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Generation of ketyl radical anions by photoinduced electron transfer (PET) between ketones and amines. Synthetic applications

Janine Cossy* and Damien Belotti

Laboratoire de Chimie Organique associé au CNRS, ESPCI, 10 Rue Vauquelin, 75231—Paris Cedex 05, France

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Abstract—Photoreduction of ketones in the presence of amines led to ketyl radicals through photoinduced electron transfer (PET). Tertiary amines, such as triethylamine (Et_3N) have frequently been used in these reactions. Different reactions can occur from ketyl radicals such as photoreduction, coupling reactions, additions on activated double bonds, cyclizations, bond cleavage of strained rings, tandem reactions such as cyclization–ring opening or ring opening–cyclization.

1. Introduction

Electron-transfer reactions are extensively studied in chemistry[1] and the photochemical approach of reactions of this type has become familiar to most organic chemists as the result of a better understanding of primary processes. Recognition of charge transfer processes in photochemical reactions, direct characterization and determination of kinetic and thermodynamic properties of radical ion intermediates, has induced a renewed interest in applications of photochemical reactions to organic synthesis.[2]

Photoinduced electron transfer (PET) processes involve two neutral molecules, a donor (**D**) and an acceptor (**A**) and an electronic excitation (Eq. 1).

$$(\mathbf{D}) + (\mathbf{A}) \xrightarrow{h\nu} (\mathbf{D}^{\bullet+}) + (\mathbf{A}^{\bullet-}) \longrightarrow \text{Products} \quad (1)$$

Production of radical ions ($\mathbf{D}^{\bullet+}$) and ($\mathbf{A}^{\bullet-}$) depends on the oxidation potential $E_{ox1/2}(\mathbf{D})$, the reduction potential $E_{red1/2}$ (**A**) of the starting molecules and on the electronic excitation energy E_{00}, according to the Rehm–Weller equation (Eq. 2) where the coulombic interaction term in polar solvents, such as acetonitrile, can be neglected in the first approximation.[3]

$$\Delta G_{set} = E_{ox1/2}(\mathbf{D}) - E_{red1/2}(\mathbf{A}) - \Delta E_{00} + \Delta E_c \quad (2)$$

When the PET is thermodynamically favourable ($\Delta G<0$), electron transfer proceeds close to a diffusion controlled rate. However, the behaviour of the formed radical ion pair depends strongly on the nature of the solvent and on the rate of the reverse electron transfer to molecules (**A**) and (**D**) in their ground state. Use of polar solvents favours the formation of solvent separated ion pairs and limits this reverse electron-transfer process. Furthermore, the selective transformation of one of the radical ion often promotes efficient chemical transformations.

PET processes between a carbonyl derivative considered as an acceptor (**A**) and an amine considered as a donor (**D**) have received considerable attention[4] since the pioneering studies on photoreduction of aromatic ketones with tertiary amines.[5] Numerous developments have appeared during the last 30 years. In this review, we will focus our attention only on the behaviour of the ketyl radical anion generated by photoreduction of ketones by amines and we will not consider the reactivity of enones and quinones. Five different processes can occur from the ketyl radical anion, e.g., abstraction of hydrogen from the reaction media to produce alcohols, coupling of two ketyl radical anions and/or coupling of the ketyl radical anion with the radical cation formed from the donor, intermolecular addition of the ketyl radical anion to an activated double bond, cyclization as in the case of ω-unsaturated ketyl radical anions, fragmentation when a Cα–X bond (X=O, C) is present. Tandem reactions can also take place such as opening of strained rings followed by cyclization or cyclization followed by opening of strained rings.

Photoreduction of ketones in the presence of amines involves charge transfer interactions between amines and ketones excited states.[5a] Kinetic studies indicate that for a given ketone, the rate constants increase when the oxidation potential of the amine is lowered [DABCO>R_3N>R_2NH>RNH_2] and the products are derived from an initial electron transfer

* Corresponding author. Tel.: +33 1 40 79 44 29; fax: +33 1 40 79 46 60; e-mail: janine.cossy@espci.fr

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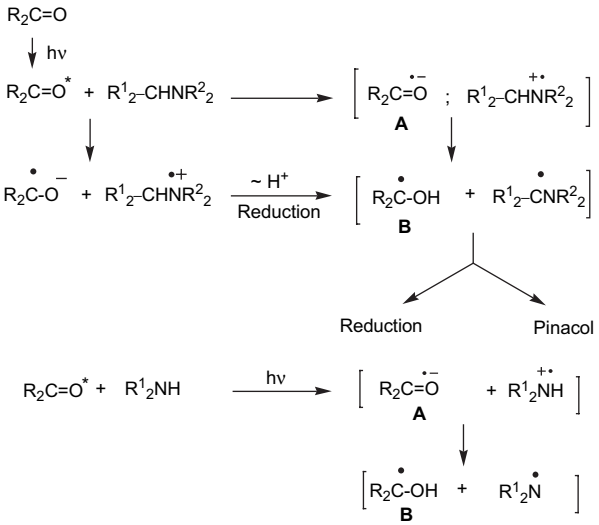
rather than from a direct hydrogen atom transfer.[6] Early studies by Cohen and co-workers[7] as well as more recent studies,[8] have demonstrated that a radical ion pair is generated through electron transfer from the ground state of the amine to the photoexcited ketone, followed by proton transfer from the amine radical cation to the ketyl species. Tertiary amines, such as triethylamine (Et_3N) have frequently been used in these reactions.[9] Electron transfer can also occur to the ground state of the ketone when the amine is excited (Scheme 1).

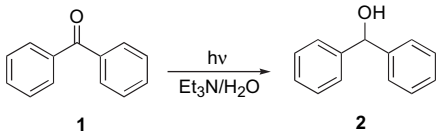


Scheme 1.

Depending on the nature of the amine, either C–H or N–H bond intervenes in the hydrogen atom transfer with the formation of the hemipinacol radical and an aminyl or α-amino radical. Furthermore, depending on the conditions and on the substrate, the abstraction of a proton by the radical anion **A** can be faster than the reactivity of the radical anion **A** itself and products can come from radical **A** or **B**.

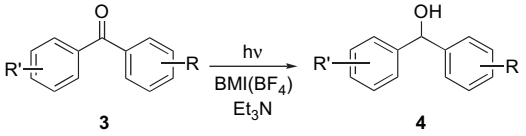
2. Photoreduction

The photoreduction of aromatic ketones by aliphatic amines has been the subject of extensive investigation.[5] In aqueous media, it was found that the reduction of aromatic ketones by amines proceeds rapidly to form secondary alcohols via a ketyl radical anion rather than a pinacol type product[5a,10] (Scheme 2).



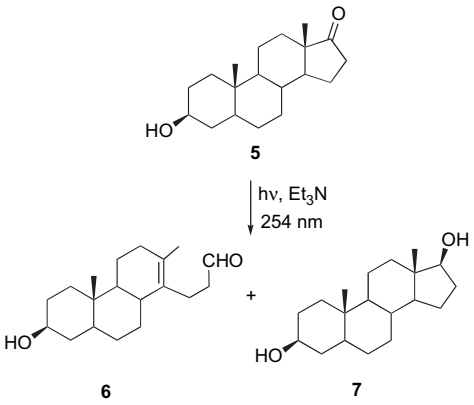
Scheme 2.

In polar solvents, as well as in ionic liquids,[11] benzydrols can be obtained from amine-mediated photoreduction of benzophenones **3** at room temperature. In ionic liquids, because the reaction consumes only 1 equiv of amine and the solvent can be easily recycled, the photoreduction allows a very clean process for the conversion of benzophenones to benzydrols (Scheme 3).



Scheme 3.

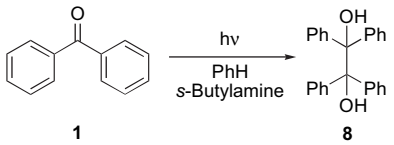
When 3β-hydroxy-5α-androstan-17-one and Et_3N were irradiated at 254 nm, such as Et_3N absorbs 99% of the incident light, one obtains products resulting from Norrish type I product, **6**, and alcohol **7** coming from the reduction of the ketone. The product ratio depends strongly on the solvent. In ether and THF, compound **6** (Norrish type I product) and alcohol **7** are observed in a ratio of 1/1 but in acetonitrile only the 5α-androstane-3β,17β-diol **7** is formed[12] (Scheme 4).



Scheme 4.

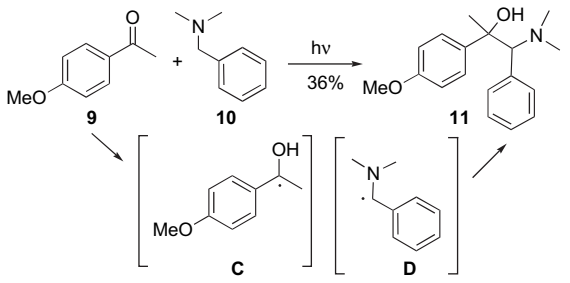
3. Coupling reactions

Coupling reactions between a radical cation and a radical anion or between two radical anions can occur. The proportion of the different products is very sensitive to the solvent and additives. For example, the irradiation of benzophenone **1** in benzene in the presence of *s*-butylamine produces the benzopinacol **8** in quantitative yield[11] (Scheme 5).



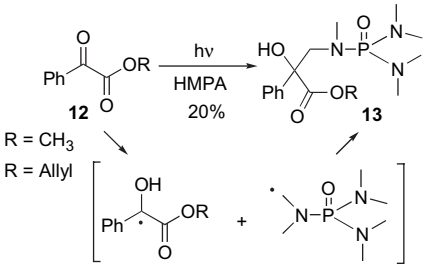
Scheme 5.

A mixed coupling product **11** is obtained when the aromatic ketone **9** is irradiated in the presence of a tertiary amine such as *N*,*N*-dimethyl *N*-benzylamine in acetonitrile. Compound **11** corresponds to the coupling of the α-amino-alkyl radical **C** with radical **D**. Both radicals possess an aromatic and an electron-donating substituent and this structure resemblance favoured the photopinacolization type reaction[13] (Scheme 6).



Scheme 6.

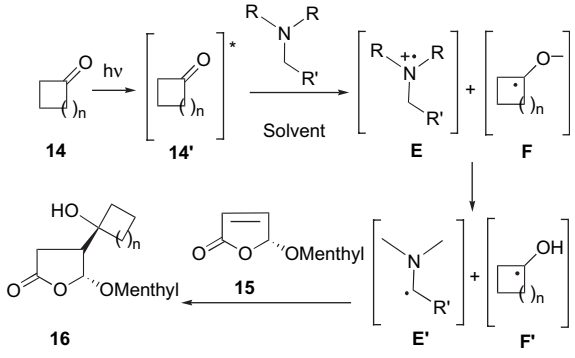
Another example of cross-coupling reaction is observed when α-ketoester **12** is irradiated in HMPA.[14] The irradiation resulted in the cross-coupling of the ketyl radical with the generation of a HMPA-derived radical according to Scheme 7.



Scheme 7.

4. Addition

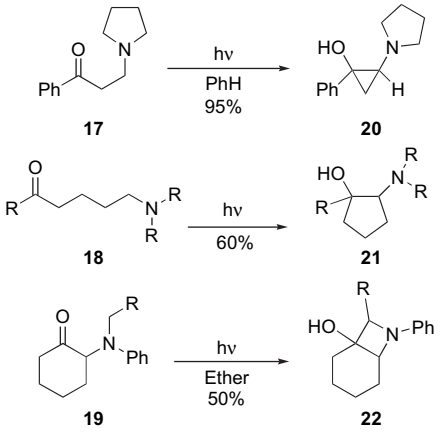
A third process that can take place is an intermolecular addition of a radical onto an activated olefin. When ketones **14** are photoreduced by a tertiary amine in the presence of an activated olefin such as (5*R*)-5-(−)-menthyloxy-2[5*H*]-furanone **15**, a ketyl radical anion is formed and after a subsequent proton transfer from the tertiary amine, a stereoselective addition of the ketyl radical to olefin **15** is observed.[13,15] It is worth noting that, due to their low reactivity, α-amino alkyl radicals, which are generated at the same time than the hydroxy radicals, do not add to **15** (Scheme 8).



Scheme 8. Amine: Et_3N; yield in **16** (n=1–9): 12–38%. Amine: $(CH_3)_2NBn$; yield in **16** (n=1–9): 37–69%.

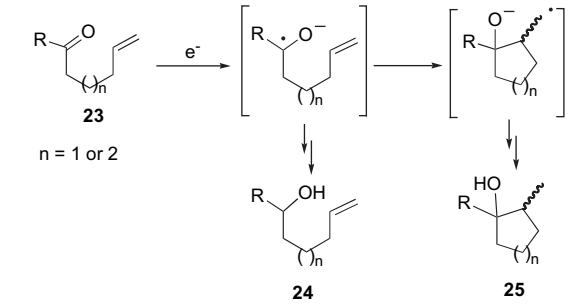
5. Cyclization

Before the 1980s, intermolecular photoreduction of ketones by amines has not provided much synthetic utility except for the production of alcohols, aminoalcohols, pinacols and polymers. More interestingly, the amino group can belong to the same molecule without disturbing the charge transfer process. Depending on the structure of the starting aminoketones **17**, **18** and **19**, α-aminocyclopropanols **20**, α-aminocyclopentanols **21** and hydroxyazetidines **22** can be, respectively, obtained in high yields[16] (Scheme 9).



Scheme 9.

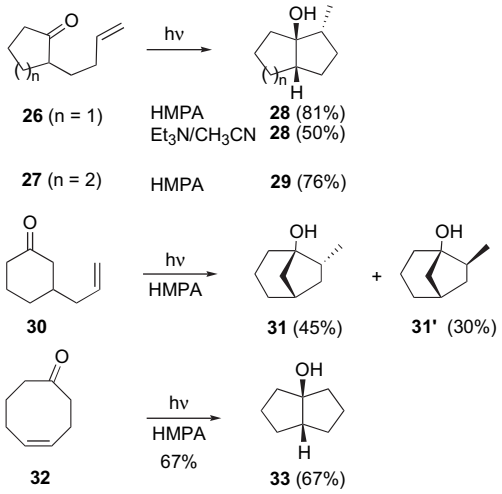
The most useful process in synthesis is probably the cyclization of ω-unsaturated ketyl radical anions, which produces functionalized substituted carbo- and heterocyclic compounds. Cyclization of δ,ε-unsaturated radicals is a very fast process,[17] which leads to cyclopentylmethyl or cyclohexyl radicals. Formation of the cyclopentane ring is highly favoured according to the literature data[18] and the Baldwin's rules.[19] According to the very fast cyclization process δ,ε-unsaturated ketyl radical anion, produced by photoinduced electron donor such as HMPA or tertiary amines such Et_3N, leads to cyclopentanol or cyclohexanol derivatives[20] rather than δ,ε-unsaturated alcohols or pinacols just as observed in the ground-state reduction[21–24] (Scheme 10).



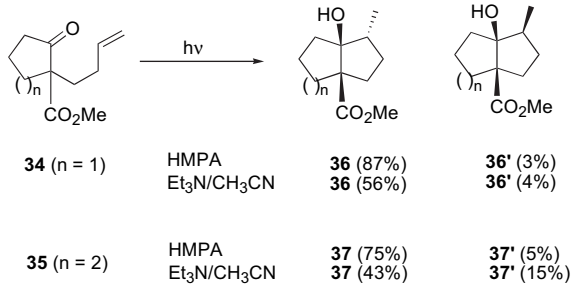
Scheme 10.

Irradiation of δ,ε-olefinic cyclopentanone **26** and cyclohexanone **27** in HMPA with low pressure mercury lamps (λ=254 nm) produced the bicyclic cyclopentanols **28** and **29**, respectively, in high yields. Analysis of the reaction mixture did not reveal any reduction compound such as ω-olefinic alcohol, other than the cyclized one. Furthermore, only one stereoisomer having the methyl and the hydroxy groups in a *trans* relationship was obtained (Scheme 11). Using Et_3N as the donor, in a polar solvent such as acetonitrile, the same reaction occurred but in lower yield. Due to the

high regio- and stereoselectivity as well as the high yield obtained in HMPA, the synthetic usefulness of the reaction toward various bicyclic cyclopentanols was tested. When 3-allylcyclohexanone **30** is irradiated in HMPA, a mixture of cyclized isomers **31** and **31′** is obtained in 45% and 30% yields, respectively. Similarly, 4-cyclooctenone **32** produced bicyclo[3.3.0]cyclooctan-1-ol **33** in 67% yield. When several functional groups are present in the starting molecule, the electron transfer from the donor occurred selectively to the most reducible group. Indeed, ketoesters **34** and **35** are transformed to the cyclized products **36/36′** and **37/37′**, respectively. In contrast to **26** and **27**, two stereoisomers were isolated, although the cyclization remains very stereoselective. A better stereoselectivity is observed in HMPA than in Et_3N/CH_3CN[20] (Scheme 12).



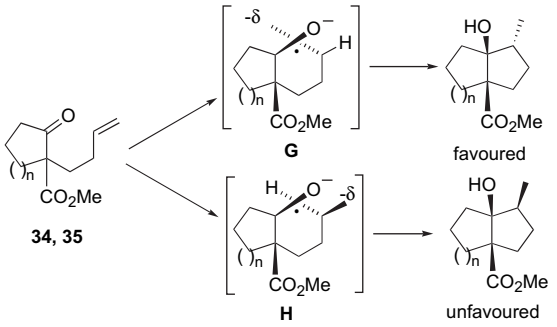
Scheme 11.



Scheme 12.

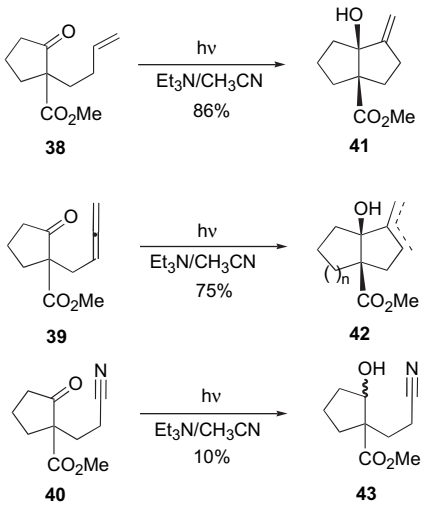
Good regioselectivities and stereoselectivities are observed and can be explained by a repulsive electrostatic interaction, which can take place between the negatively charged oxygen centre and the terminal sp^2 carbon atom in one of the two diastereomeric cyclic and polar transition states[21] (Scheme 13).

Even if HMPA gives better yields in the cyclization of unsaturated ketones than Et_3N, it is preferable to use Et_3N since this compound is less hazardous, more volatile and allows a simpler work-up (only requiring evaporation of the solvent).[25] From a preparative point of view, it was found that the procedure using Et_3N tolerates various substituents such as carbonitriles, esters, ethers, alkenes and alkynes.



Scheme 13.

For example, compounds **38** and **39**, when irradiated in acetonitrile in the presence of Et_3N, leads, respectively, to the cyclized products **41** and **42** in good yields. It is worth of note that no cyclized product was observed when ketone **40** was irradiated in the presence of Et_3N, alcohol **43** was the only isolated product[20] (Scheme 14).

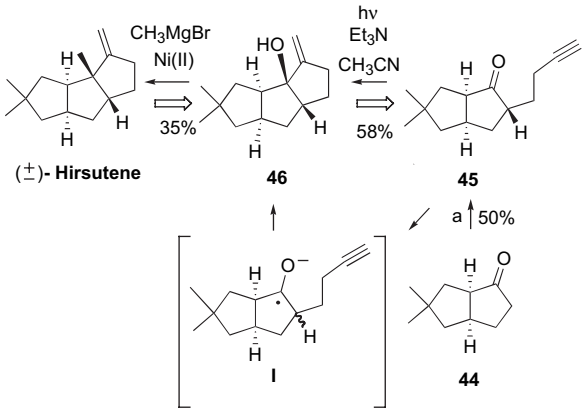


Scheme 14.

The behaviour of the intermediate radical formed from δ,ε-unsaturated ketones does not depend strongly on the method used to produce its chemical reduction, electroreduction or photoreduction. However, the latter method presents the advantage of being carried out under very mild and homogeneous conditions with few problems of reproducibility constituting a complementary and advantageous approach to cyclic compounds. For this reason, the photoreductive cyclization was applied successfully to the synthesis of cyclopentanoids, alkaloids, iridoids and sesquiterpenes.

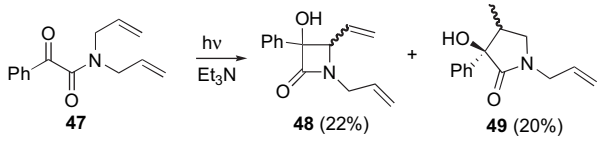
One of the first achievements based on this method was a short synthesis of (±)-hirsutene.[26] The retrosynthetic analysis shows that the tricyclic skeleton of hirsutene should come from a acetylenic ketyl radical anion cyclization, which will be issued from the photochemical reduction of ketone **45**. After the stereoselective replacement of the angular hydroxy group by a methyl group, hirsutene should be obtained. Thus, the photochemical reduction applied to compound **45**, obtained by alkylation of the bicyclic ketone **44**, afforded **46** as the only tricyclic product, which possesses the desired

cis-anti-cis stereochemistry. The highly regio-, stereo- and chemoselective replacement of the tertiary allylic alcohol in **46** with methylmagnesium bromide in the presence of a Ni(II) catalyst[27] completed the synthesis of (±)-hirsutene (Scheme 15).



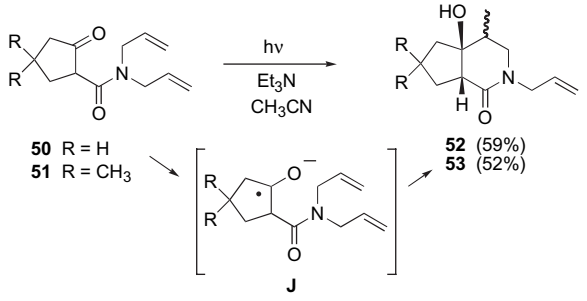
Scheme 15. (a) (1) KH/DME, $ICH_2CH{=}C(CH_3)Cl$, −78 °C; (2) $LiAlH_4$, ether, 0 °C; (3) KAPA, APA, 0 °C; (4) PCC, MS 3A, CH_2Cl_2.

Straightforward access to heterocyclic compounds can be obtained using the photoreductive cyclization of ω-unsaturated ketones. However, when *N*,*N*′-dialkyloxoamides are irradiated under reducing conditions, competition between PET and γ-hydrogen abstraction products can be observed as compounds **48** and **49** were isolated[28] (Scheme 16).



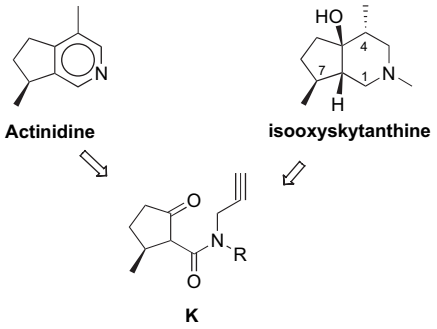
Scheme 16.

On the contrary, the photoreduction of *N*,*N*-unsaturated dialkyl β-oxamides **50** and **51** afforded only substituted 3-azabicyclo[4.3.0]nonanes, which are issued from the ketyl radical anion **J**[29] (Scheme 17).



Scheme 17.

This photoreductive cyclization is of great synthetic utility as illustrated below in the synthesis of actinidine[30,31] and isooxyskytanthine,[31,32] two rare monoterpenic alkaloids, which contain a 3-azabicyclo[4.3.0]nonane skeleton substituted by methyl groups at C4 and C7 (Scheme 18).



Scheme 18.

The synthesis of the skeleton of these two monoterpenic alkaloids and the control of the relative stereochemistry at C7 and C7a was achieved by relying on a Wolff rearrangement applied to a diazodiketone, followed by a photoreductive cyclization of unsaturated *N*-alkyl-2-oxocyclopentane carboxamides of type **K**.

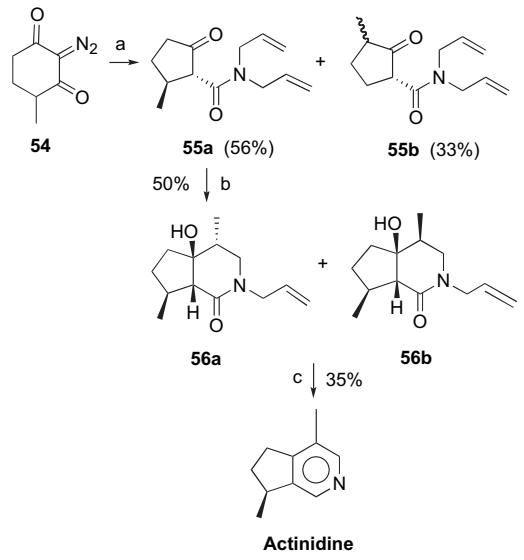
A Wolff rearrangement[33] applied to the diazodiketone **54** in the presence of diallylamine gave a 1.6/1 mixture of two regioisomeric amides **55a** and **55b**. The major product **55a**, which is the precursor of actinidine, was isolated in 56% yield. Similarly, photolysis of **54** in the presence of *N*-methyl,*N*-propargylamine gave almost quantitatively a mixture **57a** and **57b** (1.5/1). The photoreductive cyclization of **55a** carried out in the presence of Et_3N led to a 1.7/1 mixture of **56a** and **56b**, which was transformed to actinidine. Irradiation of **57a** under the same conditions led to a single product **58**, which could be converted to isooxyskytanthine (Scheme 19).

Iridoids represent a class of highly oxygenated monoterpenes characterized by a *cis*-fused cyclopentapyran ring system. In principle, synthesis of such systems could be achieved by a photoreductive cyclization of δ,ε-unsaturated β-ketoesters. Unfortunately, unsaturated β-ketoester **59** did not lead to the expected bicyclic compound **60** because of an unfavourable conformation of the ester group of **59** (Scheme 20).[34]

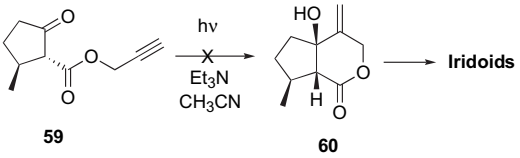
In order to overcome this conformational effect, annulation of the unsaturated β-ketoacetal **62** was investigated as a model for the synthesis of C5 oxygenated iridoids.[35] The β-ketoester, readily available from the irradiation of the diazodiketone **54** in the presence of MeOH through a Wolff rearrangement was transformed into the ketoketal **62** in a few steps. As expected, irradiation of **62** at 254 nm in acetonitrile with Et_3N led to the formation of the desired bicyclic compound **63** with a yield of 80% (Scheme 21).

The photoreductive cyclization process has been extended to unsaturated alkoxyketones to attain the furofuranic system present in antifeedant substances such as azadirachtin.[36] Ketone **65**, obtained from dihydrofuran **64**, was irradiated in the presence of Et_3N to furnish the bicyclic compound **66**. Its transformation to **68** was then achieved in five steps by using a Bamford–Stevens reaction[37,38] as a key step (Scheme 22).

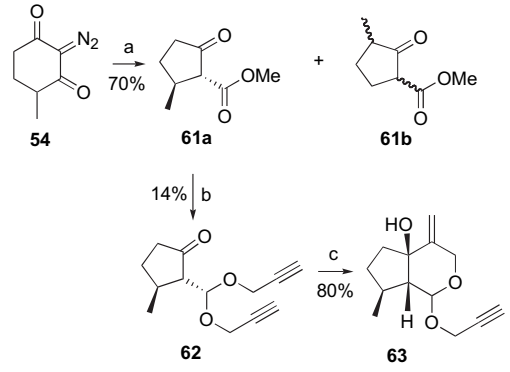
The photoreductive cyclization is very reproducible and produces stereoselectively substituted carbocyclic or heterocyclic compounds in high yields.



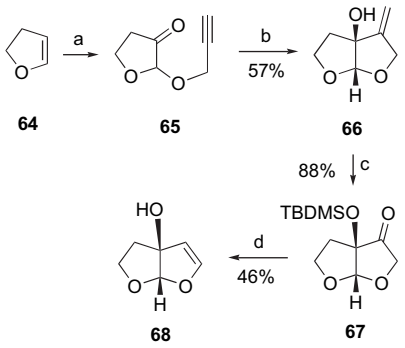
Scheme 19. Synthesis of actinidine: (a) hν, 254 nm, *N*,*N*-diallylamine, CH_3CN; (b) hν, Et_3N, 254 nm, CH_3CN; (c) i. $LiAlH_4$, ii. 10% Pd/C, xylene, nitrobenzene, MS 3A. Synthesis of isooxyskytanthine: (a) hν, 254 nm, *N*-methyl,*N*-propargylamine, CH_3CN; (b) hν, 254 nm, Et_3N, CH_3CN; (c) i. $LiAlH_4$, ii. 10% Pd/C, H_2, MeOH.



Scheme 20.



Scheme 21. (a) hν, CH_3CN, MeOH; (b) i. $LiAlH_4$, ether, 0 °C, ii. HMDS, TMSCl, CH_2Cl_2, 0 °C, iii. CrO_3, pyridine, CH_2Cl_2, iv. TMSCl, propargylic alcohol, CH_2Cl_2, v. PCC, MS 4A, CH_2Cl_2; (c) hν, Et_3N, CH_3CN.

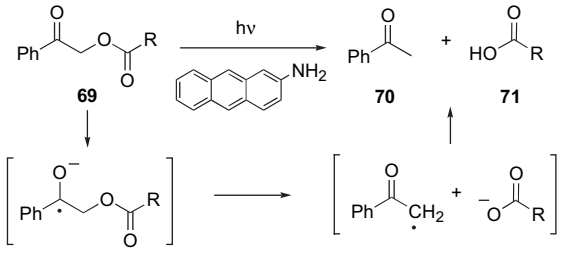


Scheme 22. (a) i. *m*-CPBA, CH_2Cl_2, 0 °C, ii. Propargyl alcohol, TsOH, iii. CrO_3, H_2SO_4, acetone; (b) hν, Et_3N, 254 nm; (c) i. *t*-$BuMe_2SiCl$, imidazole, ii. O_3; (d) i. H_2NNHTs, MeOH, H_2O, ii. Ethyleneglycol, Na, 140 °C, iii. Bu_4NF, THF.

6. Bond cleavage

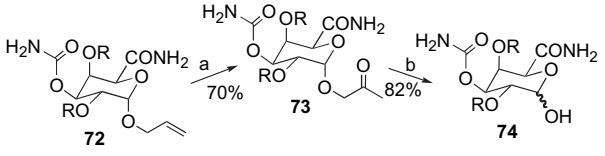
While most of the work related to PET reactions has focused on the formation of C–C bonds, the cleavage of C–O and C–C bonds has gained interest. One synthetic application of the cleavage of a C–O bond is the release of carboxylic acids upon photolysis of phenacyl esters using photosensitizers such as *N*,*N*,*N*′,*N*′-tetramethylphenylene diamine, *N*-methyl-carbazole, 2-aminoanthracene or *N*,*N*-dimethyl-aniline.[39]

It is argued that this reaction is initiated by a photoinduced electron transfer from the excited state sensitizer to the phenacyl ester. The latter process forms the ketyl anion radical of the phenacyl ester, which in turn undergoes a rapid C–O bond scission leading to the phenacyl radical and to the corresponding carboxylate anion (Scheme 23).



Scheme 23.

A second synthetic application of the C–O bond cleavage is the elimination of an allyl protection at the anomeric position of a carboxylate, which is sometimes problematic. In the case of compound **72**, the deprotection problem was solved by using a Wacker oxidation[40] followed by photolysis of **73** in the presence of Et_3N[41] (Scheme 24).

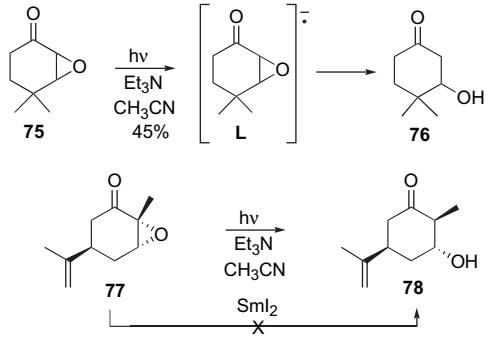


Scheme 24. (a) $PdCl_2$, CuCl, O_2, DMF/H_2O; (b) hν, Et_3N, CH_3CN, 254 nm.

The cleavage of heterocyclic strained rings can also be achieved by using a PET process. Irradiation of α-epoxy-ketones in acetonitrile in the presence of tertiary amine

[Et_3N, tribenzylamine, *N*,*N*-dimethyl,*N*-(trimethylsilylmethyl)amine, 2-phenyl-*N*,*N*-dimethylbenzimidazoline] produces the cleavage of the epoxide ring of the α-epoxyketone and leads to 3-hydroxyketone[42] (Scheme 25).

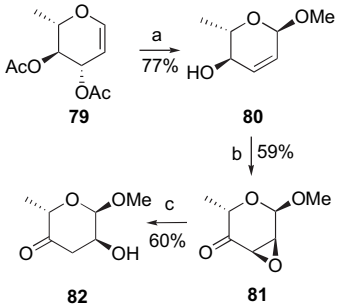
Although the exact mechanism of the epoxide ring opening from intermediate **L** has not yet been determined, a PET process seems to be involved. The observed cleavage of the C_α–O bond of an epoxyketone is similar to the reductive cleavage of the same bond using lithium in liquid ammonia,[43] Bu_3SnH[44] or by cathodic reduction.[45] Surprisingly, SmI_2 did not cleave the epoxide ring of carvone oxide[46] (Scheme 25).



Scheme 25.

The photoinduced epoxy ring opening of an α-epoxyketone, allowing stereospecific formation of a β-hydroxy ketone, has also been used in the synthesis of the methyl glycoside of cinerulose **82**, a rare sugar present in the antibiotic cinerubine B.[47]

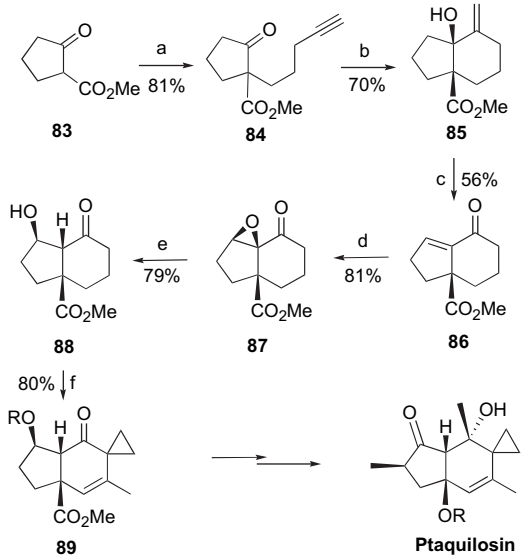
Irradiation of the epoxyketone **81**, prepared from the commercially available di-*O*-acetyl-L-rhamnam, affords the methyl glycoside **82**. The transformation of **81** to **82** considerably shortens the synthesis of this rare sugar as compared with the previous synthesis[48] (Scheme 26).



Scheme 26. (a) i. $BF_3\cdot OEt$, MeOH, ii. Resin HO^-; (b) i. *m*-CPBA CH_2Cl_2, ii. PCC, CH_2Cl_2, MS 3A; (c) hν, Et_3N, CH_3CN, 254 nm.

Ptaquilosin is the aglycone of ptaquilosine, which has been evaluated for its antitumor activity at the National Cancer Institute (NCI).[49] The photoreductive cyclization and photoreductive opening of an epoxide, which are two highly chemo-, regio- and stereoselective processes, were used to control the configurations at C5 and C9 and consequently at C1 and C7 in a total synthesis of ptaquilosin.[50] The photoreductive cyclization applied to compound **84** allows the formation of the bicyclic compound **85** (70%) in which the ester group is the precursor of the C5 hydroxy group present in ptaquilosin. Compound **85** was transformed to the enone **86**, which was epoxidized in a very stereoselective way using H_2O_2 in a methanolic potassium carbonate solution. The thus formed epoxide **87** was transformed under photoreductive conditions and hydroxy ketone **88** was isolated with a yield of 79%. In this compound all the functionalities needed are present to complete the synthesis of ptaquilosin.

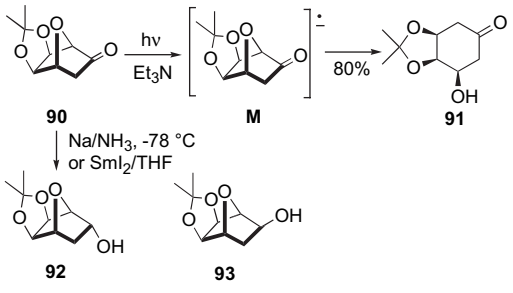
As compound **84** can be prepared in its two enantiomeric forms,[51,52] both (+)-ptaquilosin and (−)-ptaquilosin have been synthesized using this approach (Scheme 27).



Scheme 27. (a) KOH, EtOH, 1-iodopent-4-yne; (b) hν, Et_3N, CH_3CN, 254 nm; (c) i. O_3, MeOH, Me_2S, ii. Ac_2O, H_3PO_4 cat, iii. Resin OH^-, MeOH; (d) H_2O_2, K_2CO_3; (e) hν, Et_3N, CH_3CN, 254 nm; (f) i. TBDMSCl, imidazole, ii. TMSOTf, 2,6-lutidine, iii. $Pd(OAc)_2$, *p*-benzoquinone, CH_3CN, iv. $CuBr\cdot Me_2S$, CH_3Li, TMSCl, v. $Pd(OAc)_2$, *p*-benzoquinone, vi. *t*-BuOK/*t*-BuOH, $ICHCH_2SMe_2I$, KI.

Oxonorbornanones, which possess a strained oxabridge can be cleaved under PET conditions.[42,53] When these compounds are indeed irradiated in the presence of Et_3N, 3-hydroxycyclohexanones are obtained in moderate to good yields, depending on the nature of the substituents at C5 and C6. This reaction was applied to the synthesis of 3-hydroxycyclohexanones with excellent stereocontrol (transformation of **90** to **91**) (Scheme 28).

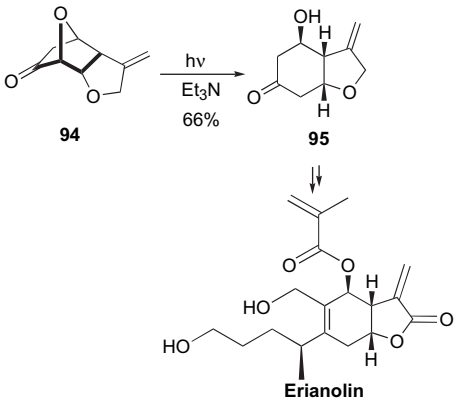
Interestingly, the treatment of **90** with Na in liquid NH_3 (−78 °C) did not induce the required C–O bond cleavage but gave a 10/1 mixture of the *endo* and *exo* alcohols **92**



Scheme 28.

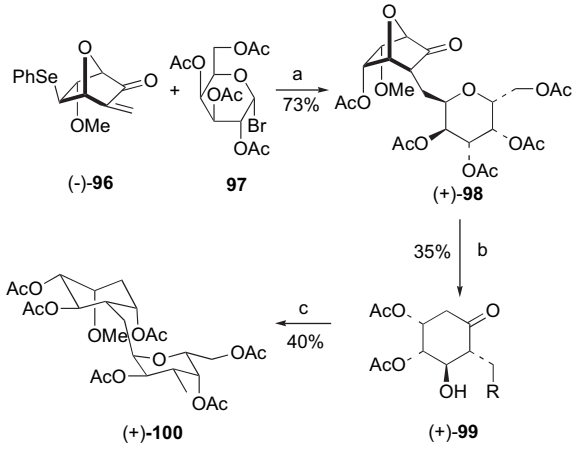
and **93**.[53] Furthermore, the treatment of **90** with 3 equiv of SmI_2 in THF led to the exclusive formation of the *endo*-alcohol **92**. These experiments show the difference in reactivity of intermediates produced by photochemistry and ground-state chemistry (Scheme 28).

The photoreductive 7-oxa ring opening method has allowed the synthesis of the erianolin skeleton from ketone **94**.[54] A new class of disaccharide mimics[55] that are α-*C*-galactopyranosides of carbo-pentopyranols[56] have been synthesized using the same approach (Scheme 29).



Scheme 29.

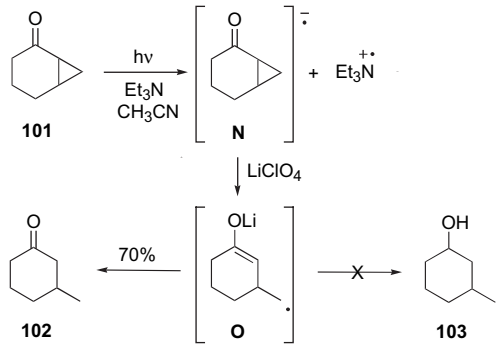
Photoinduced electron transfer from Et_3N to the all-*endo* 7-oxanorbornanone derivative (+)-**98** prepared by radical C–C bond formation between enone **96**[57] and acetobromogalactone **97**[58] led as expected to the reductive ring opening of the oxabridge and provided the tetrasubstituted cyclohexanone (+)-**99** without epimerization in the position α of the ketone. Compound (+)-**99** was then converted into **100**, a dicarba analogue of 2-*O*-(α-*O*-galactopyranosyl)-xylopyranodialdehyde (Scheme 30).



Scheme 30. (a) i. Bu_3SnH, AIBN, PhH, ii. *m*-CPBA, −78 °C, iii. Ac_2O/AcOH, iv. Bu_3SnH; AIBN; (b) hν, Et_3N, CH_3CN, 254 nm; (c) i. $NaBH_4$, MeOH, ii. Ac_2O, pyridine, DMAP.

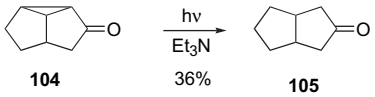
The PET induced opening of oxygenated strained rings can be extended to carbocyclic strained rings such as cyclopropanes[42a,59] or cyclobutanes. Irradiation of bicyclo[4.1.0]heptanone **101** at 254 nm in acetonitrile in the presence of Et_3N led to cyclohexanone **102** according to Scheme 31.[60]

Interestingly, the addition of $LiClO_4$ avoids further reduction of the ketone **102** to the alcohol **103** (Scheme 31).



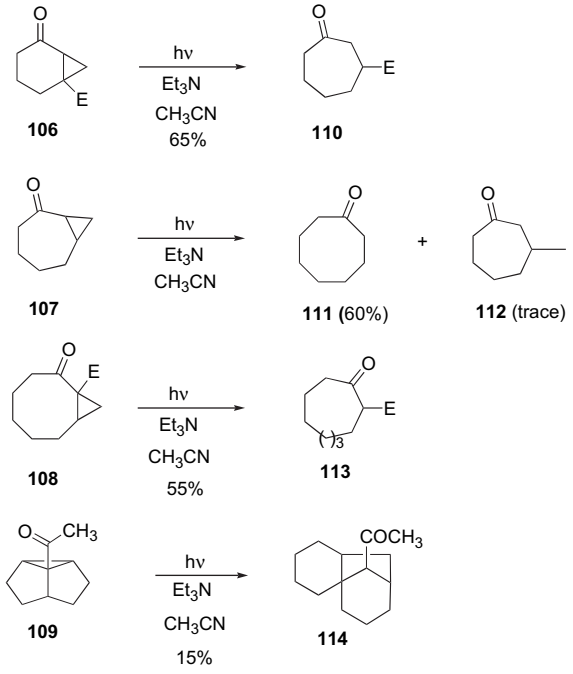
Scheme 31.

In the rigid tricyclic octanone system represented by **104**, the major product comes from the cleavage of the C2–C8 bond, arising from a better overlapping of this bond with the neighbouring carbonyl π-orbital[61] (Scheme 32).



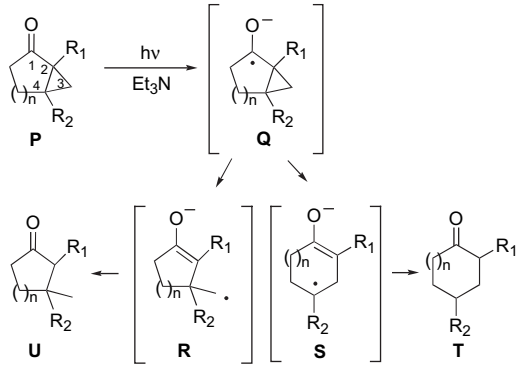
Scheme 32.

The preferred regioselectivity of the ring opening (*exo* vs *endo*) depends on the substitution pattern of the bicycloalkanones and on their ring size[62] (Scheme 33). When the bicyclo[3.1.0]hexanone and bicyclo[4.1.0]heptanone are substituted by electron-withdrawing groups at Cβ, ring-expanded products are formed. Similarly, the irradiation of bicyclo[5.1.0]octanone and bicyclo[6.1.0]nonane in the presence of Et_3N led to the ring-expanded products[62] (Scheme 33).



Scheme 33.

The radical-enolate intermediates of type **S** arising from the cleavage of the bond C2–C4 (ring enlargement process) are more stable (3.4 kcal/mol if R_2=H and 11–14 kcal/mol if R_2=CO_2Me)[62,63] than the corresponding intermediate **R** (Scheme 34). The former intermediate is a secondary radical either substituted or not by an ester moiety and the latter is a primary radical. The ring enlargement can be explained by the fact that the C2–C4 bond of the bicyclo[*n*.1.0]alkan-2-ones is weaker than that of bond C2–C3. In the case of compound **101**, the C2–C3 bond is cleaved preferentially due to stereoelectronic factors, the latter bond being better aligned with the π-system of the ketyl radical anion than bond C2–C4. In the case of compounds **106–108** the kinetic stereoelectronic factor does not compete with the highly favourable factor, which makes the ring-enlarged radical-anion intermediates highly stabilized by the carbonyl group. In compound **107**, the flexibility of the bicyclic carbon skeleton makes both the C2–C3 and C2–C4 bonds capable of proper alignment with the π-system of the ketyl radical anion, thus leading to mixtures of the corresponding methyl-cycloheptanones and ring-enlarged cyclooctanones. (Scheme 34).

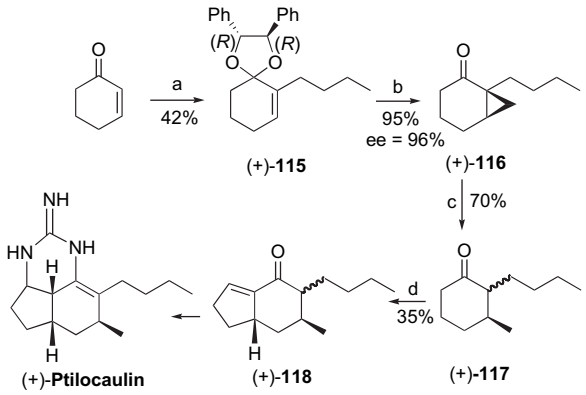


Scheme 34.

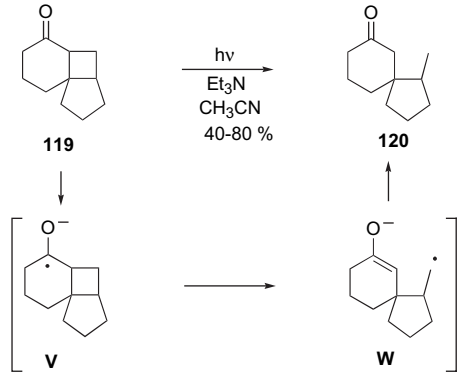
The ring cleavage of the cyclopropane ring of a chiral bicyclo[4.1.0]heptanone has been used as the key step in the synthesis of an antifungal agent, (+)-ptilocaulin.[64] Thus the chiral 2-butylbicyclo[4.1.0]heptanone was obtained by the cyclopropanation[65] of the chiral unsaturated ketal **115**[66] with high enantiomeric excess (96%). After deprotection, ketone **116** was irradiated in the presence of Et_3N and $LiClO_4$ to give the desired ketone **117**, which is the key molecule in the synthesis of (+)-ptilocaulin. The stereocontrol at C3 using this ring opening of a bicycloalkanone is much better than the addition of Me_2CuLi in the presence of a chiral inductor to the corresponding cyclohexenone.[67] Intermediate **117** was then transformed to ptilocaulin using a Sakuraï reaction,[68] a hydroboration[69] an aldolisation and a treatment of **118** by guanidine (Scheme 35).[70]

Ketyl radical anion can also induced the cleavage of a cyclobutane ring. Irradiation of compound **119** in the presence of Et_3N results in the formation of the spiroproduct **120**[59,71] (Scheme 36).

A PET mechanism was postulated for this reaction, since the cleavage of the cyclobutane ring was not observed in the absence of Et_3N. Similarly, various cyclobutylketones have been subjected to PET conditions with Et_3N. For example,

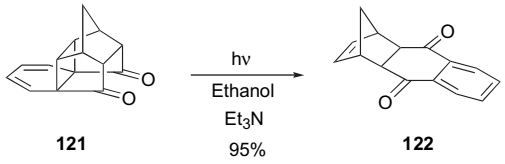


Scheme 35. (a) i. KF, Al_2O_3, *t*-BuOOH, ii. LDA, *n*-BuLi, TsOH, iii. Chiral diol, TsOH; (b) i. CH_2I_2, $ZnEt_2$, ii. TsOH; (c) hν, Et_3N, $LiClO_4$, CH_3CN, 254 nm; (d) i. LDA, NBS, ii. NaOH, iii. allylsilane, $TiCl_4$, iv. $RhCl_3$, catecholborane, v. PCC, CH_2Cl_2, MS 4A, vi. HCl, 2 N.



Scheme 36.

the irradiation of an ethanolic solution of **121** in the presence of Et_3N led to its quantitative conversion to **122**[72] (Scheme 37).

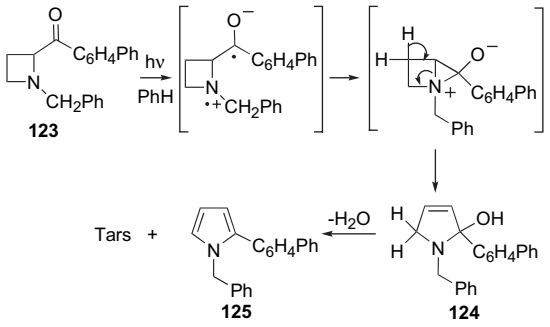


Scheme 37.

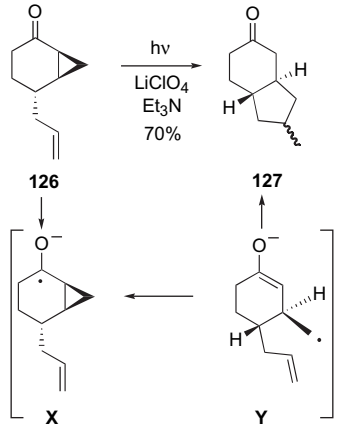
7. Tandem reactions: cyclization–ring opening and ring opening–cyclization

An intramolecular PET process in α-ketoazetidines induces an interesting rearrangement and formation of bicyclic hydroxy azetidines. These hydroxyaziridines rearrange quickly into 2-hydroxy-3,4-dihydroxypyrrole derivatives that aromatize through water elimination[73] (Scheme 38).

The radical intermediate **Y** induced by the PET fragmentation of bicyclo[*n*.1.0]alkanones can be trapped intramolecularly as shown by irradiation of the bicycloalkanone **126**[59,62] (Scheme 39).

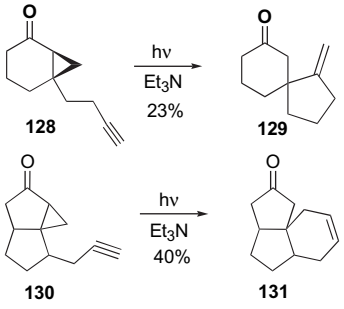


Scheme 38.

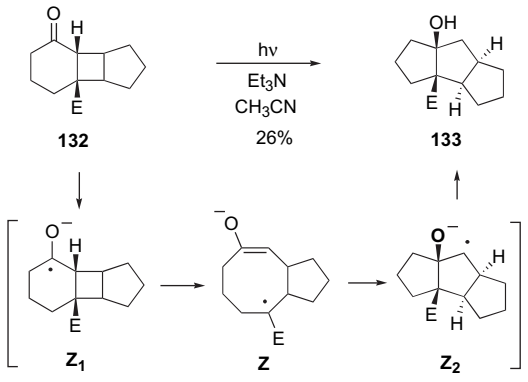


Scheme 39.

Spiro compounds can be obtained by applying a PET to compound of type **128**. Tricyclic compound **131** can also be obtained from compound **130**[74] (Scheme 40).

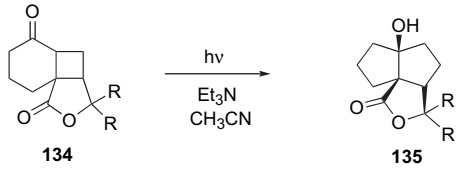


Scheme 40.



Scheme 41.

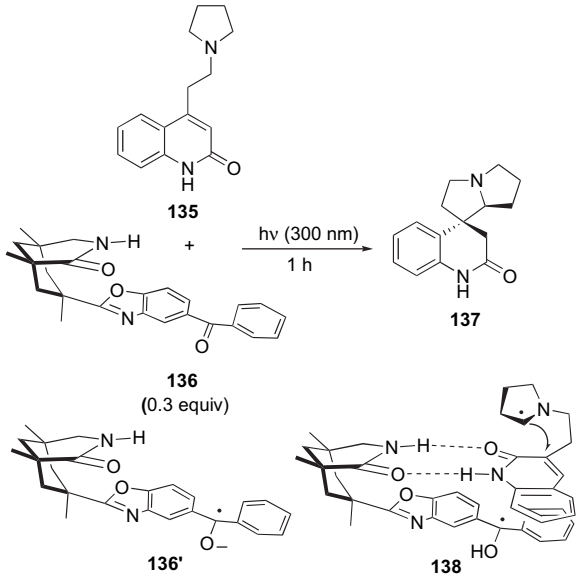
The skeleton of linear triquinanes is easily accessible from the methyl 8-oxotricyclo[5.4.0.0][2,6]undecan-1-carboxylate **132**.[71] Photoreduction of **132** implied the formation of a ring-expanded intermediate **Z**, which cyclized to produce the linearly fused triquinane **133** (Scheme 41). An extension of this reaction to heterocyclic angular tricyclic compounds has been achieved[75] (Scheme 42).



Scheme 42.

8. Miscellaneous

Even, if it is not a direct reactivity of a ketyl radical anion, and based on previously reported catalyzed conjugate additions of α-amino alkyl radicals to enones in a non-enantioselective process,[76] it is worth to point out that catalytic enantioselective reactions driven by photoinduced electron transfer can take place. Compound **137** can be obtained in 70% enantiomeric excess and in 64% yield when compound **135** is irradiated in the presence of **136**. The facial differentiation in the PET-catalyzed cyclization of the prochiral substrate is probably due to the ketyl radical anion **136′**, which can produce intermediate **138** and, it is assumed, that the facial differentiation is due to this intermediate (Scheme 43).[77]



Scheme 43.

9. Conclusion

Reactions involving PET processes are usually chemio- regio- and diastereoselective. For this reason, numerous synthetic developments have appeared during the last 30 years. At present and in spite of the interest of these

reactions, the photoreduction of ketones by tertiary amines is probably one of the most useful processes from a synthetic point of view. In the field of natural products, carbocyclic and heterocyclic molecules can be easily prepared from unsaturated ketones and PET processes cannot be neglected in synthetic schemes. The mild conditions and the high selectivity involving PET processes, make these reactions very attractive for further synthetic applications.

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25. Typical procedure: a solution of ketone (5×10^{-2} M) in acetonitrile in the presence of Et_3N (5 equiv) was irradiated at 254 nm by using a 12 TUV 15 Philips lamps merry-go-round system.
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