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A NEW METHOD IN RADICAL CHEMISTRY: GENERATION OF RADICALS BY PHOTO-INDUCED ELECTRON TRANSFER AND FRAGMENTATION OF THE RADICAL CATION

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1. PRINCIPLES OF THE METHOD

1.1 INTRODUCTION

The generation of radicals for non-chain reactions is often obtained through redox processes.[1,2] For example, anodic oxidation or the reaction with a metal compound generates the radical cation of an organic molecule,[3,4] and this fragments (often deprotonates) to yield a cation and a neutral radical, the latter species then being the active intermediate in the desired process.

$$R\text{-}X + M^{n+} \rightarrow R\text{-}X^{+\cdot} + M^{(n-1)+} \quad (1)$$

$$R\text{-}X^{+\cdot} \rightarrow R^{\cdot} + X+ \quad (2)$$

This method is widely used and it results in many synthetically useful procedures. However, it suffers some ambiguities, e.g. when X=H the metal compound may act through hydrogen atom abstraction rather than through single electron transfer followed by proton transfer,[5] or a metal-radical complex rather than the free radical may be the actual reacting species.[6,7] Furthermore, radicals are usually more easily oxidized than the substrates from which they are generated, and under the strong oxidizing conditions required for the first step they may undergo further oxidation to the corresponding cation.

$$R^{\cdot} + M^{n+} \rightarrow R^{+} + M^{(n-1)+} \quad (3)$$

Thus the chemistry of the latter species may compete with, or overcome, the desired radical chemistry. Such a two-step oxidation may of course be useful in itself, e.g. in the side-chain functionalization of aromatics (eq.4),[8] but this is not the point here.

$$ArCH_2X \xrightarrow{-e^-} ArCH_2X^{+\cdot} \xrightarrow{-X^+} ArCH_2^{\cdot} \xrightarrow{-e^-} ArCH_2^{+} \xrightarrow{+Nu^-} ArCH_2Nu \quad (4)$$

A completely different approach, and one which may overcome some of the previous limitations, is photo-induced electron transfer (PET). It is well known that electronic excited states are both strong oxidants and reductants, their redox potential differing from that of the corresponding ground states by the excitation energy, e.g. (eq.5):

$$E_{red}(\text{Excited State}) = E_{red}(\text{Ground State}) + E_{exc} \quad (5)$$

As an example, the singlet state of aromatic nitriles and the triplet state of aromatic ketones have largely positive reduction potentials (e.g. 1,4-dicyanobenzene, (DCB), Ered(S1) 2.67 V vs SCE in MeCN; trifluoroacetophenone, (TFA), Ered(T1) 1.65 V*) and thus are comparable or better oxidants than most commonly used metal compounds (e.g. CeIV, Ered 1.28 V vs SCE in water), while the corresponding ground states would hardly be considered as oxidants (DCB, Ered -1.60 V; TFA, Ered -1.38 V). This makes single electron transfer involving excited states of organic molecules (both singlet and triplet) a very common occurrence, while it is rather uncommon in ground state reactions. The process occurring is represented in eq.6.

$$R\text{-}X \xrightarrow{A^* \; A^-} R\text{-}X^{+\cdot} \xrightarrow{-X^+} R^{\cdot} \quad (6)$$

The scenario here is completely different from the previous one. The oxidant is an organic molecule, and acts as such only when excited by a photon. Thus, the reaction can be carried out in an organic solvent (provided that this is a polar one, otherwise the energy for the separation of the radical ions produced in the electron transfer step is large and must be added to the thermodynamic balance), while usually problems of mutual solubility severely limit the choice of solvent when metal compounds are used. The oxidant is continuously generated in the homogeneous solution by light absorption, and is present at a very low steady-state concentration. This makes it unlikely that it interacts with any species different from the substrate, and virtually impossible that it oxidizes the short-lived radical any further. Therefore the radical chemistry takes place free from the chemistry of the corresponding cation, and the large choice of experimental conditions available (solvent, additives, temperature) should make it easy to influence the course of the radical reaction.

Note. The acronyms DCA, DCB, DCN, TCB, and TFA, used throughout this paper, are defined in Table 1.

Some limitations of the method are also apparent, however. Thus, back electron transfer within the radical ion pair generated in the primary step is by definition a favoured process (eq.7),[13] and thus fragmentation of the radical cation will take place efficiently only if it is fast enough to compete with it.[14]

$$A^{-\cdot} + R\text{-}X^{+\cdot} \rightarrow A + R\text{-}X \quad (7)$$

Furthermore, the molecule used as the photochemical oxidants (as it appears from the examples in Table 1, this is often an aromatic derivative) as well as the corresponding radical anion formed in the electron transfer step will generally be quite reactive towards radicals. Therefore, the following reactions (eqs.8,9) are expected to be fast, and it may turn out that it is difficult to divert the radical reactivity into different paths.

$$R\cdot + A \rightarrow \text{Products} \quad (8)$$
$$R\cdot + A^{-} \rightarrow \text{Products} \quad (9)$$

The possibility that photo-induced electron transfer (PET) generation of radical cations and their fragmentation offers a novel and unusually mild method for the generation of radicals was recognized relatively early,[15] but applications of this principle are as yet limited, despite the fact that PET chemistry has developed rapidly in recent years.[9] Since the method appears promising, we thought it worthwhile to discuss the feasibility and the characteristics of each step in the desired sequence (photochemical oxidation, fragmentation, reactions of the radical). Obviously, a parallel discussion could be devoted to the generation of radicals following PET in the opposite direction, *viz* reduction of a substrate and fragmentation of the radical anion to yield a radical and an anion.

1.2 THE OXIDATION STEP

Electron transfer involving excited species has been discussed extensively elsewhere,[9-12] and we do not need to go into the theory of the phenomenon here. For all practical purposes, electron transfer between organic molecules occurs at the diffusion-controlled rate when it is exergonic, and it is still fast when slightly endergonic as calculated by the Weller equation (eq.10),[16] containing the relevant half-wave potentials, the energy of the excited state involved, and a coulombic term.

$$\Delta G = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A)\ E_{exc}(A) - 1/\varepsilon a \quad (10)$$

In polar solvents the last term is almost negligible, and this allows the definition of the redox potential in the excited state (eq.11).

$$E_{1/2}^{red}(A^*) = E_{1/2}^{red}(A) - E_{exc}(A) \quad (11)$$

Excited states count among the strongest oxidants available. Extensive compilations of the relevant parameters may be found in the literature.[9,10,12,17] Some examples are shown in Table 1, while Table 2 gives an idea of the variety of substrates which can be oxidized under these conditions. Of course, in order for electron transfer to be efficient, it is required that the substrate concentration be high enough to quench a substantial fraction of the acceptor excited state. This is usually not a problem, despite the short lifetime of such species, since PET is so fast. Furthermore, in order that side processes are minimized, it is desirable that neither A* nor the radical anion $A^{-\cdot}$ generated simultaneously with $R\text{-}X^{+\cdot}$ undergo any fast chemical reaction.

Table 1. Reduction Potentials of Some Sensitizers[a]

Acceptor	Ered	$E_{red(S_1)}$	$E_{red(T_1)}$
1,4-Dicyanobenzene (DCB)	- 1.60	2. 67	
1,2,4,5-Tetracyanobenzene (TCB)	-0.66	3.44	
1,4-Dicyanonaphthalene (DCN)	-1.28	2. 17	
9, 10-Dicyanoanthracene (DCA)	-0.89	1.97	
2,4,6-Triphenylpyrylium tetrafluoroborate	-0.29	2.53	
N-Methylacridinium tetrafluoroborate[b]	-0.43	2.32	
Tetrachloro-*p*-benzoquinone	0.02		3.33
α,α,α-Trifluoroacetophenone (TFA)	- 1.3 8		1.65

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a) in V *vs* SCE. Data from ref. 12 b) from ref. 157

Table 2. Oxidation Potentials for some Organic Substrates and Free Energy for the Fragmentation of the Corresponding Radical Cations.

Substrate	E_{ox}[a]	Fragmentation	$\Delta G(R\text{-}X^+)$[b]
$PhCH_3$	2.4[c]	$PhCH_2\cdot + H^+$	- 14.0[c]
			52[d]
$Ph_2CHCHMePh$	2.15[e]	$Ph_2CH\cdot + PhMeCH^+$	12.7[e]
cis-MeCH=CHMe	2.17[f]	$MeCH{=}CH_2\cdot + H^+$	-9.9
Me_3N	1.15[c]	$Me_2NCH_2\cdot + H^+$	6[c]
Me_20	3.1[g]	$MeOCH_2\cdot + H^+$	13
Me_4Si	3[h]	$Me\cdot + Me_3Si^+$	15[h,i]
$(Me_3Si)_20$	2.8[h]	$Me\cdot + Me_3SiOSiMe_2^+$	14[h,i]

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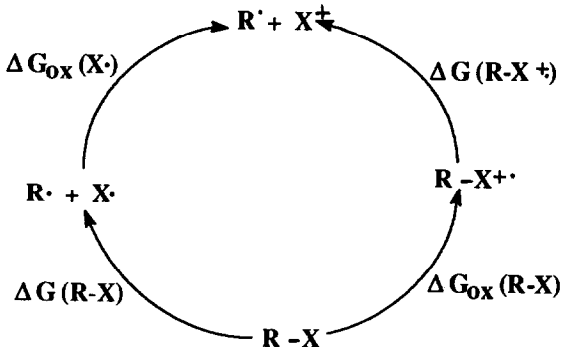
a) in V *vs* SCE b) in kcal mol^{-1}, for the calculation (based on the references given in the notes) and a caveat see the text. c) ref. 18. d) in the gas phase, ref.24. e) ref.20. f) ref. 158. g) approximated from the IP value, ref. 159 through the Miller equation, ref. 160. h) ref.21. i) calculated in the gas phase; the solution value is expected to be lower.

Aromatics, heterocycles and some ketones are well suited for this purpose, since they undergo little monomolecular photochemistry, and thus the unquenched sensitizer causes no trouble, and likewise the radical anion suffers no fragmentation. Typical examples are aromatic hydrocarbons and nitriles, pyrylium, pyridinium and acridinium salts (in these cases the oxidant is a cation and yields a neutral radical in the PET step), quinones and aromatic ketones.

1.3 FRAGMENTATION OF THE RADICAL CATION

The fragmentation of the radical cation is obviously the key step in the desired sequence and it must be a fast process in order to occur with reasonable efficiency, since it competes with back electron transfer. Thus, it is required that the barrier for fragmentation is low. The thermochemical cycle in Fig.1 and eq.12 relate the free energy change for bond dissociation in the radical cation [$\Delta G(R\text{-}X^{+\cdot})$] to the corresponding quantity for the neutral molecule [$\Delta G(R\text{-}X)$].[18-22] The difference between these two quantities is equal to the difference between the free energy for the oxidation of the neutral fragment X· to yield the obtained cation X^+ and the free energy for the single electron oxidation of the starting substrate R-X.

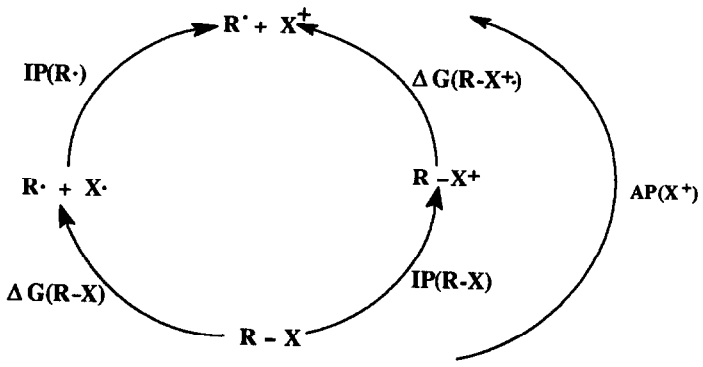


$$\Delta G(R\text{-}X^{\cdot +}) = \Delta G(R\text{-}X) + \Delta G_{ox}(X^{\cdot}) - \Delta G_{ox}(R\text{-}X) \qquad (12)$$

Figure 1. Thermochemical cycle for the oxidative fragmentation of a molecule R-X.

Application of eq.12 requires that a consistent set of thermodynamic data be used. A first possibility (Fig.2) is to make recourse to the onset ionization potentials of the substrate [IP(R-X)], which are available for a large variety of organic molecules from PES measurements, and to the appearance potential of the cation [$AP(X^+)$] from mass spectrometric measurements (IP of radicals have rarely been measured directly).[23a]

Some problems are inherent in this approach. First, measured quantities are vertical IP (IP_v) rather than the required adiabatic values (IP_a), and this leads to an overestimate of the single-electron bond energies. Second, the values obviously refer to the gas phase and, when oxidation in a condensed phase is considered, the expression must be corrected in order to take into account the interaction with the solvent (eq.16).



$$\Delta G(R\text{-}X^{+\cdot}) = \Delta G(R\text{-}X) + IP(X\cdot) - IP(R\text{-}X) \quad (13)$$

$$AP(X+) = IP(R\cdot) + \Delta G(R\text{-}X) \quad (14)$$

$$\Delta G(R\text{-}X^{+\cdot}) = AP(X^{+}) - IP(R\text{-}X) \quad (15)$$

Figure 2. Thermochemical cycle for the oxidative fragmentation of a molecule R-X in the gas phase.

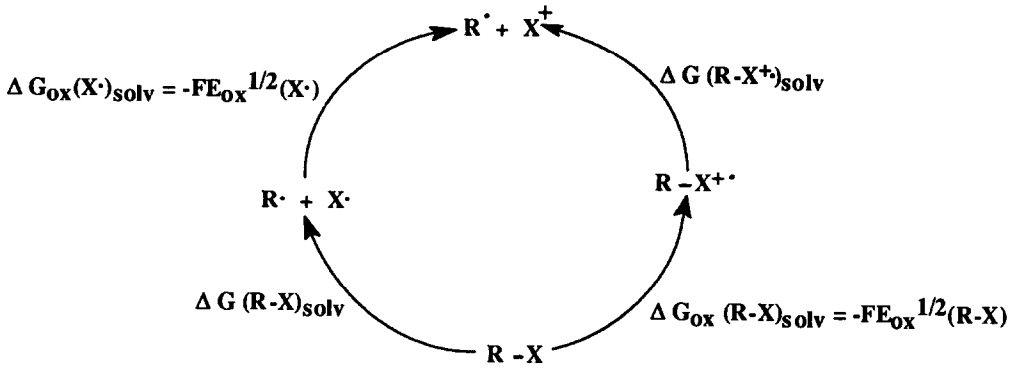
$$\Delta G_{solv}(R\text{-}X^{+\cdot}) = \Delta G_{solv}(R\text{-}X) + IP(X\cdot) - IP(R\text{-}X) + \Delta G_{solv}(X^{+}) - \Delta G_{solv}(R\text{-}X^{+\cdot}) \quad (16)$$

Solvation energies for the formation of charged species are high (as an example 48 kcal mol^{-1} for Me_3C^+).[23b] However, since the solvation terms for the two processes of eq. 17 and 18 are subtracted in

$$R\text{-}X \rightarrow R\text{-}X^{+\cdot} + e^- \qquad [\Delta G_{solv}(R\text{-}X^{+})] \quad (17)$$

$$\text{and } X^{\cdot} \rightarrow X^{+} + e^- \qquad [\Delta G_{solv}(X^{+})] \quad (18)$$

eq.15 , they may cancel out if they are of similar value. It is likely that this holds true when $R\text{-}X^+$ and X^+ are similar in size and charge distribution, e.g. when they are both π-delocalized or both heteroatom-stabilized organic cations. Indeed, it has been shown for a group of substrates actually meeting such conditions that the value for the bond dissociation energies in the gas phase and in acetonitrile are almost the same (± 1-4 kcal mol-1).[24] However, it is hardly to be expected that the two terms are equivalent when the two cations are structurally different, e.g. for the deprotonation of an organic radical cation, or for the detachment of the silyl cation (a localized σ species) from the benzyltrimethylsilane radical cation (a delocalized π species). In this case prediction is difficult.



$$\Delta G(R\text{-}X^{+\cdot})_{solv} = \Delta G(R\text{-}X)_{solv} - F[E_{ox}{}^{1/2}(R\text{-}X) - E_{ox}{}^{1/2}(X\cdot)] \qquad (19)$$

Figure 3. Thermochemical cycle for the fragmentation of a molecule R-X in solution.

Another approach is to make use of voltammetric oxidation potentials (either reversible, or corrected when irreversible) of the substrates and, when available, of the radicals (see Fig.3, eq.19). A handful of oxidation potentials for the radicals have now been measured, but since these are transient species, a cyclic measurement cannot be made, and thus it cannot be established whether these are reversible, again introducing a source of error.[18,19,24]

Finally, semiempirical or *ab initio* methods can be used to obtain an estimate of the bond strength in radical cations,[25-27] provided that the Hamiltonian used is suitable for open-shell species. In this case also the results are relevant to the free, rather than to the solvated species.

It must be noted that the thermochemical cycles of Fig.1-3 have been defined in terms of free energy in order to use oxidation or ionization potentials. However, the available tabulations contain bond dissociation enthalpies rather than energies. If eq.12 is rewritten in terms of enthalpies, eq.20 results. Here the entropic contribution is present as a difference. If the radical cation and the cation produced from it are differently solvated, the fragmentation entropy for the radical cation according to eq.2, $\Delta S(R\text{-}X^{+\cdot})$, is expected to differ from the entropy for the homolytic fragmentation of the neutral molecule, $\Delta S(R\text{-}X)$; if not, the entropic contribution can be neglected, and eq.20 simplifies to eq.21.

$$\Delta H(R\text{-}X^{+\cdot})_{solv} = \Delta H(R\text{-}X)_{solv} - T[\Delta S(RX)_{solv} - \Delta S(RX^{+\cdot})] - F[E_{ox}(RX)_{solv} - E_{ox}(X\cdot)_{solv}] \quad (20)$$

$$\Delta H(R\text{-}X^{+\cdot})_{solv} \approx \Delta H(R\text{-}X)_{solv} - F[E_{ox}(RX)_{solv} - E_{ox}(X\cdot)_{solv}] \qquad (21)$$

Activation entropies for the fragmentation of some *N,N*-dimethylaminobicumenes have been found to be in the range -12 to -27 cal $K^{-1}mol^{-1}$.[28]

When more redox data in solution become available, a general rationalization of radical cation cleavage will be possible. This is now limited to some homogeneous series of substrates. Thus, Arnold has shown that

in a series of triphenyl- and tetraphenylethanes the radical cation (formed by electron transfer to p-dicyanobenzene) cleaves at room temperature when $\Delta H(R\text{-}X^{+\cdot})$ evaluated from eq.21 is ≤16 kcal mol^{-1}.[20] Furthermore, the sense in which the radical cation cleaves (i.e. which fragment becomes the radical and which becomes the cation, eq.22 vs eq.23) is accurately predicted on the basis of the oxidation potentials of the two radicals: if $E_{ox}{}^{1/2}(ArRR'C^{\cdot}) > E_{ox}{}^{1/2}(Ar'R''R'''C^{\cdot})$ then eq.22 is followed and vice versa in the other case. When the difference is less than 0.1 V both reactions occur to a comparable extent, and the ratio between the products from the two paths has been used to estimate the relative oxidation potentials of radicals when these are not known.[20]

$$ArRR'CCR''R'''Ar'^{+\cdot} \rightarrow ArRR'C^{\cdot} + Ar'R''R'''C^{+} \quad (22)$$

$$\rightarrow ArRR'C^{+} + Ar'R''R'''C^{\cdot} \quad (23)$$

Where no solution data are available, gas-phase or theoretical results can be used. These are reasonably accurate when the structural conditions discussed above are met, and, when this is not the case, they may nevertheless be useful for obtaining a first estimate of the single electron bond energy and of the sense of the fragmentation.

The weakening of the chemical bonds on ionization is substantial. Some examples are shown in Table 2 in order to give an idea of the effect, although one should be careful in using the reported values, since, as has been mentioned above, the data used for the calculations are not always homogeneous. It is important to recognize that the ΔG for fragmentation does not depend on the characteristics of the radical formed ($R^{\cdot}$). This allows some, perhaps not intuitive, predictions. When various precursors of the same radical are compared, both $E_{ox}{}^{1/2}(R\text{-}X)$ and $E_{ox}{}^{1/2}(X^{\cdot})$ decrease when X is made a better donor. However, the effect on the first quantity is smaller than that on the second; as an example, the weakening of the bond obtained in the radical cation of methyl ß-phenethyl ether is larger than that of the corresponding amine, a better donor.

$$PhCH_2CH_2OMe^{+\cdot} \rightarrow PhCH_2^{\cdot} + MeO{=}CH_2^{+} \quad (24)$$

(calcd weakening of the bond 54 kcal mol^{-1})[29]

$$PhCH_2CH2NMe_2^{+\cdot} \rightarrow PhCH_2^{\cdot} + Me_2N{=}CH_2^{+} \quad (25)$$

(calcd weakening of the bond 48 kcal mol^{-1})[29]

Likewise, when precursors of different radicals with the same electrofugal group are compared, both $\Delta G(R\text{-}X)$ and $E_{ox}{}^{1/2}(R\text{-}X)$ change in the same sense, but, at least for large variations, the effect on the latter quantity is more important. As an example, the tetraalkylsilanes are less easily oxidized than benzyltrialkylsilanes, but they cleave more easily as the radical cation.

$$PhCH_2SiMe_3^{+\cdot} \rightarrow PhCH_2^{\cdot} + Me_3Si^{+} \quad (26)$$

(calcd $\Delta G(R\text{-}X^{+\cdot}) \approx 30$ kcal mol^{-1})[22,29]

$$CH_3CH_2SiMe_3{+\cdot} \rightarrow CH_3CH_2^{\cdot} + Me_3Si^{+} \quad (27)$$

(calcd $\Delta G(R\text{-}X^{+\cdot}) \approx 6$ kcal mol^{-1})[21,29]

To put it simply, a less easily oxidized substrate requires the choice of a stronger photochemical oxidant (which is generally possible), but will cleave more efficiently, since there is more energy accumulated in the radical cation. As the example in eq.27 shows, this means that photochemical oxidation gave access not only to resonance stabilized radicals, but also to simple alkyl radicals, and this under the particularly mild conditions illustrated above.

1.4 KINETIC AND CONFORMATIONAL FACTORS IN RADICAL CATION FRAGMENTATION

In the previous section, the fragmentation of radical cations was discussed on the basis of the thermochemical cycles of Fig.1-3. However, in order that the overall photoinduced process occurs efficently, it is also required that such fragmentations are sufficiently fast, since they have to compete with back electron transfer between the radical ions. Thus, deprotonation from a carbon atom is often predicted to be a facile, or even exergonic, process in radical cations in solution (eq.28), whereas this is not the case in the gas phase, where the reverse fragmentation (eq.29) is usually preferred.[19,24]

$$R\text{-}H^{+\cdot}_{solv} \rightarrow R^{\cdot}_{solv} + H^{+}_{solv} \qquad (28)$$

$$R\text{-}H^{+\cdot} \rightarrow R^{+} + H^{\cdot} \qquad (29)$$

The difference between the two modes is essentially on account of the solvation energy of the proton being much larger than that of the carbocation. Indeed, organic radical cations are moderate to strong acids, e.g. eqs.30,31:

$$PhCH_3^{+\cdot} \rightarrow PhCH_2^{\cdot} + H^{+} \qquad (30)$$

(calcd pK_a -12)[30]

$$PhNMe_2^{+\cdot} \rightarrow PhNMeCH_2^{\cdot} + H^{+} \qquad (31)$$

(estimated pK_a 9)[31,32]

However, the *rate* for the heterolytic cleavage of a C-H bond is relatively low also in radical cations, and depends on the nature of the proton acceptor present. The measured rates for the deprotonation in eq.30 (with substituted pyridines as bases)[33] and for that in eq.31 (bases, amines)[32,34] are well below those expected for back electron transfer to the radical anion. Therefore, other chemical processes (as well as unproductive back electron transfer) may compete with deprotonation. Indeed, a survey of the literature shows that in general fragmentations of a carbon-carbon, carbon-heteroatom, or heteroatom-hydrogen bond, provided that they are not too endergonic, occur in preference to the fragmentation of a carbon-hydrogen bond even when the latter is more exergonic.

As an example, the photochemically generated benzylic radical cations $ArCH_2X^{+\cdot}$ cleave according to eqs.32-34 in MeCN-MeOH mixed solvent:

$$ArCH_2SiMe_3^{+\cdot} \rightarrow ArCH_2^{\cdot} + Me_3Si^{+} \qquad (32)$$

$$ArCH_2COOH^{+\cdot} \rightarrow ArCH_2COO^{\cdot} + H^{+} \rightarrow ArCH_2^{\cdot} + CO_2 + H^{+} \qquad (33)$$

$$ArCH_3^{+\cdot} \rightarrow ArCH_2^{\cdot} + H^{+} \qquad (34)$$

The relative rate of these processes has been evaluated by using bifunctional donors, and it has been shown that $k_{32} > 10\ k_{33} > 10\ k_{34}$,[35] despite the fact that $\Delta G(32) \approx 30$ kcal mol^{-1} [30] and $\Delta G(34) \approx -17$ kcal mol^{-1}.[18,36] This is rationalized by assuming that the cation X^+ is in every case transfered to the same acceptor, methanol, and formation of the strong Si-O bond favours the process in eq.32. Evidence for such nucleophilic assistance to radical cation fragmentation has been found in some cases by direct kinetic measurement, e.g. $k_{35} = 5.5 \times 10^6$ M^{-1} s^{-1}.[22]

$$p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{SiMe}_3^{+\cdot} + \text{MeOH} \rightarrow \text{Products} \qquad (35)$$

Likewise, C-C cleavage and not the thermodynamically more favoured deprotonation is observed with $Ph_2CHCHPh_2^{+\cdot}$ in acetonitrile,[20,36] but with $PhCH_2CH_2Ph^{+\cdot}$ only proton transfer (to the acceptor radical anion) takes place, the fragmentation of the C-C bond being in this case prohibitively endothermic (24 kcal M^{-1}).[29,37]

In the case of $(p\text{-MeOC}_6\text{H}_4)_2\text{NMe}^{+\cdot}$ it has been observed that the activation energy for deprotonation contains a large entropic contribution.[32] Indeed, some evidence has accumulated to show that proton transfer from radical cations is faster when it occurs within the radical ion pair (or polar exciplex). Thus, the reactions of alkylbenzenes with 1,4-dicyanonaphthalene (DCN) are much more efficient when in cage proton transfer to $DCN^{-\cdot}$ than when proton transfer to an external acceptor (e.g. methanol) is involved.[38] Likewise, the C-C cleavage in an a-aminoketone has been found to occur more efficiently when the irradiation, in the presence of 9,10-dicyanoanthracene (DCA) as the acceptor, was carried out in benzene (and thus the exciplex was involved) than in more more polar solvents where the free radical ions were formed.[39]

As seen above, the rate of the proton transfer or, more generally, of the electrofugal group transfer, depends on the nature of the acceptor. Thus, deprotonation of cation radicals in the presence of strongly nucleophilic radical anions, such as those of enones, is generally efficient, while this is not the case with less basic radical anions, such as those of cyanoaromatics or α-diketones.[40-43] A useful consequence of this fact is that it is possible to determine the mode of fragmentation of radical cations by appropriate choice of the experimental conditions. Thus, with α-silylamines and enones deprotonation predominates on account of the basicity of the acceptor radical anion, but when this is diminished by solvation or coordination desilylation takes over. Furthermore, desilylation is favoured in more silophilic solvents like methanol.[41] N-H deprotonation rather than the thermodynamically favored C-H deprotonation (involving the radical anion of the acceptor) is exclusively observed in the reaction with stilbene,[44,45] which is further evidence for the importance of kinetic factors. On the other hand, the reaction of secondary amines with aromatic nitriles involves N-H deprotonation when it occurs in a strongly bonded exciplex or radical ion pair, and C-H deprotonation when it occurs from the solvated radical cation.[46]

Systematic studies of the chemistry of radical cations on the basis of product yields with intramolecular model compounds have shown that the kinetic acidity of carbon acids experiences a considerable substituent effect, and, as one may expect in view of the mechanistic differences, the effect depends on the structure of the acceptor moiety in the system considered (in the models studied either a styrene[47] or a cyclohexenone chromophore[48,49] acts as acceptor).

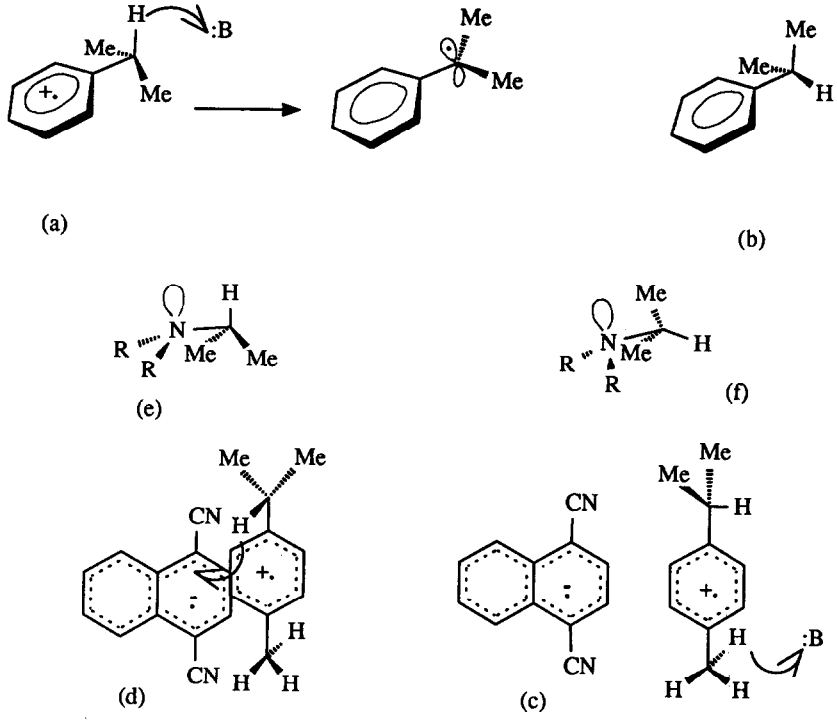


Fig.4 The favourable conformations for deprotonation of the radical cations of cumene (a) and an isopropylamine (e) are different from the lowest-energy conformation of the neutral molecules (b and, respectively, f). The reaction between DCN and *p*-cymene may involve either a tight complex (d) where the isopropyl group is forced into coplanarity or a loose radical ion pair (c), where deprotonation occurs preferentially from the methyl group since this is in the right conformation.

Steric effects are also important, and are rationalized by assuming that a fast reaction occurs when in the preferred conformation of the molecule the relevant bond is aligned in such a way that electron redistribution in the fragmentation is facilitated (Fig.4). For example, deprotonation of benzyl radical cations requires that the C-H bond overlaps with the π SOMO. Thus, when the side-chain is an isopropyl group, deprotonation is expected to be slow, since sterical hindering makes (b) and not (a) the preferred conformation. When there is intramolecular competition, as in the case of cymenes, the methyl group is expected to deprotonate faster than the isopropyl group. This is actually observed when the proton is transfered to the radical anion of a ketone or to the solvent (structure c). On the other hand, a specific donor-acceptor interaction may change the course of the reaction, and indeed the methyl-isopropyl selectivity is reversed when the proton transfer occurs in a tight complex with the radical anion of a cyanoaromatic, where the isopropyl group is forced to assume coplanarity

with the ring (structure d).[50-52] With amines or ethers the relevant σ bond must be aligned with the n SOMO on the heteroatom (from conformer e rather than conformer f), and the different efficiencies observed with different α-phenylcycloalkyl methyl ethers,[53] as well as with tertiary amines,[47] have been rationalized on the basis of the structure of the preferred conformer. Similar considerations hold for the cleavage of a carbon-carbon bond, as it is apparent in the PET induced ring cleavage of 1-phenyl-2-alkoxycyclopentanes, a reaction which does not succeed with the corresponding cyclohexanes,[53] as well as in the fragmentation of 2,2-dialkyl-1,3-dioxolanes, a reaction more efficient than that of the corresponding dioxanes or of open-chain ketals.[54]

1.5 CHEMISTRY OF THE RADICALS

It is apparent from the foregoing that photo-induced electron transfer is a powerful method for the generation of radical cations in solution. Furthermore, the conditions under which the PET initiated reactions are carried out strongly affects the subsequent chemistry of the radicals.

It has been shown above that the oxidation can be accomplished in a range of moderately polar to strongly polar solvents and often it is possible to choose among different acceptors satisfying the conditions for making the redox process occur in the excited state. Therefore, the fragmentation occurring in the radical cation can be determined at will by changing the basicity (or, more generally, the affinity for the electrofugal group) of the medium (solvent + additives) and/or of the acceptor radical ion, or by favouring the in-cage vs the out-of-cage fragmentation.

Furthermore, the evolution of the radicals generated under these conditions is often different from that occurring with conventional redox methods. Thus, when the oxidation is carried out by means of a metal compound or anodically the radical cation is generated in the presence of excess of oxidant, and thus (a) further oxidation of the radical cation to to the dication compete with fragmentation (eq.36) and (b) the neutral radical arising from the fragmentation may be oxidized to the cation (eq.37).

$$R\text{-}X^{+} \xrightarrow{-e^-} R\text{-}X^{2+} \qquad (36)$$

$$R\cdot \xrightarrow{-e^-} R^{+} \qquad (37)$$

Actually many thermal and electrochemical oxidations do occur via either eq.36 or 37.

As was pointed out in the introduction, however, under PET conditions the actual oxidant is a short-lived species generated by the absorption of the light in solution, and its interaction with other transients such as radicals is kinetically prohibited. On the other hand, in the cases we are considering in the present review the radical cation cleaves efficiently to yield a neutral radical and a cation, and thus is subtracted from back electron transfer. As a consequence, the radical anion of the acceptor may reach a significant steady state concentration. Thus, the interaction of the latter species with the radical is likely, and it leads to either of two results: reduction of the radical when thermodynamically allowed, i.e. when the radical has a high E_{red} (e.g. when it is a π–delocalized species) and the acceptor has a largely negative E_{red} in the ground state (eq.38), or addition to yield a non radical anion in the alternative case (eq.39).[20,29]

$$R\cdot + A^{-}\cdot \rightarrow R^{-} + A \qquad (38)$$

$$R\cdot + A^{-}\cdot \rightarrow R\text{-}A^{-} \qquad (39)$$

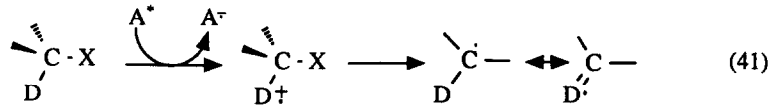
However, it is also possible that the radical is oxidized (particularly if it has a low E_{ox}, e.g. in the case of an α-aminoalkyl[55-58] or *p*-aminobenzyl radical)[28] either by the ground state acceptor (eq.40) or by an added oxidant (eq.37), e.g. a perchlorate.[59]

$$R\cdot + A \rightarrow R^+ + A^{-}\cdot \qquad (40)$$

It is apparent that, given of course certain limitations (e.g. the acceptor must have a high enough reduction potential in the excited state, and this limits either its chemical nature or its ground state E_{red}), judicious choice of the conditions allows the manipulation of the chemistry of the radical generated. Thus, both DCB [$E_{red}(S_1)$ 2.67 V vs SCE] and 1,2,4,5-tetracyanobenzene, TCB [$E_{red}(S_1)$ 3.1 V vs SCE] oxidize diphenylmethane and related substrates, but the radical anion of the former acceptor (ground state E_{red} -1.6 V) is expected to reduce the diphenylmethyl radical (E_{red} -1.14 V),[19] while the latter (ground state E_{red} 0.7 V) cannot, and can combine with it.[20,36] Likewise, both DCA [$E_{red}(S_1)$ 1.97 V] and DCN [$E_{red}(S_1)$ 2.17] oxidize amines, but the ground state of the former acceptor (E_{red} -0.89 V) oxidizes an α-aminoalkyl radical (e.g. Me_2NCH_2, E_{ox} -1.03 V),[19] while the latter (E_{red} -1.28 V) cannot, but rather combines with it.[57,58]

1.6 APPLICATIONS

In the previous sections we have shown that photoinduced electron transfer followed by fragmentation of the radical cation can be an effective method for the generation of radicals under mild conditions from a large variety of substrates. Indeed, the exceptionally high Ered of excited states allows the oxidation of even relatively poor donors, e.g. tetraalkylsilanes,[21,60] for which a thermal alternative is difficult. The chemoselectivity (e.g. C-H vs C-C or C-Si bond cleavage) as well as the stereoselectivity in the radical cation fragmentation can be predicted, and, to a certain extent, controlled by the appropriate choice of the acceptor and of the experimental conditions. Furthermore, in the same way the ensuing chemistry of the radical can be affected. In the following sections the potential of the method is demonstrated by means of some applications.



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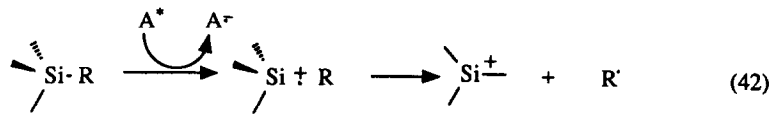

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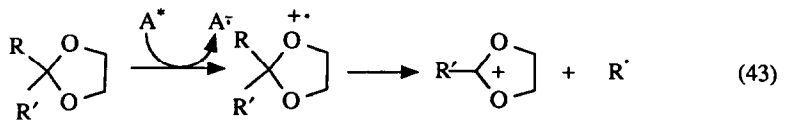


(43)

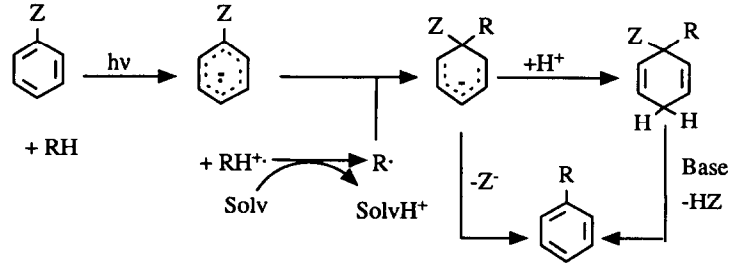
A convenient substrate for this oxidation often contains an electron donating moiety D and an electrofugal group X in an α position. The HOMO is a π or n orbital localized on the group D (a vinyl, phenyl, amino, oxy group etc.). The same group stabilizes the neutral radical arising from the fragmentation (eq.41). However, in other cases the electron donation is the same σ bond which then cleaves (e.g. with tetraalkylsilanes, eq.42) or the donor moiety is lost in the fragmentation (e.g. with aliphatic acetals, eq.43, or with aliphatic carboxylic acids). In the two last cases a non- resonance-stabilized radical is formed.

In the following survey, classification is made according to the type of radical reaction observed and the structure of the radical precursor.

2. FUNCTIONALIZATION OF AROMATICS

2.1 ALKYLATION BY DEPROTONATION OF CARBON ACIDS

Many classes of aromatic compounds show no appreciable unimolecular chemistry in their singlet excited state. Aromatics with electron-withdrawing substituents, typically the nitriles, are strong oxidants in this state, and are capable of generating the corresponding radical cations from a variety of substrates. As mentioned in Section 1.4, radical cations are remarkably acidic, and their deprotonation yields neutral radicals. Indeed, alkylbenzenes,[15,61-66] alkylalkenes,[67,68] amines,[69] ethers,[42,70] and, with particularly strong oxidants such as tri- and tetracyanobenzenes, also nitriles,[71] yield the corresponding α-stabilized radicals, and these add to the radical anion of the acceptor yielding a non-radicalic anion and the final products from it (see Section 4 for other pathways). The regioselectivity of the process is completely predictable, since the attack always involves the position(s) with the highest spin density in the radical anion. This is often a substituted position, and the reaction is then terminated either by cyanide loss, thus resulting in *ipso* substition of an alkyl for a cyano group, or by protonation, yielding a dihydrocyano derivative (eqs.44,45).



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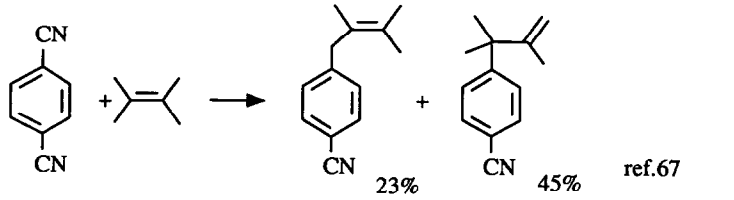
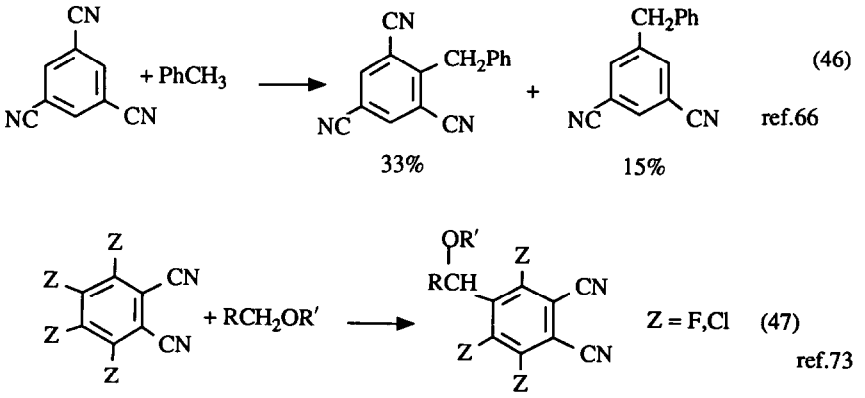
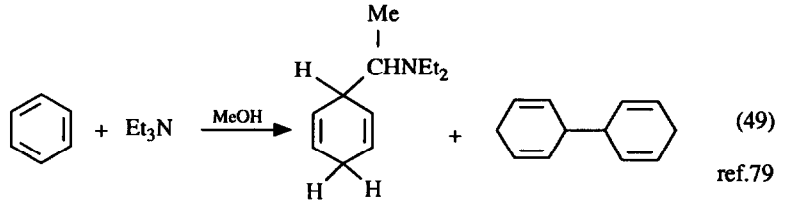


(45)

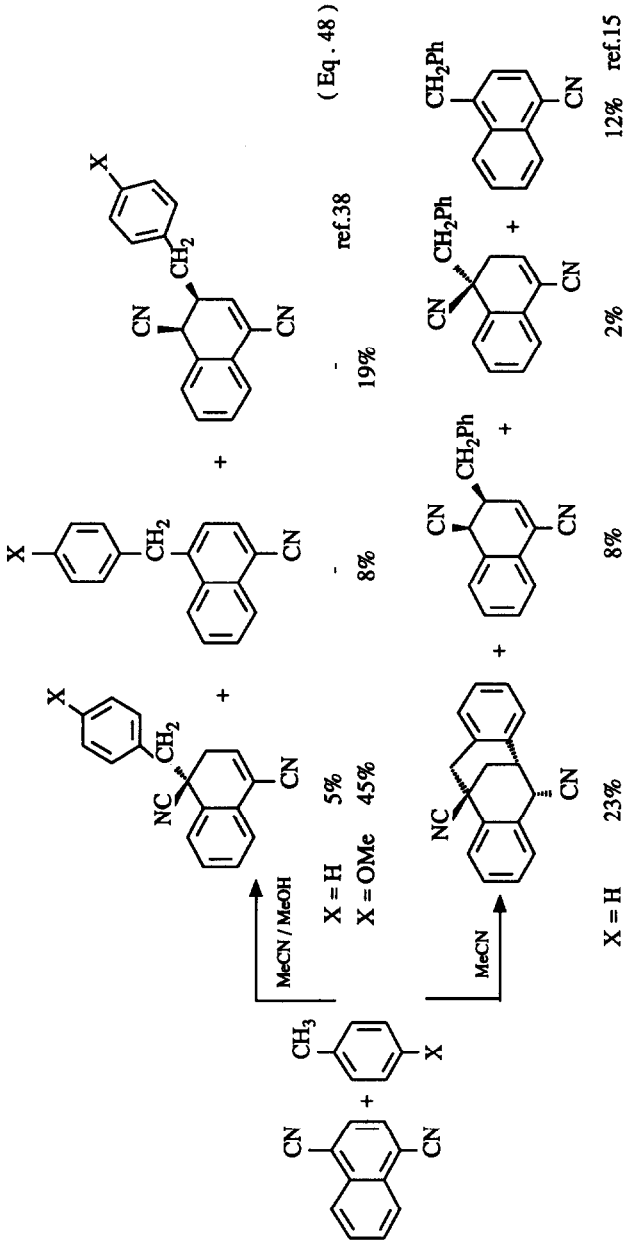
The first path is usually followed in the benzene series; the latter is often the main reaction with naphthalene, phenanthrene and anthracene derivatives. However, it is important to notice that when (one of) the position(s) of highest spin density is not substituted, attack takes place at that position too, as observed with 1-cyanonaphthalene,[72] 1,3,5-tri- and 1,2,4,5-tetracyanobenene (eq.46).[21,66] Rearomatization in this case is an oxidative process and leads to alkylated derivatives retaining the cyano group.[72] Similar alkylation have been observed with halobenzonitriles and with cyanophthalimides (eq.47).[73,74]



Because of the low basicity of the radical anions of aromatic nitriles, the proton is usually transferred to the solvent (typically acetonitrile). However, in some cases proton transfer occurs within the radical ion pair, probably because the donor-acceptor interaction is particularly strong and makes diffusion of the radical ions slower. A case in point is the reaction between DCN and alkylbenzenes. This leads to the normal alkylation in position 1 (that with the highest spin density) in nucleophilic media, e.g. MeCN-MeOH mixtures (eq.48).[38] However, in neat acetonitrile in-cage proton transfer takes place, and the main products are a tetracyclic derivative, apparently arising from a peculiar coupling of the radicals with formation of two C-C bonds, accompanied by the adduct at position 2, and only minimal amounts of the adduct at 1.[15,36,37,64,75-77] The difference between the tight complex leading to the tetracyclic derivative and the normal alkylation path is shown also by the contrasting methyl - isopropyl selectivity observed for the various products when cymenes are used (see Fig.4).[50,52]

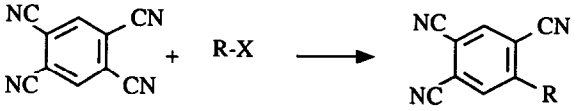


Proton transfer in the initially formed ion pair occurs also in other cases, and is similarly followed by alkylation. This is the case for the system stilbene - tertiary amine[47,78] and probably also for the reaction between unsubstituted aromatics, e.g. benzene (or naphthalene) - tertiary amines (eq.49).[79,80]


MeCN / MeOH
X = H 5%
X = OMe 45%
-
8%
-
19%
ref.38
(Eq. 48)
MeCN
X = H 23%
8%
2%
12%
ref.15

2.2 ALKYLATION BY RADICALS ARISING FROM DIFFERENT FRAGMENTATIONS

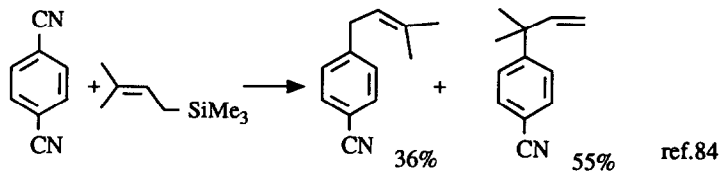
Benzyl radicals are formed also from phenylacetic acids and they alkylate DCN (and to a lesser extent also 1-cyanonaphthalene).[35,81] Strong oxidants like TCB are alkylated also by aliphatic acids (eq.50).[82] Fragmentation of the carbon-carbon bond and alkylation take place starting from some bibenzyl derivative[76] and arylated pinacol ether[77] using DCN, and from aliphatic acetals when TCB is used.[54] Fragmentation of a C-C bond and radical addition are involved also in the reaction of phenylcyclopropane with DCA.[83]



(50)

R	X		
Me	$SiMe_3$	80%	ref.21
Me	$SiMe_2OSiMe_3$	90%	ref.21
Bu	$SnBu_3$	84%	ref.60
Me	COOH	55%	ref.82
t-Bu	$MeCOCH_2CH_2O$	70%	ref.54

Benzyl- and allyl-silanes, -germanes and -stannanes effectively alkylate dicyanobenzenes (eq.51),[84,85] DCN (eq.52),[36,86] 9-cyanophenanthrene (eq.53) and DCA,[87] while the reactions with 1-cyanonaphthalene



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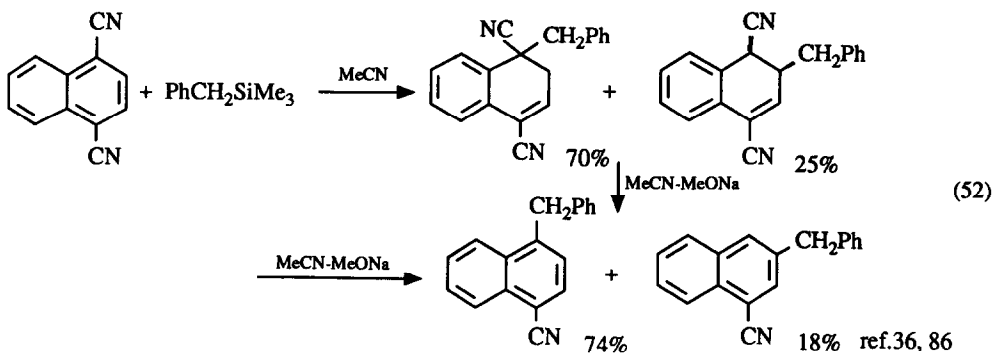
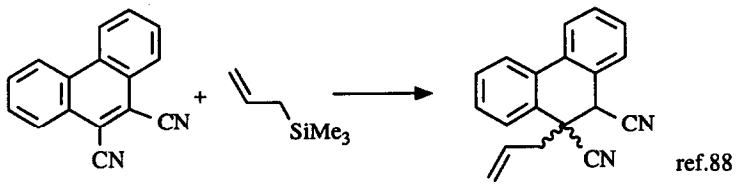


(52)

and allyltrimethylsilane are more complex.[72] Dicyano- and tetracyanobenzene are alkylated also by tetraalkylsilanes or stannanes (eq.50,54). With TCB the reaction works well also with siloxanes, silyl ethers,

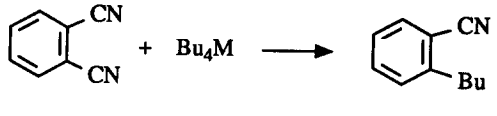


(53)

ref.88

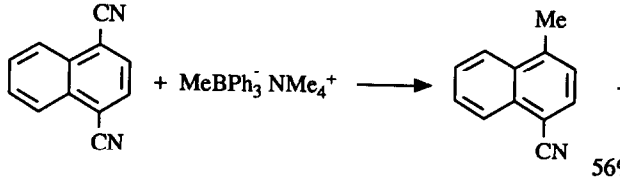
80%

and silyl amines (eq.50).[21,60,72] Alkyltriphenylborates alkylate DCN (eq.55).[88,89] Notice that with asymmetric donors, e.g. with acetals,[54] silanes,[21,60] or stannanes[38,60] containing different alkyl groups, the more branched alkyl group is selectively detached, with usually only a trace of the product arising from the alternative alkylation. As in the previous section, the final step is either protonation to yield a dihydroaromatic derivative (usually predominating in the naphthalene and anthracene series) or rearomatization, usually predominating in the benzene series (when the irradiation is carried out under basic conditions dehydrocyanation to give the aromatic derivative takes place in all cases, eqs.52,55).



M = Si 38%
M = Sn 46% ref.60

(54)



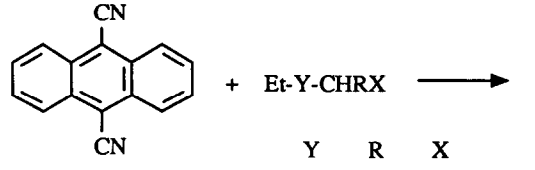
56%

44%

ref.89

(55)

Since arene radical anions are weak bases, deprotonation of carbon acids is usually not observed when there are other potential electrofugal groups in the radical cation. Thus, α-aminosilanes undergo desilylation when irradiated with DCA (eq.56),[41] whereas they are deprotonated when irradiated with enones since in the latter case the radical anion is more basic (see Section 4).



(56)

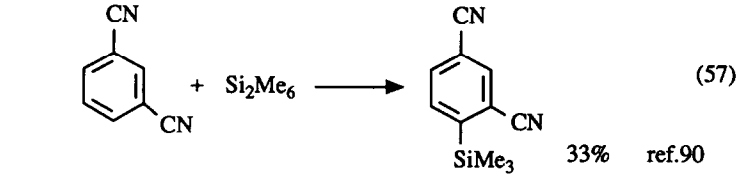
ref.41

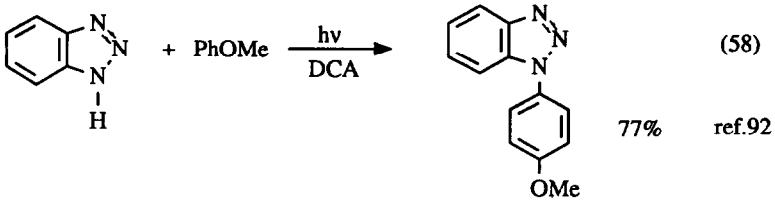
Y	R	X	
O	H	$SiMe_3$	89%
S	H	$SiMe_3$	90%
O	Me	H	93%

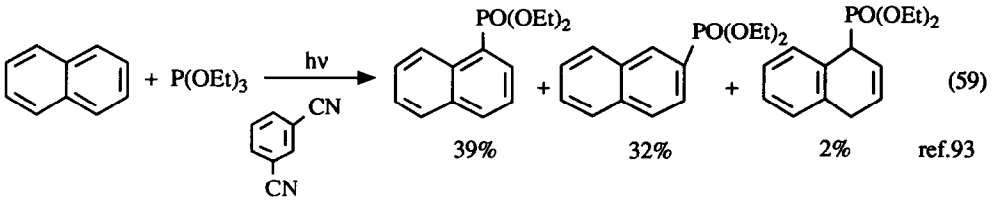
As mentioned before, the order of electrofugacity for the group E in benzyl radical cations $ArCH_2E^{+\cdot}$, as deduced from the results of alkylation of DCN in MeCN-MeOH, is Me_3Si > COOH > H.[3]

2.3 OTHER FUNCTIONALIZATIONS

Heteroatom-centered radicals are formed in a similar way. Silylation of aromatic nitriles occurs efficiently with suitable substrates, such as disilanes (eq.57)[90] or diphenylpinacol silyl ethers.[91] With primary amines amination of aromatics occurs, in some cases in interesting yields.[79] 1-Arylbenzotriazoles are obtained from triazole and aromatic hydrocarbons by irradiation in the presence of DCA as the electron transfer sensitizer (eq.58).[92] Arylphosphonates are obtained from arenes and trialkylphosphites by irradiation in the presence of *m*-dicyanobenzene (eq.59).[93]

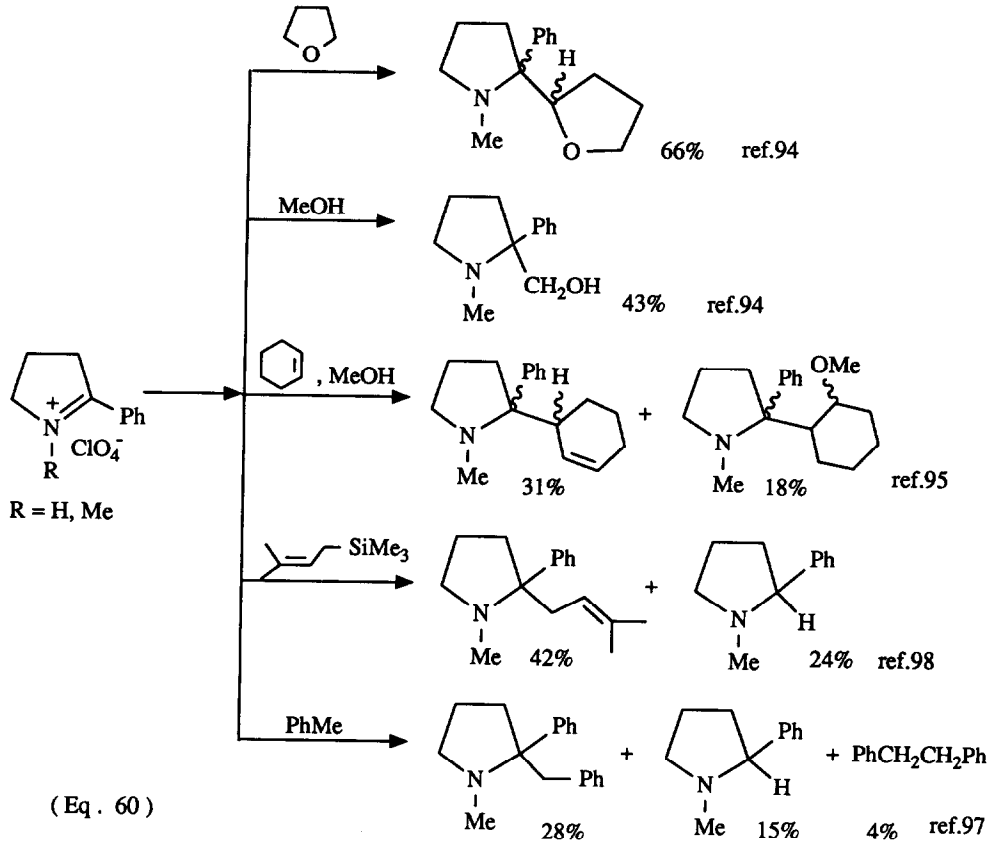


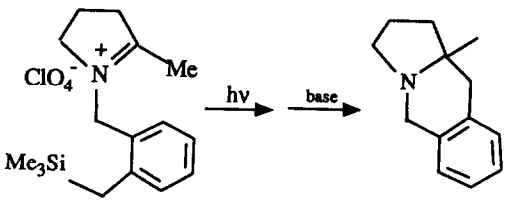




3. FUNCTIONALIZATION OF HETEROCYCLES

Pyrroleninium salts are convenient substrates for PET induced alkylation and have been extensively investigated using ethers, alcohols,[94] alkenes,[95] alkylarenes,[96,97] silanes and stannanes[96,98] as substrates (eq.60). The electron transfer - desilylation - alkylation strategy is useful in the intramolecular case for building new heterocycles from pyrroleninium (eq.61),[97] 3,4-dihydroquinolinium (eq.62)[99-101] and open chain iminium precursors (eq.63),[102] e.g. for the synthesis of the erithrane,[100] protoberberine[101] and harringtonine[102] skeletons.

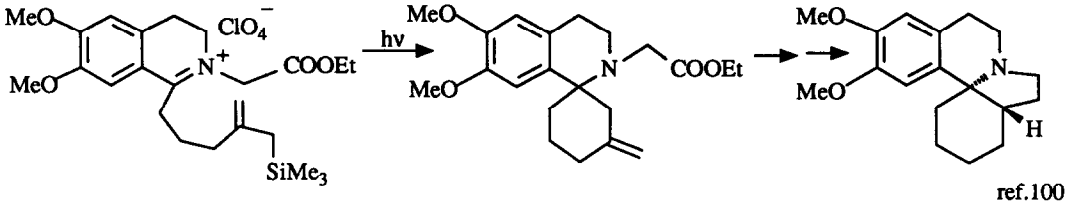




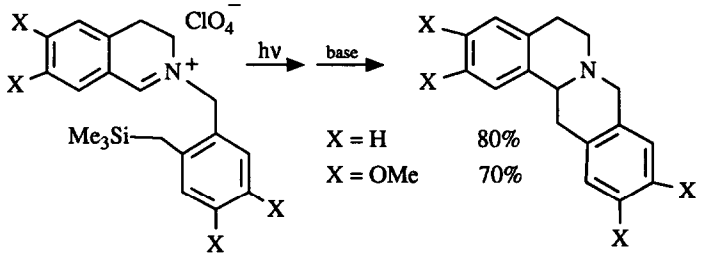
(61)

A related tandem PET reaction has been carried out with amines. DCN oxidizes amines to iminium salts, and simultaneously oxidizes and fragments allylsilane, so that the net result is a-allylation of an amine (eq.64).[103]

Quinolinium salts are similarly alkylated with stannanes (or distannanes) (eq.65), and the same holds for neutral 2,4-dicyanopyridine.[104] *N*-Methylacridinium perchlorate is reductively alkylated by hexamethyldisilane (eq.66),[105] while it undergoes reductive dimerization with the corresponding digermanes, distannanes,[106] and silylated pinacol ethers (the latter donors *N*-silylate *N*-methylphenazinium triflate).[91]

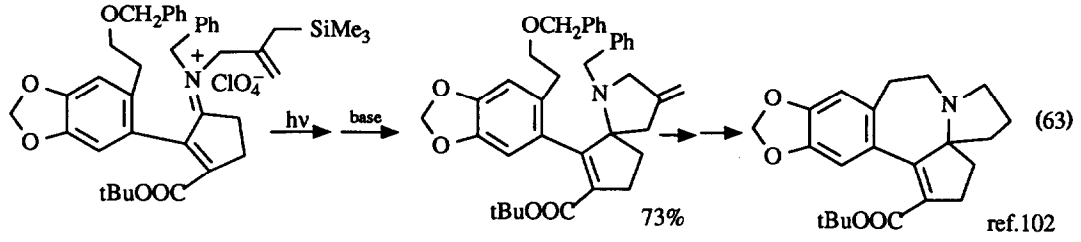


ref.100



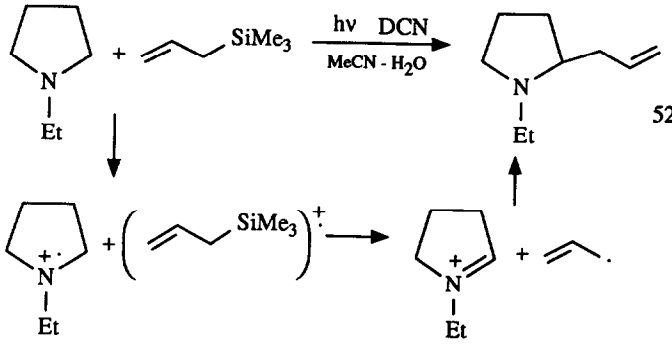
X = H 80%
X = OMe 70%

ref.101 (62)



(63)

ref.102



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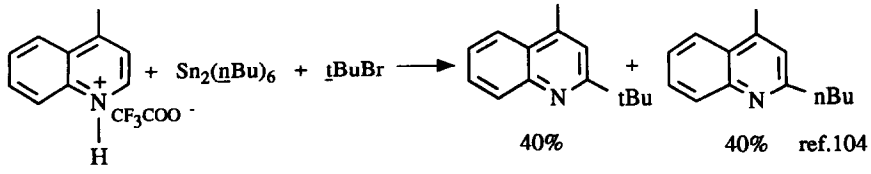
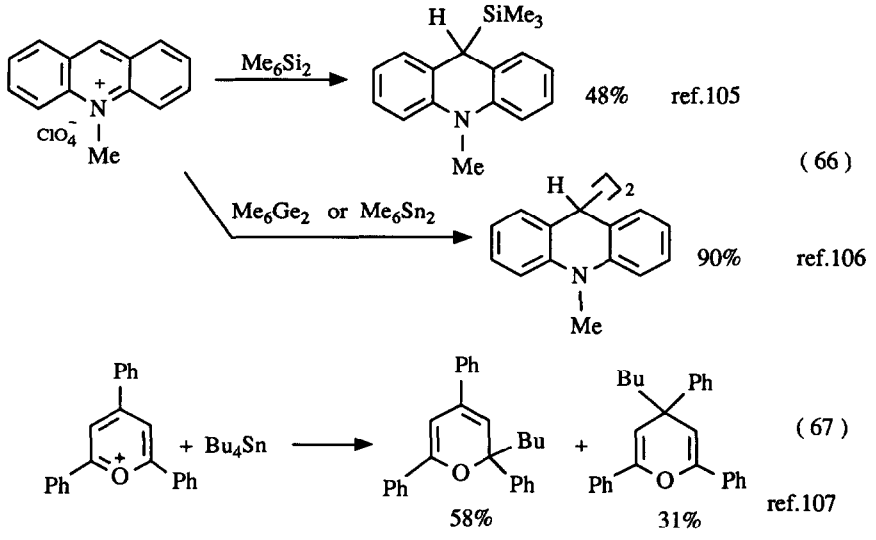


(65)

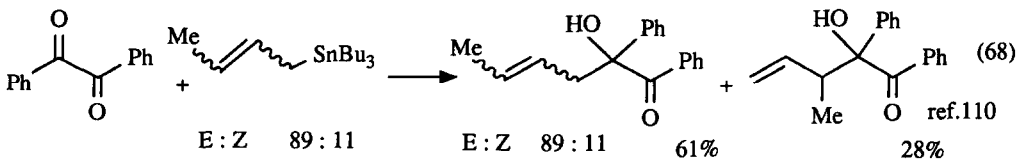
40% 40% ref.104

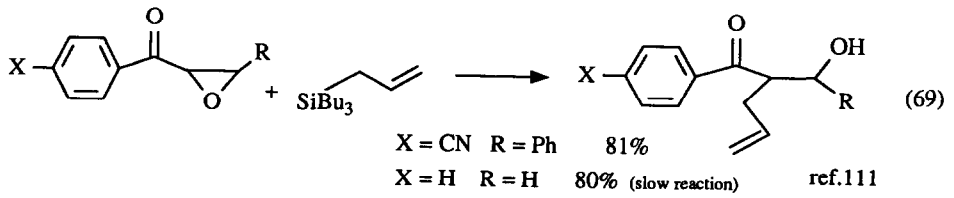


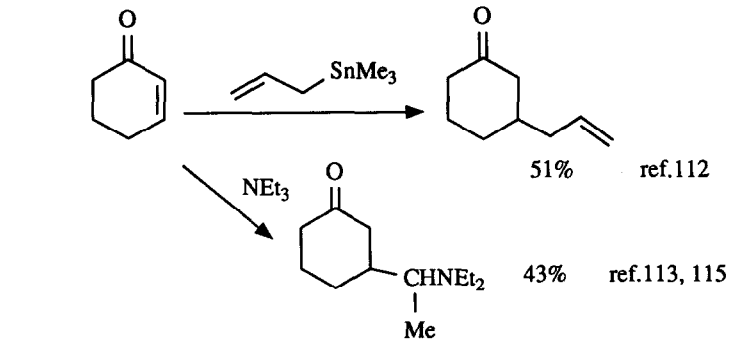
Alkylation/reduction of pyrylium salts is observed with stannanes (eq.67), and less efficiently with Ge and Si analogues.[107]

4. ADDITION TO KETONES, ENONES AND QUINONES

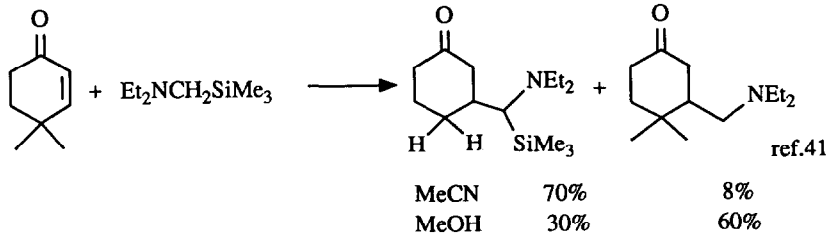
Aromatic ketones[108] and α-diketones[109] give the corresponding homoallylic alcohols in fair yield when irradiated in the presence of allylstannanes (eq.68). Interestingly, the stereochemistry of the double bond is conserved. [110] α,β-Epoxyketones undergo allylation with ring-opening (eq.69).[111]





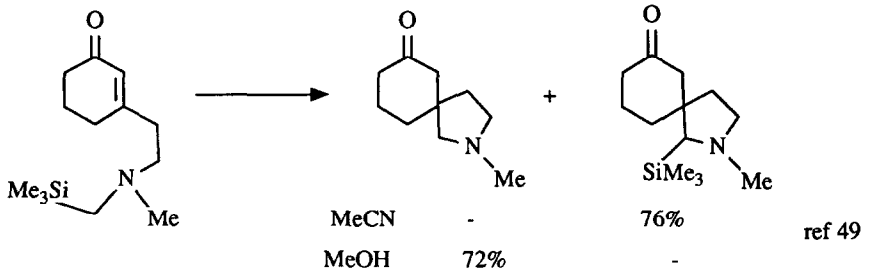


(70)



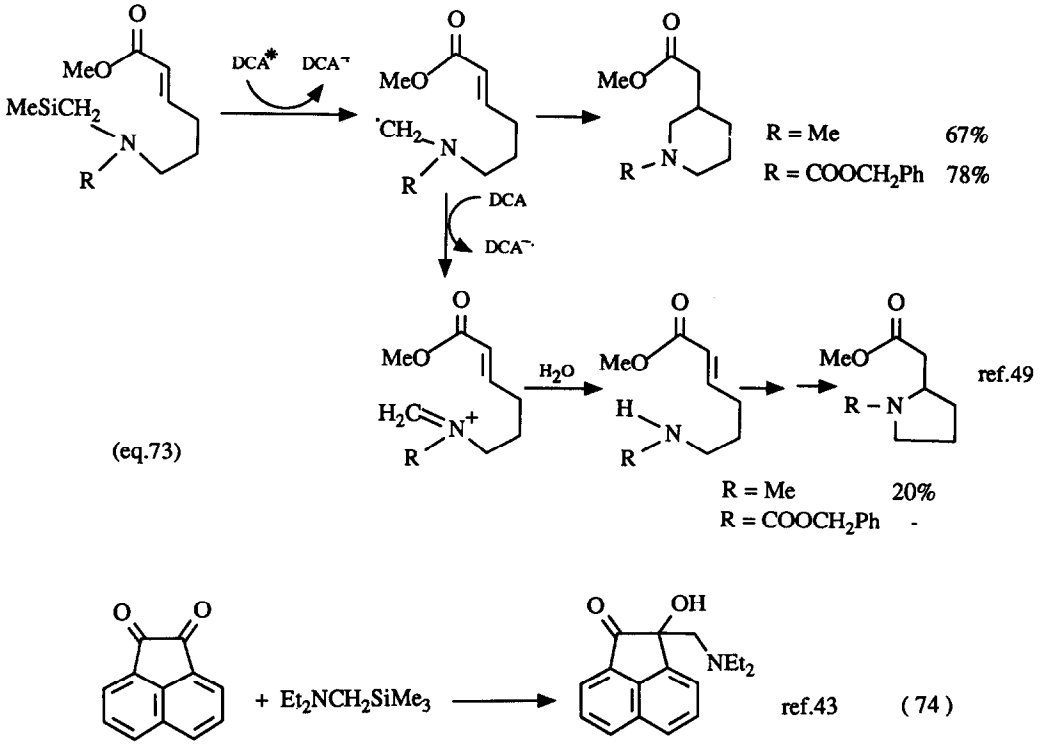
(71)

Enones are allylated at the ß position both by allylstannanes[112] and by tertiary amines (eq.70).[113-115] An interesting situation arises when α-silylamines are used: here the chemical outcome depends on the relative rate of deprotonation vs desilylation for the amine radical cation, and these in turn are governed by the basicity of the enone radical anion (eq.71). Proton transfer to the latter species is fast in aprotic media such as MeCN, and thus silicon-containing adducts predominate under these conditions, whereas when the basicity is decreased by hydrogen-bonding to protic solvents or complexation with cations, desilylation is faster and silicon-free products predominate.[40,41,116]



(72)

The dual fragmentation of α-silylamines has been exploited for intramolecular cyclizations (eq.72), where the chemoselectivity is higher (notice also that when deprotonation occurs, this involves only the silicon substituted carbon, an example of the effect substituents have on the kinetic acidity of cation radicals).[48,49] It can be convenient to carry out the reaction by electron transfer sensitization, e.g. with DCA, rather than by direct irradiation; in this case the aminoalkyl radical adds to the neutral enone moiety rather than to the DCA

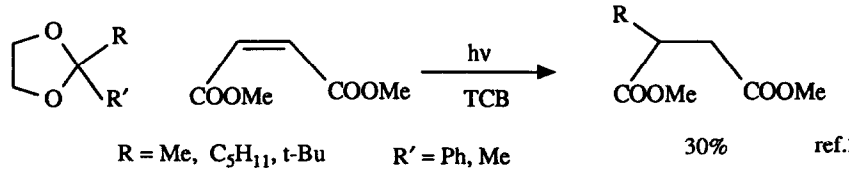


radical anion. This is advantageous in terms of stereoselectivity in product formation[117] and furthermore it induces cyclization also in derivatives where direct irradiation causes only cis-trans isomerization.[57,58] A limitation of the method is that the easily oxidizable α-amino radical can be converted into the cation by ground-state DCA; this path is apparent in the desilylmethylation observed in some cases, due to the formation of the secondary amine by hydrolysis of the iminium cation.[48,49] This can be obviated either by using a different electron acceptor sensitizer, chosen such that its ground state is a milder oxidant, e.g. DCN or DCB (with these molecules, however, some alkylation of the sensitizer itself takes place, see Section 2), or by using urethanes rather than amides, in order to have a less oxidizable radical. The latter solution works beautifully, and can be extended to α,ß-unsaturated esters (eq.73). On the other hand, when the radical anion of the acceptor is less basic than that of enones (e.g. with phthalimides[118] or acenaphthenequinone,[43] besides, obviously, cyanoaromatics - see Section 2.1) α-silylamines undergo C-Si cleavage exclusively (eq.74).

Tetrachloro-*p*-benzoquinone is reductively alkylated by alkylbenzenes[119] and silylated by hexamethyldisilane[120] and arylpinacol silyl ethers.[121]

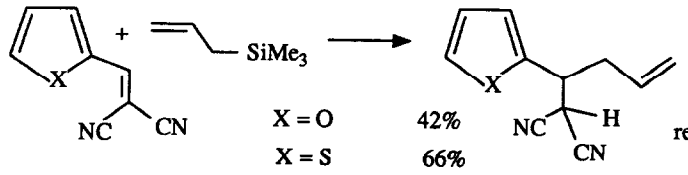
5. ADDITION TO ALKENES

α,ß-Unsaturated esters are intramolecularly alkylated by α-silylamines (or urethanes) when sensitized by cyanoaromatics (see Section 4).[48,49] Likewise, when sensitized by TCB, maleates are alkylated by ketals



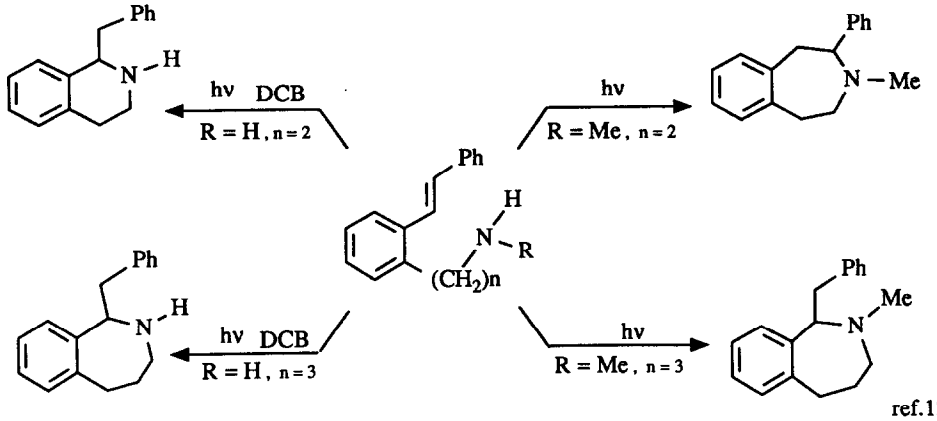
(75)

R = Me, C_5H_{11}, t-Bu R′ = Ph, Me 30% ref.38



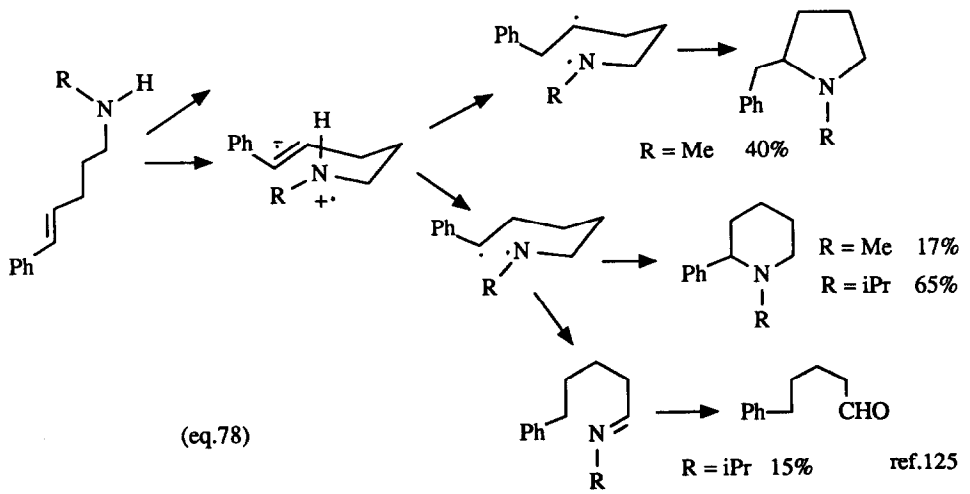
(76)

ref.122



(77)

ref.124



(eq.78)

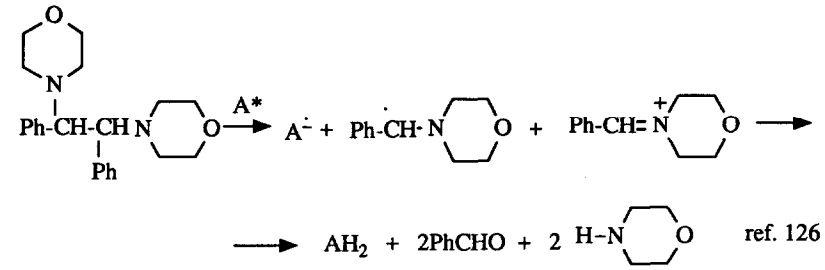
ref.125

(eq.75).[38] Some unsaturated nitriles have been allylated by irradiation with allylstannanes (eq.76)[122] and tetracyanoquinodimethane is alkylated by alkylarenes.[123]

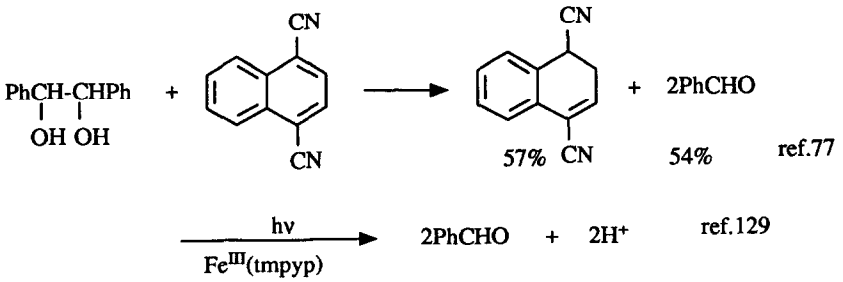
Both tertiary and secondary amines add to stilbenes via an electron-transfer, proton-transfer, radical coupling mechanism.[45] The addition of amines to styrenes is synthetically useful in the intramolecular case. *ortho*-*N*-Methylaminoethylstilbenes and the corresponding aminopropyl derivatives both cyclize to a seven-membered ring via an exciplex mechanism, whereas the corresponding primary amines cyclize only under DCB sensitization to yield tetrahydroisoquinolines or tetrahydrobenzazepines respectively (eq.77).[124] ß-Alkylaminopropylstyrenes cyclize photochemically. The bulk of the *N*-alkyl group determines the preferred conformation of the intermediate, and thus the type of cyclization occurring (eq.78).[125]

6. SOLVOLYTIC OR OXIDATIVE FRAGMENTATION OF σ BONDS

The radical cations of aryl α-diamines (eq.79),[126] α-aminoalcohols[55,56,127] as well as vicinal diols[77,128,129] and their silyl ethers[91,121] easily fragment under PET conditions. Proton transfer follows and the net result is generally two-electron reduction of the sensitizer and oxidative cleavage of the substrate, unless a further thermal oxidation takes place. For example, a porphirinato iron complex has been found to oxidize pinacols stoichiometrically in the absence of oxygen and catalytically in its presence (eq.80).[129]

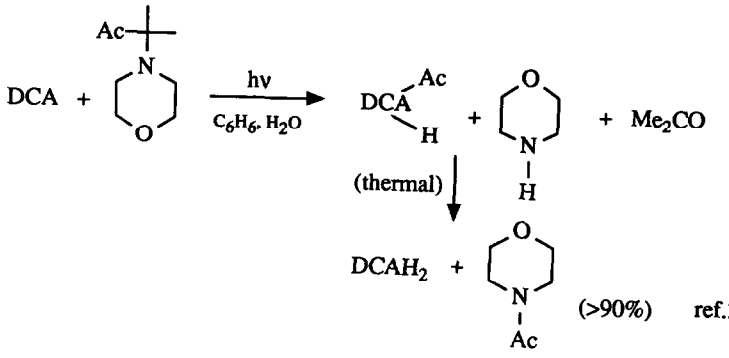


(79)

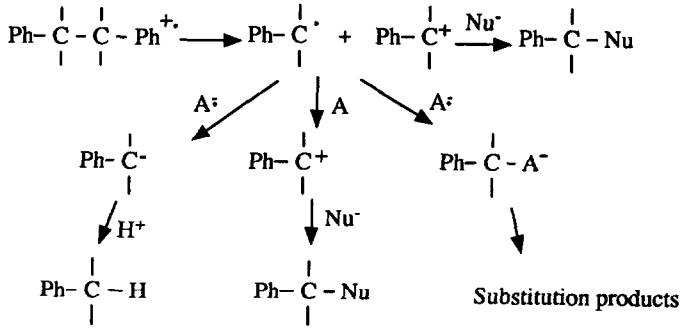


(80)

C-C bond fragmentation has been observed also with 2-(*p*-aminophenyl)-1-phenylethanol,[128] 2,2-diphenylethyl ethers,[130,131] 3-methyl-3-morpholino-2-butanone (eq.81),[39] and 2,3-diphenylaziridines.[132] Interesting stereoelectronic effects determine the ring opening of 1-phenyl-2-alkoxycycloalkanes.[133-135] C-C bond fragmentation has been extensively studied with bibenzyls (eq.82).[20,28,136-140] Here, depending on the

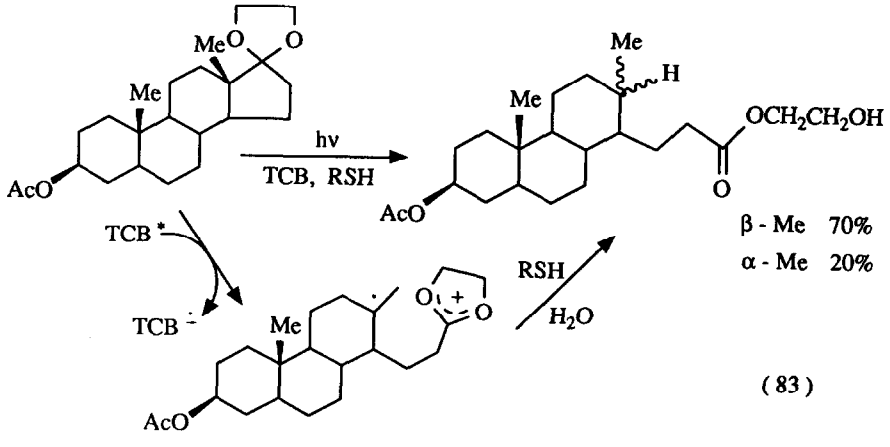


(81)



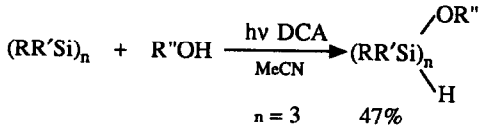
(82)

characteristics of the radical formed and the sensitizer used, the former species may be reduced by $A^{-\cdot}$ (and the net result is solvolysis of the C-C bond),[20] oxidized by ground state A (e.g.for *p*-aminobenzyl radicals, and then the net result is oxidative solvolysis),[28] or add to $A^{-\cdot}$, when the net result is aromatic alkylation, see Section 2.1. With a fragmentable radical anion, as in the case of tetranitromethane, further possibilities arise.[139]

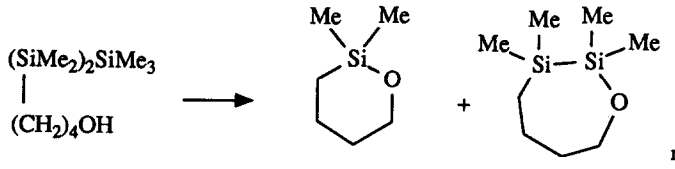


(83)

Solvolytic C-C fragmentation has been observed also with some aliphatic derivatives, e.g. spiro acetals (eq.83).[38] A Si-Si bond is similarly cleaved in cyclic polysilanes (eq.84).[141-142]



ref.141



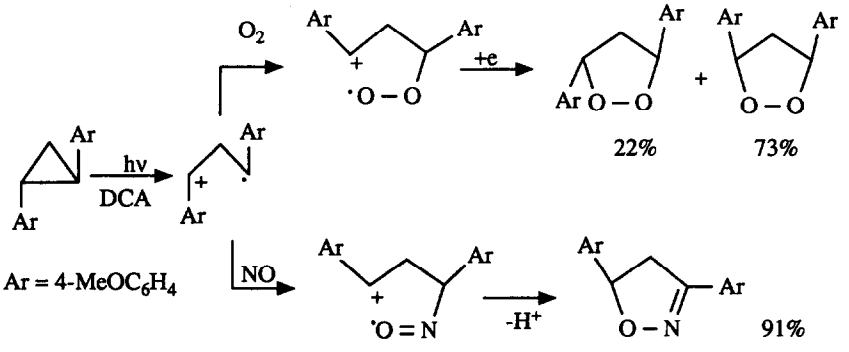
(84)

ref.142

Deprotonation of benzylic radical cations is involved in the cis-trans isomerization of some 1-phenyl-2-alkoxyindanes[133,134] and in the PET sensitized deconjugation of 1-phenylalkenes to the 3-phenyl isomers in the presence of a hindered pyridine.[143]

Very stable radicals formed by fragmentation, e.g. cumyl[137] or acenaphthenyl[144] radical, dimerize when alternative addition paths are too slow.

Finally, addition of oxygen to radicals formed *via* PET-induced cleavage is a significant feature in photochemical oxidations.[145] Thus, alkylbenzenes,[146-8] bibenzyls, arylpinacols[146] and benzylsilanes[149] all give the expected carbonyl derivatives by fragmentation of a C-H, C-C, or C-Si bond in the presence of electron-acceptor sensitizers. This may be a useful method for preparing aromatic aldehydes.



(85)

Oxygenation of aryl substituted cyclopropanes, to form 1,2-dioxolanes (eq.85),[150-152] of the corresponding epoxides to give ozonides,[150,153,154] and of aziridines to give 1,2,4-dioxazolidines[150,155] also proceeds via cleavage of the radical cation, and with the heterocycles possibly it involves the corresponding ylids. The similar reaction of diarylcyclopropanes with NO yields isoxazolines (eq.85).[156]

7. CONCLUSION

The reported examples are sparse, not necessarily mechanistically homogeneous, and mostly not optimized from the preparative point of view. We believe, however, that they are sufficiently numerous and varied to allow the recognition that the generation of radicals *via* photoinduced electron transfer - radical cation fragmentation offers new opportunities to the synthetic chemist. Futher exploratoration studies, synthetic developments and applications to complex synthetic plans based on this method are expected to reveal new fascinating chemistry.

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