CHAPTER 4

Radical Reactions: Part 2

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Structure and Stability

Carbon-centred Radicals

The Whiffen effect in EPR spectroscopy and the relevant aspects of the H−C and M−C (M = metal) hyperconjugation in radicals and spin-paired molecules has been reviewed.[1] A paper on the resonance structures of benzoid conjugated radicals has been published. The number of resonance structures (SC) in radical benzoid hydrocarbons is larger than the numbers of resonance structures in Kekuléan (closed-shell) benzoid hydrocarbons. Analytical expressions for the SC of benzoid radicals have been derived.[2] Enthalpies of formation of 20 cyclic and conjugated hydrocarbon radicals were calculated.[3] Proton and electron affinities were calculated for a series of aliphatic and alicyclic carbanions and radicals using MP2/6−31 and B3LYP methods. Structural and electronic factors that control anion and radical stabilization were examined by natural bond orbital analysis. Structural analyses of several systems showed the importance of C−H and C−C hyperconjugation effects in both radicals and anions. No correlations between the % *s*-character of ionizing C−H bonds and proton affinity existed.[4] The mechanisms of decomposition of primary arsines and dialkyl R_2E,

where E = S, Se, Te, as precursors for metal organic vapour-phase epitaxy has been reviewed.[5]

A CAS-MCSCF and CCSD(T) theoretical study on the mesolytic dissociations of methyl- and silyl-cyclopropenyl radical cations and anions has shown that the radical cations dissociate into c-$C_3H_3^+$ and $XH_3^\bullet$ (X = C, Si). The radical anions fragment into c-$C_3H_3^\bullet$ and XH_3^- (X = C, Si).[6] The cleavage reactions of but-1-ene and 4,4-dimethyl pent-1-ene molecules and their cations to form neutral and charged hydrocarbon products were investigated using Hartree–Fock/density-functional theory. For the radicals studied, the isotropic coupling constants are reported and are comparable to experimental data. It was found that the experimental hyperfine properties of the but-1-ene cation could be explained by rotational averaging caused by the flat potential surface for the rotation about the C(2)–C(3) bond.[7]

Ab initio MO and B3LYP hybrid Hartree–Fock/density-functional (HF/DF) calculations of benzene and toluene nitrosation confirm that nitrosation proceeds through initial formation of intermediate electron-acceptor π-complexes.[8] Transformation of (benzene–NO)$^+$ and (toluene–NO)$^+$ π-complexes into *N*-protonated nitroso derivatives in B3LYP and MP2 calculations occur by a novel migratory insertion of nitrogen into the aromatic C–H bond. The IMOMO (integrated MO + MO) method has been used to calculate single-bond dissociation energies for the C–H bond of benzene, the C–F bond of fluorobenzene, the C–CH_3 bond of toluene, the Si–H bond of phenylsilane, the O–H bond of *n*-propanol, isopropanol, *n*-butanol and *t*-butanol, the C–S bond of $PhCH_2$-SCH_2, and the O–O bond of SF_5O–OSF_3.[9] The PM3 method has been used to study the 'breakage mechanism' of N–NO_2 and the 'cleavage mechanism' of C-NO_2 for the decomposition of *o*-nitroazidobenzene.[10] *Ab initio* calculations on the gas-phase decomposition of nitroethylene have revealed that the first stage involved the formation of a four-membered cyclic intermediate, the decomposition of which to H_2CO and HCNO proceeds via a biradical intermediate.[11] A coupled-cluster analysis of the electronic states of 4-aminobenzonitrile and 4-(*N*,*N*-dimethylamino)benzonitrile has been reported.[12]

Polarity reversal catalysis by tri-*t*-butoxysilanethiol has been applied to promote radical-chain epimerization selectively at carbon centres of the type $R^1R^2C^*HOR$.[13] B3LYP and post-HF computations performed on α-substituted carbocations $CH_3\overset{+}{C}HR$, (R = H, CH_3, CH=CH_2, C≡CH, F, and Cl) revealed that the substituents stabilize the cations compared with R = H in the order CH=CH_2 > CH_2 > C≡CH > Cl > F.[14]

The interactions of acetone with liquid sulfuric acid solutions have been described.[15] A theoretical analysis of the reaction of H with C_2H_5 has shown three barrierless pathways, two leading to association and one for abstraction.[16] Similarly, the reaction H + $CH_2CO \rightarrow CH_3$ + CO has been studied at high temperatures and pressures.[17] An ESR study of the radical species formed by pyrrole reaction with cyanoacetylene in the system KOH–DMSO was carried out.[18] The effect of bridgehead substituents on the stability of 1-norbornyl radical (**2**) generated by electrochemical reduction of a series 4-X-substituted bicyclo[2.2.1]heptan-1-yl bromides and iodides (**1**) (X = H, F, Cl, Br, I, $SnMe_3$) has been investigated by cyclic voltammetry.[19] The variations in the peak reduction can be translated to values for the weakening of the C–Br and C–I bond dissociation energies upon replacement of X = H by all the substituents

(1) → **(2)**
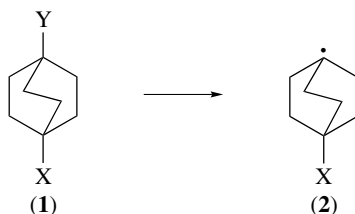
X = H, F, Cl, Br, I, SnMe$_3$
Y = Br, I

X, using dissociative electron-transfer theory. A through-space stabilizing interaction (homohyperconjugation) in the 4-X-substituted bicyclo[2.2.1]heptane radical species has been shown to exist.
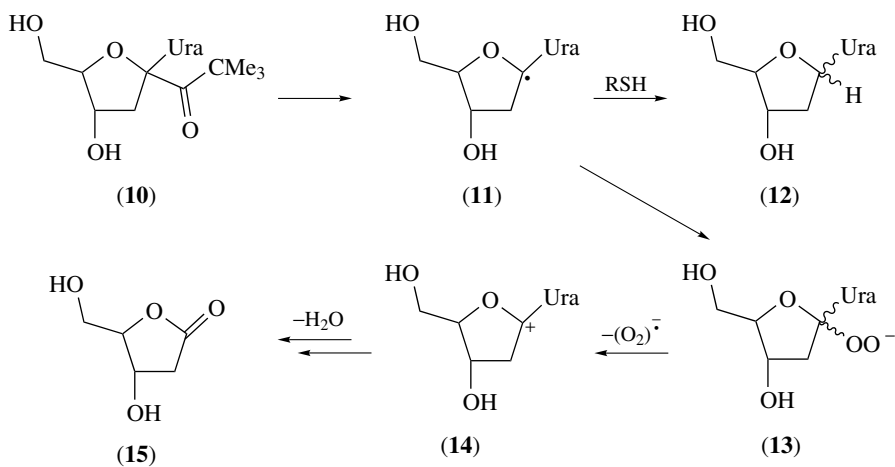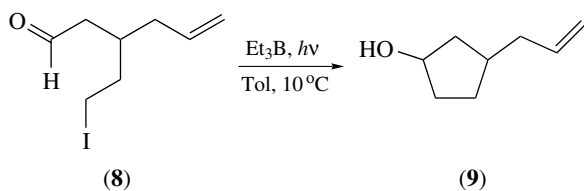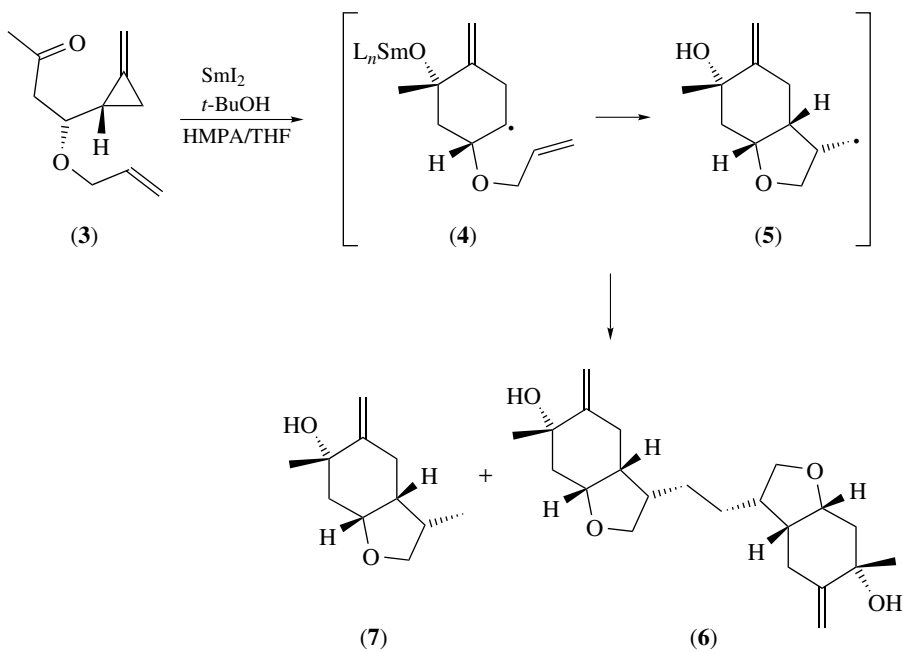
The reactions of sodium dimethyl and diisopropyl phosphite with 4-nitrobenzyl chloride, 9-chlorofluorene, and diphenylchloromethane provided information that supported the proposed reaction mechanism. The R$_2$PO$^-$ anion acts towards an arylmethyl chloride as a base and abstracts a proton to form a carbanion, which can then participate in single-electron transfer processes to produce carbon-centred radicals.[20]

The 2-glycyl radical H$_2$NĊHCO$_2$H has been generated by collisional neutralization of the stable 2-glycyl cation (H$_2$NCHCO$_2$H)$^+$ and is stable on the microsecond time-scale.[21] Losses of CO, water, and an amine hydrogen were calculated to be the lowest energy dissociations by combined density-functional theory and *ab initio* calculations. The authors concluded that depletion of the glycyl radicals in biological systems most likely occur via a bimolecular reaction.

A samarium(II) iodide-mediated cascade sequence, that leads to a highly stereoselective dimerization, has been reported. This sequence begins with an SmI$_2$-mediated formation of a ketyl radical and leads to an alkyl radical which appears to be partially protected from further reduction to the organosamarium by ligation to the ketyl oxygen-bound samarium. This radical instead undergoes dimerization (**6**) and reduction to a smaller extent (**7**).[22] The cyclization of the initially formed ketyl radical may proceed via a chair-like transition state to give the intermediate radical as a single diastereoisomer which then cyclizes to give the alkyl radical.

ω-Iodo-aldehydes (**8**) or -ketones in the presence of triethylborane as a radical initiator and in the presence of oxygen or light as terminator undergo 5-*exo*-trig cyclization to give (**9**).[23] In these conditions a 5-*exo*-trig cyclization on an aldehyde is faster than on an alkene. The high reactivity of carbonyl derivatives may be attributed to the Lewis acidity of triethylborane.

The kinetics of the reaction of 2′-deoxyuridin-1′-yl radicals (**11**) with thiols, with superoxide release from the peroxyl radical (**13**) generated, have been reported.[24] Radical (**11**) is produced by photolysis of precursor (**10**). When the radical is produced in the presence of thiols, (**12**) is formed. Second-order kinetics were found for the reactions with thiols. Peroxyl radical (**13**) is formed in the presence of oxygen. This undergoes heterolytic fragmentation to the superoxide anion O$_2$$^{\cdot-}$ and cation (**14**), which ultimately leads to 2-deoxyribonolactone (**15**).

(**3**) (**4**) (**5**)

(**7**) + (**6**)

(**8**) (**9**)

(**10**) (**11**) (**12**)
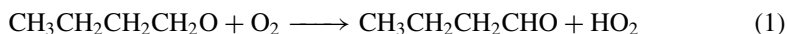
(**15**) (**14**) (**13**)

A kinetic and mechanistic study of the reaction between toluidine blue (TB) and sulfite has shown a first-order dependence on both reactants, a stoichiometric ratio of 1:1 and pH dependence.[25] The reactive species are TB^+ and SO_3^{2-} ions and Cu(II) acted as a promoter by facilitating the formation of a ternary complex with TB^+ and SO_3^{2-}.

Miscellaneous Radicals

The spin-density distribution in carbon-based peroxyl radicals was studied by density-functional theory at the B3LYP level. Electronegative substitution at the carbon α to the peroxyl group results in an increase of terminal hyperfine coupling and spin-density shortening of the C—O bond and lengthening of the O—O bond. In cases of steric hindrance, the C—O bond-shortening was prevented. Thiyl peroxyl radicals were reinvestigated and it was confirmed that the addition of an electron-pair donor (hydroxide) to $CH_3SOO^{\bullet}$ alters the spin-density contribution in the peroxyl group.[26]

The reaction of $HO^{\bullet}$ radical with a number of dialkyl sulfides was reported to be affected by the pH, the nature of the functional group, and the chain length.[27] The presence of the CH_2CH_2OH group results in the formation of α-thio radicals and dimer radical cation in neutral and acidic conditions. In the case of the $CH_2CH_2CH_2OH$ group, an intramolecular radical cation, with *p*-orbital overlap between oxidized sulfur and O, is observed that forms a five-membered ring. The reaction with 2,2′-thiodiethanoyl chloride leads to the formation of α-thio radicals in neutral conditions and in acidic conditions an intramolecular cation forms a four-membered ring between the oxidized sulfur and chlorine. The hydroxyl radical-induced decomposition of 2′-deoxycytidine has been reported and the products were identified.[28] An explanation of the decomposition mechanism was provided. The Bell–Evans–Polanyi principle and CASSCF wavefunctions were used to locate transition structures for the unimolecular decomposition of methyldioxirane into $MeCH(O^{\bullet})_2$ and of $MeCH(O^{\bullet})_2$ into AcOH, HCO_2Ac, and $CO_2 + CH_4$.[29] Semiempirical UHF/PM3 calculations examined three possible mechanisms for the diphenylcarbonyl oxide (Ph_2COO) bimolecular decay.[30] The 'head-to-tail' interaction of two Ph_2COO molecules has been found to be the most favourable pathway.

A report considers the reactions of 1-butoxy and 1-pentoxy radicals with oxygen (eqs 1 and 2) and of their isomerizations by 1,5-H-shift (eqs 3 and 4) using direct and time-resolved monitoring of the formation of NO_2 and HO radicals in the laser flash-initiated oxidation of 1-butyl and 1-pentyl radicals.[31]

$$CH_3CH_2CH_2CH_2O + O_2 \longrightarrow CH_3CH_2CH_2CHO + HO_2 \qquad (1)$$

$$CH_3CH_2CH_2O + O_2 \longrightarrow CH_3CH_2CHO + HO_2 \qquad (2)$$

$$CH_3CH_2CH_2CH_2O \longrightarrow CH_2CH_2CH_2CHOH \qquad (3)$$

$$CH_3CH_2CH_2CH_2O \longrightarrow CH_3CHCH_2CHOH \qquad (4)$$

Their rate coefficients were determined and showed that the primary alkoxy radicals have slightly higher rate coefficients for the reaction with O_2 than the secondary

radicals and the isomerizations abstracting H atoms from CH_2 group are faster than those which abstract the H-atom from a methyl group.

Highly stable 4-(benzimidazol-2-yl)-2,6-di-*t*-butylphenoxyl radicals have been synthesized. Their hydrogen-bonding functionality offers prospects for use in molecular magnetic materials.[32]

p-Chlorophenyl derivatives of *N*-alkoxy-4-arylthiazolethiones (**16**) were selected for precursors of oxygen-centred radicals after a study of their physical and chemical properties. Thiazolethiones (**17**) efficiently liberate free alkoxy radicals (**18**) upon irradiation or heating in the presence of Bu_3SnH as a radical trap. These reactive intermediates (**18**) undergo intramolecular cyclization by selective 5-*exo*-trig or 6-*endo*-trig pathways to the olefinic bonds to afford tetrahydrofurans or tetrahydropyrans as the major products in good yields.[33]
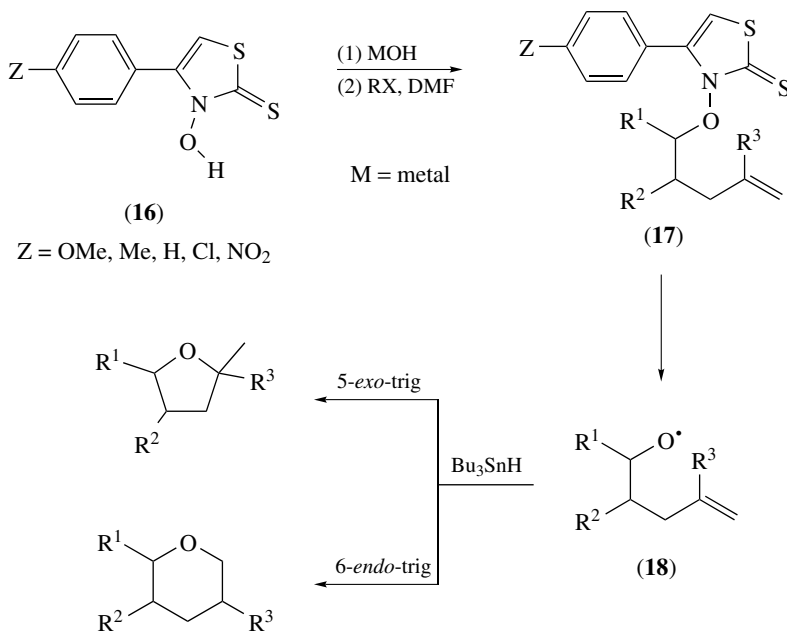

The thermochemistry of sulfur radicals in the gas phase has been reviewed.[34] Methylsulfonyl radicals and cations have been produced by femtosecond collisional electron transfer in the gas phase.[35] When formed by vertical collisional electron transfer from cation $CH_3SO_2^+$, radical $CH_3SO_2^•$ dissociates to $CH_3^•$ and SO_2. Radical $CH_3OSO^•$ exists as a mixture of *syn* (**19a**) and *anti* (**19b**) isomers which are stable when formed by collisional electron transfer to the corresponding cation. Dissociation of both isomers of $CH_3OSO^•$ formed $CH_3^•$ and SO_2 via isomerization to methylsulfonyl radical. An *ab initio* study on the formation of the thiyl peroxyl radical has also been reported.[36] Julolidylthiyl radicals (**20**) were formed by femtosecond photo-dissociation of the corresponding disulfide and have been observed

with pumb/supercontinuum probe spectroscopy.[37] Two forms of the radical were distinguished by their kinetics and by their spectra. Semiempirical calculations predict a radical doublet state D_2, optically dark, close to bright and a more polar ground state D_0.


(**19a**)   (**19b**)   (**20**)
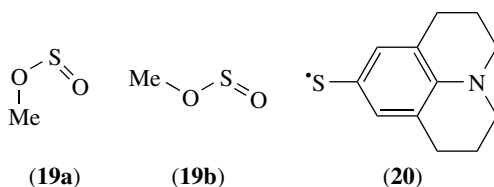
Tin hydrides containing one or two pyridyl groups have shown selective reactivity towards organic iodides, bromides, and chlorides. Those containing one pyridyl group smoothly reduce primary alkyl bromides but were completely inactive towards primary and secondary alkyl or aromatic chlorides. Tin hydrides with two pyridyl groups reduced iodides easily, bromides much more slowly, and were unreactive towards organic chlorides. This selective reactivity has been attributed to the intramolecular coordination of the tin to the pyridyl group.[38]

Stable thioaminyl radicals have been studied by ESR, X-ray crystallography and magnetic resonance.[39] Cationic aminyl radicals produced from *N*-chloroalkenylamines (**21**) by using Lewis acids (CuCl:CuCl$_2$, FeCl$_2$:FeCl$_3$, and TiCl$_3$:TiCl$_4$) underwent intramolecular cyclization to give pyrrolidines in excellent diastereoselectivity (depending on the type of *N*-substituent and Lewis acid).[40]

(**21**)
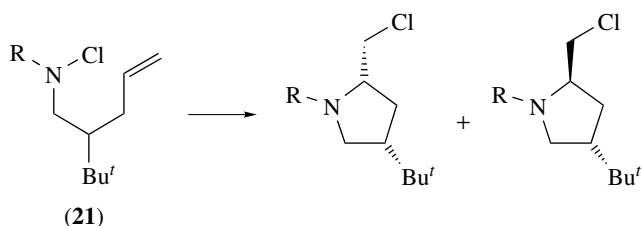
A free-radical mechanism has been suggested for the nitrosation of 1,2-phenylenediamine (**22**) by peroxynitrite PN/CO$_2$.[41] 1,2,3-Benzotriazole (**26**) was formed as a result of an intramolecular nucleophilic displacement on the diazo hydroxide (**25**) by the neighbouring amine group. The authors suggest that the mechanism involves an initial H-atom abstraction or one-electron oxidation from (**22**) by CO$_3^{\bullet-}$, followed by the reaction of the product (**23**) with NO$^{\bullet}$. The inhibitory effects of azide support a free-radical mechanism of the reaction.
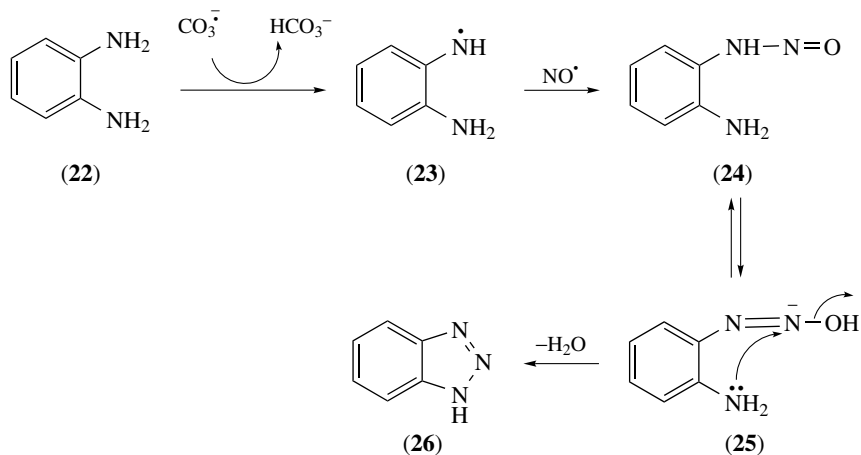
A study of the HeI photoelectron spectroscopy (PES) on the electronic structure of the $(CH_3)_2N$ radical, which was produced through the pyrolysis of $(CH_3)_2NNO$, has been reported. The PES bands were assigned using density functional theory calculations based on the Amsterdam density function program.[42] A triphenylamine triradical containing three N-t-butyl-N-oxylamino radical groups in the *para* position has been found to contain a doublet ground state, as shown by ESR and magnetic susceptibility measurements.[43] This was supported by MO calculations. The structure, conformational behaviour, and magnetic properties of the oxoverdazyl radical (**27**) and of the biradical obtained by joining two identical units have been investigated by hybrid HF/DFT electronic method.[44] A non-planar structure is predicted for the biradical *in vacuo* and in solution and a planar conformation in the solid state which is ascribed to the packing effect.


(**27**)
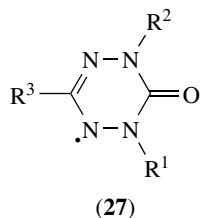
The 3-picolyl and 2,5-lutidyl radicals were isolated and studied by mass-resolved and fluorescence excitation. The 3-picolyl radical has a much shorter D1 life (9 ns) compared with that of 2,5-lutidyl radical (245 ns). The addition of a CH_3 group to the picolyl radical to form lutidyl suggests that the presence of the CH_3 group alters or eliminates a non-radiative pathway in the picolyl radical. *Ab initio* calculations suggest that ring expansion through a seven-membered radical ring could account for

the missing 2- and 4-picolyl radicals and lutidyl counterparts if the D1 lifetimes for the excited-state species are short.[45]

A paper has reported that nitrogen-centred radicals (**29**) have been generated by one-electron reduction (at carbon or metal electrodes) of stable nitrenium ions of the general structure (**28**). The reactivity of the radicals is influenced by the substituents attached to the two nitrogen atoms that are directly linked to the ion nitrenium centre.[46]


(**28**)   (**29**)
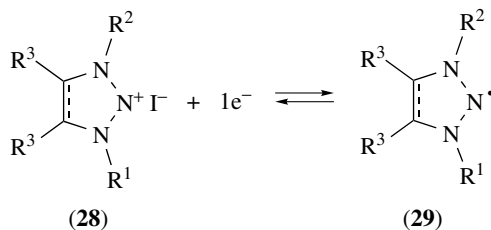
Quinolin-8-ols (**31**) and 1,2,3,4-tetrahydroquinolin-8-ols (**32**) were synthesized from 2-(3-hydroxyphenyl)ethyl ketone *o*-2,4-dinitrophenyloximes (**30**).[47] Treatment with NaH and then DDQ and acetic acid afforded quinolin-8-ols (**31**). When the reaction was carried out in the presence of Na[BH$_3$(CN)], 1,2,3,4-tetrahydroquinolin-8-ols (**32**) were obtained. The cyclization proceeds via alkylideneaminyl radical intermediates generated by single electron transfer between the 3-hydroxyphenyl and 2,4-dinitrophenyl moieties to generate an anion radical intermediate (**33**). The nitrogen−oxygen bond of the oxime cleaves to provide an alkylideneaminyl radical (**34**). Intramolecular coupling of biradical (**34**) gave (**31**) after isomerization. The magnetic properties of terpyridine-like ligands bearing appended nitronyl nitroxide or imino nitroxide radicals have been studied.[48] An EPR study of the behaviour of stable β-phosphorylated cyclic aminoxyl radicals in the presence of SDS micelles has been reported.[49] The radicals, except in the case of strongly hydrophilic radicals, were found to exchange between water and micelles. Their partition coefficients were evaluated from computer stimulations of the EPR spectra. *N*-*t*-Butylhydroxylamine reacted with an acceptor alkene, substituted by at least one conjugatively electron-withdrawing group, in the presence of *t*-BuNO as an oxidant to give aminoxyls identical with those formed in the thermal or photochemical reaction between the alkene and α-phenyl *N*-*t*-butyl nitrone (Scheme 1).[50]
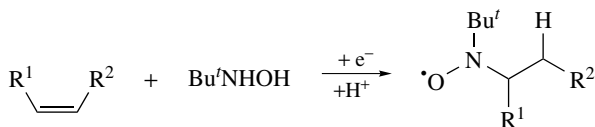

R^1 and R^2 = electron-withdrawing groups

SCHEME 1

(**30**)

(**31**)

(**32**)

(**33**)

(**34**)

(**35**)

(**36**)
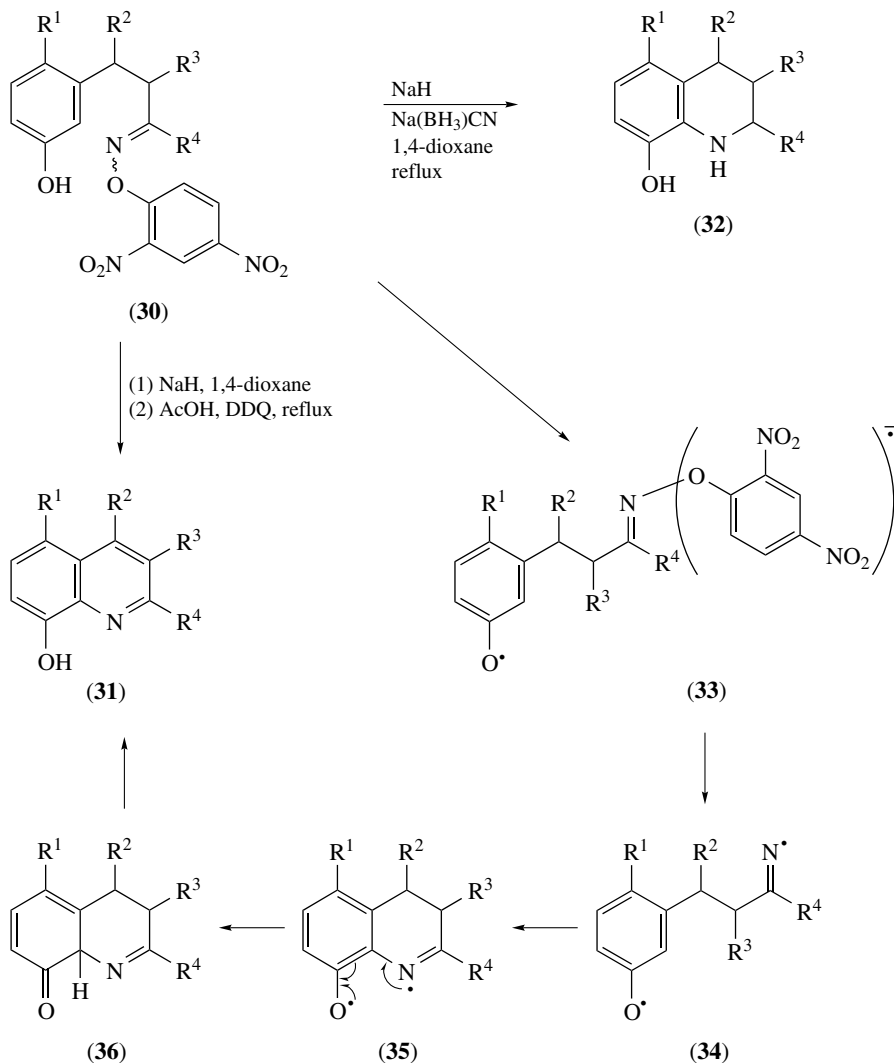
1,2-Organolithium additions to 2-phenyl-3,3-dimethyl-3H-indole (**37**), followed by oxidation of indolines (**38**) with m-chloroperoxybenzoic acid, gave indolinic aminoxyls (**39**) in 20–30% yield.[51] The organolithium addition does not occur when groups other than phenyl are present at C(2). Attempts to synthesize suitable precursors such as 1,2-dihydro-2-phenyl-2-alkylbenzothiazole, 1,2-dihydro-2-phenyl-2-alkylbenzoxazole, and 1,2-dihydro-2-phenyl-2-alkyl-4H-3,1-benzoxazin-4-one for other new aminoxyls failed.

A report was concerned with the ability of nitroxyl radicals, such as TEMPO and other related structures, to act as catalysts in the asymmetric oxidation of alcohols. Cyclic voltammetry was used to measure the oxidation potentials of the nitroxyl

(**37**)　　　　　　　(**38**)　　　　　　　(**39**)
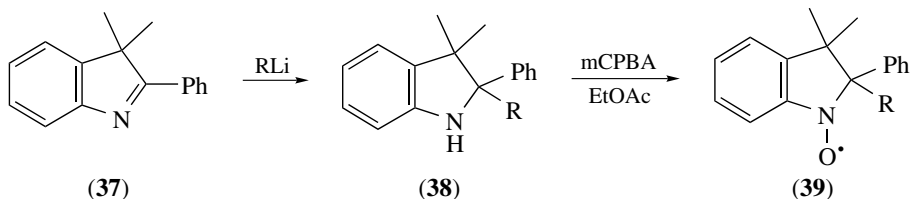
radicals and provided information on the stability of the *N*-oxo ammonium salts. Those with the lowest redox potentials and with half-lives greater than a few minutes were the best catalysts.[52] Aryl(heteroaryl)ethynylphenyl-2-imidazoline nitronyl nitroxyl (**40**) radical and imino nitroxyl (**41**) radicals have been synthesized. The *g* tensor and HFI components for imidazoline-1-oxyl were found to depend on the properties of the substituents at the 2-position.[53]


(**40**)　　　　　　　　　　　　　　　(**41**)
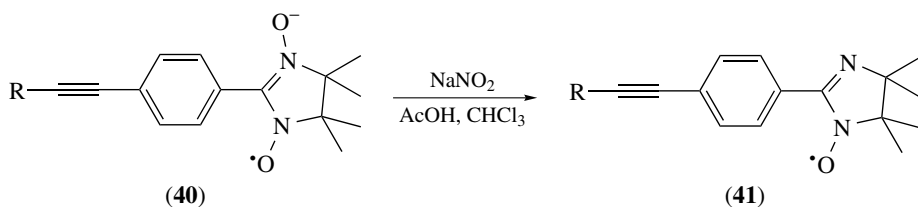
Nitroxides and Spin Trapping

In situ radiolysis time-resolved ESR was used to measure the reaction rate constants of the nitrone spin trap 5,5-dimethyl-1-pyrrolidine–*N*-oxide (DMPO) with a number of small alkyl and σ parent radicals in dilute aqueous solution. Electron-releasing α-hydroxyalkyl radicals reacted more rapidly than the unsubstituted radicals while the electron-withdrawing carboxymethyl radical was slower. σ-Radicals such as sulfite anion and carboxyl anion were trapped rapidly. Polar effects and steric considerations only weakly influence spin adduct formation. The reaction rates of alkyl and hydroxyalkyl radicals with DMPO are similar whether electron-withdrawing or electron-releasing substituents are present. The measured trapping rate constants with DMPO are slower than the corresponding rates with a nitroso spin trap MNR. This is due to the weakly nucleophilic character of DMPO, the strongly electrophilic character of MNP and the unfavourable steric factors in the DMPO–radical encounter complex.[54] The formation of the hydroxy radical spin adduct, HO–DMPO•, has been studied by EPR spectroscopy under conditions where the hydroxy radical is not involved. One method was the photo-sensitized oxidation of DMPO to its radical cation followed by reaction with water using quinines as sensitizers. A second method involved nucleophilic addition of water to DMPO followed by reaction of the intermediate hydroxylamine by mild oxidants such as quinones and Fe(III). The observation of HO–DMPO• was dependent on the acidity of the medium and decreased

by increasing acidity. Use of buffered neutral or slightly alkaline solutions or ethyl acetate increased the formation of the adduct.[55]

A series of $2H$-imidazole-1-oxides, isoquinoline-N-oxides and pyrrolidine-N-oxides were investigated as to their specificity and efficiency at spin trapping HO$^\bullet$ and $O_2^{-\bullet}$ as well as the stability of the corresponding spin-trapped adducts.[56] 2,2-Dimethyl-4-methoxycarbonyl-$2H$-imidazole (**42**) has been found to be the most selective of the spin traps investigated for the *in vivo*, *in situ* detection of HO$^\bullet$ at the expense of $O_2^{-\bullet}$.

The reaction of two 4-R-triazolinediones (**43**) (RTAD; R = Me and Ph) with DMPO was investigated by UV–visible, FT-IR, ^{1}H and ^{13}C NMR and EPR spectroscopy.[57] The reaction sequence involved the spin-adduct formation via a modified version of the Forrester–Hepburn mechanism and the rate-determining step was the oxidation of the spin adduct by RTAD, leading to the final product (**44**). An ESR spin-trapping study of the decomposition of sodium trioxodinitrate (Angeli's salt) in the presence of 5,5′-dimethyl-1′-pyrrolidine N-oxide (DMPO) suggest that its hydrolysis is associated with the generation of OH radicals.[58] The hydrolysis of AS in the presence of either ethanol or DMSO produces 1-hydroxyethyl and methyl radicals which add to DMPO to give ESR spectra of the DMPO/hydroxyethyl and DMPO/Me$^\bullet$ nitroxides. It is anticipated that NO$^-$ generated by the decomposition of AS dimerizes to *cis*-hyponitrous acid which is unstable and decomposes via an azo-type homolytic fission (Scheme 2).

(**42**)   (**43**)   (**44**)
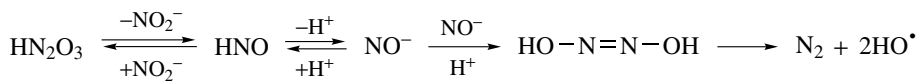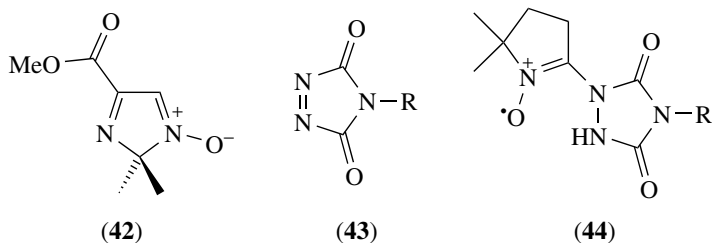
SCHEME 2

1-Methyl-2-substituted-5-pyrrolylcarbonyl fluorinated nitroxides, generated by the H-abstraction/spin-trapping reaction of 1-methyl-2-substituted-pyrrole-5-carbaldehydes with the H-abstracting agent [Rf(NO$^\bullet$)Rf] and the spin trapping agent RfNO, were studied by EPR.[59] The a_N values (hyperfine splitting constants) were affected by the polar effect of the 2-substituent and the spin-delocalization effect also existed (Scheme 3).

SCHEME 3

(45)　(44)

(46)　(47)
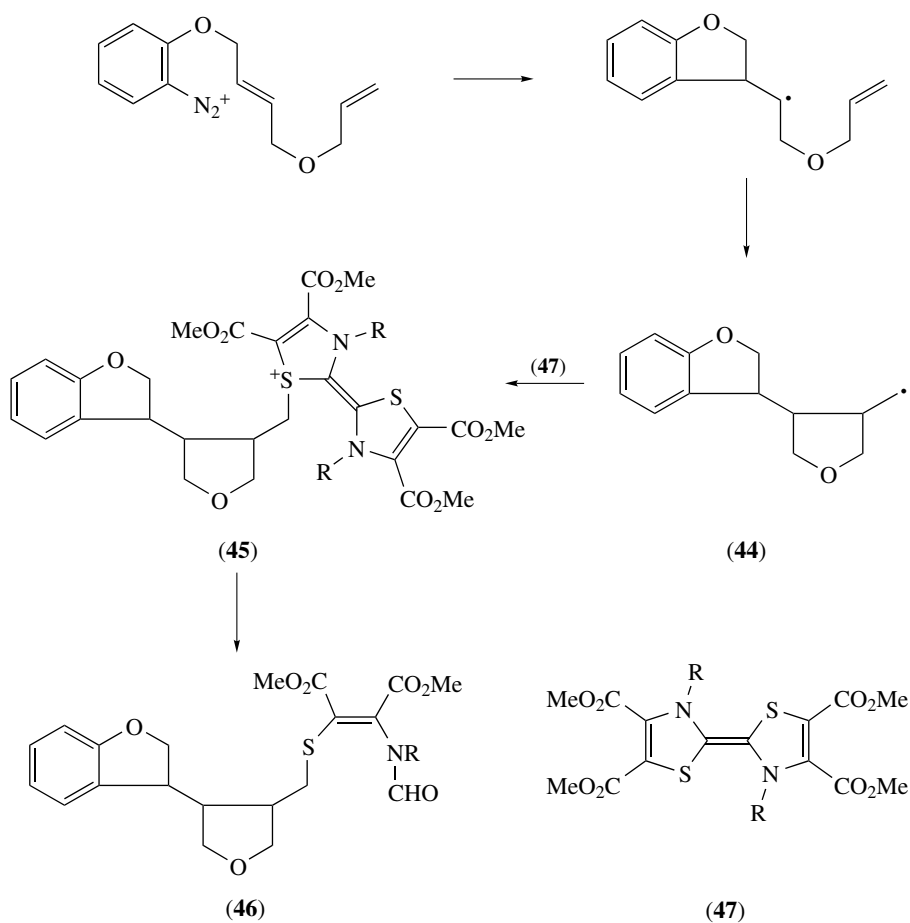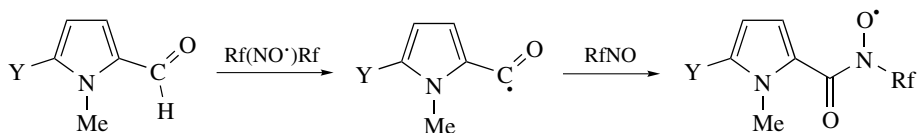
The radical cations of diathazadithafulvalenes DDTF (**47**) trap primary carbon radicals and afford isolable products.[60] These products feature cleavage of the DDTF ring system. Their radical cations couple more slowly with secondary carbon radicals allowing a second cyclization affording the final radical (**44**). This primary radical reacts with the radical cation of DDTF to afford (**45**), which after cleavage of the ring gives formamide (**46**).

The copolymerization of styrene and maleic anhydride was studied by the spin-trapping technique using 2-methyl-2-nitrosopropane as a spin trap. Four types of ESR spectra were obtained, of which three corresponded to trapping of the growing polymer chain at a centre originating from the styrene part or from two centres originating from the maleic anhydride part. The fourth EPR spectrum may be due to a cyclic five-membered aminoxyl or a six-membered 1,2-oxazine radical cation.[61]

Oxidation and Reduction

Perturbation theory was utilized to predetermine the regioselectivity of free-radical benzylic and allyl oxidation reactions of unconjugated π-systems.[62]

The chemistry of radical cations generated via cerium(IV) ammonium nitrate (CAN) oxidation of cyclopropylarenes and their potential as ion probes have been investigated. Oxidation of cyclopropylbenzene and 1- and 2-cyclopropylnaphthalenes leads to cyclopropane ring-opened products whereas 9-cyclopropylanthracene yields a radical cation that does not undergo cyclopropane ring opening. The results suggest that the cyclopropylarene radicals cannot be utilized as single-electron transfer probes because the cyclopropane ring opening does not occur at an appreciable rate.[63] Radical cations of 2-alkyl-5-t-butyl-1,4-dimethoxybenzene (**48**; 2-alkyl = Me, Et, i-Pr, and PhCH$_2$) were generated in one-electron oxidation of their parent compounds by pentafluorobenzoyl peroxide or cerium(IV) sulfate.[64] These radical cations were shown to collapse through two competitive pathways i.e deprotonation and de-t-butylation. The deprotonation was confirmed by EPR observation of the corresponding benzyl radicals. The relative importance of the two pathways is greatly dependent on the structure of the alkyl substituents, the nature of solvents, and the reaction temperature. For deprotonation, the reactivity order is found to be Me > PHCH$_2$ > Et $\gg$ i-Pr.

Small changes in the solvent or in the conditions of oxidation can lead to changes in the electronic and molecular structure of aryldiazo radical cations, from a linear allylic π- to a bent σ-radical state.[65] Both states have been observed in the radical cations of diphenyldiazomethane (**49**) and 5-diazo-10,11-dihydro-5H-dibenzo[a,d]cycloheptene


(**48**)

(**49**)

(**50**)   (**51**)   (**52**)
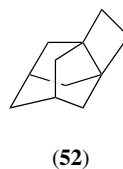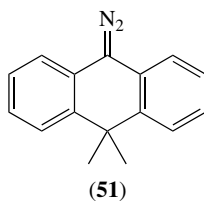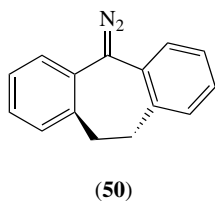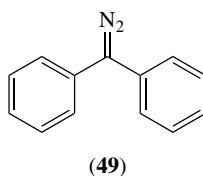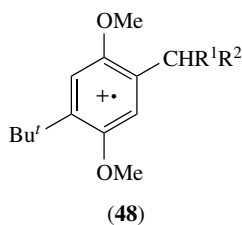
(**50**) whereas only the π-radical state could be formed in the radical cation of 9-diazo-9,10-dihydro-10,10-dimethylanthracene (**51**) in which the two phenyl rings are forced into a position coplanar with the $(C_{ipso})_2-CN_2$ plane. Quantum-chemical calculations have shown that observed small energy differences between the π- and σ-radical states of aryldiazo radical cations are due to solvent and/or counterion effects (see above).

The oxidation of 3,6-dehydrohomoadamantane (**52**) with $NO^+BF_4^-$, photo-excited tetracyanobenzene, and under anodic conditions has been found to involve a common radical cation intermediate. The study has shown that the activation of propellane σ_{C-C} bonds with strong oxidizing electrophiles occurs by a sequence of single-electron transfer steps. These findings are supported by *ab initio* computations showing that the isomeric radical cations can equilibrate with low barriers and lead to a common product.[66]

Chiral 2-imidazoline dianions undergo one-electron oxidation in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) to form a radical anion that is either trapped stereoselectively by TEMPO or undergoes dimerization.[67] Oxidation of bis-diazene oxides leads to novel *O*-stabilized 4N/3e radical cations and 4N/2e dications. These were detected by ESR spectroscopy and cyclic voltammetry. B3LYR/6−31G calculations confirmed the nature of the 4N/3e and 4N/2e systems.[68]

The oxidation of isopropylidenequadricyclane (**53**) with the electron-transfer catalyst tris(*p*-tolyl)aminium hexafluoroantimonate, $TTA^+ \cdot SbF_6^-$ (**54**), gave the bicyclo-heptatriene (**55**). Epoxidation of the isopropylidene group (**56**) changes the reactivity of the quadricyclane and oxidation with $TTA^+ \cdot SbF_6^-$ produces the norbornadiene (**57**).[69] A histidine radical cation and a histidine peroxy radical were formed by oxidation of histidine with the Ti^{3+}/H_2O_2 Fenton system. Isotropic hyperfine coupling constants of β-protons and three ring protons and two nitrogen nuclei have been determined.[70] The radical anion of acepentalene (**58**) was generated by photo-oxidation of the ace-pentalene dianion.[71] The spin population appears to be evenly distributed over the

(**53**) $TTA^+ SbF_6^-$ (**54**) →   (**55**)

(**56**)   (**54**) →   (**57**)
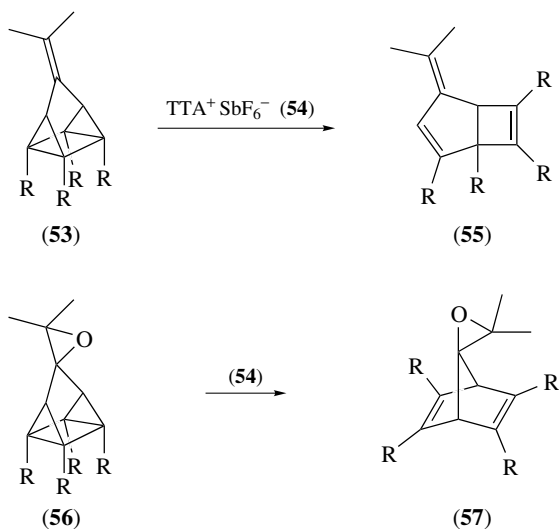
nine-membered perimeter due to a rapid interconversion between two bowl-shaped C_s forms and a relative low-lying planar C_{2v} transition structure.
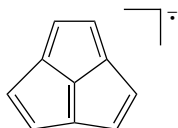

(58)

Oxidation of benzyl alcohol catalysed by chloroperoxidase exhibits a very high prochiral selectivity involving only the cleavage of the *pro-S* C−H bond.[72] The reaction mechanism involved the transfer of a hydrogen atom to the ferryl oxygen of the iron-oxo complex. An α-hydroxy-carbon radical and the iron-hydroxy complex P−Fe^{IV}−OH form. They may lead to the hydrated benzaldehyde or stepwise with the formation of the intermediate α-hydroxy cation.

Hantzsch 1,4-dihydropyridines were oxidized quantitatively to give the corresponding pyridine derivatives by irradiation in CCl$_4$. A photo-induced electron-transfer mechanism is involved. The critical step in this mechanism is the fast dechlorination of CCl$_4$ (Scheme 4).[73]

In the photochemical one-electron oxidation of aromatic sulfides, dimer radical cations were formed in rapid equilibrium with monomeric radical cation **(59)**. The complex formation of σ- and π-types has been shown to be sensitive to the steric and electronic influence of substituent. For the case of *p*-(methylthio)anisole the formation of π-type dimer was shown to be reduced due to steric hindrance of two methyl groups. No formation of dimer radical cation was observed for *p*-(methoxy)thioanisole and diphenyl disulfide where the corresponding monomer radical cations are stabilized by the delocalization of positive charge on the sulfur atom. Density-functional calculations supported the experimental results. The intramolecular formation of similar radical


SCHEME 4

(59)
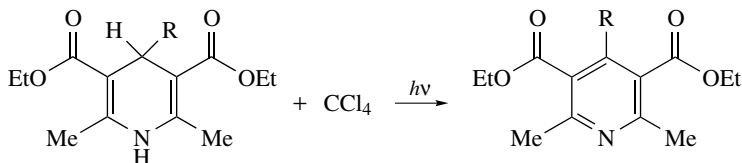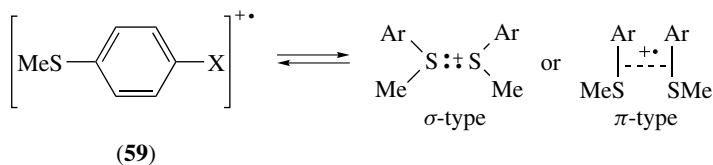
ion π and σ complexes for the 1,n-bis(phenylthio)alkanes with $n = 3$ and 4 was reported.[74]

Br-atom initiated oxidation of dimethyl sulfide (DMS) in a large-volume reaction chamber gave SO_2, CH_3SBr, and DMSO.[75] A rapid addition of Br atoms to DMS takes place, forming an adduct that mainly reforms reactants but also decomposes unimolecularly to form CH_3SBr and CH_3 radicals. DMSO is formed from the reaction of BrO radicals with DMS. The reaction $CH_3O_2 + Br \rightarrow CH_3O + BrO$ is postulated as the source of BrO radicals.

The HO-initiated oxidation of isoprene[62] and propene in the presence of nitrogen oxides has been the subject of two reports. Oxidation of isoprene in the presence of NO and O_2, and regeneration of the OH radicals by the reaction of isoprene-based peroxy radicals with NO, were measured and compared with simulations of the kinetics of this system.[76] CH_2O and CH_3CHO were produced from the oxidation of propene.[77] Reaction of the β-hydroxypropylperoxy radicals with NO leads to the formation of chemically activated β-hydroxypropoxy radicals which, according to theoretical calculations, decompose to CH_2O and CH_3CHO. The most stable conformations of the oxy radicals are found to contain intramolecular hydrogen bonds. Similarly, the hydroxyl radical oxidations of the azo dyes methyl orange (**60**) and calmagite (**61**) were found to be extremely fast with second-order rate constants. Methyl orange reacted with the hydroxyl radical by one-electron reduction at the nitrogen centre forming the anilino cation radical. Hydroxyl radicals reacted with calmagite by addition to the benzene ring producing hydroxycyclohexadienyl radicals, which rapidly decomposed to phenoxyl-type radicals by water elimination.[78]

(**60**)

(**61**)
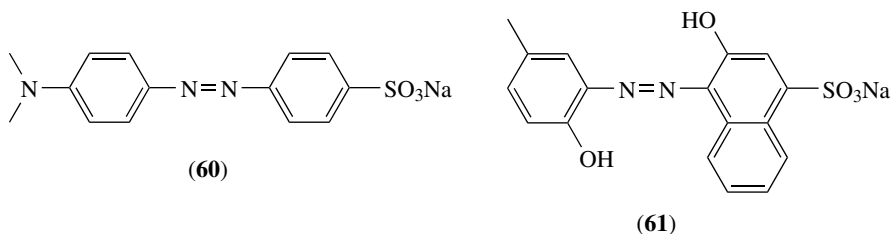
A one-electron oxidation study of quercetin (see structure below) and quercetin derivatives (rutin) by DPBH, CAN, or dioxygen in protic and aprotic solvents has shown that quercetin radicals quickly disproportionate to generate quercetin and produce a quinone.[79] This quinone adds water molecules and is then degraded. Oligomerization might be a minor route in media of low water content. Oxidation of quercetin–serum albumin complex retarded water to the quercetin quinone. The role of the quercetin 3-OH was established as follows: (1) allows the formation of p-quinonoid compounds, quickly converted into solvent adducts which still react with one-electron oxidants, and (2) in its deprotonated form stabilizes radicals, allowing autoxidation to proceed under mild conditions.

quercetin
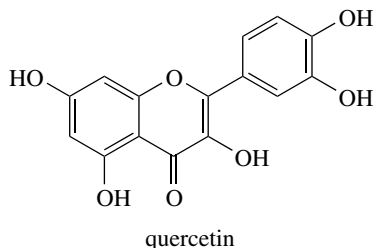
The photo-oxidation of the aryl-substituted cycloheptatrienes 7-(*p*-methoxy-phenyl)cycloheptatriene and 7-, 1- and 3-(*p*-dimethylaminophenyl)cycloheptatrienes to the corresponding radical cations in de-aerated acetonitrile solution was accomplished by electron transfer to the electronically excited acceptors 9,10-dicyanoanthracene, *N*-methylquinolinium perchlorate, *N*-methylacridinium perchlorate and 1,1'-dimethyl-4,4-bipyridinium dichloride.[80] In the case of 7-(*p*-methoxyphenyl)cycloheptatriene (**62**), deprotonation of the radical cation occurs successfully, compared with back electron transfer, to give a cycloheptatrienyl radical (**63**) which undergoes a self-reaction forming a bitropyl. If the photo-oxidation is done in air-saturated acetonitrile solution containing HBF$_4$ and one of the acceptors, the tropylium cation is formed. Back electron transfer dominates in the *p*-dimethylaminocycloheptatrienes and the formation of the cycloheptatrienyl radical is prevented.

(**62**)   (**63**)
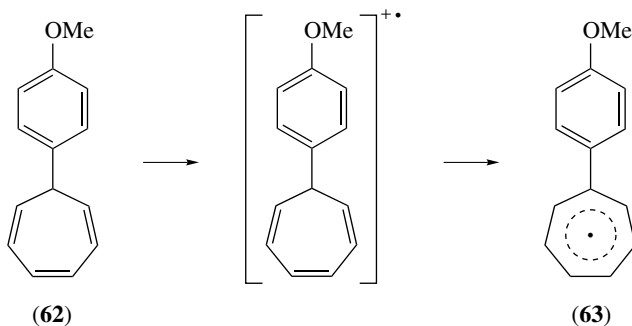
Photo-oxidation of 1,1-dialkyl-2-arylhydrazines by single-electron transfer with trimethylsilyl cyanide (TMSCN) as cyanide ion source leads to regio- and stereo-selective α-hydrazino nitriles.[81] This stereoselective cyanation of hydrazines takes place on the more substituted carbon atom compared with the results obtained with tertiary amines (Scheme 5).

The reductive dehalogenation of polyfluoroarenes by zinc in aqueous ammonia gave products derived from the removal of one or two halogen atoms.[82] A radical anion is suggested to form initially by direct electron transfer from the zinc to substrate which then fragments. C$_{60}$ undergoes single-electron reduction by the electron-rich,

$$R = H, Me; n = 1,2$$

SCHEME 5

(64)
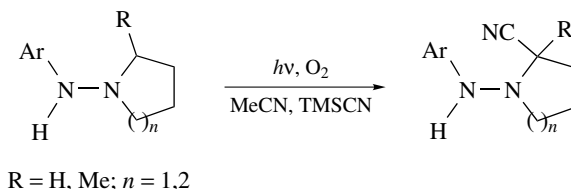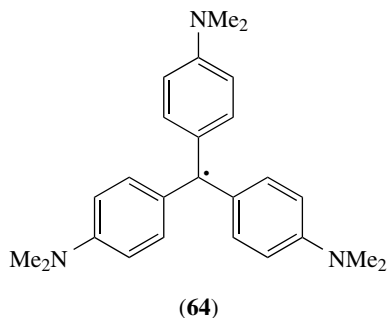
sterically hindered Crystal Violet radical (**64**) leading to a carbocation–carbanion salt $(64)^+(C_{60})^{\cdot-}$ which is stable in solution and in the solid state.[83]

First-order kinetics have been found for the reductions of pinacolone by borane-dimethyl sulfide in THF, which proceeds via a monoalkoxyborane complex.[84] In contrast, the kinetics were second order for the reduction with catecholborane and the reactive species was found to be a catecholborane dimer present in small concentrations.

The reduction of several phosphaallenes has attracted a lot of attention. Bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphoshaallene (**65**) was electrochemically reduced in THF to give diphosphaallyl radical (**67**), which would originate through protonation of the radical anion (**66**) immediately after its formation. The radical (**67**) was identified by EPR spectroscopy and was supported by DFT calculations.[85] Monophosphaallene $ArP=C=C(C_6H_5)_2$ (Ar = 2,4,6-*t*-$Bu_3C_6H_2$) underwent irreversible reduction to the neutral monophosphaallylic radical Ar-$\overset{\bullet}{P}$-CH=CPh$_2$ as shown by EPR. Comparison of the hyperfine tensors with those obtained from *ab initio* calculations for the radical anion $(HP=C=CH_2)^{\cdot-}$ and the monophosphaallylic radical $(H\overset{\bullet}{P}-CH=CH_2) \leftrightarrow (HP=CH-\overset{\bullet}{C}H_2)$ indicate that the species observed by EPR is the monophosphaallylic radical Ar-$\overset{\bullet}{P}$-CH=CPh$_2$.[86] The radical anion of *p*-phosphaquinone was successfully

$$ArP=C=PAr \longrightarrow [ArP=C=PAr]^{\cdot-} \longrightarrow$$

(**65**) (**66**) (**67**)
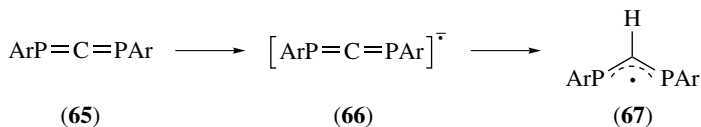
generated *in situ* by reduction with Na in THF (Scheme 6). Comparison of the isotropic and anisotropic coupling constants of the radical anion with those of the phosphorus atoms suggest that about 2% and 64% of the unpaired electron are localized on the $3s$ and $3p$ orbitals of phosphorus, respectively.[87]
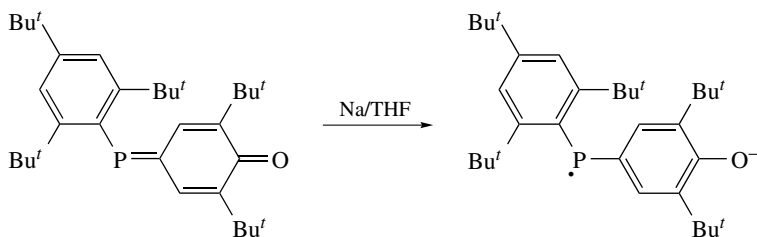
SCHEME 6

The reductive cleavage of iodobenzene and 3-methyliodobenzene was studied by cyclic voltammetry in both DMF and acetonitrile at 21 and 56 °C at different scan rates and has shown that there is a transition between stepwise and concerted mechanisms at lower scan rates. 1-Iodonaphthalene undergoes a stepwise reductive cleavage with mixed kinetic control by electron transfer and follow-up bond breaking, whatever the scan rate.[88]

The kinetics of hydride and organometallic additions to benzaldehyde-H and -D were determined at −78 °C using a variety of hydride reagents, Grignard reagents and organolithiums.[89] The additions of hydride, methyl-Grignard reagents, and methyl- and phenyl-lithiums showed an inverse deuterium kinetic isotope effect. Little effect was observed was observed with phenyl-Grignard and *n*-butyl- and *t*−butyl-lithium. Allyl-Grignard and allyllithium showed a normal secondary deuterium effect. The results showed that the rate-determining single-electron transfer occurs with allyl reagents but direct nucleophilic reaction occurs with all other reagents. The extent of bond formation is dependent on the reactivity of the reagent.

Electron-transfer Reactions

Photo-induced Electron Transfers

Photo-induced electron-transfer decarboxylation reactions have been reviewed.[90] A variety of methyl- and methoxy-substituted phenol radical cations have been generated by either photo-induced electron transfer or photo-ionization in dry solvents such as acetonitrile.[91] In the presence of small amounts of water the radical cations are not detected and the phenoxyl radical is the only transient species observed. The 2-methoxyphenol radical cation was found to be more reactive than the 4-methoxy radical cation.

The reactivity and π-facial selectivity of CH_3OH and H_2O additions to the radical cations of 7-benzhydrylidenenorbornene derivatives (**68**), generated by photo-induced

electron transfer, were investigated. It was found that, amongst the $\pi-\pi$ interactions in the radical cations of 7-benzhydrylidenenorbornene derivatives, the interaction between the 7-benzhydrylidene group and the *endo* alkene induces efficient nucleophilic capture of a radical cation at the benzhydrylidene group with the *anti* selectivity at the *endo* alkene.[92]

(68)
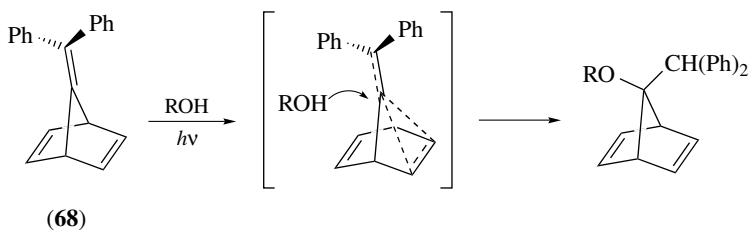
The electron-transfer-induced cyclization of homochrysanthemol proceeds via a five-membered transition state, from intramolecular substitution at the quaternary cyclopropane carbon, to generate the five-membered cyclic ethers (**69**) and (**70**).[93] In contrast, the intramolecular photo-induced cyclization of chrysanthemol goes via a six–membered transition state involving attack at the terminal vinyl carbon.
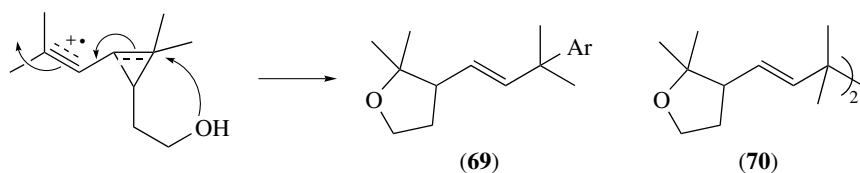

(69) **(70)**

Photo-induced electron-transfer radical-cation Diels–Alder reactions of indole with aromatic or heteroaromatic substituted exocyclic dienes using tris(4-methoxyphenyl)pyrylium tetrafluoroborate as a catalyst proceed with complete regioselectivity to form [*b*]-annelated tetrahydrocarbazoles (Scheme 7). The regio- and diastereo-selectivities were rationalized using potential energy surface calculations. The mechanism and the potential energy hypersurface of the radical-cation Diels–Alder reaction was investigated using quantum chemical methods. The potential surface demonstrates non-synchronous and non-concerted reaction pathways. The energies of the different long-bond intermediates have been calculated with semiempirical molecular and density-functional methods.[94]

A photo-induced electron transfer (from either the sensitizer in its excited state to the oxadiazole in its ground state or from the electron-donor reagent such as triethylamine to the excited oxadiazole) has been suggested as an explanation for the breaking of the O–N bond of 5-aryl-3-methoxy-(or 5-aryl-3-phenyl-)-1,2,4-oxadiazoles (**71**) upon irradiation.[95] The resulting oxadiazole radical anion underwent either a heterocyclization to give quinazolin-4-ones or reduction to give open-chain products.

SCHEME 7

(**71**)
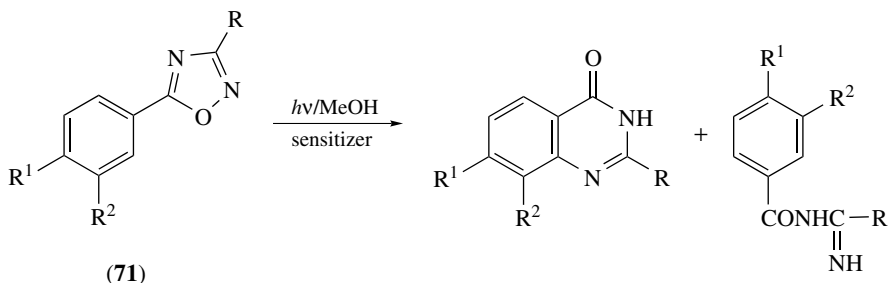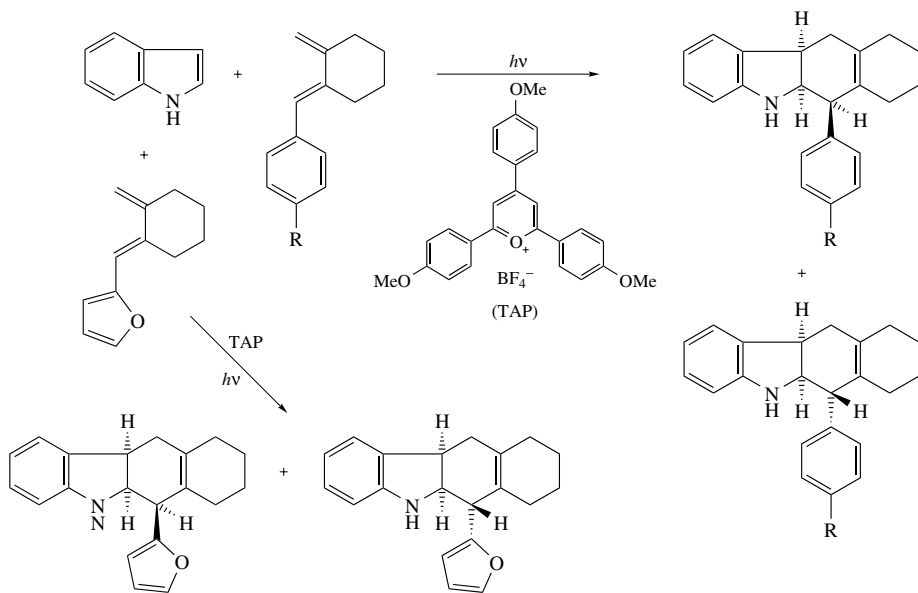
Other Electron Transfers

The kinetic isotope effect in the one-electron transfer from 1-benzyl-1,4-dihydronicotinamide to 9-fluorenylidenemalononitrile was studied and the rate constants of the reactions were calculated.[96] The electron affinities (EA) for a series of methyl benzoates, acetophenones, benzaldehydes, and benzophenones were determined by applying the electron-transfer equilibrium method in the gas phase.[97] The substituent effect on the stability of aromatic radical anions has been analysed.

ESR, IR and Raman spectroscopic studies on the ^{14}N/^{15}N and ^{12}C/^{13}C equilibrium isotope effects on the electron-transfer reaction between *N*-methylphenothiazine and the radical cation of its ^{15}N- and/or *N*-^{13}C-methyl-substituted analogues have been reported.[98] ^{15}N and ^{13}C substitution of methylphenothiazine increases the ionization potential of the molecule, making it difficult to lose an electron to form the corresponding radical cation.

Evidence of a single transfer process from the nucleophile to the aromatic substrate has been found for the nucleophilic aromatic substitution (S_NAr) reaction of different polynitrobenzenes with nucleophiles such as alkoxides, thiolates, and tertiary amines.[99] The two radical species that are generated within the solvent cage have been detected by EPR spectroscopy. *Ab initio* calculations have been performed in the investigation of the electron transfer reaction between biphenyl radical anion and neutral biphenyl.[100] Aromatic compounds substituted with an electron-donating group, such as methoxy, hydroxy, or amino, were regioselectively iodinated with iodine in the presence of tetrabutylammonium peroxodisulfate in CH_3CN via an electron-transfer mechanism.[101] The *p*-positions of methoxybenzenes and phenols were exclusively iodinated whereas *o*-iodination only occurred when the *p*-position was blocked.

Chlorides RMe_2CCH_2Cl [(a) R = Me, R = Ph and (b) R = CH_2Ph] reacted with diphenylphosphide ions in liquid ammonia, via a proposed $S_{RN}1$ mechanism and their reactivities were measured. The higher reactivity of (a) has been attributed to efficient intramolecular electron transfer from the phenyl ring to the C−Cl σ^* bond (intra-ET catalysis). The lower reactivity of (b) is ascribed to a decrease in the rate of the intra-ET by elongation of the bridge by one methylene unit. The relative reactivity of (a) versus (b) is proposed to indicate the ratio of the intra-ET rates of the radical anions of both compounds.[102]
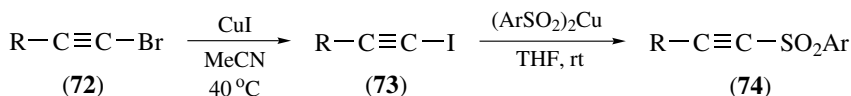
Chloride dioxide (ClO_2) forms red charge-transfer complexes with piperidine and imidazoline nitroxyl radicals that slowly transform into oxoammonium salts.[103]

The aminium salt-induced cyclodimerization of stilbenes in 1,1,1,3,3,3-hexafluoropropanol gave mixtures of indane and tetrahydronapthalenes. The solvent effects are consistent with an electron-transfer mechanism via a radical cation.[104]

The Patterno−Buchi coupling of various stilbenes (S) with chloroanil (Q) to yield *trans*-oxetanes is achieved by the specific charge-transfer photo-activation of the electron donor−acceptor complexes (SQ). Time-resolved spectroscopy revealed the (singlet) ion−radical pair[$S^{+\bullet}$, $Q^{\bullet-}$] to be the primary reaction intermediate and established the electron-transfer pathway for this Patterno−Büchi transformation. Carbonyl quinone activation leads to the same oxetane products with identical isomer ratios. Thus, an analogous mechanism is applied which includes an initial transfer quenching of the photo-activated (triplet) quinone acceptor by the stilbene donors resulting in triplet ion−radical pairs.[105]

The electron-transfer reactions between the β-cyclodextrin (β-CD) *N*-substituted phenothiazine derivatives and β-CD.ATPO (4-acetoxy-2,2,6,6-tetramethyl-1-oxopiperidinium hexachloroantimonate) were found to be influenced by the conformations of the phenothiazine derivatives restricted by the β-CD cavity. *N*-Phenylphenothiazine (PPT) and *N*-phenylethylphenothiazine (PEPT), included by β-CD, can transfer an electron to the β-CD.ATP complex. No electron transfer was observed between the β-CD.*N*-benzylphenothiazine (β-CD.BPT) complex under the same conditions. The conformation of the β-CD.BPT complex is such that the oxidation centre was shielded by the β-CD wall and the substituent. However, electron-transfer reactions between γ-CD.BPT and β-CD.ATP and nitric acid occurred.[106]

Copper iodide acts as an efficient reagent for the nucleophilic displacement of 1-haloalkynes. It transforms 1-bromoalkynes (**72**) into 1-iodoalkynes (**73**) which, on further treatment with copper(II) bis(arenesulfinate), are converted into the corresponding alkynyl aryl sulfones (**74**).[107] An electron transfer between 1-haloalkynes and copper(I) salts is believed to take place for the copper-assisted halogen-exchange reaction at the acetylenic carbon atom.

$$R-C\equiv C-Br \xrightarrow[\substack{MeCN \\ 40\,^{\circ}C}]{CuI} R-C\equiv C-I \xrightarrow[THF,\ rt]{(ArSO_2)_2Cu} R-C\equiv C-SO_2Ar$$

$$\quad\ \ (\mathbf{72}) \qquad\qquad\qquad (\mathbf{73}) \qquad\qquad\qquad\qquad (\mathbf{74})$$

Substituent effects on the electron-transfer processes between pyrrolidinofullerenes and tetrakis(dimethylamino)ethylene (TDAE) were studied in both the ground state and excited triplet state.[108] Equilibrium constants and rate constants for forward and backward electron-transfer processes in the ground state, in addition to rate constants of the forward electron transfer in the excited triplet state were measured.

An inner-sphere electron reduction has been proposed as a possible mechanism for the Fe(II)-induced decomposition of 1,2,4-trioxolanes (ozonides) (**75**) and (**76**).[109] Benzoic acid was found to be the major product. The nucleophilic Fe(II) species attack the ozonide from the less hindered side of the electrophilic O—O σ^* orbital to generate exclusively the Fe(III) oxy-complexed radical (inner-sphere electron transfer). After selective scission of the C—C bond, the resulting carbon-centred radical produced the observed product. The substituent effect determine the regioselective generation of one of the two possible Fe(III)-complexed oxy radicals. The bond scission shown will occur if R^2 is bulkier than R^1.

The mechanism of the Gibbs reaction has been investigated.[110] It has been concluded that *N*-chloroimine radical anion (**80**), generated in a single-electron transfer

(**75**)   (**76**)
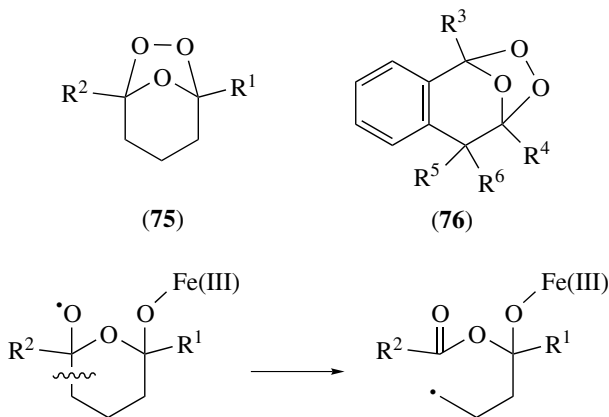
from the anion of phenol (**78**) to *N*-chloroimine (**77**), can produce indophenol dye (**79**) in three distinct routes. For more reactive reagents/substrates, a fast combination of the radical pair in the solvent cage is involved. For less reactive reagents, the *N*-chloroimine radical anion (**80**) escapes the solvent cage to initiate a chain reaction. The mechanism of the chain reactions has been termed $S_{RN}2$. In the case where the anion of (**80**) is less active, a competitive reaction along a third route can proceed in which the haloimine radical anion (**80**) yields a benzoquinone imine (**81**) by elimination of halide and the abstraction of an H-atom from the medium. Compound (**81**) could also give indophenol.
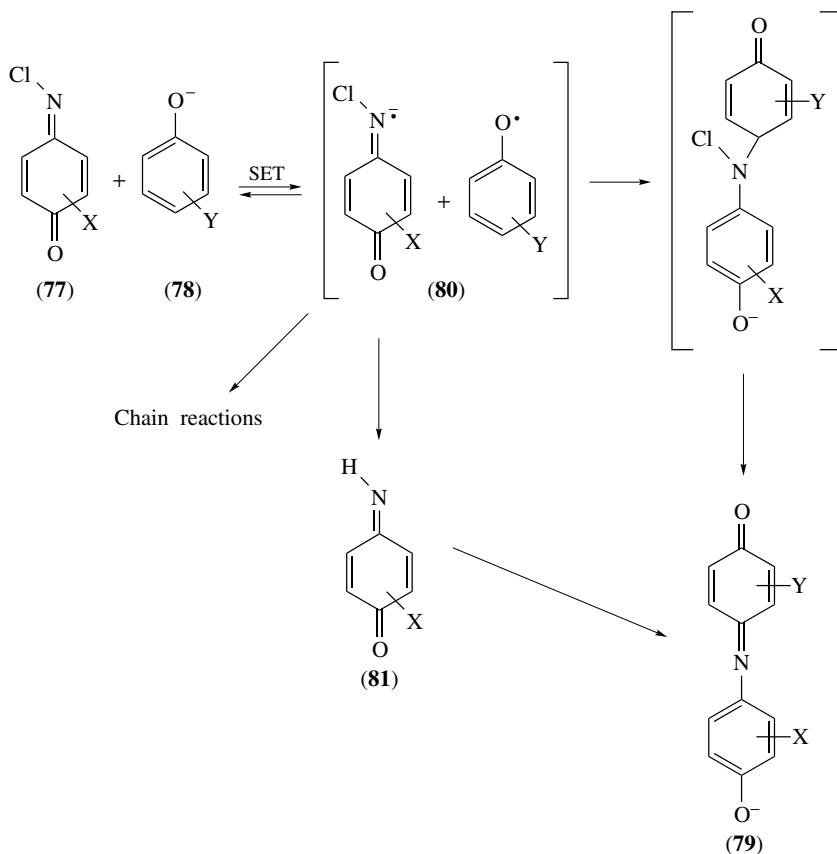
Radical Cations

A review considering the generation and characterization of radical ions, their reactions, formation of species with three-electron bonds, and radical cations of strained systems has been published.[111] The redox and acidity properties of a number of substituted benzene radical cations were studied by pulse radiolysis.[112]

Radical cations of toluene, *p*-, *o*-, and *m*-xylene and their deuteriated analogues, generated in $CFCl_3$ and CF_3CCl_3 matrices by X-irradiation, have been investigated by ESR and high-resolution ENDOR spectroscopy.[113] The ESR and ENDOR spectra are dominated by large axially symmetric hyperfine splitting due to methyl group protons. The hyperfine coupling constants of methyl and ring protons for toluene and *p*-xylene were accurately measured by ENDOR spectroscopy. Theoretical calculations of the isotropic and dipolar hyperfine coupling constants were in agreement with experiment. From spin-density calculations, the methyl-substituted benzenes were classified in two groups: toluene and *p*-xylene are of the $^2B_{2g}$ and *o*- and *m*-xylene are of the $^2B_{1g}$ type. The hybrid density-functional method B3LYP and the cc-pVDZ basis set have demonstrated that the naphthalene radical cation isomerizes to azulene radical cation via the Dewar–Becker mechanism at energies lower than its dissociation limit for acetylene elimination. The hydrogen-shifted naphthalene isomer is a proper interme- diate whereas the norcadiene isomer of the Dewar–Becker mechanism was found to be a transition structure in the ionic system.[114]

Ab initio calculations have been used to determine the parameters that govern the rate of spin-forbidden interconversion of the triplet and singlet states of a series of *p*-X-substituted aryl cations (X = H, CN, CH_3, F, OH, NH_2). The cations, where X = H, CN, CH_3 and F, were found to be ground-state singlets; X = NH_2 has a triplet ground state and the OH derivatives were almost isoenergetic. The minimum- energy crossing points between the two surfaces were found to lie very little above the higher of the minima in all cases and spin–orbit coupling was significant at these points. Therefore, it is expected that aryl cations will rapidly convert into their most stable spin states, and in the case of near degeneracy, such as for p-$HOC_6H_4{}^+$, the states may interconvert rapidly enough to be accessible in thermal reactions.[115]

The regio- and diastereo-selectivities in the rearrangement or strained cyclopentane- 1,3-diyl radical cations, generated by electron transfer, and the mechanism of this novel 1,2-migration have been reviewed.[116] A different theoretical study of the 1,2- rearrangement of housane radical cations suggested that the ground-state potential- energy surface of the housane radical cations is centred around a conical intersection at a planar, symmetric cyclopentane-1,3-diyl symmetry.[117] The computations show that the reaction proceeds in two steps: breakage of the one-electron bond of the reactants, which produces the asymmetric, quasi-planar intermediate, and subsequent 1,2-rearrangement, which is essentially barrierless. The reaction results in the selective 1,2-migration of the original *endo* substituent of the reactant.

A number of papers have reported studies on pyrimidine radical cations. 1- Methylthymine radical cations generated via a triplet-sensitized electron transfer to anthraquinone-2,6-disulfonic acid were detected by Fourier transform electron paramagnetic resonance (FTEPR). The parent 1-methylthymine radical cation, and its transformation to the N(3)-deprotonated radical cation, were observed. Radical cations formed by addition of HO^- and $PO_3{}^-$ at C(6) were also detected depending on the pH.[118] Similarly, pyrimidine radical cations deprotonated at N(1) and C(5)-OH were detected from the reaction of $SO_4{}^{\bullet-}$ with various methylated pyrimidines.[119] These radicals are derived from the initial $SO_4{}^{\bullet-}$ adducts of the pyrimidines. Radical cations of methylated uracils and thymines, generated by electron transfer to parent ions of

solvents such as *n*-butyl chloride and acetone, have also been detected. They show a transient tautomerism and exist in *n*-butyl chloride in the lactam and in acetone in the lactim form.[120] A kinetic study of the proton-transfer reactions between methylarene radical cations (**82**) and (**83**) and pyrimidine bases implicated a mechanism in which a complex is first formed that then undergoes proton transfer, followed by separation of the product.[121]

2,7-Diaminonapthalene radical dications (**84**) and (**85**) were prepared by oxidation of the equivalent amines.[122] Oxidation with thianthrenium perchlorate yielded ESR-active solutions. The ESR studies and effective magnetic moment measurements suggest a triplet ground state for (**84**$^{2+}$) whereas (**85**$^{2+}$) has a possible singlet ground state in CDCl$_3$ at 30 K. The thianthrene cation radical perchlorate (Th$^{+\bullet}$ClO$_4^-$) adds to

(**82**)   (**83**)

(**84**)

(**85**)
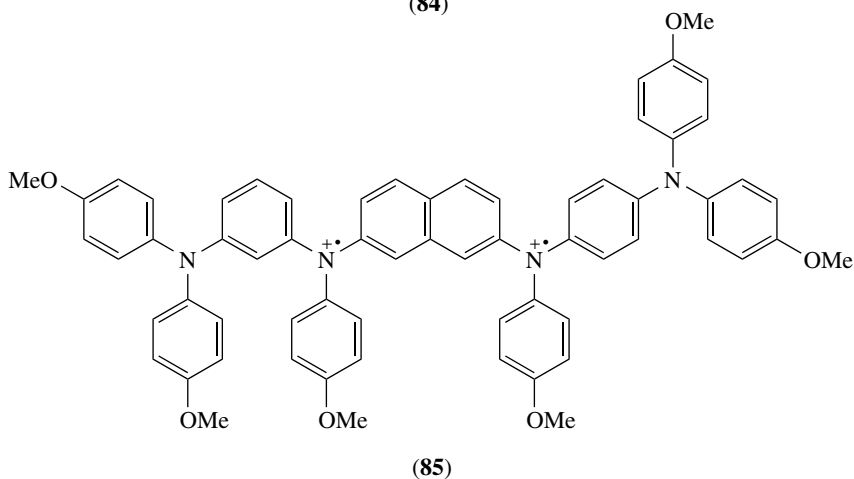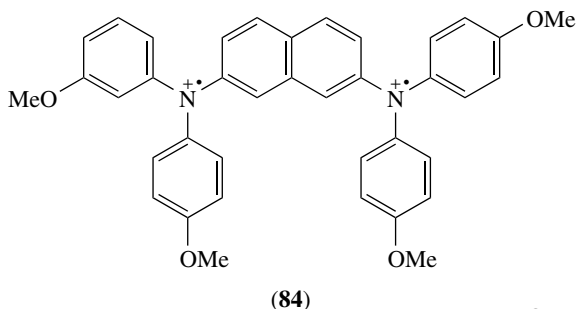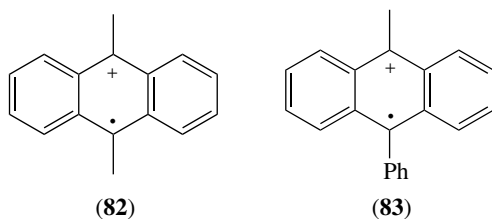
cyclostomes to give the monadic 1,2-(5,10-thianthrenium-diyl)cyclostomes. Addition of Th$^{+\bullet}$ClO$_4^-$ to cyclopentene and cycloheptene gave mixtures of mono- and bis-adducts, the monoadduct to a small extent for the former (17%) and a large extent (50%) for the latter.[123]

The tricyclopropylamine radical cation has been generated by γ-irradiation of cyclopropylamine in a mobile CF$_2$ClCFCl$_2$ matrix and was studied by EPR.[124] A planar geometry at the nitrogen atom has been revealed. The minimum-energy geometry has a C_{3h} symmetry with the three cyclopropyl groups in the bisected orientation. The geometries of the radical cations of cyclopropyldiisopropylamine, di-*t*-butylcyclopropylamine, dicyclopropylisopropylamine, and tricyclopropylamine were examined by ESR spectroscopy. All the radical cations were shown to be planar. Amines that have cyclopropyl substituents assume a perpendicular conformation in the neutral amines and a bisected orientation in the corresponding radical cations.[125]

Exposure of dilute solutions of triethylamine–boron hydride (Me$_3$N-BH$_3$) in Freon (CFCl$_3$) to ionizing radiation gave a radical cation whose EPR spectrum was that of the radical cation (Me$_3$N$-$BH$_3^{+\bullet}$). Electron loss from B$-$H bonds is clearly favoured over loss from the N$-$B bond.[126] The gas-phase reactions of the methylamine radical cation with mono- and di-haloethenes occur by substitution of one halogen substituent and by formal hydride abstraction yielding the ion (H$_2$CNH$_2$)$^+$ and a halogenated ethyl radical as products.[127] High-level *ab initio* calculations were carried out to establish the minimum-energy path of the reaction of methylamine radical cation and chloroethene along both reaction channels. EPR spectra have been obtained for the radical cations of a series of fluorinated ethylenes and propenes that were generated by irradiation with γ-rays in solid halocarbon matrices.[128] The spectra consist of a hyperfine structure with a nearly axial symmetry due to fluorine nuclei. The trifluoroalkene cations CF$_2$=CFX$^+$ (X = H, CH$_3$) have a planar structure. For the mono- and di-fluoroalkene radical cations the optimized geometry was calculated by an *ab initio* MO method. The results show that fluorinated ethene and propene cations have planar structures.

Ab initio molecular-orbital calculation on the isomerization of [C$_3$H$_5$N]$^{+\bullet}$ radical cation reveal that acetonitrile-*N*-methyl [CH$_3-$CN$-$CH$_2$]$^{+\bullet}$ and *N*-methylketenimine [CH$_3-$NC$-$CH$_2$]$^{+\bullet}$ are the most stable species among the 15 isomers considered.[129] The study revealed that the two isomers constituted distinct species in the gas phase and that isomerization takes place prior to dissociation during high-energy CID experiments. Methoxy isothiocyanate (CH$_3$ON=C=S)$^{+\bullet}$ and methyl cyanate *N*-sulfite (CH$_3$OCN$^+-$S$^-$) radical cations, derived from dissociative ionization of heterocyclic precursors, have been fully characterized by mass spectrometric methods in the gas phase.[130]

The effects of temperature on the shape of intervalence charge-transfer bands for the radical cations of bis(2-*t*-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)hydrazines that are bridged by 2,5-xylene-1,4-diyl, durene-1,4-diyl, naphthalene-1,4-diyl, biphenyl-4,4-diyl and 9,9-dimethylfluorene-2,7-diyl aromatic rings were studied by ESR.[131]

The X-ray crystal structure of the hexafluoroantimonate salt of 1,4-diithin radical cation stabilized by bicyclo[2.2.2]octane annelation revealed a planar ring and was in agreement with theoretical calculations.[132] Tertiary aminium radical cations underwent facile 5-*exo*-cyclization to give distonic 2-substituted pyrrolidinium radical cations.[133]

These can be further oxidized to 1,3-dications and trapped by nucleophiles such as water, alcohols, or chloride ion.

The metastable dimethoxyethane radical cation $[CH_3OCH_2CH_2OCH_3]^{+\bullet}$ eliminates methanol to give a $[C_3H_6O]^{+\bullet}$ fragment.[134] The reaction involves a sequence of 1,4-H shift, leading finally to the radical cation $[CH_3\overset{+}{O}(H)CH_2\overset{\bullet}{C}HOCH_3]$, which eliminates methanol to give $[CH_2CHOCH_3]^{+\bullet}$.

The radical cation of 2,5-dimethylhexa-2,4-diene was generated and some of the Raman spectrum bands were assigned using theoretical methods such as UHF, CASSCF, UBLYP and UB3LYP procedures. A small amount of the less stable *gauche* conformer of the radical cation was identified and its bands assigned.[135] *Ab initio* calculations on the isomerization of butene and pentene radical cations indicate that the lowest barrier for a rearrangement to the most stable ion structure is below the dissociation limit.[136] The linear butene radical cation isomerizes to the isobutene via the $(CH_3CC_2H_5)^{+\bullet}$ structure, whereas in the pentene case the isomerizations proceeds via the 1,2-dimethycyclopropane radical cation.

The gaseous dichlorocarbene radical cation reacted with alkyl halides via a fast electrophilic addition to form a covalently bonded intermediate $(Cl_2C-X-R)^{+\bullet}$ in a Fourier transform ion cyclotron resonance mass spectrometer.[137] This intermediate fragments either homolytically or heterolytically to produce net halogen atom or halogen ion transfer product. Addition of carbonyls to the carbene ion is followed by homolytic cleavage of the C−O bond to yield a new carbene radical cation.

The solvent effects on the ring opening of the cyclobutene radical cation by implementation of the polarizable continuum model have been studied.[138] The authors concluded that the reaction leads directly to *trans*-butadiene radical cation via a cyclopropenyl-carbinyl type of radical cation, in contrast to expectations of a normal 'electrocyclic' pathway leading to *cis*-butadiene radical cation. MO and DFT calculations on the $2 + 2$-cycloreversion reaction of the cyclobutane radical cation have revealed three distinct but energetically similar structures for the radical cation: a parallelogram that corresponds to the minimum, on the Jahn−Teller surface, a rhombus, corresponding to a transition structure connecting two parallelograms, and a rectangle that is a second-order saddle point. The reaction was shown to proceed in a concerted fashion, and is not consistent with a putative acyclic intermediate, but the two ethylene fragments are brought relative to each other. The transition structure connects the product complex to the parallelogram structure of the cyclobutane radical cation.[139]

Reaction pathways for the addition of ethylene to butadiene radical cation involving H-shifts have been investigated at the coupled cluster UCCSD(T)/DZP//UMP2(fc)/DZP + ZPE level of theory.[140] Several rearrangement reactions have been found to occur below the energy limit of separated ethylene and butadiene radical cation. The cyclopentenyl cation $(C_5H_7)^+$ in the gas phase may originate from various pathways.

The Diels−Alder reaction of either *m*- or *p*-substituted aryl *cis*-prop-1-enyl ethers (**87**) with 2,3-dimethylbutadiene (**88**) catalysed by tris(2,4-dibromophenyl)aminium hexachloroantimonate (**86**$^{+\bullet}$) at $0\,^\circ C$ are non-stereospecific and occur via an indirect Diels−Alder reaction.[141] When the reaction is carried out at $-78\,^\circ C$, the vinylcyclobutane adducts are observed and these are efficiently converted into the

Diels–alder adducts at 0 °C. This cation radical–vinylcyclobutane rearrangement is non-stereospecific, thus accounting for the formation of a *cis–trans* mixture of Diels–Alder adducts. Kinetic studies revealed (Scheme 8) that the ionization of these ethers involves an inner-sphere electron-transfer mechanism involving strong covalent (electrophilic) attachment to the substrate via oxygen (oxonium ion) or carbon (carbocation).
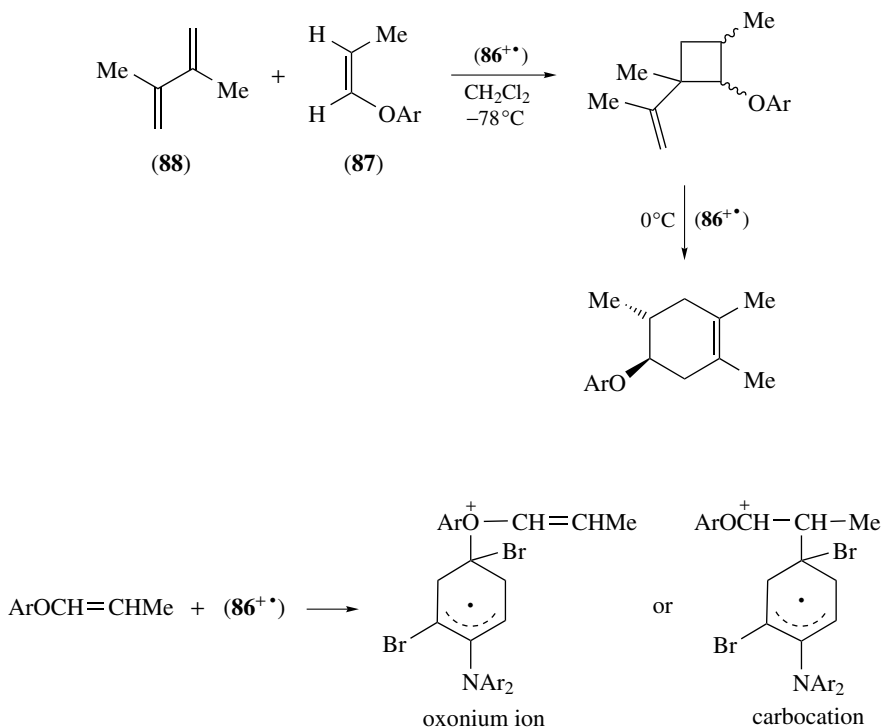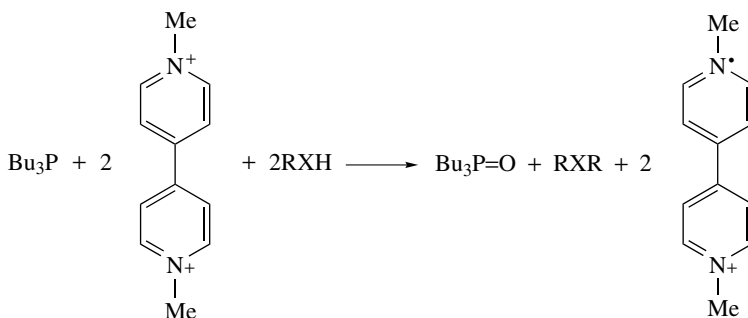

SCHEME 8

The cation radical Diels–Alder cycloadditions of *cis-* and *trans*-prop-1-enyl aryl ethers to cyclopenta-1,3-diene catalysed by tris(4-bromophenyl)aminium hexachloroantimonate are stepwise processes involving an intermediate distonic cation radical in which the carbocationic site is stabilized by the electron-donating functionality (Scheme 9).[142]

A cation radical chain cycloaddition–polymerization catalysed by tris(4-bromophenyl)aminium hexachloroantimonate has been reported to afford polymers with an average molecular weight up to 150 000. Both cyclobutanation and Diels–Alder polymers were obtained.[143] The reactivity of the phospine radical cation towards nucleophiles was studied. Tributylphosphine reacted with 1,1-dimethyl-4,4-bipyridinium (methyl viologen, MV) in the presence of an alcohol or thiol (RXH; X = O, S), which resulted in the gradual formation of the one-electron reduced form
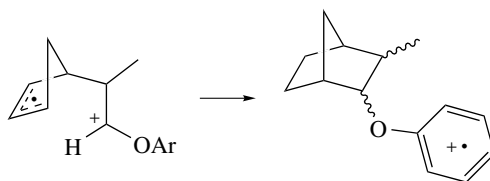
SCHEME 9

of the MV (Scheme 10). Tributylphosphine was oxidized to the tributylphospine oxide. The increase in the amount of the MV$^+$, which was followed spectrophotochemically and with tributylphosphine and RXH in excess, did not follow first-order kinetics. A single-electron transfer takes place from tributylphosphine to MV, to generate tributylphospine radical cation and MV$^+$. The resulting phosphine radical cation undergoes ionic reaction with RXH and back electron transfer from MV$^+$ with comparable efficiency. The kinetic data show that the reaction of the tributylphosphine radical cation with nucleophile RXH is governed by both electronic and steric factors.[144]

SCHEME 10

Transformations of the radical cations of 2,3- and 2,5-dihydrofuran (DHF), radiolytically generated in Freon matrices, were investigated by low-temperature EPR. The 2,3-DHF$^{+\bullet}$ radical cation is stable at 77 K but at higher temperatures is transformed into dihydrofuryl radical, DHF$^\bullet$. The oxygen-centred radical cation 2,5-DHF$^{+\bullet}$ is unstable at 77 K and transforms via an intramolecular H-shift into a transient distonic radical cation 2,4-DHF$^{+\bullet}$ which at higher temperatures yields the DHF$^\bullet$ radical.[145]

Radical Anions

EPR was used for the determination of equilibrium constants K_1 for

$$Q + QH_2 \rightleftharpoons Q^{\bullet-} + Q^{\bullet-} + 2H^+$$
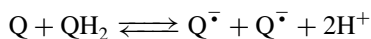
from a steady-state concentration of semiquinones ($Q^{\bar{\bullet}}$) in mixtures of 11 alkyl-, methoxy-, and chloro-substituted 1,4-benzoquinones and 1,4-naphthaquinone (Q) and hydroquinones (QH$_2$).[146]

Rate constants K_H for proton transfer from a series of substituted phenols to anthracene and phenanthrene radical anions formed in DMF have been measured by the voltammetric method. The homolytic bond dissociation energy D for ArH$^\bullet \to$ Ar + H$^\bullet$ was evaluated and the values were in agreement with experiment.[147] Cyclic voltammetry and EPR spectroscopy have shown that the stability of the anion radicals of dialkylbenzene-1,3-dicarboxylates, dialkyl pyridine-2,6-dicarboxylates, and their corresponding dithio-S, S−diesters is due to a reversible dimerization mechanism. The EPS data confirmed the existence of relatively stable anion radicals formed from one-electron reduction of the diesters, the simple spectra of which suggested that the radicals responsible were the primary anions.[148] The solvent-induced intramolecular electron-exchange (IEE) reaction within the conjugated 1,4-dinitrobenzene radical anion has been studied in linear alcohols.[149] The rate constants were determined from alternating line-broadening effects in EPR spectra and were found to be smaller than the rate constants for the 1,3-dinitrobenzene radical anion due to the conjugation of the nitro groups. A semiempirical AM1 study of the fragmentation of the radical anions of *o*-, *m*-, and *p*-halonitrobenzenes and some alkyl-substituted derivatives in relation to their $\sigma-\pi$ orbital isomerism and the energy of their interconversion was reported.[150]

The solvent effects on the C−Cl bond cleavage in the aromatic radical anions of 9-chloroanthracene, 3-nitrobenzyl chloride, and 3-chloroacetophenone were described by applying the Savéant model.[151] The results showed that the bond dissociation energy is not strongly solvent dependent.

An EPR and AM1 molecular modelling study of the structure of the radical anion of β-ionone (**89**) was carried out to investigate the structure and magnetic properties of one-electron transfer reactions of carotenoids. The temperature dependence of the EPR spectrum of the radical anion helped to reassign the coupling constant of 16 G from the 7-*H* to the 4-*H* proton in the axial orientation. The previous assignment failed to account for the rate of the cyclohexene ring inversion. The EPR showed that the coupling for the 7-*H* proton is approximately 9.5 G. The rate of cyclohexene ring inversion in the radical anion was estimated.[152]

(**89**)
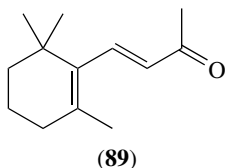
The stability of radical anions of disulfides [RS−SR]$^{\bar{\bullet}}$ and their ease of dissociation into thiolate anions and thiyl radical were studied as a function of pH with alkyl substituents of different structures:[153]

$$RS^\bullet + RS^- \rightleftharpoons [RS-SR]^{\bar{\bullet}}$$
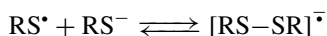
The radical anion stability increased when protonated amino groups were present and rose with their proximity to the S−S group. The presence of electron-donating methyl groups on the α-carbon caused a small reduction in stability. Ionized $CO_2{}^-$ groups on the β-carbon reduced the stability significantly. In the absence of protonated amino groups, the strength of the $(S-S)^-$ bond increased with the electron-withdrawing ability of the groups attached to S atoms.

A series of alkoxycyclooctatetraene radical anions was synthesized by lithium reduction of the corresponding ethers in hexamethylphosphoramide. The radical anions of *n*-propoxycyclooctatetraene and ibuprofoxycyclooctatetraene exhibit a small splitting for the γ-proton on the sp^3-hybridized carbon connected to the oxygen atom. The EPR pattern is consistent with a homohyperconjugative interaction involving overlap of the σ-bond to the γ-hydrogen and the π-system of the conjugated cyclooctatetraene ring.[154]

The EPR spectra of electrolytically produced anion radicals of α-aminoanthraquinones were measured in DMF and DMSO. The isotropic hyperfine coupling constants were assigned by comparison with the EPS spectra of dihydroxy-substituted antraquinones and molecular-orbital calculations.[155] Isomerically pure phenylcarbene anion (PhCH$^\bullet$) has been generated in the gas phase by dissociative electron ionization of phenyldiazirine.[156] PhCH$^\bullet$ has strong base and nucleophilic character. It abstracts an S atom from $CS_2{}^-$ and OCS, an N atom from N_2O, and an H atom from $(CH_3)_2NH$, propene, and $(CH_3)_2S$. Nucleophilic displacement of Cl^- from CH_3Cl occurs at a 41% collision rate. It also exchanges both the carbene hydrogen and a hydrogen in the phenyl ring upon reaction with ND_3 and D_2O. The rate constants for the H-atom abstraction reactions of the dichloride radical anion $(Cl_2{}^\bullet)$ with oxygenated hydrocarbons, ethanol, methanol, propanol, formaldehyde, diethyl ether, tetrahydrofuran, and acetone in dilute aqueous solutions were determined by the laser flash photolysis−long-path laser absorption technique.[157]

Comparison of the standard potentials of the radical anion of three α-nitrocumenes (α-nitrocumene, *p*-cyano-α-nitrocumene and *p*-nitro-α-nitrocumene) revealed that the nitroallyl portion occurs in (**90a**) and (**90b**), while in (**90c**) the electron is added to the nitrophenyl group. It was concluded that homolytic cleavage takes place for the radical anions of (**90a**) and (**90b**) to give nitrite and the cumyl radical whereas the cleavage of radical anion (**90c**) is heterolytic.[158]

The radical anions of various phenyldiphosphaalkenes (Scheme 11) were studied by EPR.[159] Their reduction is easier than that of monophosphaalkenes and is dependent on the nature of the isomer. Both EPR spectra and DFT calculations showed that in the radical anion the unpaired electron belongs to a π^* orbital and that its delocalization is dependent on the relative position of the two phosphaalkene moieties and on the nature of the bridging group. The spin density on the phosphaalkene carbon is higher for the *meta* compound than for the *ortho* and *para* compounds.
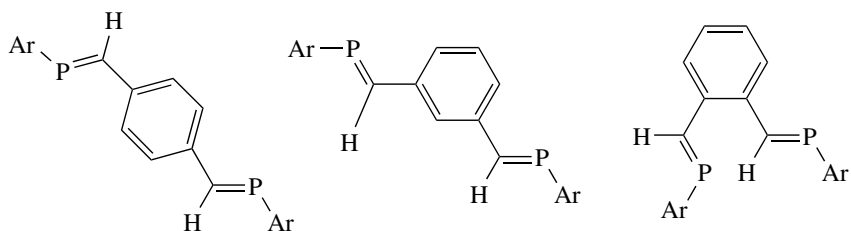
Radical anions of acyclic vicinal oligo-ketones with up to five CO units, generated by reduction of the parent compounds with potassium in the presence of Kryptofix 222, were shown to be extended π-systems by ESR measurements.[160]
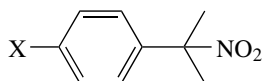
(**90**)

a; X = H
b; X = CN
c; X = NO$_2$

SCHEME 11

The kinetics of the rearrangement of radical anions derived from aliphatic cyclopropyl ketones (**91**) have been studied by homogeneous redox catalysis and compared with the neutral radicals. For radical anions (**92**), rearrangement is actually faster than that of the free radicals.[161] Placement of a phenyl group on the α-carbon of either a neutral radical or radical anion retards the rate of rearrangement because of delocalization of spin. For the radical ion the delocalization of charge is also important. In the ring-opened form (**93**), the negative charge no longer enjoys the stabilization afforded by the aromatic ring and the radical anion rearrangement is three orders of magnitude slower than that of the neutral radicals. In summary, the delocalization of spin affects the rates of rearrangement, and for radical anions charge plays an important role.

(**91**)   (**92**)   (**93**)
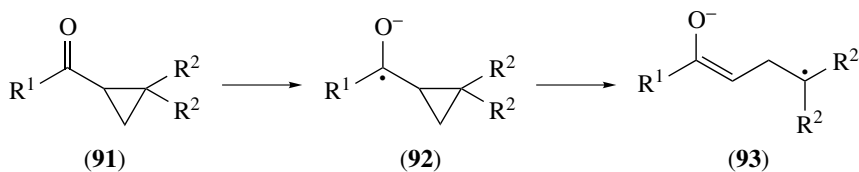
Biradicals

The matrix isolation and spectroscopic characterization of *m*- and *p*-benzynes and their derivatives have been reported.[162] Fourier transform ion cyclotron resonance mass spectrometry has been employed to investigate the reactivity of *m*-benzyne biradical with a pyridinium charge site in the 5-position.[163] The chemical properties of *m*-benzyne in the gas phase differ from those of the monoradical and

o-benzyne. *m*-Benzyne undergoes radical and addition reactions characteristic of *o*-benzyne but is less reactive. This reduced reactivity is rationalized by the strong coupling of the unpaired electrons, which results in a reduced thermodynamic force and increased barrier for radical reactions. The greater distance between the reactive centres in *m*-benzyne hinders alkyne-type addition reactions characteristic of *o*-benzyne.

Aromatic diradicals have attracted a lot of interest since the discovery that 1,4-diradicals are likely to be the key intermediates in the biological action of the enediyne group of anti-tumour antibiotics. A series of heteroaromatic arylazo esters with different numbers of ring nitrogens adjacent to the azo ester have been synthesized and their methanolysis in chloroform has been studied by EPR spectroscopy in order to investigate whether radical intermediates play an essential role in DNA cleavage.[164] Evidence from EPR spectroscopy shows that radicals are formed by methanolysis of the monoazo esters (Scheme 12). Methanolysis of 1,4-bisazo esters has also been studied in an effort to generate a diradical similar to that produced by enediynes. No EPR signal was observed. A diradical has been proposed as an intermediate (Scheme 13). These diradicals have been shown to be unstable and undergo retro-Bergman cyclization to form nitriles. The decomposition product 1,2-dicyanobenzene was isolated in 25% yield and is consistent with a diradical intermediate.
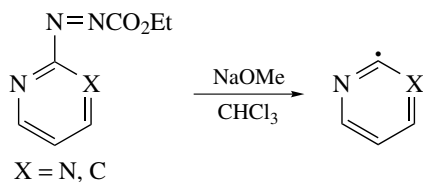
SCHEME 12
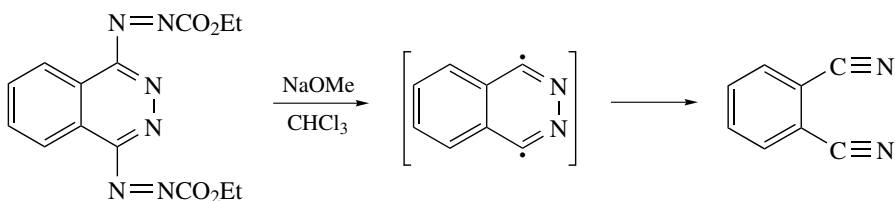
SCHEME 13

The behaviour of triplet acyl–diphenylmethyl biradicals $O=C^{\uparrow}-(CH_2)_{n-2}-C^{\uparrow}Ph_2$, generated from the Norrish type-I reaction of 2,2-diphenylcycloalkanones $(CK)_n$ with various ring sizes, $n = 6, 7, 9, 11, 12, 13$, was the subject of a study. For 2,2-diphenylcycloalkanones where $n = 6$ and 7 an intramolecular disproportionation takes place giving rise to a diphenylalkenal (**94**). The primary products in the photolysis

of $(CK)_n$ ($n \geqslant 9$) are the *para*-coupling products of biradicals, 4-methylenecyclohexa-2,5-denienyl ketone $(P)_n$, which are converted thermally into $(PC)_n$ (for $n = 11-13$) or photolysed to give decarbonylation products upon prolonged irradiation $(PH)_{n-1}$.[165]

(**94**)

PH-($n-1$)   PC-n P-n
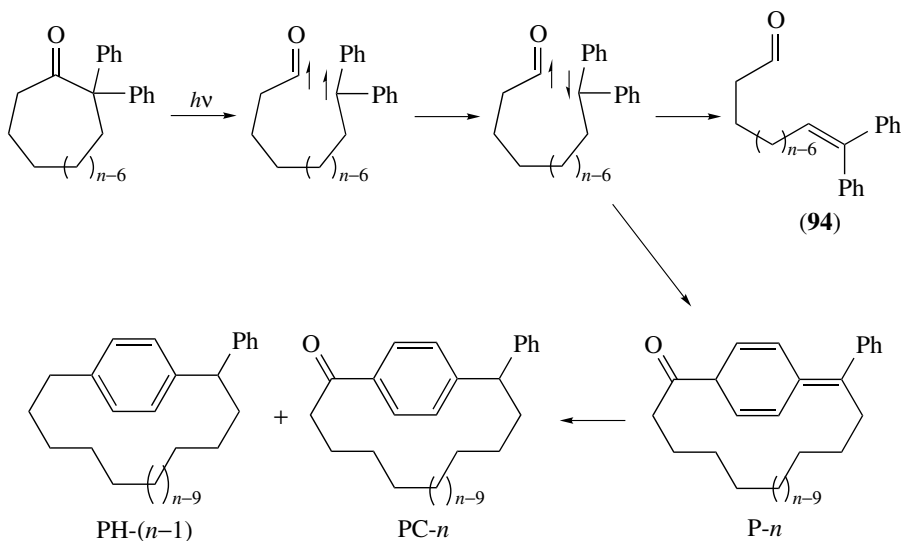
The Myers–Saito cycloaromatization of enynallenes has been proposed to consist of two parallel mechanisms, one involving a biradical and the other with dipolar character.[166] The competitive trapping experiments with cyclohexa-1,4-diene and cyclopentadiene are incompatible with a single-intermediate mechanism and suggest that there two parallel pathways for the cycloaromatization of (**95**). One pathway involves a biradical (**96**) but the nature of the intermediate is uncertain. MCSCF calculations suggest that a cyclic allene (**98**) is the more likely intermediate. Attempts to trap this cyclic allene with dienes, such as cyclopentadiene, butadiene, and cyclohexadiene, did not give the Diels–Alder cycloadduct. A reaction of one molecule of (**95**) with two molecules of diene was observed. The obvious mechanism involves the sequential reaction of the biradical intermediate with two equivalents of diene to close the macrocycle. It is possible, though, that a Diels–Alder reaction occurred but the bond homolysis in the cycloadduct could lead to the diradical (**99**) that reacted with a second molecule of cyclopentadiene. The zwitterions could be the second intermediate. The solvent effects on the product ratio in more non-polar reaction media support a more polar intermediate but the calculated energies indicate that (**97**) would not be energetically competitive with the biradical (**96**). The authors concluded that the cyclic allene is the most likely second intermediate.
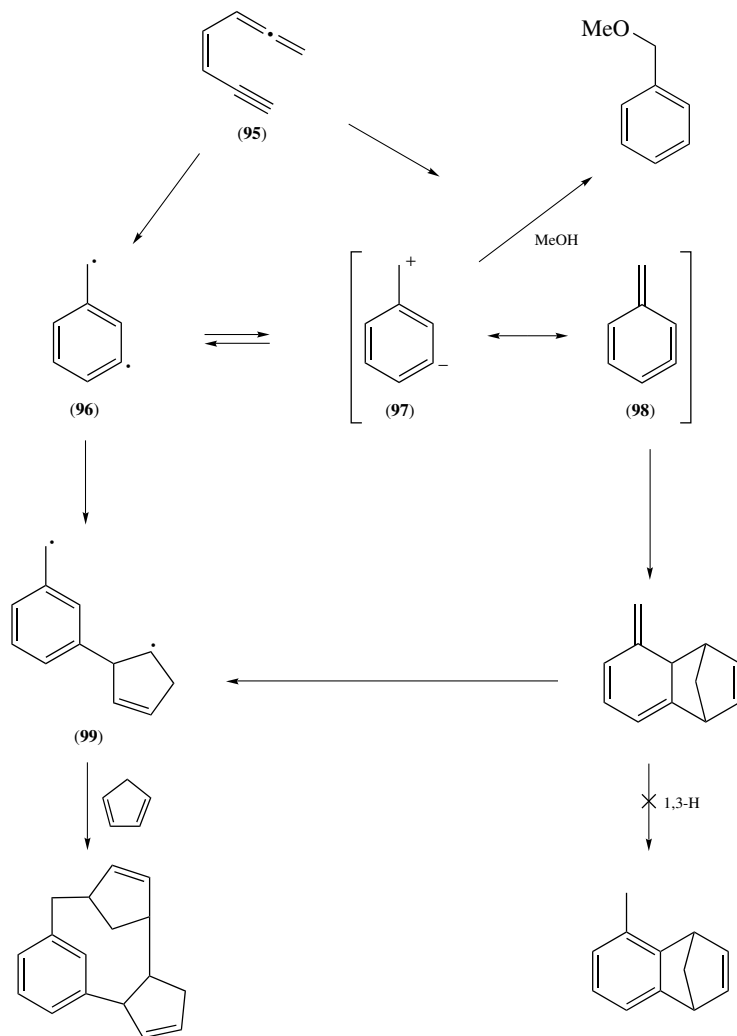
Several trimethylenemethane-type (TMM) dinitroxide diradicals have been prepared that differ in *t*-butylaminoxylphenyl ring-torsion angles by virtue of different steric demands of their 'spin-protecting groups.'[167] A TMM-type dinitroxide (**100**) having a planar π-system was synthesized. EPR spectral characterization revealed that neither N- nor H-hfcc varied. This indicated that there is no apparent relationship between N- or H-hfccs and conformation. All the biradicals, apart from one, exhibited linear Curie plots that are consistent with both triplet ground states and singlet–triplet degeneracies.

(**100**)
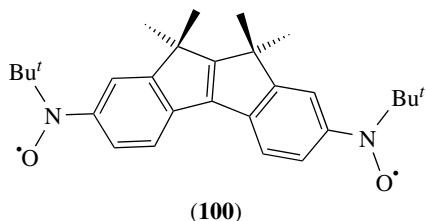
4,6-Bis(trifluoromethyl)-*N*,*N*′-di-*t*-butyl-1,3-phenylenebis(aminoxyl)   biradical, upon quenching in 2-methyltetrahydrofuran from ambient temperature to 5 K or below, produced the biradical in its singlet state, which slowly converts at low temperatures into the triplet ground state.[168] *Ab initio* calculations on the lowest singlet and triplet states of 2,2-disilylcyclopentane-1,3-diyl indicated the singlet lies well below the triplet.[169] Density-functional calculations indicated that the ground state of the tetramethyleneethane (TME) diradical in the gas phase is the singlet, whereas the triplet state should be metastable. In the vibrational spectra of the two states of TME the symmetric scissoring vibrations have the same frequencies as the vibrational modes of the photoelectron spectrum of the (TME)⁻ anion.[170]

Ab initio calculations on spiropentane (**101**) and *cis*- and *trans*-1,2-dimethylspiropentanes (**103**) and (**106**) have shown that, in the diradicals (**102**), (**104**), and (**105**) which are formed by the cleavage of the peripheral bond between C(1) and C(2) in the spiropentanes, the weakly electron-donating cyclopropane ring results in conrotation as the preferred pathway for ring opening of (**101**), (**103**), and (**106**),[171] in agreement with experimental results. The calculations indicated that the *s-cis*-methyl conformation in diradical (**105**) is lower in energy than the *s-trans*-methyl conformation in diradical (**104**). A long-range attraction between *s-cis*-methyl group at C(1) and the non-bonding *p*-π AO at C(3) in (**105**) contributes to stabilizing the diradical.
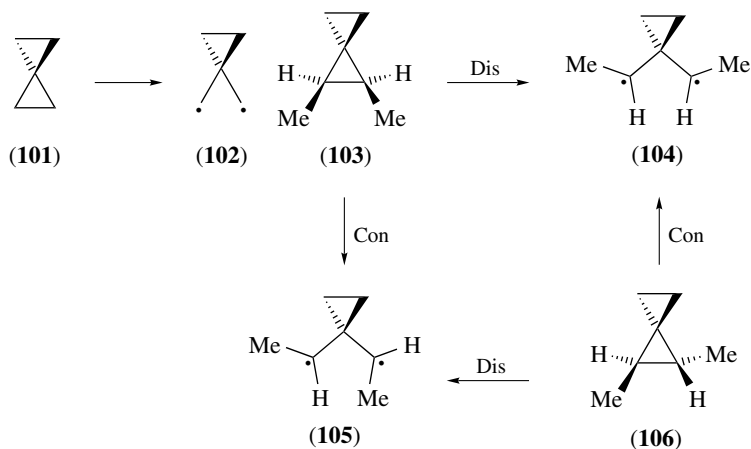
Similarly, *ab initio* calculations on the thermal reaction of propene forming methyl-cyclopentane suggested a three-step biradical reaction with 1,4-biradical and 1,5-biradical as intermediates.[172] Quantum-chemical calculations have been carried out for the cyclization of the neocarzinostatin chromophore cyclonona-1,2,3,5-tetraen-7-yne to 1,5-didehydroindene biradical.[173] The degree of stereoselectivity of the Diels–Alder reaction of 2-methylfuran and maleic acid in water has been found to reduce significantly in the presence of heavy atoms. Taking into account the relatively low concentration (3.5–7 M) of heavy-atoms, and the rapid fall off of the heavy-atom effect with distance, these results show that a large portion of the Diels–Alder reaction occurs via diradical intermediates.[174]

The relative stabilities of singlet and triplet electronic states of three different oxyallyl systems and the closed form of cyclopropanone, bicyclo[1.1.0]butanone, and bicyclo[2.1.0]pentan-5-one have been studied by density-functional calculations (B3LYP/6–31 G*). The results of these calculations are in good agreement with predictions of calculations based on multi-determinant methods.[175]

Pyrolysis and Thermolysis

The mechanism of the thermal $S_{RN}1$ reaction, using 4-nitrocumyl chloride and 2-nitropropanate ion as a model has been investigated. The results provided unambiguous evidence that a decrease in driving force is able to change the mechanism of homogeneous reductive cleavage reactions from stepwise to concerted.[176]

The thermolysis of a variety of 1,2,4-trioxanes in methanol has been followed by mass spectrometry and provided evidence of the corresponding products.[177] A study of the thermal decomposition of 3,6-diphenyl-1,2,4,5-tetroxane in toluene and methanol revealed a significant solvent effect that supported a homolytic stepwise mechanism instead of a concerted process.[178]

Ab initio calculations were carried out to elucidate the possible mechanism for decomposition reactions of dioxetane and dioxetanone and related species. The computational results indicate that endothermic O−O cleavages, followed by charge transfers, are operative for the chemiluminescence reactions of these peroxides with several anion species such as phenols, indoles, and luficerins. The chemically initiated electron-exchange luminescence mechanism requires complete one-electron transfer for the formation of excited carbonyl fragments.[179] Another theoretical study of the thermal decomposition of 1,2-dioxetane has re-examined the singlet/triplet surface-crossing regions and computed the spin–orbit coupling and energetics.[180] The barrier to O−O cleavage on the ground-state surface has been found to lie at nearly the same energy as the transition structure for the C−C biradical cleavage on the triplet energy surface. The computational results indicate that the singlet and triplet surfaces do not cross along the minimum-energy path between the ground state O−O cleavage and the singlet biradical. The authors have evidence for a singlet/triplet crossing 'line' that spans the ground-state O−O cleavage valley and lies a few kcal mol^{-1} higher in energy. The computed spin–orbit coupling between the ground state and triplet $^3(3\pi)$ surfaces is larger throughout the crossing region. It has been suggested that facile intersystem crossing from the ground state to the triplet state can occur anywhere

along the minimum-energy path, which could lead to a $^\bullet$OCHCH$_2$O$^\bullet$ triplet biradical. This could either fragment to form triplet products or undergo intersystem crossing back to the ground-state surface. Along these lines *m*-silyloxyphenolate-substituted 1,2-dioxetanes (see below) containing the substituent directly attached to the peroxidic ring or separated by a methylene group were treated with fluoride. The released phenolate anion acts as an intramolecular electron donor to the dioxetane moiety, inducing dioxetane cleavage and formation of an electronically excited singlet state, which emits fluorescence.[181]
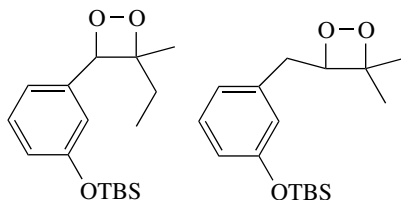
The thermal unimolecular decomposition of ethoxy radicals (C$_2$H$_5$O$^\bullet$) was investigated at different temperatures and pressures. Under these conditions the β-C$-$C scission CH$_3$CH$_2$O$^\bullet$ + M $\rightarrow$ CH$_2$O + CH$_3$$^\bullet$ + M is the dominant decomposition channel. Excellent agreement between the experimental and calculated rate constants has been found.[182]

A number of reports on the thermal decomposition of peroxides have been published. The thermal decompositions of *t*-butyl peroxyacetate and *t*-butyl peroxypivalate,[183] of HCOH[184] and a kinetic study of the acid-induced decomposition of di-*t*-butyl peroxide[185] in *n*-heptane at high temperatures and pressures have been reported. Thermolysis of substituted *t*-butyl (2-phenylprop-2-yl) peroxides gave acetophenone as the major product, formed via fragmentation of intermediate alkoxy radicals RCH$_2$C(Ph)(Me)O$^\bullet$.[186] A study of the thermolysis mechanism of di-*t*-butyl and di-*t*-amyl peroxide by ESR and spin-trapping techniques has been reported.[187] The di-*t*-amyloxy radical has been trapped for the first time. β-Scission reaction is much faster in di-*t*-amyloxyl radicals than in *t*-butoxyl radicals. The radicals derived from di-*t*-butyl peroxide are more reactive towards hydrogen abstraction from toluene than those derived from di-*t*-amyl peroxide.

The flash vacuum pyrolysis of alkynes, arynes, and aryl radicals has been reviewed. A discussion of secondary reactions and rearrangements is included.[188] The pyrolysis of cyclopentadienes has also been examined.[189] The rates for the initial C$-$H bond fission and the decomposition of *c*-C$_5$H$_5$ have been calculated. A single-pulse shock study on the thermal decomposition of 1-pentyl radicals found alkene products that are formed by radical isomerization through 1,4- and 1,3-hydrogen migration to form 2- and 3-pentyl radicals.[190] The pyrolysis of *t*-butylbenzene in supercritical water was the subject of a report.[191]
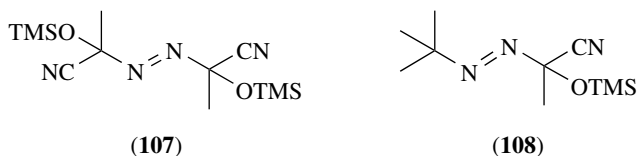
The kinetics of the thermal isomerization of methylcyclopropane to four isomeric butanes have been determined from rate-constant measurements over a wide range of temperatures 695–1154 K. The kinetic parameters are consistent with the formation

of the two but-2-enes through a diradical intermediate. Kinetic data for but-1-ene and 2-methylpropene formation are also presented. The higher activation energy for the formation of but-1-ene and of *cis-* and *trans-*but-2-ene is due to the higher energy required to break the C(2)-C(3) bond compared with the methyl-substituted C(1)−C(2) bond.[192]

An *ab initio* RHF/3−21 G study has shown that the decomposition of 3-hydroxy-3-methylbutan-2-one is a concerted process with hydrogen transfer and bond breaking via a five-membered cyclic transition state.[193] AM1 and PM3 methods using UHF calculations were applied to study the thermolysis of 2-cyanofuroxan.[194] The reaction proceeds via a two-step pathway in which the second step is rate determining. The effect of solvent in the thermal decomposition reaction of *trans-*3,3-dimethyl-5,6-tetramethylene-1,2,4-trioxacyclohexane was studied.[195]

The kinetics of the pyrolysis of CF_3CHFCF_3 in a single-pulse shock tube over the temperature range 1200−1500 K have been studied. The most important products detected were C_2F_6, $CF_2=CHF$, C_2F_4, C_3F_6, cyclo-C_3F_6, and CF_3CHFCF_2H. Traces of CF_3H, CF_4, C_2F_5H, C_3F_8, and C_4F_6 were identified. Modelling results showed that the major initiation step was the C−C bond-fission reaction. The abstraction of a secondary H atom by F atoms was predicted to be important, whereas 1,2-HF elimination was slower.[196] New completely fluorinated intermediates have been identified from spectroscopic studies of thermal reactions of perfluorinated alkenes, carbocycles and oxiranes in the gas phase.[197] A theoretical study of the thermal decomposition mechanism of fluoromethanethiol (FCH_2SH) and of CH_3SF at the G2(MP2) level of theory has shown that the most energetically favourable channel is the formation of HF and CH_2S via a four-centre elimination mechanism for both molecules.[198]

The thermal decomposition of azoalkanes bearing geminal α-cyano and α-trimethylsiloxy groups has been the subject of a report.[199] The symmetrical compound (**107**) decomposes near room temperature to afford entirely C−C dimers, whereas the unsymmetrical azoalkane (**108**) requires heating to 75 °C. A ^{13}C NMR product study of photolysed (**107**) in the presence of TEMPO showed that the fate of caged *t-*butyl-1-trimethylsiloxy-1-cyanoethyl radical pairs is disproportionation (17%), cage recombination (20%), and cage escape (63%).

(**107**)   (**108**)

The kinetics and mechanism of pyrrole pyrolysis were investigated by *ab initio* quantum-chemical calculations. It was revealed that pyrrole undergoes tautomerization to form 2*H*- and 3*H*-pyrroles prior to any thermal decomposition. It has been shown that the major product, HCN, arises from a hydrogen migration in pyrrole to form a cyclic carbene with the NH bond intact. Ring scission of the carbene leads to an allenic imine of HCN and propyne which is the lowest energy pathway. The 2*H*-pyrrole

undergoes CN fission to form an open-chain biradical species which leads to *cis*- and *trans*-crotononitrile and allyl cyanide. The biradical can also undergo facile H-fission to form cyanoallyl radical that leads to acetylene, acetonitrile, acrylonitrile, and H_2.[200]

A similar study using density-functional B3LYP theory and *ab initio* calculations was done by other researchers.[201] The pyrrole was found to tautomerize to $2H$-pyrrole which, via 1,2-hydrogen migration, yields $3H$-pyrrole; $3H$-pyrrole can rearrange to *cis*-isocyanocrotonitrile via a concerted transition state of C(2)−C(3) bond cleavage and 1,2-hydrogen migration from C(2) to C(3). *cis*-Isocyanocrotonitrile isomerized to *cis*-crotonitrile. Allyl cyanide was proposed to form from $2H$-pyrrole through a concerted transition state of C−N bond cleavage and 1,2-migration. This study failed to identify a decomposition pathway for HCN generation.

The thermolysis of 2-methoxyphenol in the presence of cumene as a radical scavenger occurs via two possible pathways. A homolytic cleavage of the methoxyl O−C bond leads to methane and 1,2-dihydroxybenzene whereas an induced route starting with abstraction of the phenolic hydrogen by cumyl radicals leads, after a cascade of reactions, to phenol, 2-hydroxybenzaldehyde, and 2-hydroxybenzyl alcohol.[202]

A gas-phase study of the decomposition mechanisms of nitromethane (CH_3NO_2), methyl nitrite (CH_3ONO), dimethylnitramine, and 1,3,3-trinitroazetidine [$(NO_2)_2C_3H_4NNO_2$] revealed that, after the initial bond fission, several reaction centres develop when very active radicals such as CH_3, H, NO, OH, HCO, and HNO combine to form the final mixture of products.[203] CH_3ONO decomposition gives large amounts of NO_2 and CH_3OH which are not produced in the CH_3NO_2 decomposition. The results indicate that the nitro−nitrite isomerization is minimal for the CH_3NO_2 system. The thermal decomposition of nitromethane in shock tubes (Scheme 14) has been analysed and the rate constants for the reactions (*a*) and (*b*) below (Scheme 14) were re-examined.[204] The rate constants for reaction (*b*) decreased slightly with temperature.

$$CH_3NO_2 \; \overset{a}{\rightleftharpoons} \; CH_3 \; + \; NO_2 \qquad\qquad CH_3 \; + \; NO_2 \; \overset{b}{\rightleftharpoons} \; CH_3O \; + \; NO$$

<div align="center">SCHEME 14</div>

A kinetic modelling study on the decomposition of benzene near 1000 K revealed that the presence of CH_4 product and the enhanced yields of H_2 above the predicted values could only be explained by invoking the reaction with 0.1% toluene impurity. The decomposition reaction is dominated by the unimolecular dissociation of C_6H_6 followed $H + C_6H_6 = C_6H_5 + H_2$ and $C_6H_5 + C_6H_6 = C_{12}H_{10} + H_2$ by the short chain process which results in the dehydrogenation of C_6H_6 producing $C_{12}H_{10} + H_2$.[205]

Propyne pyrolysis was studied in a flow reactor at 1210 K and 1 atm. Pressure-dependent rate coefficients of several reaction steps in propyne and allene pyrolysis were determined by *ab initio* calculations. The reactions include the mutual isomerization of propyne and allene, the chemically activated reactions with the H atom and of acetylene with methyl on C_3H_5 potential-energy surface. The reaction mechanism predicts the acetylene and methane production rates determined in the flow reactor.[206]

The pyrolysis of acetonitrile in a single-pulse shock tube over the temperature range 1400–2100 K was investigated. The major products detected were HCN, C_2H_2,

CH$_4$, and H$_2$ while minor products such as HCCCN, H$_2$C=CHCN, C$_2$H$_4$ and C$_4$H$_2$ were also detected. *Ab initio* chemical calculations revealed that the pyrolysis of acetonitrile is initiated by CH bond fission, forming a cyanomethyl radical. Products such as HCCN and H$_2$C=CHCN have been shown to arise from the decomposition of succinonitrile, that forms by the recombination of two cyanomethyl radicals.[207]

The kinetics of thermocyclization of 2,3-diethynylquinoxaline (**109**) (Bergman cyclization) have been studied in various solvents. Non-polar solvents give shorter half-lives and better yields. The cyclization rates observed were found to be solvent dependent.[208]


(**109**)

X = H, Cl
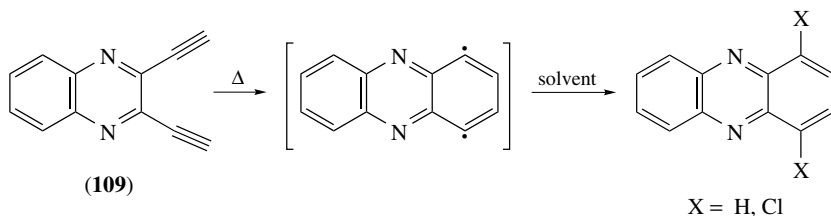
Other researchers have reported that the cyclization step is believed to be rate determining in the cycloaromatization (Bergman) reaction of aliphatic enediynes.[209] It has been found that the rate-limiting step is hydrogen abstraction by benzannelation. This effect should be attributable to the faster rate of retro-Bergman cyclization from the aromatic ring-condensed 1,4-didehydrobenzene diradicals and/or the slower rate of hydrogen abstraction by them.

The intramolecular thermal cyclotrimerization of dodeca-1,6,11-triyne (**110**) at 450–600 °C afforded 1,2,3,6,7,8-hexahydro[*a*5]indacene (**112**) and dehydro derivatives. An exothermic cycloaromatization mechanism has been proposed. An initial formation of a single bond gives diradical (**111**) which is then trapped by an alkyne.[210]

(**110**)   (**111**)   (**112**)
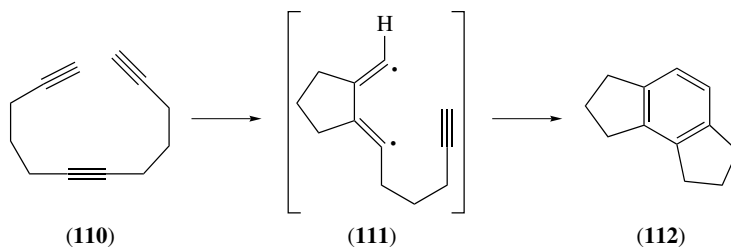
Thermolysis of benzoenyneallene (**113**) in cyclohexadiene at 75 °C produced the cycloaromatized adduct (**116**) in 22% yield. A biradical is believed to form through a cascade sequence involving an initial Myers cyclization. Trapping of the aryl radical centre in (**114**) with the tetrarylallenic moiety intramolecularly affords (**115**), having two triaryl radical centres. Hydrogen abstraction from cyclohexa-1,4-diene by (**115**)

(113) → **(114)**

↓

(116) ← **(115)**

(117) → **(118)**
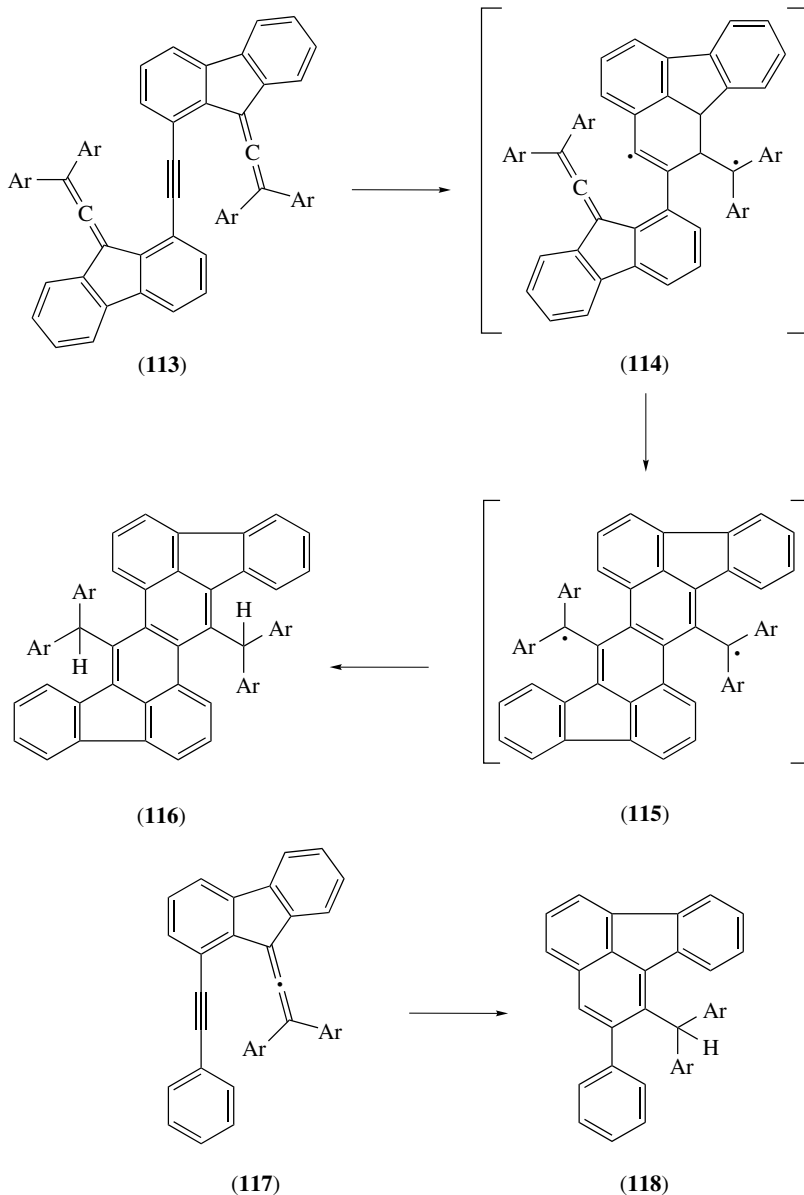
gives (**116**). Thermolysis of benzoenyneallene (**117**) furnished fluoroanthenes (**118**). The presence of the five-membered ring in (**113**) and (**117**) is essential to direct the initial biradical-forming step towards the Myers cyclization reaction. Without the five-membered ring, as in (**119**), the C(2)–C(6) cyclization reaction becomes the preferred pathway leading to benzofluorenes (**120**).[211]

(**119**) (**120**)

(**121**) (**124**)

R = H

(**122**) (**125**)

(**123**) (**126**)
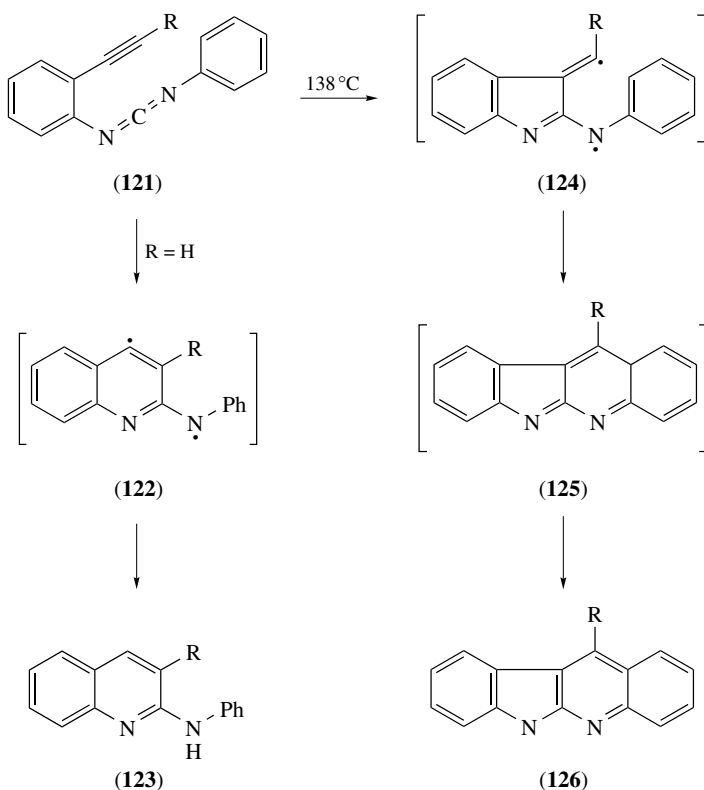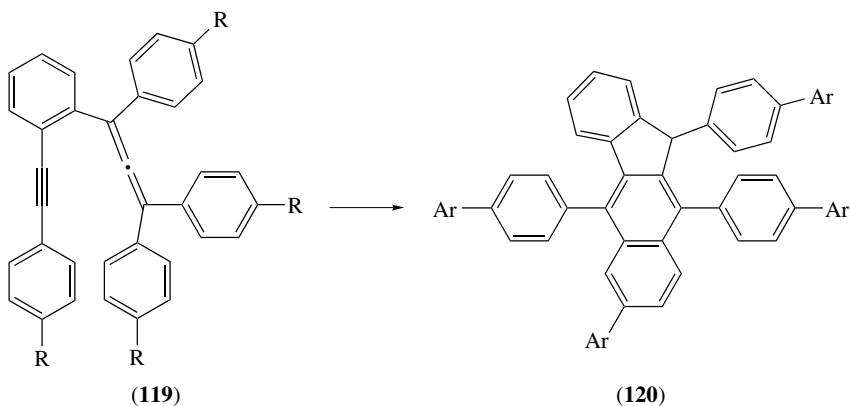
In a similar way, thermolysis of *N*-[2-(1-alkynyl)phenyl]-*N*′-phenylcarbodiimides (**121**) provides a new route for the synthesis of 6*H*-indolo[2,3-*b*]quinolines.[212] Thermolysis of (**121**) for R = H, in γ-terpinene at 138 °C produced (2-phenylamino)quinoline (**123**; 49%) and 6*H*-indolo[2,3-*b*]quinoline (**126**; 16%); (**123**) was produced via biradical (**122**) followed by hydrogen abstraction from γ-terpinene.

A two-step biradical pathway through (**124**) or one-step intramolecular Diels–Alder reaction could furnish (**125**), which underwent tautomerization to give (**126**). For R = TMS, Me, Pr, *t*-Bu, and Ph, 6*H*-indolo[2,3-*b*]quinolines (**126**) were obtained exclusively and in high yields.

The flash vacuum pyrolysis of *N*-benzylbenzotriazoles (**127**), [(2-benzotriazol-1-ylmethyl)benzonitrile and methyl 2-(benzotriazol-1-ylmethylbenzene)] and the corresponding *N*-benzylisoxazolones (**128**) has been studied.[213] The benzotriazoles lose nitrogen to give diradicals which undergo intramolecular hydrogen-atom transfer to give the benzaldehyde *N*-phenylimine when R = CN (**129**), or undergo cyclization (**130**, R = CO₂Me). The benzisoxazolones (**128**) rearrange initially to the corresponding benzaldehyde *N*-(2-carboxyphenyl)imines (**131**), which then undergo subsequent intramolecular addition reactions.
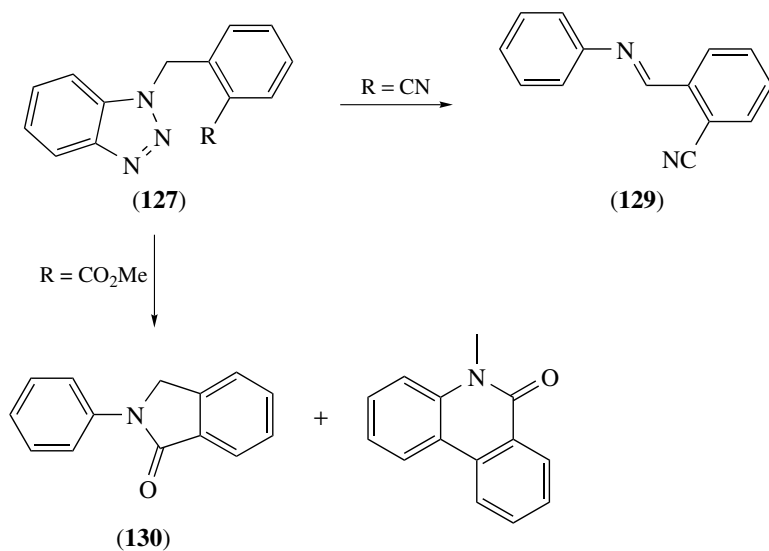
The same researchers have also studied the flash vacuum pyrolysis of *N*-acylbenzotriazoles (**132**) and of the corresponding *N*-acylbenziisoxazolones (**133**).[214] The benzotriazole derivatives gave compounds whose origin suggests a triplet diradical intermediate (**134**) formed by loss of N₂. The benzotriazole derivatives R = CO₂Me and R = CN gave benzoxazoles and the isoindolo[1,2,3,5]benzotetraazepine (**135**) for R = CN. For R = CH₂Cl, acrinidine was the only product. At lower temperatures the benzisoxazolones gave benzoxazole products, consistent with a singlet carbene intermediate. Thus, at low temperatures indolo[1,2*b*]benzoxazole is the major pyrolysis product, but this had triplet diradical properties at higher temperatures leading to the formation of acrinidine for the chloromethyl compound.

(128)

(131)

R = CN

R = CO₂Me

MeO₂C

(132)

R = CN, CO₂Me, CH₂Cl

(134)

R = CN, CO₂Me

R = CH₂Cl

R = CN

(135)
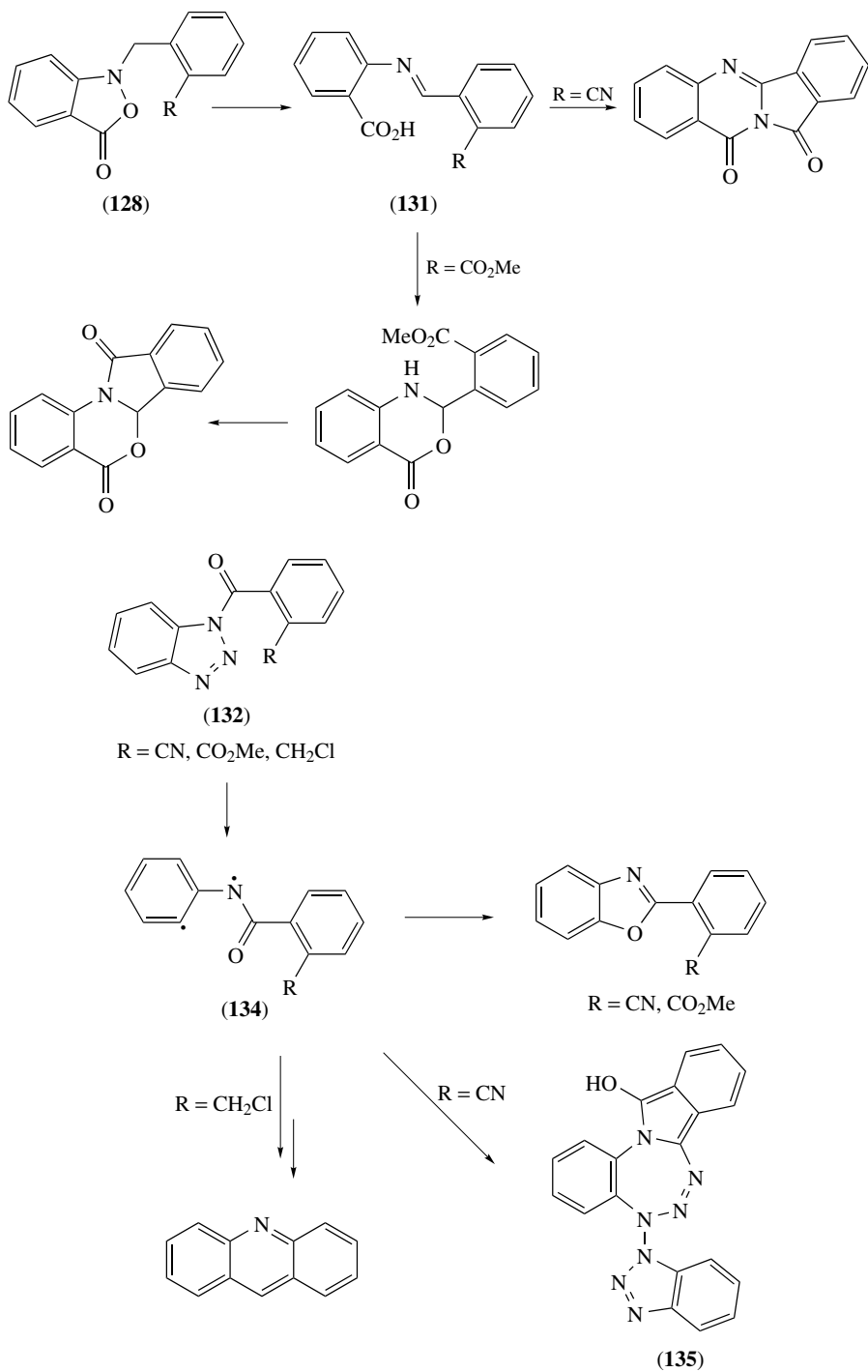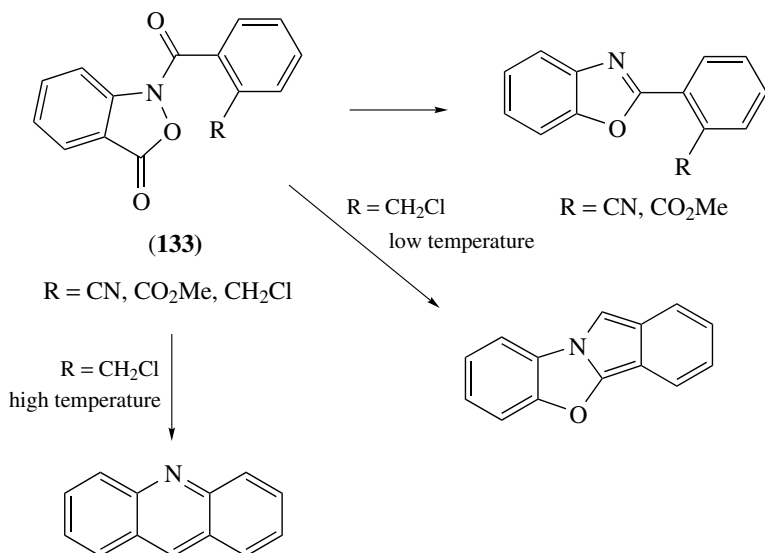
Photolysis

Two examples of enone/alkene photo-cycloaddition involving a rearrangement of the intermediate 1,4-diradical have been reported.[215] The photo-Fries rearrangement of 1-naphthyl acetate in aqueous solution of the novel antenna polyelectrolyte poly(sodium styrenesulfonate-co-2-vinylfluorene) (PSSS-VF) was studied. Three copolymers of different fluorine chromophores were synthesized. It was demonstrated that electronic excitation energy could migrate along the polymer chain before being transferred to the solubilized molecule. The reaction of naphthyl acetate is sensitized by light absorbed by the polymeric fluorine chromophores. The product contribution was dependent on the content of fluorine in the copolymer. The reaction in aqueous solution of PSSS-VF rich in fluorine chromophores occurs with high sensitivity to form the caged product, 2-naphthol, in 95% yield whereas sensitizers with low fluorine content gave 90% yield of the non-caged product, 1-naphthol.[216]

Photolysis of vinyl halides can induce both heterolysis of the C−X bond, thereby generating vinyl cations, and homolysis giving vinyl radicals. This competition between the two mechanisms was studied for 3-vinyl halides, 1,2,2-triphenylbromoethane (**136**) and 1-phenyl-2,2-bis(*o*-methoxyphenyl)-1-bromoethene and β-styrene.[217] Incursion of the photo-induced $S_{RN}1$ process, through the intermediate vinyl radical, is verified in the presence of reducing nucleophiles, such as the enolate ions of ketones and in part with $(EtO)_2PO^-$. Incursion of the heterolytic pathway and the intermediacy of the radical cation, occurs in the presence of weak electron-donor anions, such as NO_2^-, N_3^- and Cl^-. The vinyl cation of β-styrene gives phenylacetylene via an $E1$-type elimination.

(**136**)
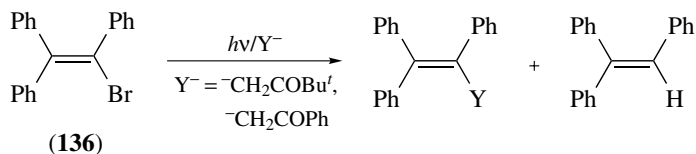
Photolysis of 1-(*o*-tolyl)-1-benzoylcyclopropane (**137**) and 1-(*o*-tolyl)-1-benzoyl-oxirane (**138**) resulted in hydrogen-transfer reaction to produce a 1,5-biradical intermediate (**139**). The biradical from (**137**) cyclized before cyclopropyl ring opening to give spiroindanol (**140**). However, with the biradical derived from (**138**), the oxiranyl ring opens up immediately after the initial hydrogen abstraction to give (**141**).[218]

(**137**) X = CH$_2$
(**138**) X = O

(**139**)

X = CH$_2$ X = O

(**140**)   (**141**)
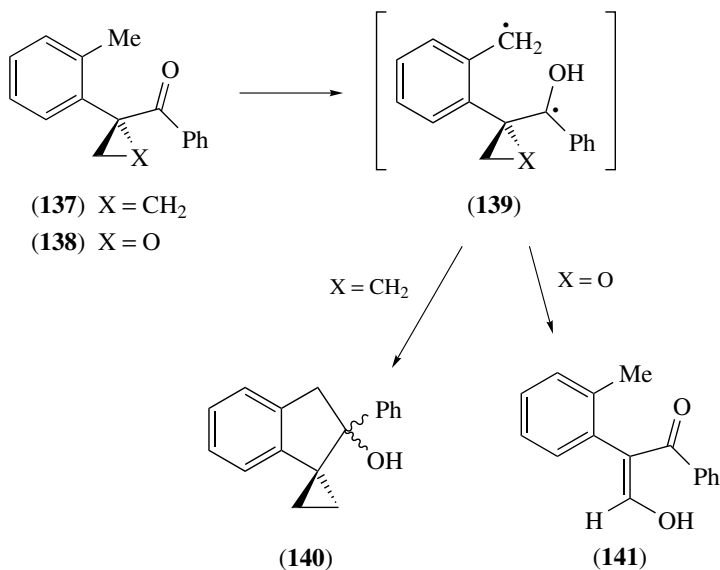
The photolysis of the diazobicyclo[2.2.2]heptene derivative (**142**) was studied at different temperatures and was found to give mixtures of *syn* (**143**) and *anti* (**144**) products.[219] The experimental data support the homolytic (S_H2) pathway as the prevalent reaction channel at elevated temperatures for the generation of the sterically encumbered *syn* product, whereas at low temperatures the triplet pathway operates and loss of the *syn* selectivity is observed. The loss of *syn* selectivity at low temperatures is due to efficient intersystem crossing in the singlet-excited azoalkane to afford the planar, nitrogen-free triplet diradical which unselectively ring closes.

(142)   (143)

double inversion

(144)
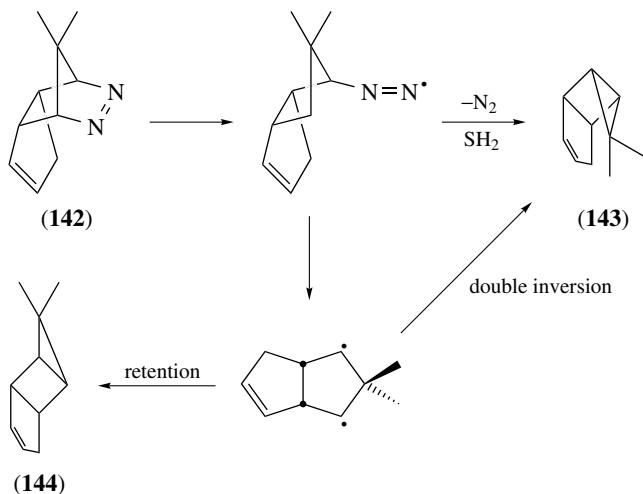
Copper(II), at very low concentrations, modulates the distribution of tolmetin stable photo-products (**145**) and (**146**), as well as inhibiting the DNA cleavage photo-induced by the drug. An electron-transfer process from the triplet carbanion (generated in the tolmetin photolysis) to the copper is involved.[220]

(145)

(146)
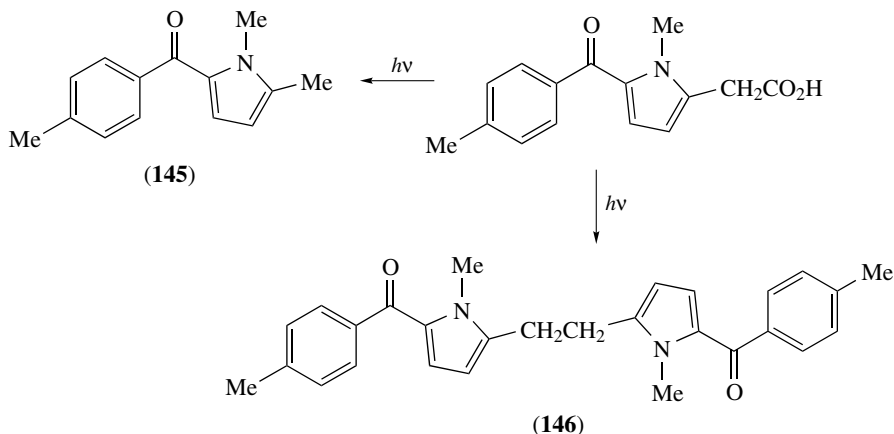
Radioloysis

A review of aromatic substitution by the $S_{RN}1$ reaction has been published.[221] The reactions of enolate ions of 2-acetyl-(**147**) and 3-acetyl-1-methylpyrroles (**148**) with aryl iodides and neopentyl iodides under irradiation conditions afforded good yields of substitution products by $S_{RN}1$ mechanisms, without the need for initiator.[222] These
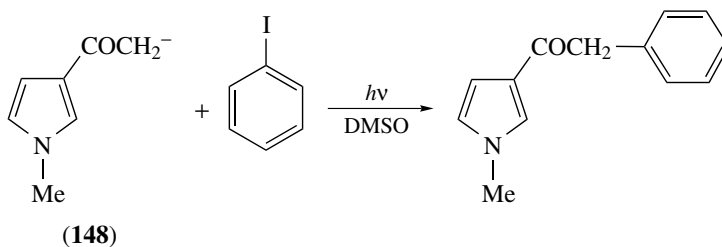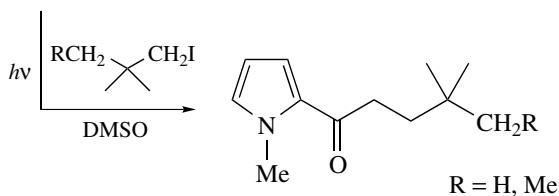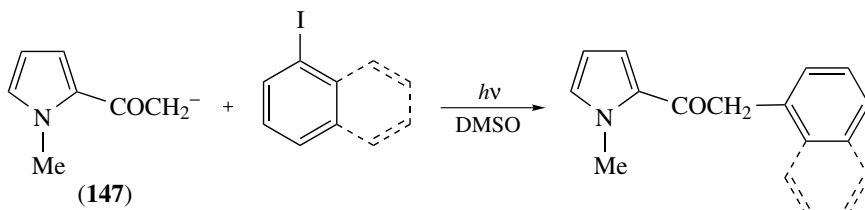
anions were found to be more reactive than the enolate ion of acetophenone and are able to participate in initiation in contrast to the enolate ions of the five-membered ring analogues 2-acetylthiophene and 2-acetylfuran. The reactions of 2-iodo- and 1,2-dihalo-adamantanes with carbanions under $S_{RN}1$ conditions have been reviewed.[223] The reactions of 2-iodoadamantane with two carbanions ($^-CH_2COPh$) and ($^-CH_2NO_2$) by the $S_{RN}1$ mechanism under irradiation by entrainment with the enolate ion of acetone or by induction with FeBr$_2$ have been examined (Scheme 15). A decrease in reactivity of 2-adamantyl radicals with bulky carbanions (such as anthrone and 2-naphthyl methyl ketone) and with less-reactive nucleophiles has been observed.

Chloroadamantanes (149) and (150) reacted with $^-CH_2COPh$ to afford the monosubstitution products (151) and (152) as intermediates, the intramolecular electron-transfer reaction of the radical anion intermediate being a slow process. Product (151) with chlorine in the 1-position reacted further to give (153), whereas (152) with chlorine in the 2-position is unreactive, showing that the 1-position is the more reactive. 1,2-Diiodoadamantane (154) reacted with $^-CH_2NO_2$ to give the monosubstitution products (155) and (156). This implies that the intramolecular electron-transfer reaction of the radical anion is a slow process. The fact that (155) was formed as major product and (156) was the minor product shows that, when (154) accepts an electron, fragmentation occurs faster at the 1-position than the 2-position.

SCHEME 15

(**149**)   (**151**)   (**153**)

(**150**)   (**152**)

(**154**)   (**155**)   +   (**156**)
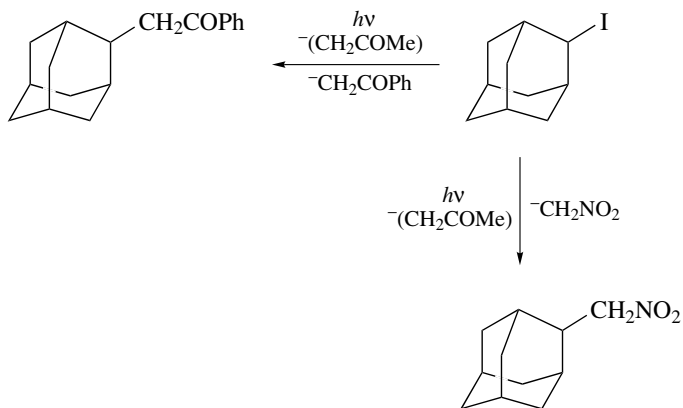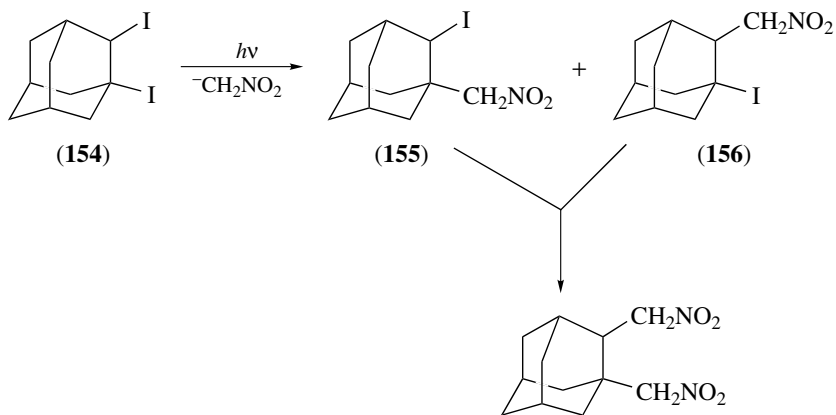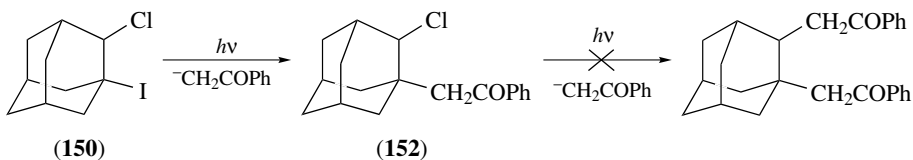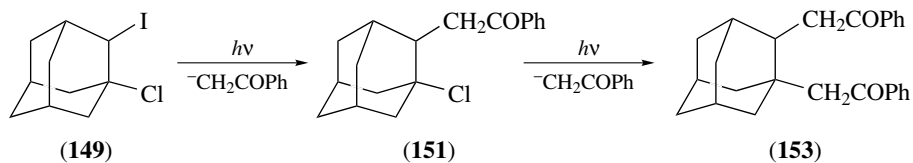
The 1,4-diphenylbutane-1,4-diyl biradical (**157**) was generated from 1,4-dichloro-1,4-diphenylbutane or 2,5-diphenylcyclopentanone under irradiation conditions giving rise to styrene, 1,2-diphenylcyclobutane, and 1-phenyl-1,2,3,4-tetrahydronaphthalene.[224] Tetrahydronaphthalene forms from 1,4-biradicals that have a phenyl group attached to one of the radical centres. Irradiation of 2-phenylcyclopentanone resulted in the formation of tetrahydronaphthalene.
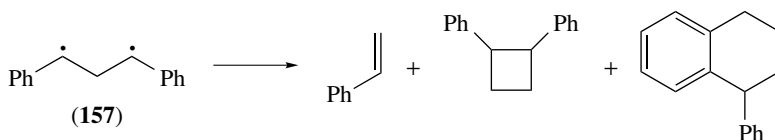
Hydroxyl radicals were generated radiolytically in N_2O-saturated aqueous solutions of thiourea and tetramethylthiourea.[225] Conductometric detection showed that HO^- and a dimeric radical cation were produced. The dimeric radical cation is formed by addition of a primary radical to a molecule of thiourea. In basic solution, the dimeric radical cation decays rapidly to a dimeric radical anion, which is formed via neutralization of the cation and subsequent deprotonation of the neutral dimeric radical (Scheme 16). This was not observed in tetramethylurea. These dimeric radical cations of thiourea and tetramethylurea are strong oxidants and readily oxidize the superoxide radical, phenolate ion, and azide ion.
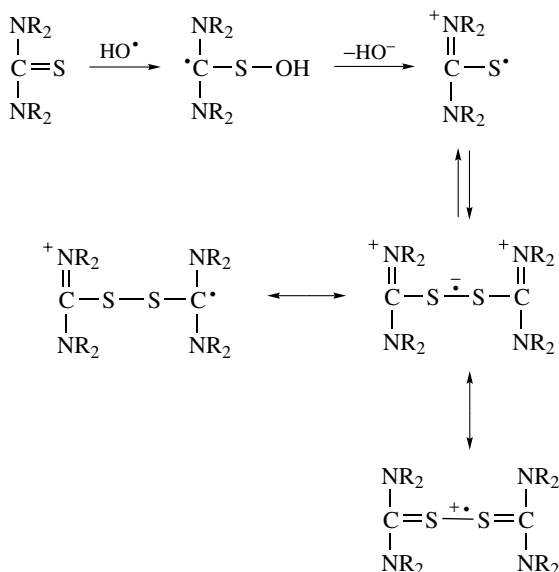
SCHEME 16

The nature and redox properties of the transient species formed on pulse radiolysis of aqueous solutions of 2-(phenylthio)ethanol have been reported.[226] Radiolytic reduction has been used to study the substituent effect on nitrobenzyl carbamate fragmentation designed as triggers for bioreductve prodrugs. A series of 2,3- and α-substituted 4-[*N*-methyl-*N*-(4-nitrobenzyloxycarbonyl)amino]phenylacetamides (**158**) were studied. The hydroxylamines were generated by ^{60}Co γ-irradiation of the nitro compounds in aqueous phosphate-buffered propan-2-ol. Electron-donating substituents in the 2-position of the benzyl ring accelerated fragmentation of the hydroxylamines.[227]

(**158**)
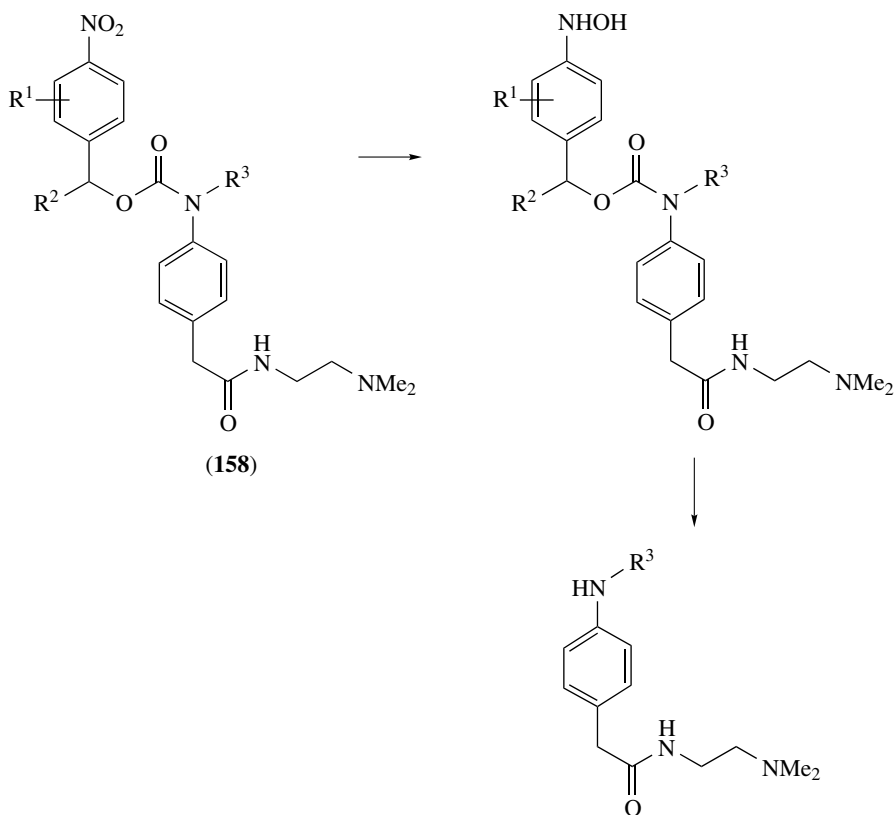
The solute benzene radical cation was formed on pulse radiolysis of an acidic aqueous solution of benzene. The transient optical absorption bands ($\lambda_{max} = 310$, 350–500 nm) were assigned to the solute benzene radical cation which is formed on acid-catalysed dehydration of the OH adduct. The radical cation is able to undergo an electron-transfer reaction with Br$^-$ and was found to be a strong electron oxidant.[228]

Pulse radiolysis has been used to study the complex reaction that follows electron addition to hydroxybenzophenones (HOBPs).[229] The various radical species involved have been characterized spectrally and their pK_a values evaluated. The differences

observed for *p*-, *o*-, and *m*-derivatives have been explained. Reduction of hydroxy-benzophenone was also studied using dimethyl ketyl radicals as reductants in mixed water–acetone–propanol solvents. These radicals have been found to react via adduct formation with the HOBPs, whereas H-atom transfer reaction have been identified in the reactions with ⁻OBPs.

A pulse radiolysis study of the reactivity of the radical cations generated from 2-, 3- and 4-(4-methoxyphenyl)alkanols (**159**), where the OH group is separated from the aromatic ring by an increased number (from 2 to 4) of carbon atoms, has shown that the cations react with HO^- forming products of $C_\alpha–C_\beta$ bond cleavage. Either O–H deprotonation is coupled to C–C bond cleavage or a radical zwitterion is first formed which undergoes intramolecular electron transfer coupled to C–C bond cleavage. An oxyl radical intermediate is suggested for the base-catalysed decay of 3-(4-methoxyphenyl)propanol radical cation. This radical undergoes 1,2-H atom shift leading to the formation of 3-(4-methoxyphenyl)propanal. The oxygen acidity disappears when four carbon atoms are interposed between the OH group and the aromatic ring. These systems behave as carbon acids both in acidic and aqueous solutions.[230]

$(CH_2)_nOH$

OMe

(**159**)

n = 2, 3, 4
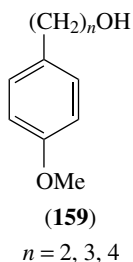
A similar kinetic and product study of the side-fragmentation reactions of a series of radical cations [$4\text{-MeOC}_6\text{H}_4\text{CH(OH)R}^{+\bullet}$] has also been carried out in acidic and basic solution.[231] At pH 4, the radical cations undergo C_α-H deprotonation for R = H, Me and Et and $C_\alpha–C_\beta$ bond cleavage for R = *t*-Bu, CH(OH)Me and CH(OMe)Me. Both types of cleavage are observed for R = *i*-Pr. Hydrogen bonding of the α-OH group with the solvent stabilizes the transition state of the C–C bond fragmentation but not of the deprotonation process. In the presence of ⁻OH the 1-arylalkanol radical cations become oxygen acids and deprotonation involves the alcoholic C_α-OH bond. The proton is transferred to the base to give the benzyloxy radical either via radical zwitterions (which undergo intramolecular electron transfer) or directly (electron transfer coupled with deprotonation.) The benzyloxy radical can then undergo a β-C–C bond cleavage to form 4-methoxybenzaldehyde and R• or a formal 1,2-H shift to form an α-type radical.

Irradiation of 1-phenylcycloalkenes (**160**) with cyano-aromatics electron-accepting sensitizers in MeCN and benzene containing 1 M methanol gave *trans*-(**161**) and *cis*-isomers (**162**) of anti-Markovnikov adducts.[232] The (**161**)/(**162**) isomer ratio was found to depend on the ring size of 1-phenylcycloalkene but not on the sensitizer used. The mechanism of the reactions was studied by semiempirical MO calculations.
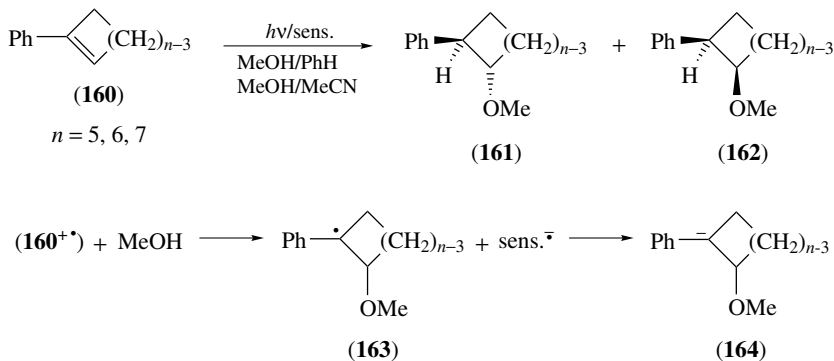
The stereoselectivity of anti-Markovnikov adducts (**161**) and (**162**) produced through photo-induced electron-transfer reaction of (**160**) with MeOH in MeCN depends on the optimum structures and stabilities of the corresponding radical and carbanion intermediates (**163**) and (**164**). In PhH, steric hindrance in an exciplex, comprising an excited singlet sensitizer and (**160**), forced *cis* addition of MeOH to (**160**) to give *trans*-isomer (**161**) as the major addition product.

Photochemical irradiation of α,β-unsaturated ketones in the presence of $Me_3SiOP(OR)_2$ (R = Me, Et) gave phosphonosilylation products of 1,4-conjugate additions which are hydrolysed to the phosphono ketones (**165**).[233] The envisaged initiation step is electron transfer to the triplet excited state of the enone to generate a radical ion pair.

Photo-irradiation of the tryptamine (**166**) produces an intermediate diradical cation that leads to the formation of an azonino[*cd*]indole.[234] This is the first example of a vinylogous Witkop cyclization.
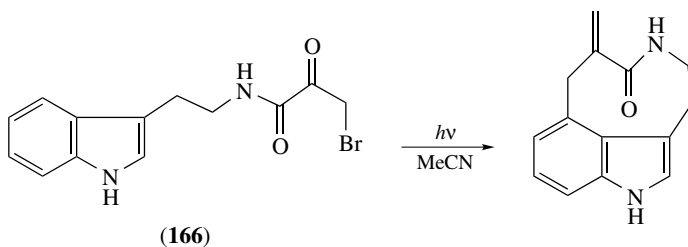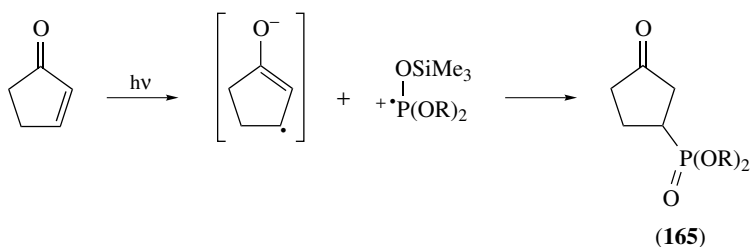
N-Substituted-1-aza-1,4-dienes (**167**) undergo the di-π-methane rearrangement to give cyclopropane derivatives when irradiated in the presence of 9,10-dicyanoanthracene (DCA) as an electron transfer sensitizer. It is the second example of a rearrangement of the di-π-methane type that takes place in the ground state of the radical cation intermediate.[235]

(**167**)
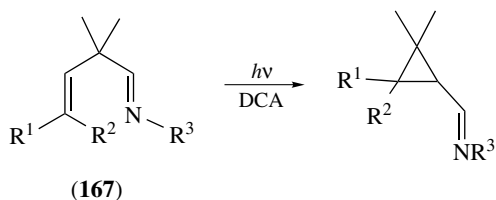
Autoxidation

The $Mo(CO)_6$–TBHP system promoted autoxidation of 5-alkylidenene-4,5-dihydrofurans (**168**) under mild conditions, allowing the preparation of primary, secondary and tertiary furyl hydroperoxides.[236] A radical mechanism has been proposed and was supported by the experimental data.

(**168**)
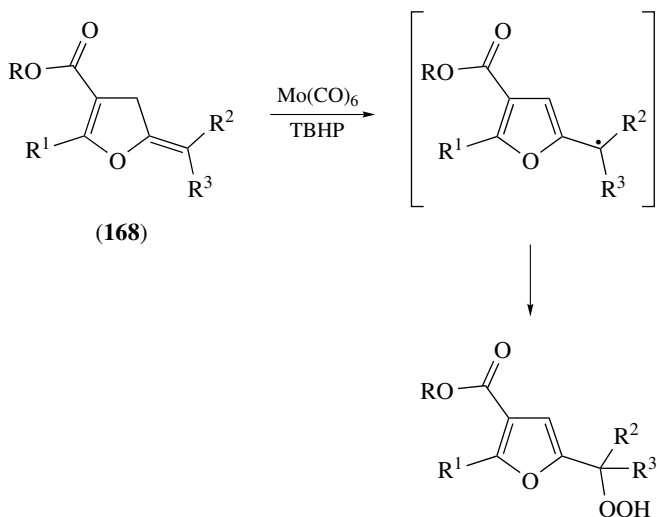
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