112)

B. Intramolecular Hydrogen Abstraction

The Norrish type 2 reaction has been observed[124] for aliphatic carboxylic acids, with the abstraction being of necessity from the alkyl chain of the acid (eq 113). Simple aliphatic amides[31,124] are either not photochemically active or else reaction involves α-cleavage of the (O=)C—N bond. However, *N*-stearoylimidazoles and similar amides do undergo[125] a type 2 photoelimination, with the hydrogen abstracted from the acid chain (eq 114). The other major products of this reaction arise from initial α-cleavage of the amide bond followed by recombination of the radicals (see section IV.B).



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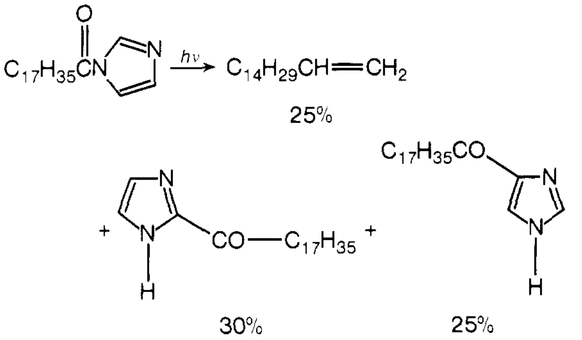
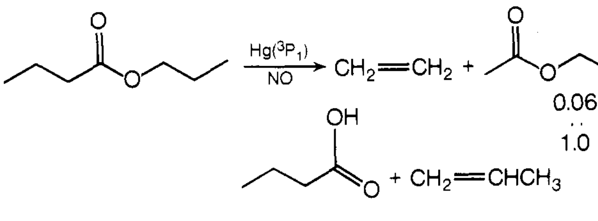


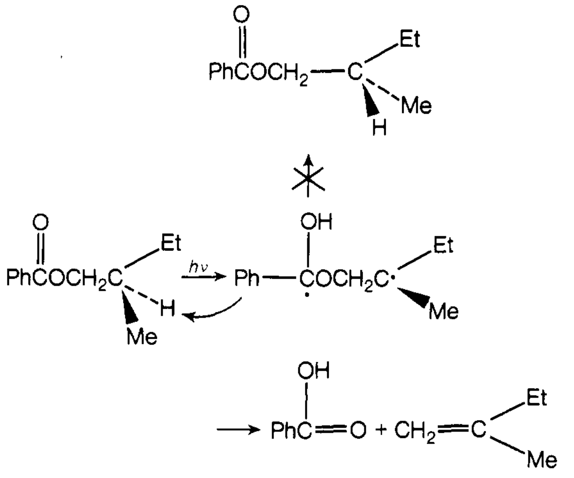
(114)

The photoelimination reactions of esters have been more widely investigated. With completely aliphatic esters reaction can be brought about by direct irradiation or using triplet mercury as a sensitizer. In many cases the intramolecular hydrogen abstraction products constitute only a very small part (1–10%) of the total photochemical reaction, although (as for ketones) the ratio of type 2 reaction to α-cleavage is higher at lower temperatures,[126] but trapping of the free radical (C—C(=O) α-cleavage) derived products by nitric oxide allows the hydrocarbons from the intramolecular process to be studied. Abstraction occurs[127] from both the acid and the alcohol units (eq 115), though the latter products are usually formed in greater amounts. Dialkyl carbonates and thiolcarbonates undergo similar reactions.



(115)

Benzoate esters and other similar aromatic esters undergo a Norrish type 2 photoelimination to give the aromatic acid and an alkene. The chemical yield is moderate to high (*n*-propyl benzoate gives 45% benzoic acid, together with 4% of the α-cleavage product benzaldehyde;[13] 1,1-dihexylheptyl benzoate gives 93% benzoic acid[75]), but the quantum yield is very low (for *n*-propyl benzoate,[128] ϕ_{acid} = 0.006). The reaction occurs[128] through both the lowest (π,π*) triplet state and the lowest (π,π*) singlet state, and the inefficiency is probably a result of the fact that the conformations of the intermediate 1,4-biradical are such that reversion to ground-state ester is greatly preferred over cleavage to give products. Although the lack of extensive racemization[129] in the optically active esters (eq 116) and the low yield of interconversion (≤2%)[130] of threo and erythro isomers of suitably substituted esters (eq 117) do not support this interpretation, these results could well be ascribed to relatively slow bond rotation in the biradical.



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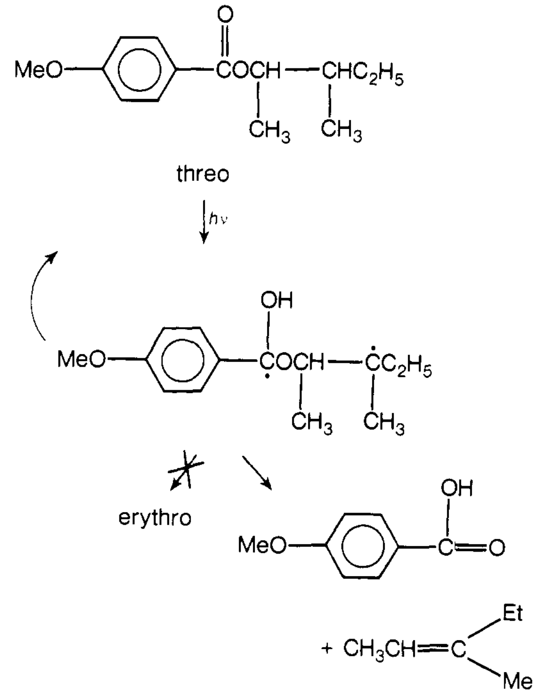
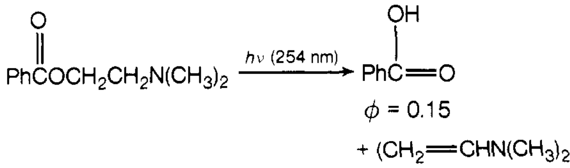


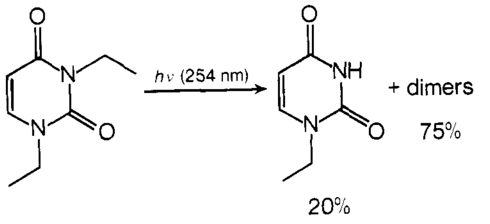
(117)

If the side chain contains an electron-donor group such as dialkylamino adjacent to the site of abstraction, photoelimination can become quite efficient (eq 118) because an electron-transfer/proton-transfer mechanism is available.[7] Similarly, even though *N*-alkylbenzamides produce benzamide on irradiation only with extremely low quantum efficiency (ϕ_{254} = 0.0006 for *N*-isobutylbenzamide), a considerably increased (though still low) efficiency can be achieved[7] when the alternative mechanism can operate (ϕ_{254} = 0.023 for $PhCONHCH_2CH_2NEt_2$).



(118)

The Norrish type 2 reaction is responsible[131] for the dealkylation of *N,N*-diethyluracil (eq 119). With 5-alkyluridines a more complex process is postulated (eq 120) in which the initial biradical cyclizes onto the double bond of the ring to give a fused cyclobutane product which then cleaves photochemically to give an alkene and uridine.[132] The normal Norrish type 2 route is not followed here because bond cleavage in the biradical would give a tautomer of uridine which is a six-membered cyclic allene. With



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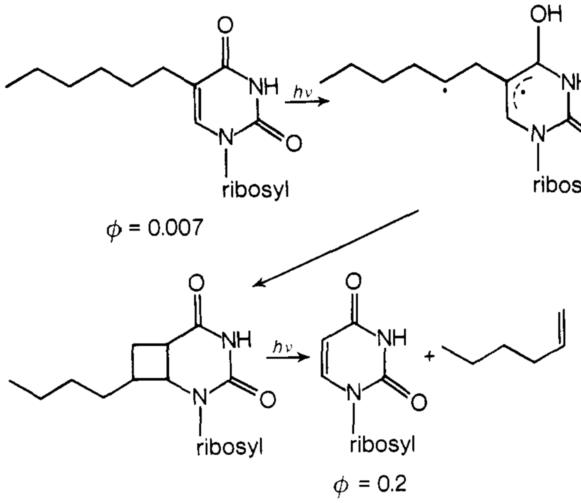
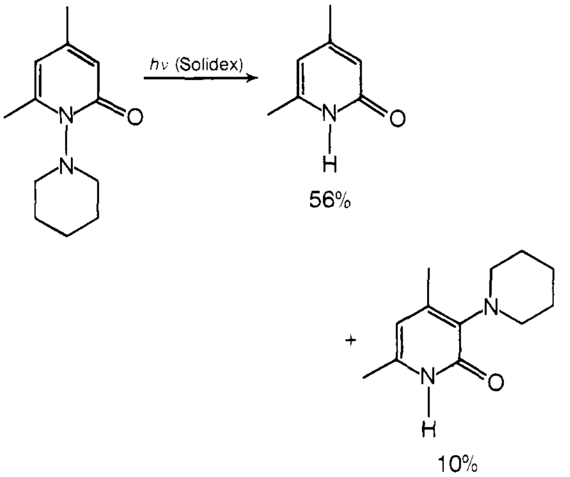


(120)

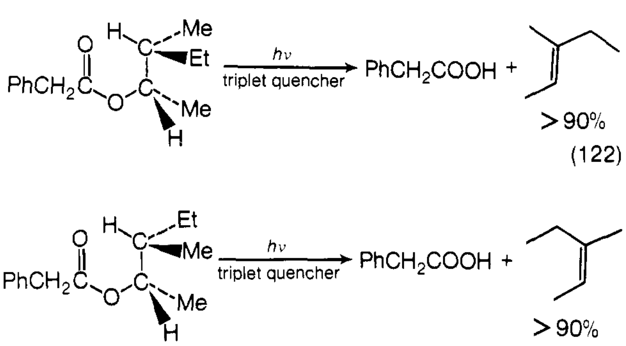
5-ethyluridine the cyclobutane intermediate has been isolated by the choice of the right irradiation wavelength (<265 nm).

When a nitrogen–oxygen or nitrogen–nitrogen bond is present in the α,β position, as in some substituted 2-pyridones (eq 121), the major product[133] is formally that expected on a hydrogen abstraction and cleavage mechanism, but no Δ^1-tetrahydropyridine (the other Norrish type 2 product) could be detected, and the minor product suggests that a free radical (β-cleavage) process is occurring.



(121)

In the series of phenylalkanoate esters $Ph(CH_2)_nCO_2CH_2CH_2OEt$, the phenylacetate ($n$ = 1) shows[134] an enhanced quantum efficiency for photoelimination (ϕ_{254} = 0.009 for n = 0, 0.098 for n = 1), and phenylacetates in general show this property. It is for this reason that they have been widely used in investigating the mechanism of the Norrish type 2 reaction of esters. The process seems to involve mainly a singlet state of the ester, and in the presence of triplet quencher the reactions[135] of diastereoisomeric phenylacetates are strongly, though not completely, stereoselective (eq 122). This is interpreted in terms of an intramolecular hydrogen abstraction process which requires a close approach of the carbonyl oxygen and the relevant hydrogen atom and which gives rise to a short-lived 1,4-biradical (this is a different mechanism from that involved in the thermal production of alkenes from esters). Studies[136] on the stereoisomers of conformationally restricted esters (eq 123, R = H) and on deuterated analogues (eq 123, R = D)[137] support this view, although there is some debate about whether syn or anti elimination is preferred in the cyclohexane systems. Both of these latter studies indicate that α-cleavage (benzyl–carbon) may occur to a small extent but it is not responsible for the major reaction products.



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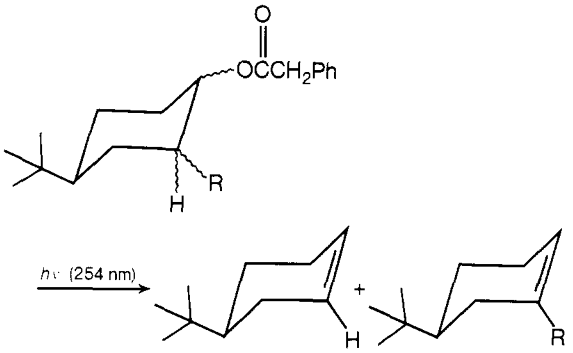
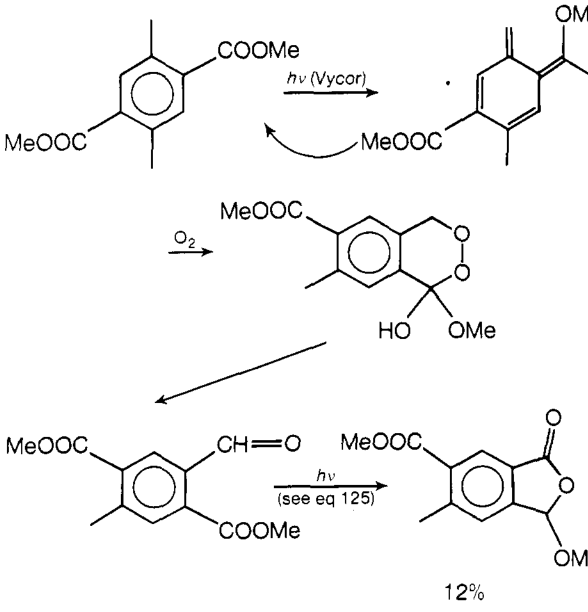


(123)

Photoenolization can occur in some o-alkylbenzoates and related esters, although as yet there is no evidence for it with simple esters such as those of o-toluic acid. The enol can undergo deuterium exchange with EtOD or D_2O which results in deuterium incorporation into the o-alkyl group, or it can be trapped by oxygen (eq 124)[138] or a dienophile (eq 125).[139]

A related process, probably involving overall proton transfer, is responsible for the photochromic behavior[140] of o-(p-nitrobenzyl)benzoate salts (eq 126).



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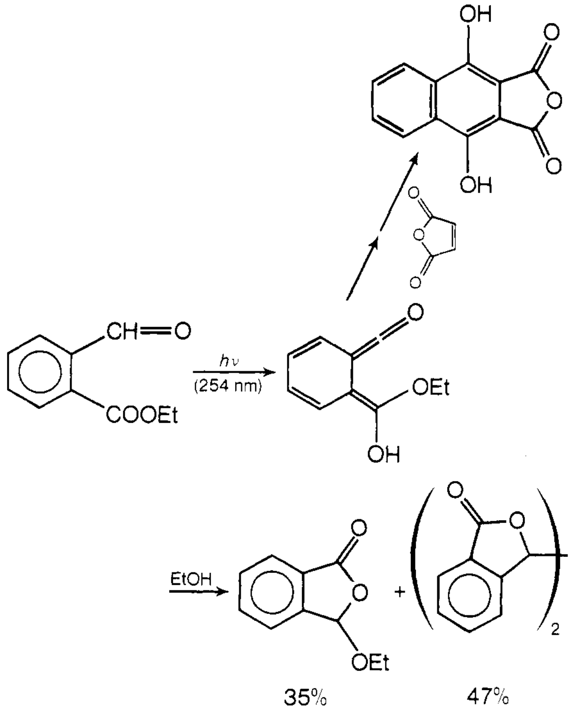

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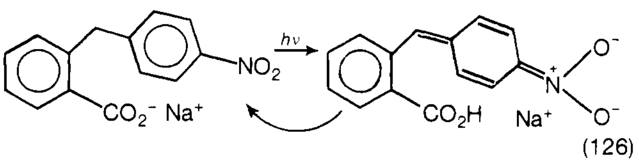
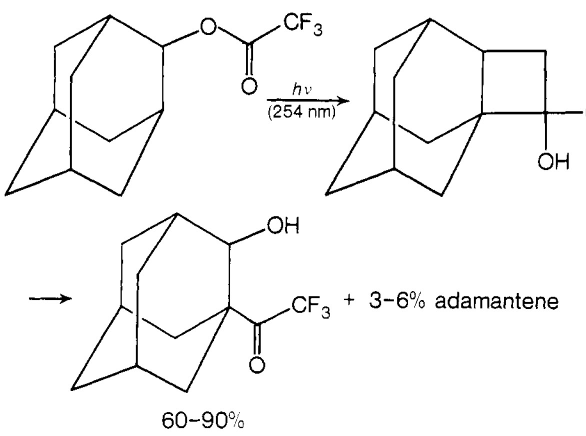


(126)

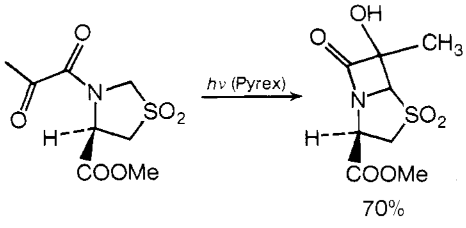
C. Cyclization

Cyclobutanol formation is commonly encountered in the photochemistry of ketones as a process in competition with Norrish type 2 elimination, but the analogous 2-oxetanol (a cyclic hemiketal) formation is rare for esters. Only one report has appeared[141] in which the oxetanol is not isolated but decomposes to give a β-hydroxy ketone (eq 127).



(127)

The process in which α-ketoamides[142] give β-lactams (eq 128), or β-ketoamides[143] give γ-lactams (eq 129), is a photoreaction of the ketone group, although the amide is involved in the new ring. Pyruvate esters give only the Norrish type 2 elimination products on irradiation (eq 130), and this has been proposed as a covenient way of oxidizing primary alcohols to aldehydes.[144] The carbonyl group of a cyclic acylimine does seem to be directly involved[145] in a photochemical abstraction/cyclization process used in corrin synthesis (eq 131).



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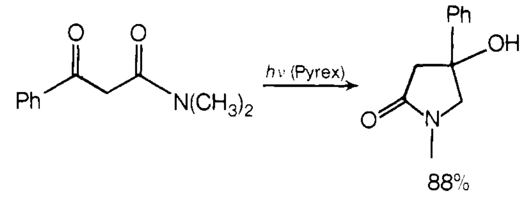

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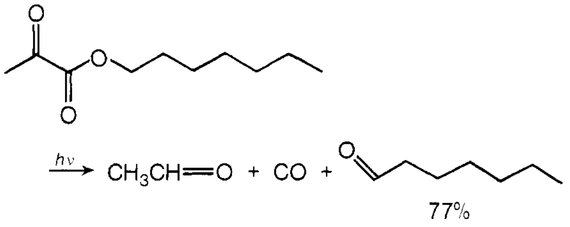

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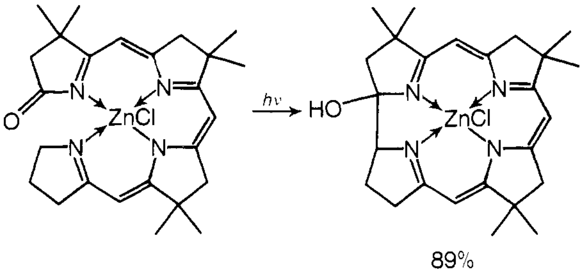
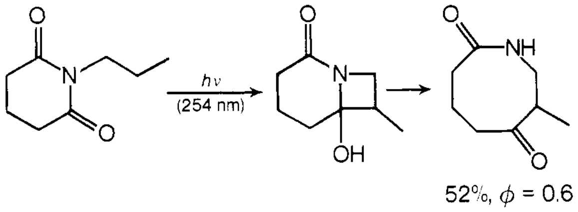


(131)

In contrast to esters and amides, cyclic imides provide a wide range of hydrogen abstraction/cyclization reactions. The 2-azetidinols formed from *N*-alkyl aliphatic imides (eq 132)[146] or *N*-alkyl aromatic imides (eq 133)[147] undergo ring opening to give medium-ring ketoamides, which in some systems can undergo further photochemical reaction.



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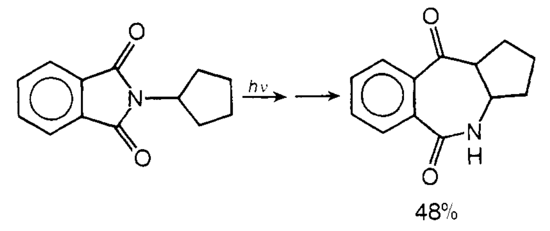
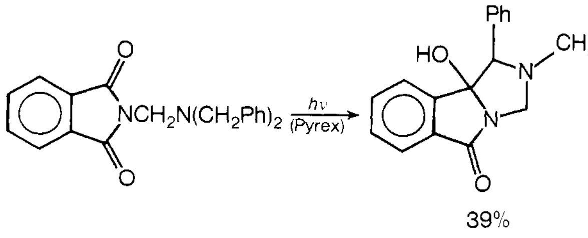


(133)

Different sizes of new rings can be formed in the imide photocyclization reactions, ranging from five-membered (eq 134)[148] to 21-membered (eq 135).[149] The directing influence of an electron-donor group such as $-NR_2$ or especially $-SMe$ is quite



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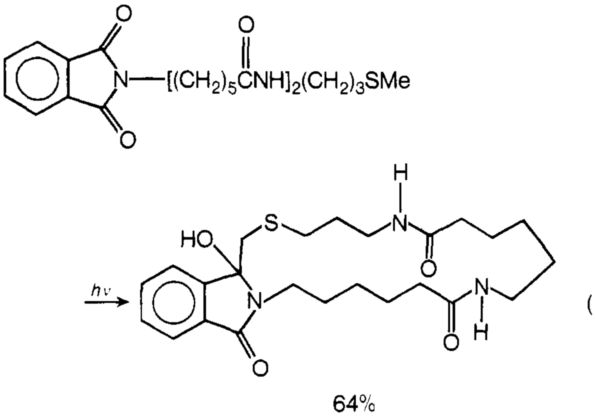
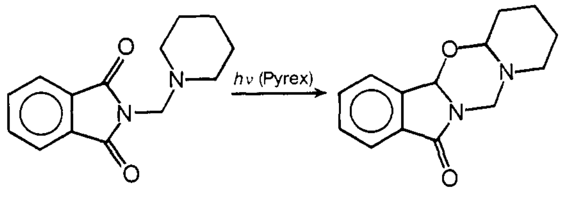


(135)

64%

remarkable, and good yields of many medium- or large-ring heterocycles can be obtained. It is suggested that the electron-donor group brings the remote part of the alkyl chain close to the imide group by a charge-transfer interaction.

In one report[150] of systems of this kind there is one product which incorporates the carbonyl oxygen in the new ring (eq 136), which is unusual in that it suggests that an abstraction by carbon has occurred or that a 1,2-hydrogen shift is involved at some stage.

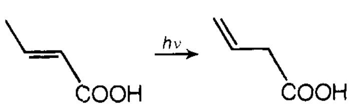


(136)

15%

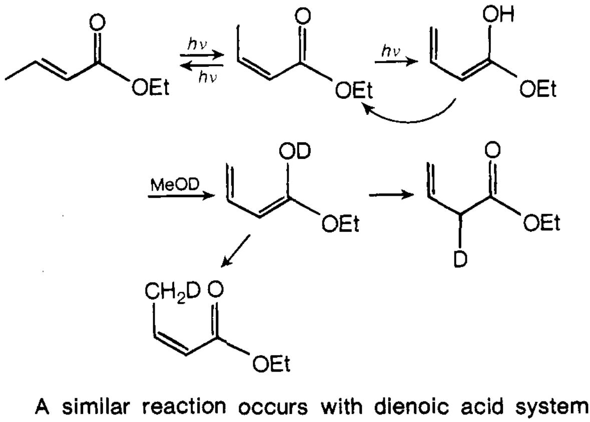
D. α,β-Unsaturated Acid Derivatives

α,β-Unsaturated acids and esters with a hydrogen atom on the γ-carbon can undergo photochemical isomerization[151] to the β,γ-unsaturated isomer (eq 137). The reaction presumably occurs through the geometrical isomer in which the acid (or ester) and hydrogen-bearing groups are on the same side of the double bond. The reaction involves hydrogen abstraction to give an enol of the β,γ-unsaturated compound, and the enol can undergo hydrogen/deuterium exchange which is detected[152] as deuterium incorporation into product and into recovered α,β isomer (eq 138).



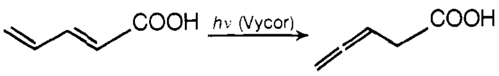
(137)

100%



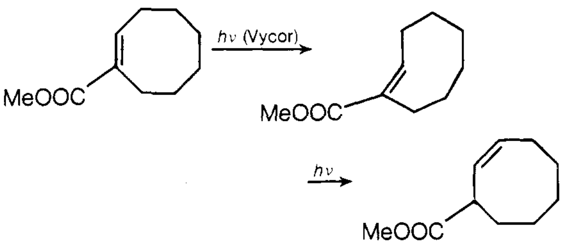
(138)

A similar reaction occurs with dienoic acid systems (eq 139),[153] and also with cycloalkene-1-carboxylates (eq 140) if the ring is at least eight-membered.[154] The steric requirement for intramolecular reaction is that the geometrical isomer must be such that close approach of the carbonyl group and the site of abstraction is possible. Because of ready photochemical cis ⇄ trans isomerization about the C=C double bond (a photoreaction typical of alkenes), this does not normally pose a serious restraint. Acyclic systems usually react through the cis isomer (eq 138), and cyclic systems through the trans isomer (eq 140), though methyl *trans*-cycloheptene-1-carboxylate[154] reacts in a concerted process with ground-state cis isomer to give a cyclobutane dimer (eq 141) rather than undergoing photochemical positional isomerization. The α,β → β,γ isomerization reaction[155] of compounds such as methyl cyclopentene-1-carboxylate (eq 142) is almost certainly not intramolecular, and it is likely that intermolecular hydrogen abstraction is responsible for this process.



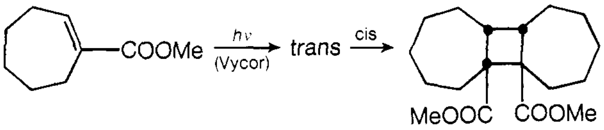
(139)

32%



(140)

70%



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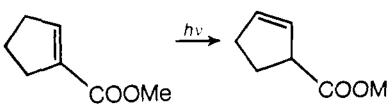
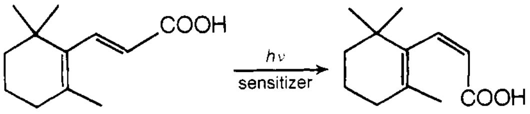


(142)

~100%

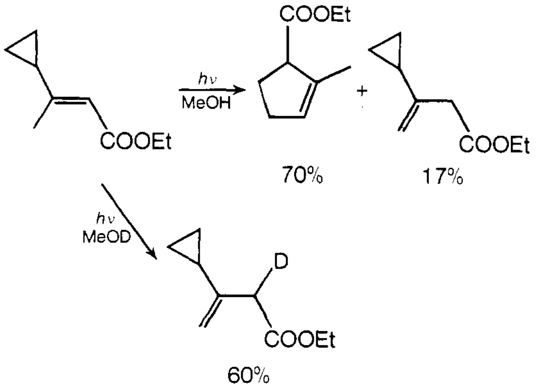
The α,β → β,γ isomerization is a singlet state reaction; triplet sensitization produces only geometrical isomerization about the double bond, though this is frequently a desirable process (eq 143).[156]



(143)

100%

When a cyclopropyl group is conjugated with the α,β-unsaturated system, ring enlargement to a cyclopentene-3-carboxylate system (eq 144) competes with the α,β → β,γ reaction.[157]

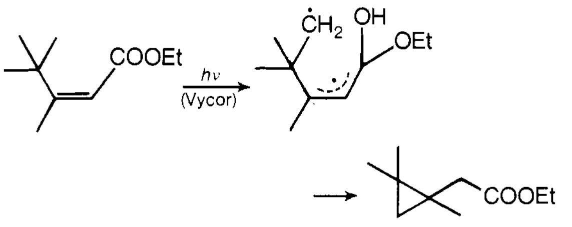


(144)

70% 17%

(145)

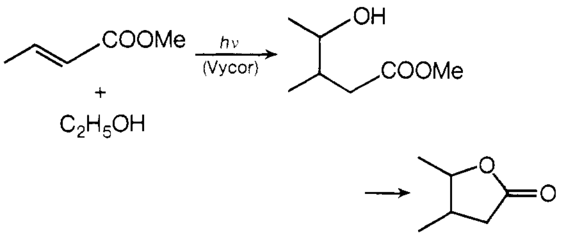
60%



(146)

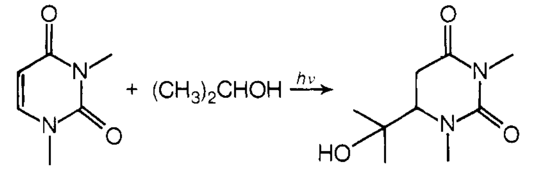
Rather surprisingly, a deuterated alcohol solvent has a large effect[157,158] on the hydrogen abstraction pathway (eq 145). When no γ-hydrogen is available for abstraction, δ abstraction may occur[158] in aliphatic systems to give a cyclopropyl compound (eq 146).

Intermolecular hydrogen abstraction by the carbonyl oxygen seems to be responsible for the photoaddition of alcohols to acyclic[159] α,β-unsaturated carboxylate compounds (eq 147) or to cyclic compounds such as 1,3-dimethyluracil (eq 148),[160] although in the latter systems a different mechanism sometimes competes[161] which leads to alkoxy-substituted products (eq 149). Ethers (eq 150)[162] and hydrocarbons (eq 151)[163] can be added in a similar way; with these a competitive reaction leads to α-substituted products, and the results of deuterium-labeling studies suggest that the β carbon in the excited state abstracts a hydrogen atom to give these alternative products, since the use of perdeuteriocyclohexane[163] leads to an α-substituted product with one deuterium in the β position. A radical which arises from a similar hydrogen abstraction process by a carbon atom of the C═C double bond of a substituted maleimide has been identified by ESR spectroscopy.[164]

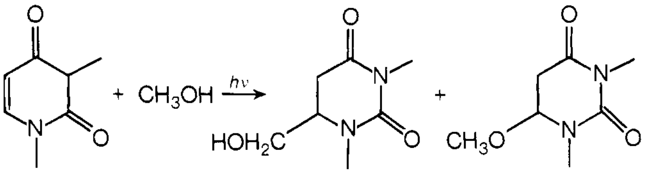


(147)

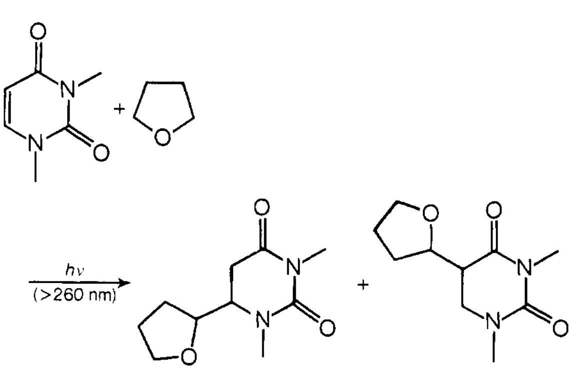
59%



(148)

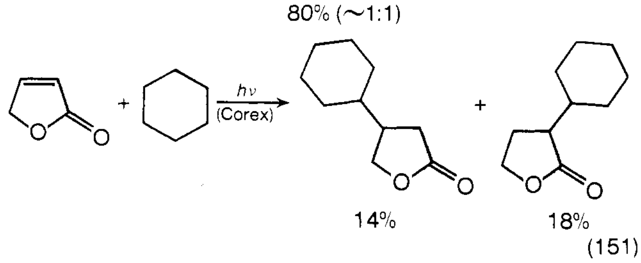


(149)



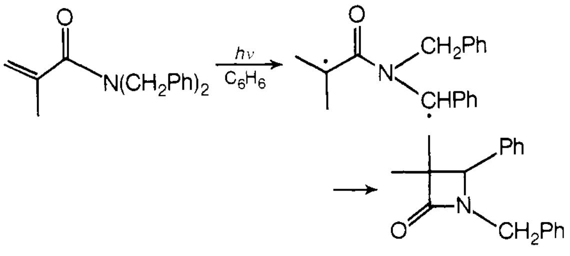
(150)

80% (~1:1)



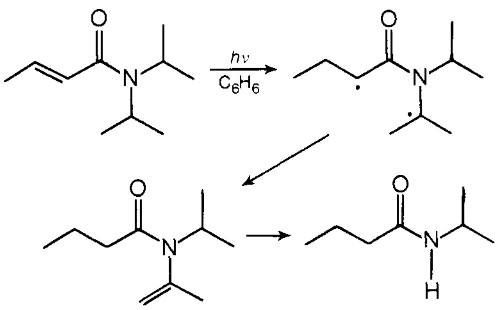
(151)

Intramolecular hydrogen abstraction by the β carbon is held to be responsible[165] for the reaction in which β-lactams are formed from α,β-unsaturated amides (eq 152). The intermediate biradical can isomerize by a 1,5-hydrogen transfer in certain cases to give an enamide which hydrolyzes in the work-up procedure (eq 153).



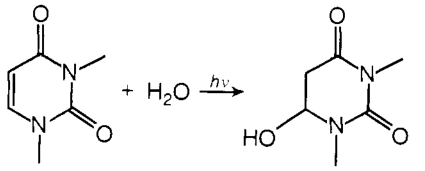
(152)

84%



(153)

Finally, mention must be made of the photohydration of pyrimidines (e.g., eq 154) which has received widespread attention for its photobiological significance.[166] Unlike the photodimerization process of these compounds (see section VII.B), the photohydration is a singlet state reaction and probably involves nucleophilic attack by water on the partly positive β-carbon atom.



(154)

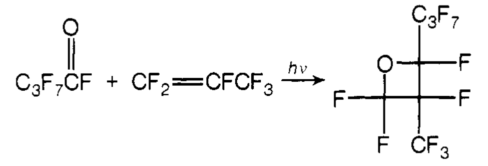
$\phi \sim 0.01$

VII. Cycloaddition

A. Oxetane Formation (C═O Cycloaddition)

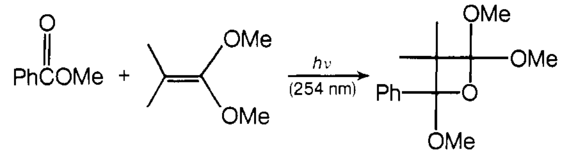
The Paterno-Büchi reaction in which an aldehyde or ketone undergoes photochemical cycloaddition with an alkene to give an oxetane has been known for a long time. Examples of the reaction which involve an acid derivative as the carbonyl component are much less common. In part this is because there are other photochemical processes open to acid derivatives, especially when there is an α or β bond weaker than typical carbon-carbon bonds in ketones. Taking this into account, such derivatives as acyl fluorides or some esters are the most likely acid derivatives to give rise to oxetanes. Another question which arises is the electronic nature of the excited state. The Paterno-Büchi reaction is typical of (n,π*) excited states, whereas many acid derivatives have lowest (π,π*) excited states. However, this need not be a complete barrier to reaction, especially if electron transfer plays a significant role in the mechanism.

Typical oxetane-forming reactions are those of perfluoroacyl fluorides (eq 155)[167] or of aromatic esters (eq 156).[168] In other systems an intermediate oxetane has been proposed to account for the products isolated, as in the metathesis[169] which leads to formaldehyde and an enol ether from an ester and a 1,1-disubstituted ethylene (eq 157), or in the formation[170] of a ketone from an aroyl halide and an alkene (eq 158). In the latter case infrared evidence from low-temperature irradiations provides support for the intermediacy of the oxetane.



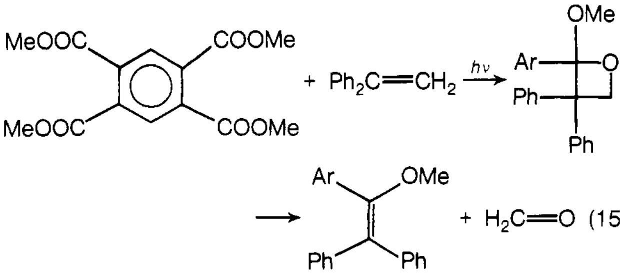
(155)

73% (~ 1:1 cis:trans)



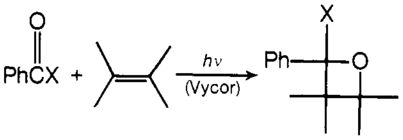
(156)

65%

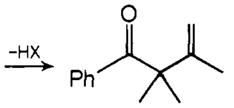


(157)

(Ar = 2,4,5-(MeOOC)$_3$C$_6$H$_2$)



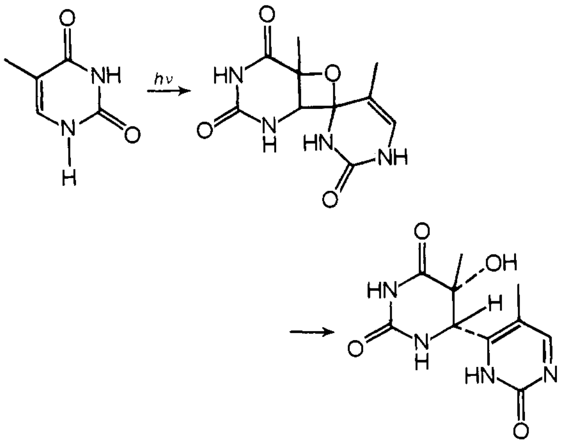
(X = Br or Cl)



(158)

41%

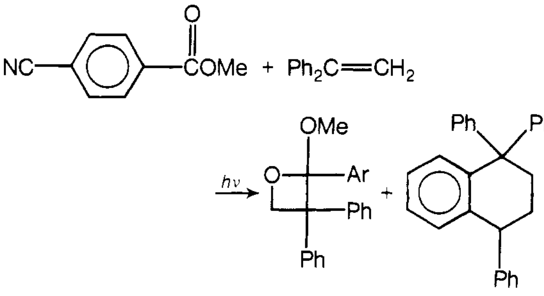
An unusual photodimer of thymine[58] arises from a first-formed oxetane (eq 159), and again low-temperature studies allow the oxetane to be detected.



(159)

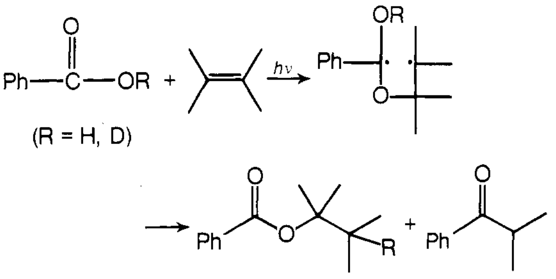
$\phi < 0.001$

Many of the reports of oxetane formation from esters involve esters with electron-withdrawing groups attached, such as diethyl oxalate, ethyl cyanoformate, or cyano- or alkoxycarbonyl-substituted benzoates. Mechanistic studies[168,171] involving esters of aromatic carboxylic acids suggest that a singlet (π,π^*) state of the ester is the reactive state and that an exciplex is formed first between this state and the alkene. The need for electron-rich alkenes is indicative of electron-transfer involvement, and the radical cation of 1,1-diphenylethylene is implicated[172] in forming a triphenyltetrahydronaphthalene as by-product in some reactions (eq 160). In the reaction between benzoic acid and 2,3-dimethylbut-2-ene there is evidence for biradical formation[173] because the major product arises by a 1,5-hydrogen transfer in the biradical (eq 161). Such a process is possible because of the OH group of the acid, and the whole reaction is a "reverse" Norrish type 2 process going through a hydroxy 1,4-biradical. In a similar way[174] the biradical from cyclohexene-1-carboxylic acid and the alkene can undergo intramolecular trapping (eq 162) in competition with hydrogen transfer.



(160)

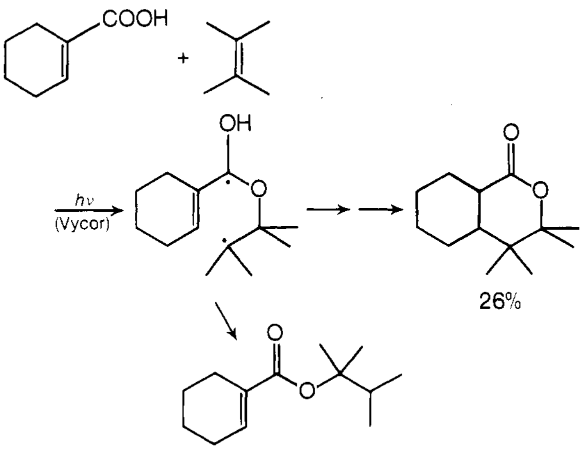
(Ar = p-NC—C$_6$H$_4$)



(R = H, D)

(161)

46%, ϕ = 0.22 22%

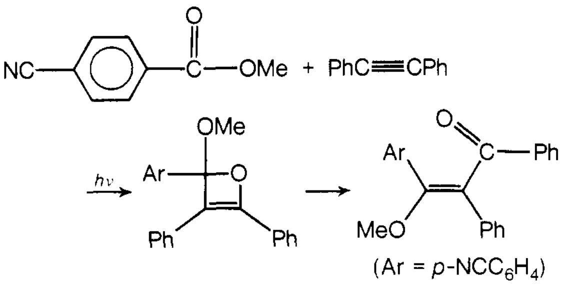


26%

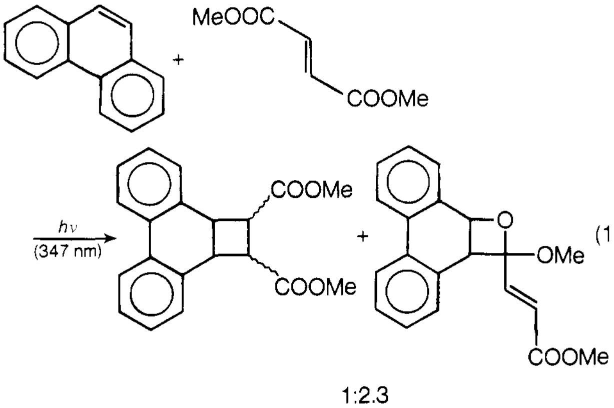
(162)

32%

The isobutyrophenone (PhCOCHMe$_2$) formed as a second product from benzoic acid (eq 161) may well arise by cleavage of the oxetane. Alkynes undergo a photoaddition with esters (eq 163) that parallels the reaction of alkynes with ketones, and it is likely that an unstable oxetene is formed first.[175] α,β-Unsaturated esters with alkenes offer the opportunity for competition between oxetane and cyclobutane formation, and in several



(163)

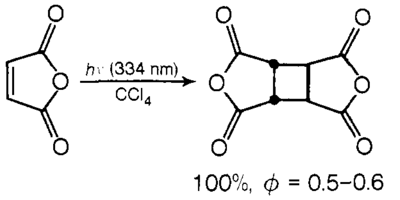


(164)

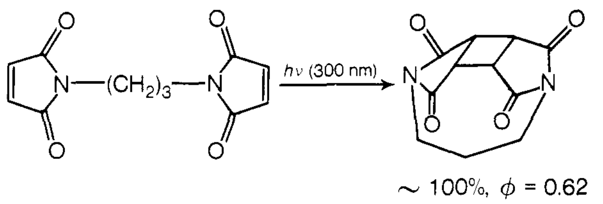
systems[176] both types of product are formed (eq 164). In this phenanthrene/fumarate system both singlet and triplet states contribute to the reaction.

B. Cyclobutane Formation (C=C Cycloaddition)

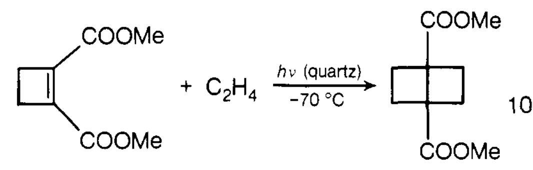
There is a wide range of photochemical reactions in which α,β-unsaturated acid derivatives react with alkenes, alkynes, or aromatic compounds to give cyclobutanes or other carbocyclic systems. In the overall equation for reaction the carboxylic acid function appears to be a "trivial" substituent, but in practice the C=O group is involved in the process. For reactions which take place on direct irradiation, the carbonyl group is involved in extending the chromophore so that radiation of moderate wavelengths (>220 nm) can be used and also in promoting intersystem crossing to the triplet manifold. For triplet-sensitized reactions the carbonyl group assists by providing a triplet excited state of sufficiently low energy for successful energy transfer. In this section an attempt is made to illustrate briefly the variety of systems that can be employed and produced by these processes. Cyclobutanes can be formed in high yield by intermolecular (eq 165)[177] or intramolecular (eq 166)[178] dimerization reactions of α,β-unsaturated acid derivatives on direct irradiation, or by reaction of these derivatives with alkenes (eq 167).[179] In the case of maleic anhydride and cyclohexene (eq 168) the mechanism involves[180] excitation of a ground-state charge-transfer complex between the reactants and subsequent two-step addition. Triplet sensitization yields similar products in many cases.



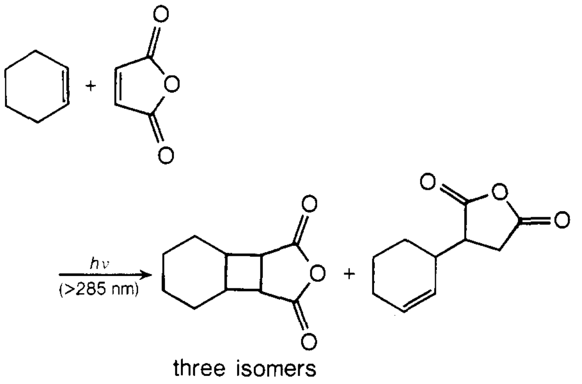
(165)



(166)

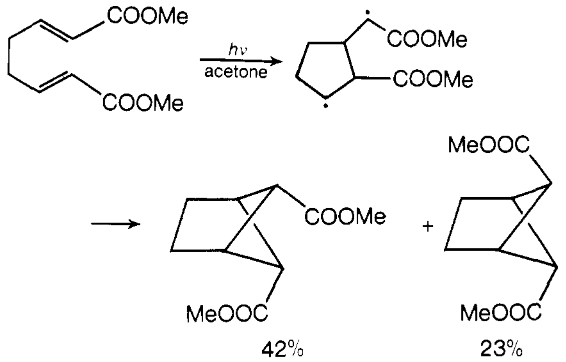


(167)



(168)

For some acyclic α,β-unsaturated esters direct irradiation gives isomerization products (e.g., cis ⇄ trans isomerization or $\alpha,\beta \rightarrow \beta,\gamma$ isomerization) as well as cyclobutane adducts or dimers. Triplet sensitization is usually effective in enhancing cyclobutane formation, although cis ⇄ trans isomerization still occurs and the overall result is a nonconcerted process leading to mixtures of stereoisomers. For intramolecular cycloaddition in acyclic systems the orientation is governed largely by the ring size (preferably five-membered) of the first-formed biradical, and whereas 1,5-diene units give bicyclo[2.1.1]hexanes (eq 169), 1,6-diene units give bicyclo[3.2.0]heptanes (eq 170).[181]



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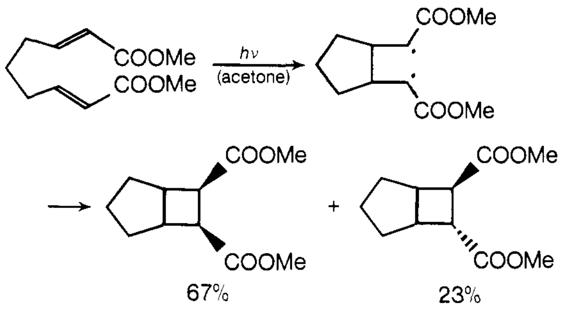
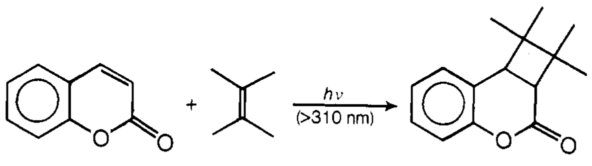


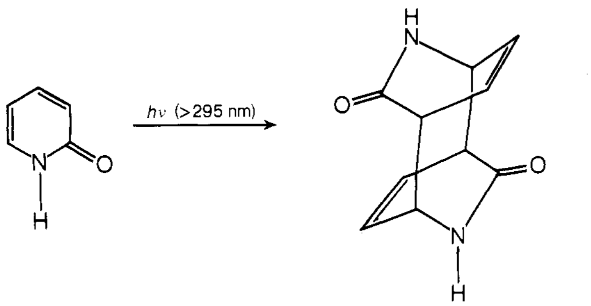
(170)

Systems such as α-pyrones, coumarins, 2-pyridones, and 2-quinolones can take part in these cycloaddition reactions. For instance, coumarin reacts with 2,3-dimethyl-2-butene (eq 171) to give a cyclobutane adduct in high yield by way of singlet and triplet excimers.[182] In the absence of added alkene head-to-head [2 + 2] dimers are formed, mainly through a singlet state reaction. 2-Pyridone can also give adducts, mainly across the 3,4 bond, when irradiated with alkenes,[183] but the dimers formed on irradiating high concentrations without alkene are largely of



(171)

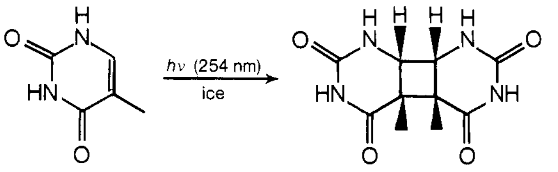
$\phi \sim 0.003$



(172)

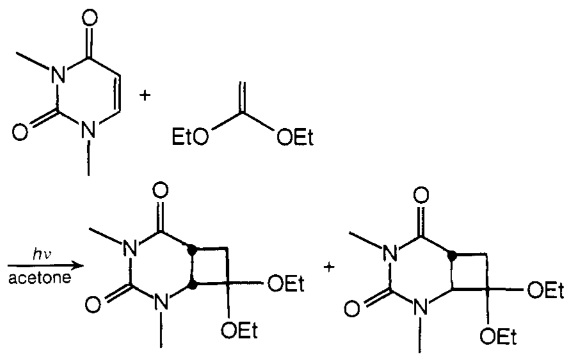
the head-to-tail [4 + 4] type (eq 172), again by way of a singlet state process.[184]

A much studied area in which photochemical reactions of this kind play an important part involves pyrimidines such as those in nucleic acids, and pyrimidine photodimerization is held to be responsible for most photobiological effects of the ultraviolet irradiation of DNA. These processes have been well reviewed,[166,185] and only two illustrative examples will be given here. Compounds such as thymine or uracil undergo photodimerization, but in solution the quantum yield is quite low ($\phi_{265} \sim 0.005$ for uracil), though the chemical yield is often high; a mixture of stereoisomers is formed through the triplet state. In the solid state, or in a matrix such as ice where aggregation can occur, the quantum yield is much higher (eq 173) and the stereoselectivity is greater. The photodimerization is reversible, and while dimer formation predominates at long wavelength, the reverse process occurs efficiently ($\phi \sim 1.0$) at short wavelength. Cross-addition between different pyrimidines is possible, as is photoaddition to alkenes (eq 174). The latter reaction in solution is again a triplet state process,[186] and a mixture of stereoisomers is formed although only one orientation of product is obtained.



(173)

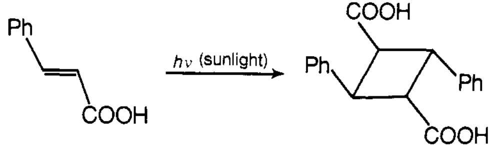
85%, $\phi > 0.2$



(174)

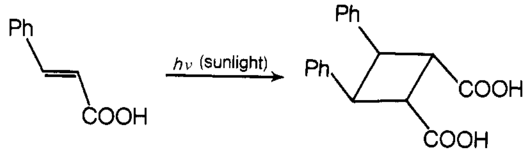
86% 14%

The orientation and stereochemisty of cyclobutane formation seems to be governed by a number of factors. For a triplet state reaction which goes through a biradical intermediate the orientation is normally that corresponding to the most stable of the alternative biradicals, and the reaction is not stereospecific. When a complex between the two reagents is involved (whether ground state/ground state or ground state/excited state), the orientation of the product is determined by the preferred orientation for the interaction in the complex. In the solid state "topochemical" control operates. The orientation and stereochemistry of the products are determined by the orientation of the molecules in the crystal. The classic example of this is cinnamic acid.[187] Of the three crystal modifications, one gives a head-to-head dimer on irradiation (eq 175), one gives a head-to-tail dimer (eq 176), and the third is photochemically inactive.



(175)

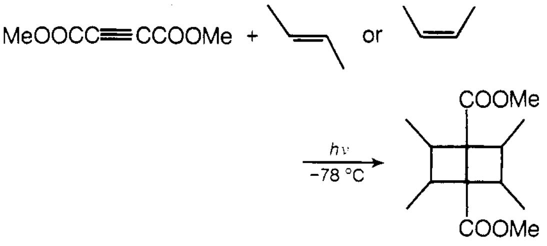
α-solid 74%



(176)

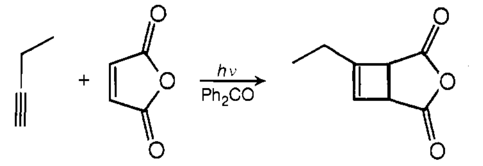
β-solid 80%

An α,β-acetylenic acid derivative forms a cyclobutene on irradiation with an alkene, though very often a second molecule of alkene reacts rapidly with the cyclobutene. This is the case with dimethyl acetylenedicarboxylate and 2-butene (eq 177), where 1:2 adducts are isolated.[188] The reaction occurs through the triplet state of the ester, and the same four stereoisomers are produced from either cis or trans alkene. Cyclobutenes are



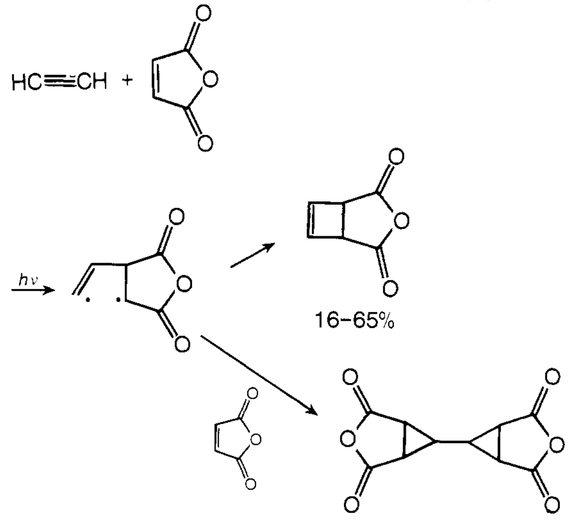
(177)

4 isomers



(178)

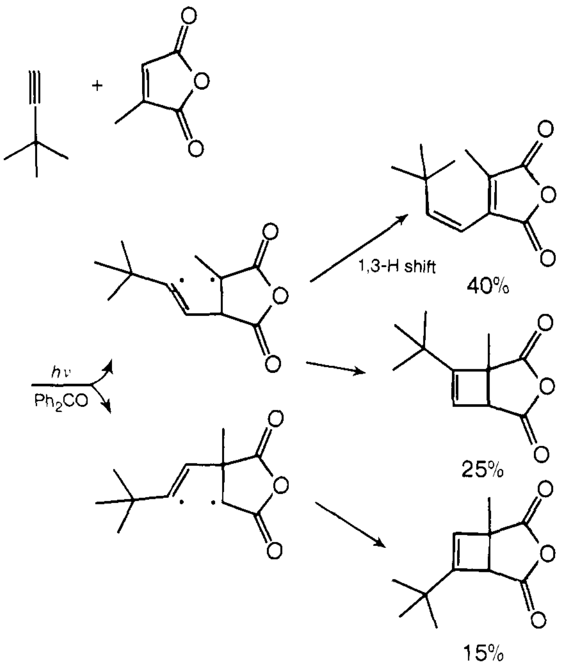
75%



16–65%

(179)

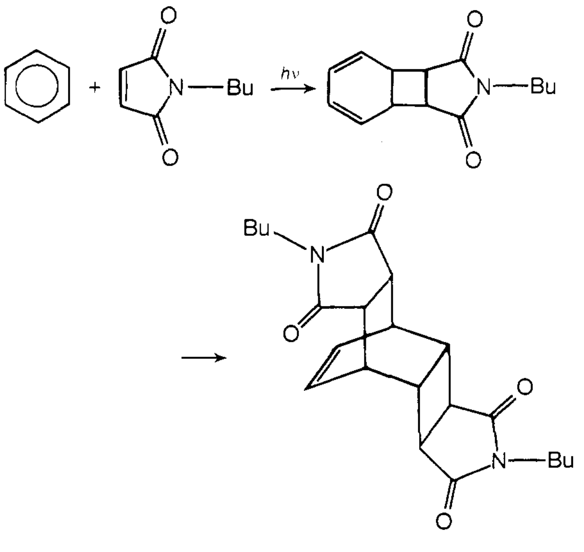
84–35%
(3 isomers)



(180)

formed as the isolated product when compounds such as maleic anhydride are irradiated[189] with an alkyne (eq 178). The reaction is triplet sensitized and proceeds by way of a biradical intermediate. Evidence for this intermediate comes[190] from the nature of the 2:1 adduct formed in a competing process in some systems (eq 179), and from the isolation[191] of a product derived from the biradical by a hydrogen shift when 3,3-dimethylbutyne reacts with citraconic anhydride (eq 180). The orientation of addition in the major products of this latter reaction is also indicative of biradical intermediates.

The photocycloaddition of alkenes to benzenoid compounds gives a variety of product types. Electron-poor alkenes such as α,β-unsaturated acid derivatives generally give [2 + 2] cycloadducts, although with maleic anhydride and maleimides the initial 1:1 adduct rapidly undergoes Diels–Alder reaction with a second molecule of alkene (eq 181).[192] The 1:1 benzene: maleimide adduct can be intercepted with an added dienophile, but until a few years ago the corresponding maleic anhydride adduct had not been successfully trapped. This has now[193] been achieved (eq 182). The maleic anhydride reaction differs from the maleimide reaction in that a ground-state charge-transfer species is excited (whereas imide excitation is required in the other reaction), and also in that proton acids are capable[194] of diverting the reaction to give phenylsuccinic anhydride (eq 183) by trapping of a dipolar intermediate on the pathway to the 1:1 adduct. In both systems triplet-sensitized reaction is possible.



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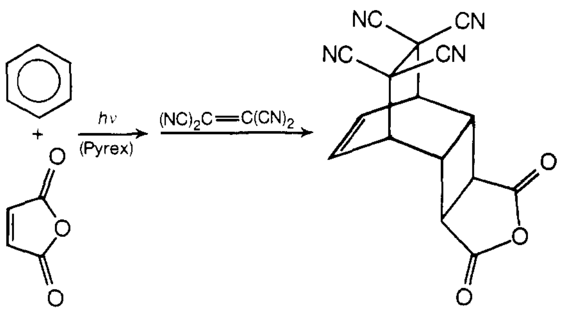
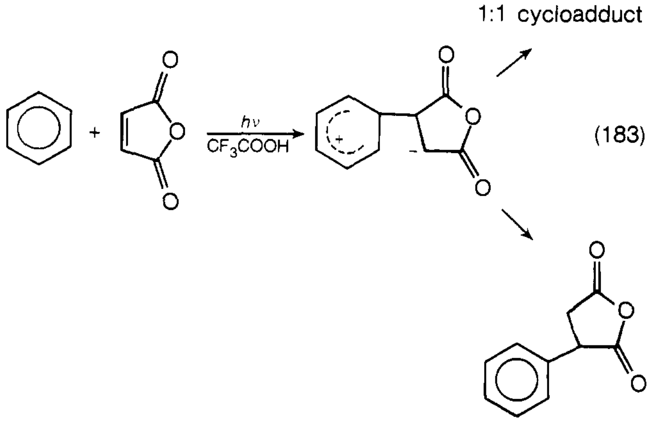
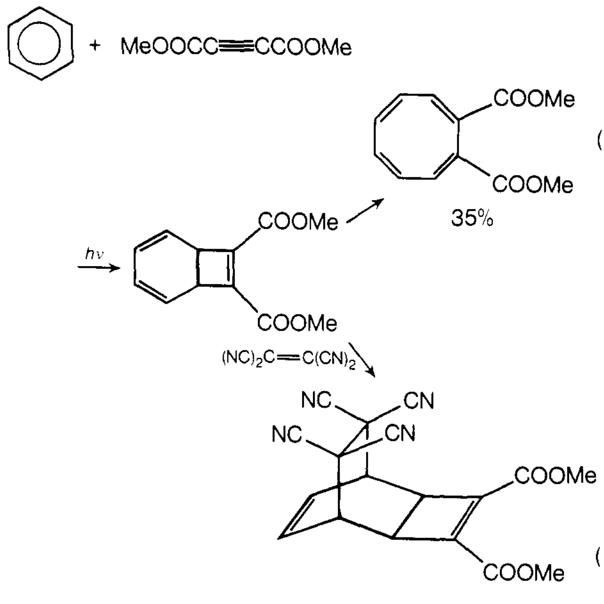


(182)



(183)

Irradiation of α,β-acetylenic esters with benzene gives rise to cyclooctatetraenes (eq 184) on irradiation, by ring-opening of an initially formed bicyclooctatriene[195] which can be trapped[196] by added dienophile (eq 185).

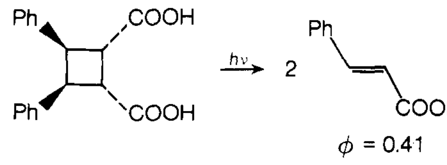


(184)

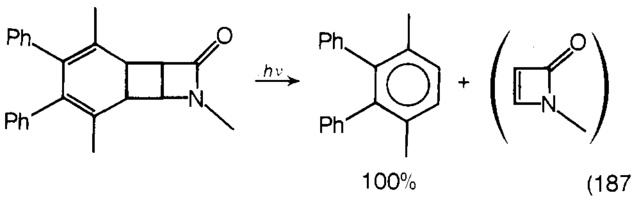
(185)

C. Cycloreversion

The reverse of cycloaddition, in which a cyclobutane undergoes cleavage to two alkenes, can be brought about photochemically in some systems, and it has already been mentioned in connection with pyrimidine photodimers. Another example is seen in the reaction[197] of cinnamic acid dimers which revert to the monomer (eq 186) with short-wavelength irradiation. This type of process can be employed to generate reactive species



(186)



(187)

such as[198] an unsaturated β-lactam (eq 187), although in this example the light is undoubtedly absorbed initially by the diphenyldiene unit. Formally these cycloreversion reactions involve bond cleavage β to the carbonyl group (see section IV), though there is little evidence about the concertedness or stepwise nature of the mechanism.

Note Added in Proof. α-Cleavage of a (O=)C—N bond is involved in the photoaddition of *N*-methylphthalimide with conjugated dienes[199] to give benzazepines, and a similar cleavage in a six-membered unsaturated lactam leads to a ring-opened imine/ketene which is trapped by molecular oxygen.[200] The γ-cleavage reaction in glycidate esters (53) has been shown[201] to be catalyzed by small amounts of metal ion impurities. The cyclization reactions of iodobenzanilides (99) have been reported in much more detail.[202] Intramolecular oxetane formation occurs[203] on irradiation of *N*-alkenylimides.

VIII. References

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