

Chapter 2

Photochemical Synthesis

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Abstract Photochemical reactions are generally easily carried out, at least in laboratory scale, and require no expensive apparatus. Some general reactions, e.g. the cycloaddition of enones to alkenes and various oxygenations have been extensively investigated and represent an excellent choice for preparative applications. Many other possibilities are known—and a few are presented below. This suggests that photochemical steps should be considered more often in synthetic planning.

2.1 Role of Photochemistry in Synthesis

Of all the diverse applications of photochemistry, the most *chemical* one, that is chemical *synthesis* has been actively investigated for over a century, but has probably still much to reveal with future development [1]. In fact, photochemical synthesis is less widely used than it may be. This may appear surprising since chemical synthesis is actually based on the generation of high-energy intermediates for forming new bonds and electronic excitation offers a wonderful opportunity by activating molecules in a controlled way. Unfortunately, practitioners of organic synthesis sometimes feel that photochemical reactions are interesting from the mechanistic point of view, but ill-suited for preparative purposes because they

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require expensive instruments, tend to give mixtures and at any rate their course is difficult to rationalise.

Some of the known photochemical reactions may appear appealing, but also 'unexpected'. As a matter of fact, even a scientist such as Georg Büchi, who played a major role in the relaunch of organic photochemistry after World War II and rediscovered the photochemical carbonyl + alkene cycloaddition that now bears his name along with that of the original discoverer, Emanuele Paternò, was not convinced of the viability of the photochemical approach in synthesis. In an interview he declared that "...*useful applications were not forthcoming...*" from that side and he felt that "...*the course of the transformations could rarely be predicted, thus robbing the investigator of the pleasure derived from designing new reactions*" [2]. Several decades later, it is still felt that it is not always simple to teach this topic. As it has been recently expressed, sometimes this seems to involve a "*somewhat mysterious effect*" so that, "*by simply absorbing a UV/Vis photon, a molecule becomes something different, and in many cases behaves in a way completely opposite to that of its ground state*" [3].

In the opinion of the present contributors there are still many prejudices, but nowadays there is sufficient support, if not widespread application, in the literature for the important role that photochemistry can have in organic synthesis.

2.2 Carrying Out a Photochemical Synthesis

As a matter of fact, carrying out a preparative photochemical reaction is a simple and inexpensive procedure [4]. It is important that some precautions are taken, however, in order to avoid a disappointment. First of all, it must be checked that light is absorbed by the compound that is meant to. Thus, the lamp should have an emission spectrum (available from the maker) overlapping at least in part with the absorption of the reagent and not be hindered from reaching it. Thus, e.g. the walls of the vessel must be transparent to the wavelength used, as must the solvent. The correct choice of the lamps also helps to minimise expenses. Low pressure mercury arcs emitting at 254 nm (or, when phosphor-coated, in the near UV or the visible, being available for various wavelength ranges) are quite inexpensive and long-lived. Along with the slightly more expensive medium-pressure mercury lamps (125–400 W) these are fully sufficient for virtually all of the photochemical syntheses in the scale of some grams. The emission spectra for low and medium pressure Hg lamps may be found in [Chap. 14](#) (Fig. 14.2).

Further precautions are that heating by the lamp (that is important with high pressure lamps or incandescent lamps emitting in the visible) is controlled and that the reaction is monitored by UV/Vis spectroscopy, besides as by the preferred analytical method. This is because it must be ascertained whether (one of) the photoproduct(s) absorb(s) competitively with the reagent; in that case the reaction may stop much before completion. Furthermore, the solutions should be not overly concentrated (this would cause a strongly decreasing absorption when proceeding

from the illuminated surface to the inner volume, a condition that tends to give 'dirty' reactions. However, circulating the solution to be irradiated around the lamp may give a significant advantage and an even better way is using a microreactor, an example of which is shown in [Chap. 14](#) ([Fig. 14.3](#)).

It is noteworthy that photochemical reactions are often little affected by the temperature and by small amounts of impurities (in both cases, because of the short lifetime of electronically excited states, which precludes reactions that have a sizeable activation energy or bimolecular reactions when the trap concentration is low). However, the above holds for excited states, not for ensuing intermediates, such as radicals or unstable species that often are the primary products in photochemical reactions and are usually quite sensitive to conditions. Furthermore, some impurities may specifically interact with the excited state at a very high (diffusion controlled, $\sim 1 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) rate.

Typical examples are compounds having low lying triplets, which can function as acceptors in an energy transfer process and thus 'quench' the photoreaction (see [Chap. 1](#)). The most obvious case is oxygen for which the lowest-lying excited state is lower in energy with respect to practically all organic molecules and thus inhibits photoreactions, or at least most triplet states, while short-lived singlets are less affected. This makes it advisable that irradiations are carried out on a 'deaerated' solution (that is flushed for some minutes with an inert gas such as nitrogen or argon) at least in the initial tests, until the effect of oxygen has been established. On the other hand, this relative independence of the primary photochemical step on the temperature and on conditions is an advantage because it leaves more freedom for directing the chemistry of the following intermediates, e.g. radicals, thus making the photochemical method generally more versatile than thermal methods involving the same intermediate.

2.3 Photochemical Reactions

As for which reactions to do or to explore, it is certainly true that photochemical reactions have been much less applied than thermal ones, but a large number of these are perfectly known and, what is most important, have been rationalised by taking into account their electronic structure in the same way as it is customary to do for ground state reactions [5, 6]. Thus, as soon as the chromophore involved is identified, one may roughly predict the chemical behaviour. As an example, a $n \rightarrow \pi^*$ transition in a carbonyl group leaves a single electron in the n_{O} orbital, which makes such excited states quite similar to oxygen-centred radicals. Indeed, the chemistry observed is the same as that of alkoxy radicals and involves α -cleavage, hydrogen abstraction and electrophilic attack to π -bonds.

A brief survey of the general classes of photochemical reactions is given below. Some recent examples, in most of which a photochemical step is incorporated in a complex synthetic plan, are reported, in order to give at least a flavour of the (potential) role of photochemical synthesis.

2.3.1 Hydrocarbons

Non-conjugated alkenes do not absorb in the near UV, but polyenes or arylalkenes do and the absorption maximum progressively moves towards longer wavelengths and becomes more intense upon extending the conjugation. Furthermore, these derivatives have low-lying triplet states that can be populated by sensitizers (including those adventitiously present). $\pi\pi^*$ excited states are formed, where the double bond is broken. As a result, the molecules lose planarity and alkenes are most often characterised by efficient *E-Z* photoisomerism in the excited state, except when torsion is hindered by molecular constraint. A (mainly) one-way isomerisation can be obtained by exploiting the different absorption spectra of the two diastereoisomers—and thus by selective excitation, or by the appropriate choice of the sensitizer or by complexation [7].

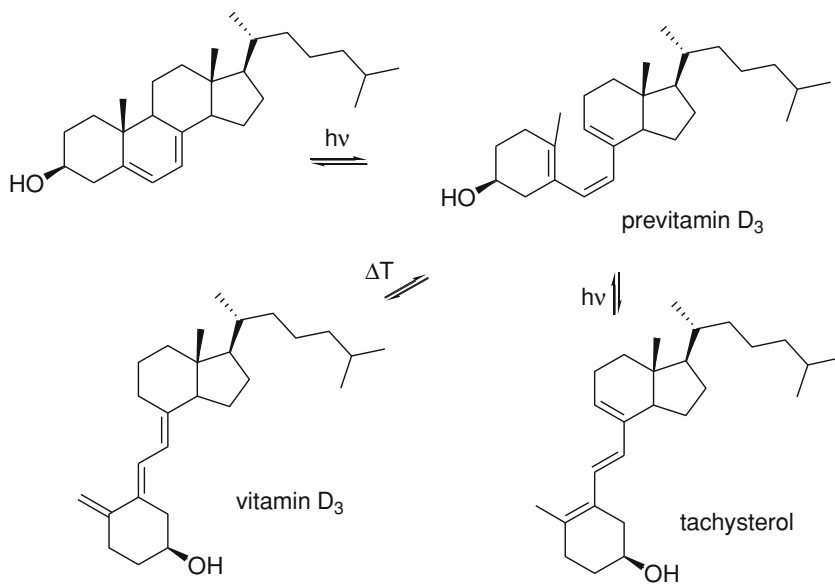
Geometrical isomerism is a general reaction, applying not only to C=C bonds, but also to carbon-heteroatom and heteroatom–heteroatom double bond, as in oximes, hydrazones and azo compounds.

With conjugated polyenes, electrocyclic reactions are generally observed. Due to the stereochemical control, these are often considered among the most representative photochemical reactions, although the occurrence of such processes in both directions means that mixtures are often obtained. A case of industrial importance is the synthesis of vitamin D. The competition between different π^6 electrocyclic reactions and sigmatropic hydrogen shift is shown in the scheme below for the case of the formation of a mixture of previtamin D₃ and tachysterol. The reaction has been recently enhanced by using a photomicroreactor combined with a thermal-microreactor. Heating converts the provitamin into the desired vitamin, and this causes a shift of the equilibrium towards the latter compound in the photoisomerisation of tachysterol to previtamin D₃ (see Scheme 2.1) [8].

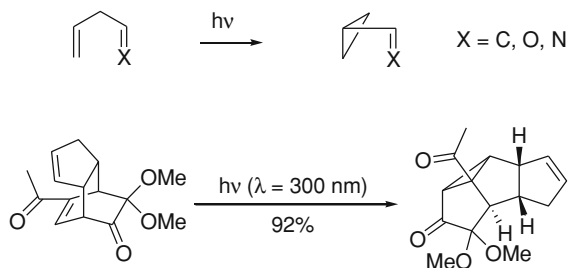
Not less useful is the photochemistry of non-conjugated dienes. Thus, 1,4-dienes undergo a typical photo-rearrangement to vinyl cyclopropanes, which may be a valid way for building a three-membered ring, particularly in a complex structure (this is known as the di- π -methane rearrangement, see Scheme 2.2). β,γ -Unsaturated ketones and imines rearrange in the same way to cyclopropylketones and imines respectively [9].

On the other hand, 1, ≥ 5 dienes undergo intramolecular 2+2 cycloaddition. Different modes are possible and mixtures may be obtained. However, at least when the relative arrangement of the two double bonds is fixed, either because freedom is restricted by the structure of the diene or because complexation by metal ions has been effected, the selectivity may be excellent (see Scheme 2.3) [10–12].

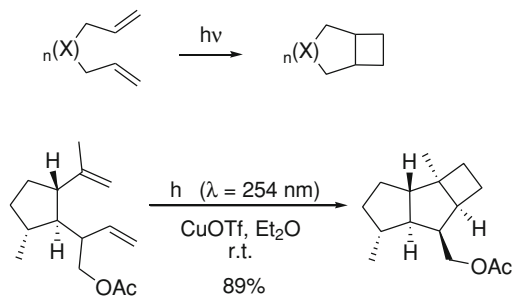
Aromatic compounds absorb strongly in the UV, with larger aromatic derivatives extending out to the visible. Extended conjugation and geometrical constraints make them less photoreactive than alkenes, or at least less efficiently reactive. However, the increased stability does not deter excited states from exhibiting their attitude for remarkable reactions. Among unimolecular processes, photo-rearrangements to polycyclic compounds, as in the benzene \rightarrow benzvalene



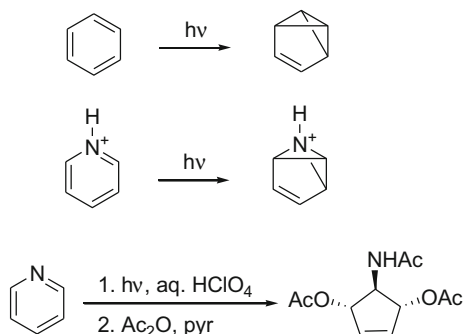
Scheme 2.1 Electrocyclic photoreactions and photoisomerization in the synthesis of vitamin D₃



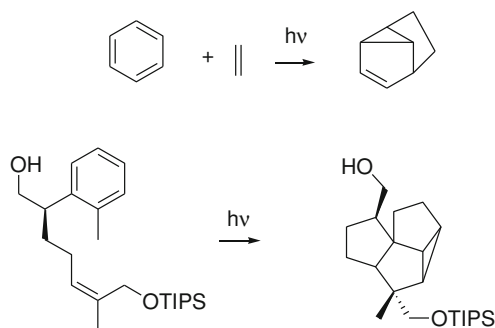
Scheme 2.2 (Oxa)-di- π -methane rearrangement



Scheme 2.3 [2+2] Olefin cycloaddition



Scheme 2.4 Benzene to benzvalene rearrangement and aza analogue



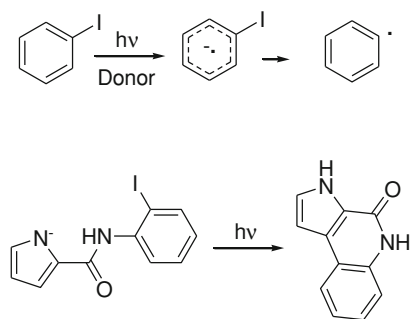
Scheme 2.5 *Meta* benzene-olefin cycloaddition

case (see Scheme 2.4), are well known. This is synthetically useful with heteroaromatics, in particular pyridine or rather pyridinium salts, where the three-membered ring undergoes nucleophilic opening [13, 14].

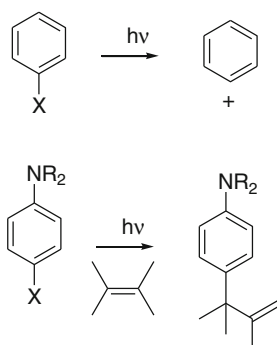
Remarkable also is the related case of the *meta* benzene-alkene cycloaddition. Here again, mixtures are formed, but at least when the alkene moiety is tethered to the benzene ring and a preferred conformation exists, regio-selective processes have been found where several new stereocenters are formed in a single step and in a rigorously controlled way—and thus are synthetically highly valued (see Scheme 2.5) [15].

In the field of (hetero)aromatic photochemistry substitution reactions are also quite useful. The two most useful classes are the $S_{RN}1$ reaction [16] and S_N1 reaction [17], involving respectively the aromatic radical anion and the aryl cation as the key intermediates. In the former case, (generally photoinduced) electron transfer generates the radical anion of an aryl halide. With less strongly bonded derivatives (usually iodides) the intermediate cleaves to an aryl radical that gives the new product *via* a chain process (see Scheme 2.6).

Aryl cations, on the other hand, are the typical example of ground state intermediates that cannot be generated thermally, whereas these are smoothly accessed photochemically by irradiation of phenyl chlorides and fluorides, or at least of the



Scheme 2.6 The photo $S_{RN}1$ reaction



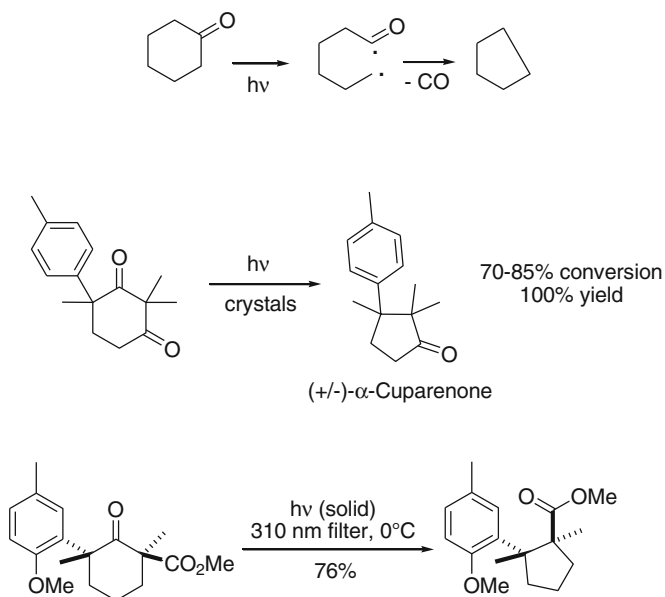
Scheme 2.7 The photoarylation of alkenes *via* S_N1

electron-donating substituted types, in polar solvents (see Scheme 2.7). The reaction has been applied for the arylation of alkenes, alkynes, benzenes and heterocycles, offering a metal-free alternative to catalysed reactions largely used in synthesis.

2.3.2 Ketones and Related Chromophores

The lowest-lying excited state of ketones most often corresponds to a $n_O \rightarrow \pi^*_{C=O}$ transition. The maximum of this band is around 280 nm with simple aldehydes or ketones and is shifted to the red for conjugated or aryl derivatives. As hinted above, the unpaired electron on the n_O orbital gives to these states electrophilic properties similar to those of alkoxy radicals, and indeed the observed chemistry is similar in the two cases. Typical reactions are α -fragmentation, inter- or intramolecular (from the easily accessible γ position) hydrogen abstraction and attack of alkenes (finally resulting in a formal 2+2 cycloaddition to give an oxetane, the Paternò-Büchi reaction).

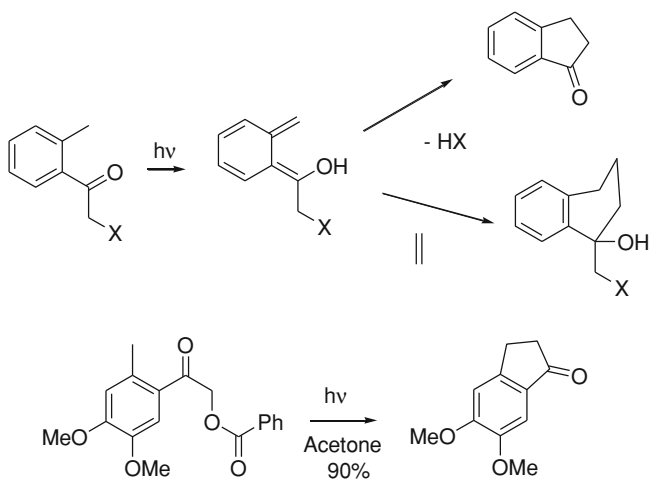
Fragmentation has given synthetically useful results particularly in the solid state for α -(poly)substituted ketones, where both α -bonds are cleaved and the



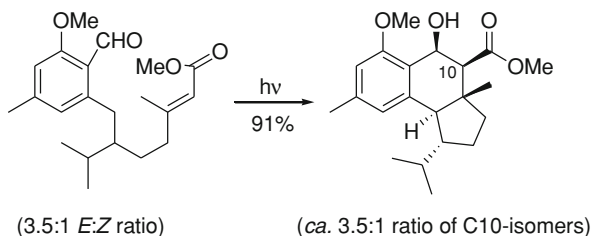
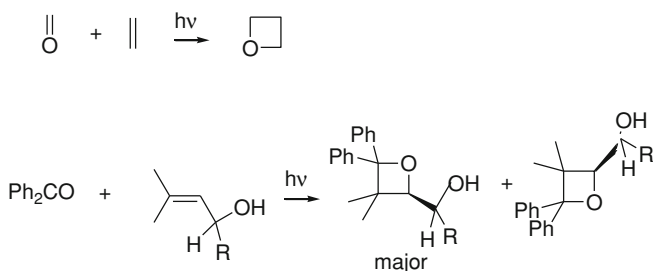
Scheme 2.8 Decarbonylation reactions

recombination of the adjacently formed radical centres is more easily controlled leading to the chemo- and stereoselective photo-decarbonylation reactions (see Scheme 2.8) [18, 19].

When conformationally favored, intramolecular hydrogen abstraction is very effective. This reaction has been observed in *o*-methylbenzophenone and related

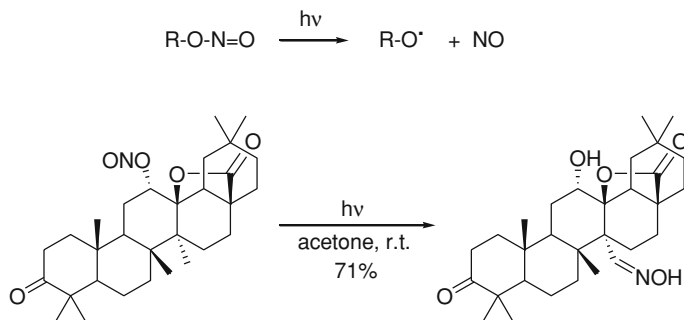


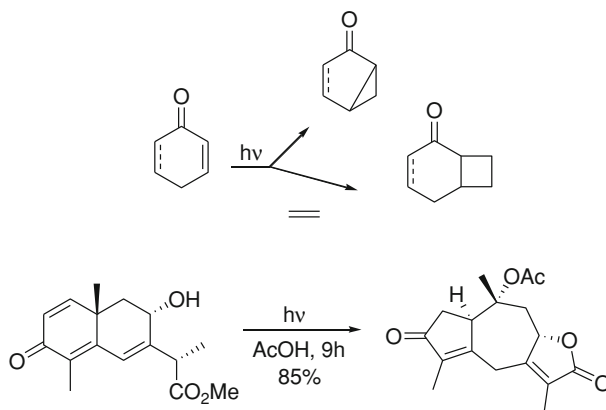
Scheme 2.9 Enolisation and fragmentation

**Scheme 2.10** Enolisation and [4+2] cycloaddition**Scheme 2.11** Synthesis of oxetanes

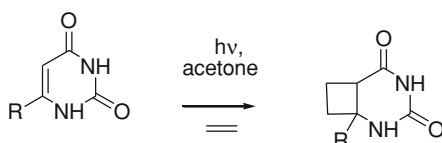
compounds and has been frequently used for producing the enol form of the starting material, and thus access to the high reactivity of such a group. In a typical application, this is trapped by an alkene, whether intra- or intermolecularly, leading to a 4+2 cycloaddition regenerating aromaticity [20]. In the presence of a suitable leaving group, an elimination reaction can also take place (see Schemes 2.9, 2.10) [21]. The photocycloaddition to alkenes, a regioselective but not stereospecific reaction, offers a useful entry to oxetanes (see Scheme 2.11) [22].

The nitro group has an electronic structure similar to the carbonyl and likewise a $n\pi^*$ lowest state that again shows radicalic properties (hydrogen abstraction). Interesting is the case of nitrites that generally undergo easy homolytic cleavage of

**Scheme 2.12** Photolysis of a nitrite



Scheme 2.13 Enones rearrangement



Scheme 2.14 Intermolecular enone cycloaddition

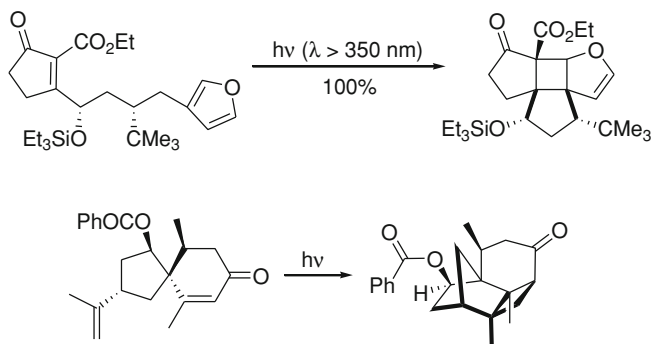
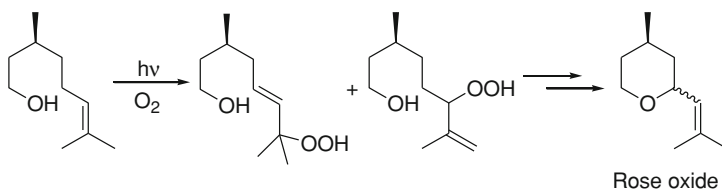
the N–O bond. This is often followed by intramolecular hydrogen abstraction by the alkoxy radical and addition of NO molecule leading to function exchange (Barton reaction) (see Scheme 2.12) [23].

As one would expect, conjugated ketones are mostly poor hydrogen abstractors. This is a fortunate circumstance, because it leaves room for a variety of reactions that are quite useful from the preparative point of view. These include rearrangements [24], addition reactions and 2+2 cycloaddition with alkenes. An example of rearrangement of a cross-conjugated cyclohexadienone is shown above. This gives a cyclopropylcyclopentenone that opens up in the reaction medium (see Scheme 2.13).

As for the synthesis of acylcyclobutanes by cycloaddition, this is often a very efficient process and is one of the most largely used synthetic procedures in organic photochemistry. An example is the addition of uracil to alkenes (see Scheme 2.14) [25]. The intramolecular version is most often used and gives excellent results (see Scheme 2.15) [26, 27].

2.3.3 Oxidations

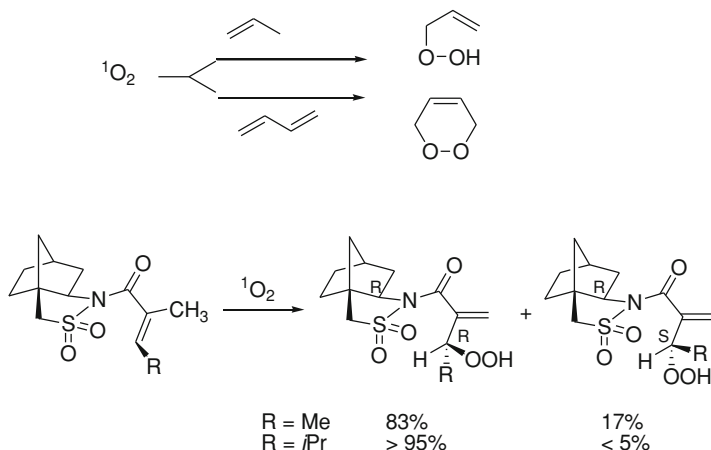
Along with the cycloaddition of enones, photooxidation is probably the most consistently used photochemical reaction for synthetic purposes. This is also one

**Scheme 2.15** Intramolecular enone cycloaddition**Scheme 2.16** Synthesis of rose oxide

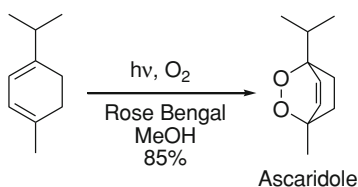
of the few that have found application in an industrial context, notably in the case of rose oxide. This fragrance is produced in Germany in a considerable yearly tonnage, making recourse to photochemistry in one of the first steps. This involves the oxidation of citronellol in the presence of a sensitiser (Rose Bengal) using molecular oxygen (see Scheme 2.16). The thus generated excited (singlet) oxygen is a highly electrophilic species that attacks alkenes in a very mild process [28]. The resulting hydroperoxides are then reduced to the alcohols, which then are transformed into the corresponding cyclic ethers.

Oxygenation *via* singlet oxygen is often convenient [29] and occurs according to two processes; the ene (Schenck) reaction to give allylhydroperoxides with alkenes [30] and the cycloadditions with dienes to give 1,2-dihydrodioxins (see Scheme 2.17) as in the case of the synthesis of ascaridole (see Scheme 2.18). The cycloaddition occurs effectively also with electron-donating substituted aromatics (e.g. phenols and naphthols, see Scheme 2.19) [31] or multi-ring aromatics (quite effectively with anthracenes and higher homologues, see Scheme 2.20) [32].

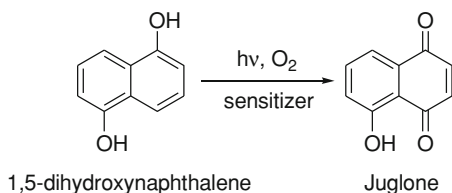
The addition of oxygen to furans to form ozonides and hydroxyfuranones (Scheme 2.21) has been largely exploited in view of the ensuing easy elaboration of these versatile intermediates [33–35].



Scheme 2.17 Modes of reaction of singlet oxygen



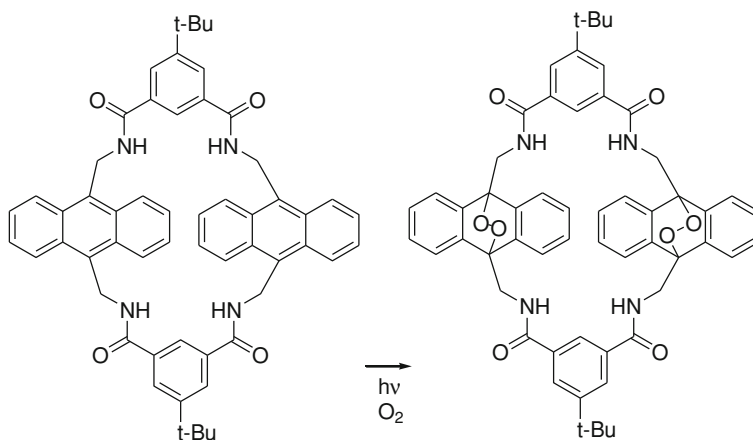
Scheme 2.18 Synthesis of ascaridole



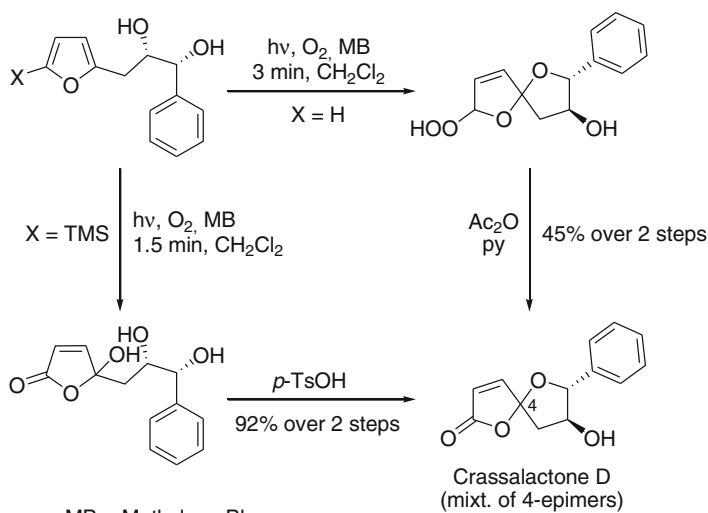
Scheme 2.19 Oxygenation of naphthol

2.3.4 Miscellaneous

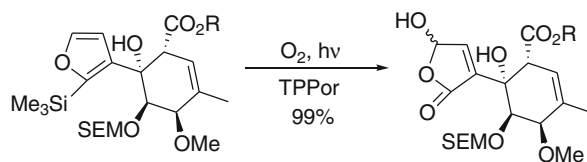
There are many more preparatively useful classes of photochemical reactions that could be addressed in this short presentation. Perhaps, one should at least mention halogenation, sulfonation and sulfochlorination that have large industrial significance for the preparation of surfactants. As an example, the sodium salts of secondary alkanesulfonamidoacetic acid were synthesised using *n*-alkanesulfonyl



Scheme 2.20 Oxygenation at the anthracene ring



MB = Methylene Blue

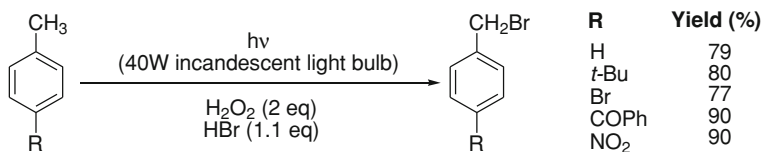


R = $(\text{CH}_2)_2\text{SiMe}_3$

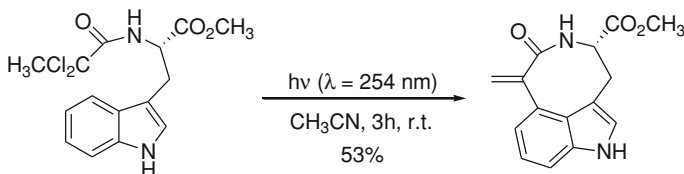
SEM = trimethylsilyloxyethyl

TPPor = 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine

Scheme 2.21 Oxygenation of furans



Scheme 2.22 Photoinduced halogenation



Scheme 2.23 An example of *N*-chloroacetamide cyclisation

chlorides as starting materials. These surfactants, having the formula $R-SO_2-NH-CH_2-COONa$, with $R=C_{12}$, C_{14} , C_{16} and C_{18} derived from the corresponding *n*-alkylsulfonyl chlorides obtained by photochemical sulfochlorination of the alkanes under visible light using sulfuryl chloride [36]:



Photochemical halogenations may also be convenient on the laboratory scale. As an example, benzylic bromination is conveniently carried by using HBr/H_2O_2 under irradiation with a common incandescent lamp (see Scheme 2.22)[37]. Apropos halides, it may be added that fragmentation of the carbon-halogen bond has been considered above for aromatic derivatives, but is useful also for aliphatic derivatives. A typical example is the photocyclisation of *N*-phenyl chloroacetamides and *N*-arylalkyl chloroacetamides (see Scheme 2.23)[38].

2.4 Conclusions

The variety of chemical reactions reported above is impressive. Most of them hardly have a simple thermal alternative. When it is further considered that these reactions are usually more easily carried out than many modern synthetic reactions, it may be concluded that the role of photochemistry in chemical synthesis is bound to further develop.

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