The Influence of Aminium Radical Heterolytic Fragmentation Rates on the Nature and Efficiencies of SET-Promoted Photochemical Reactions

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Two important types of α-heterolytic fragmentation reactions of aminium radicals are discussed. In these fragmentation processes, transfer of electrofugal groups from the aminium radicals to either Lowry-Bronsted or Lewis bases produces α-amino radicals. The results of recent studies that provided key information about the dynamics of the important aminium radical fragmentation reactions, deprotonation, desilylation, are summarized. Finally, selected examples, which demonstrate how knowledge of the relative rates of aminium radical cleavage can be used to design synthetically relevant SET-promoted photocyclization reactions, are presented.

key words: aminium radicals, SET-Photochemistry, α-Silylamines, phthalimides

INTRODUCTION

Single electron transfer (SET) is a key mechanistic event in a number of interesting photochemical reactions [1]. In contrast to classical photochemical reactions, those initiated by SET proceed via the intermediacy of charged radical species. The chemistry of these radical ion intermediates plays a major role in governing the nature and efficiencies of SET-promoted excited state processes. α-Heterolytic fragmentation processes are among the most common types of ion radical reactions and, as a result, they play pivotal roles in the SET photochemistry of organic substrates. In pathways where α-heterolytic fragmentation processes participate, departure of electrofugal or nucleofugal groups from the respective cation or anion radical intermediates often competes with back electron transfer or alternative reaction modes to generate carbon centered radical intermediates, which react further to produce the observed photoproducts. Therefore, knowledge about the nature and dynamics of ion radical fragmentation reactions and their dependence on structure, substituents, and the reaction medium is crucial for understanding numerous SET-photochemical processes.

In this review [2-4], we will discuss several α-heterolytic fragmentation reactions of aminium radicals (Scheme 1) that

Scheme 1.

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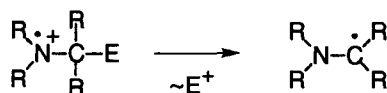
are derived by one electron oxidation of amines and their derivatives. In these fragmentation processes, transfer of electrofugal groups from the aminium radicals to either Lowry-Bronsted or Lewis bases produces α-amino radicals. Recent studies have provided key information about the dynamics of two important aminium radical fragmentation reactions, including deprotonation, desilylation. The focus of the discussion below will be on the question of how the rates of aminium radical cleavage influence the nature and efficiencies of SET-photochemical reactions involving amine substrates.

DISCUSSION

Photochemical Generation of Aminium Radicals

Amines are among the most easily oxidized classes of neutral organic substances. This is reflected by their low oxidation potentials. As expected, oxidation potentials of amines are significantly altered by N-substituents. Amines bearing N-electron donating substituents that are capable of stabilizing the formed amine cation (aminium) radicals have lower oxidation potentials than those with N-electron withdrawing substituents. In addition, α-substituents can bring about stabilization of amine cation radicals. Accordingly, α-trialkylsilylamines and α-trialkylsilylcarbamates have significantly lower oxidation potentials than their non-silicon substituted counterparts [5,6]. This phenomenon is a consequence of hyperconjugative stabilization of the aminium radicals by interaction of the half vacant nitrogen nonbonding p-orbital with the carbon-silicon σ-orbital [7].

Owing to their low oxidation potentials, amines serve as electron donors in a variety of SET-promoted photochemical processes. Some common methods of promoting SET-photo-reactions of amines include (1) SET from amines to excited

states of acceptors that participate as substrates in photochemical reactions with the amine (e.g., α,β-unsaturated ketones), (2) SET from amines to excited states of acceptors that serve as photosensitizers (e.g., cyanoarenes) for photochemical reactions occurring between amines and other substrates, and (3) SET from amines to preformed radical cations (redox photosensitization) [8].

Common Heterolytic Fragmentation Reactions of Aminium Radicals

By far the most common heterolytic fragmentation reaction followed by tertiary aminium radicals is α-CH deprotonation, which results in the production of α-amino radicals (Scheme 2). Closely related to this process are other fragmentation reactions involving the transfer of electrofugal groups to Lowry-Bronsted bases or Lewis bases. One example of this is base induced retro-aldol cleavage of cation radicals derived from tertiary β-aminoalcohols. Decarboxylation, with or without simultaneous deprotonation, is common reaction of aminium radicals derived by SET oxidation of α-amino acids or their carboxylates. Finally, silophile promoted α-desilylation of α-trialkylsilylaminium radicals is the yet another fragmentation process observed for these reactive intermediates. In all cases, the driving force for fragmentation is provided by a combination
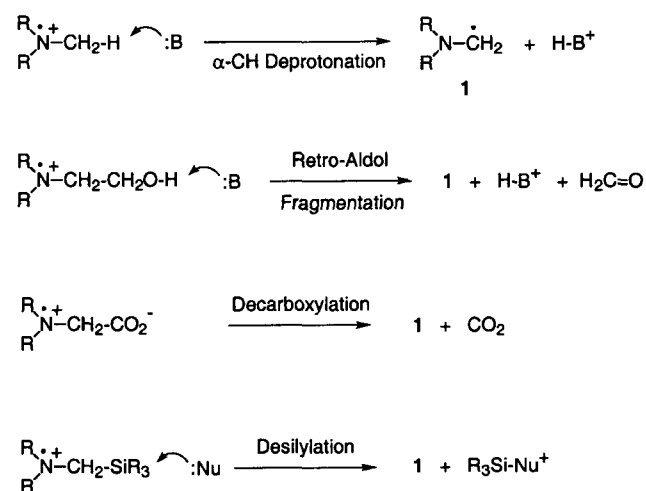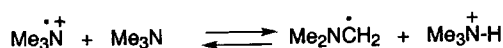
of factors including (1) delocalization of the N-centered positive charge density into the α-C-H, α-C-C or α-C-SiR$_3$ σ-bonds, and (2) the thermodynamics associated with formation of carbonyl π-bonds or silicon-silophile σ-bonds.
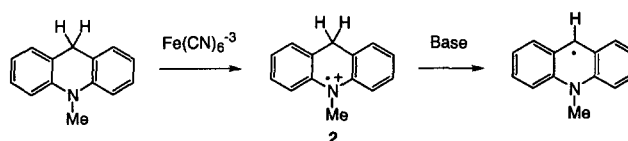
Direct Measurements of the Rates of Tertiary Aminium Radical α-CH Deprotonation

The acidity of tertiary aminium radicals is a consequence of the presence of α-CH protons. The importance of aminium radical α-CH deprotonation in electrochemical and SET photoinduced oxidation reactions of amines stimulated detailed kinetic studies. In one investigation, Das and Von Sonntag [9] used pulse radiolysis methods to determine that the bimolecular rate constant for proton transfer from the trimethylaminium radical to Me$_3$N (Scheme 3) is $7 \times 10^8 M^{-1}s^{-1}$. Equally informative results come from a kinetic investigation of ferricyanide oxidation reactions of 1,4-dihydropyridines and N-methylacridanes by Bruice and his coworkers [10,11]. This effort demonstrated that rate limiting deprotonation of the aminium radical intermediate **2** by imidazole and acetate occurs with rate constants in the $1 \times 10^7 M^{-1}s^{-1}$ range (Scheme 4).

More thorough evaluations of the dynamics of tertiary aminium radical α-CH-deprotonation have been carried out by employing stopped-flow, time resolved laser flash photolysis and electrochemical techniques. In one study, Dinnocenzo and Banach [12] probed base induced deprotonation reactions of the stable aminium radical **3** by using stopped-flow kinetic methods. The results showed that the bimolecular rate constants for α-CH deprotonation of **3** by quinuclidine bases **4** (Scheme 5) are in the range of $1 \times 10^2 - 6 \times 10^4 M^{-1}s^{-1}$.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

$$1,4\text{-}(CN)_2C_6H_4 \; + \; p\text{-}X\text{-}C_6H_4NMe_2 \; \xrightarrow[\text{MeOH-MeCN}]{hv} \; [1,4\text{-}(CN)_2C_6H_4]^{\overset{-}{\bullet}} \; + \; p\text{-}X\text{-}C_6H_4\overset{\bullet+}{N}Me_2$$

5   **6**

$$\overset{-}{O}Ac \; \Big| \; \sim H^+$$

$$p\text{-}X\text{-}C_6H_4\overset{\bullet}{N}\text{-}CH_2$$
$$|$$
$$Me$$

Scheme 6.

$$Ph_2N\overset{R_1}{\underset{R_2}{\overset{|}{C}}}\text{-}H \; \xrightarrow[1,4\text{-}(CN)_2C_6H_4]{hv} \; Ph_2\overset{\bullet+}{N}\overset{R_1}{\underset{R_2}{\overset{|}{C}}}\text{-}H \; \xrightarrow[\overset{-}{O}Ac]{\sim H^+} \; Ph_2N\text{-}\overset{R_1}{\underset{R_2}{\overset{\bullet}{C}}}$$

7   **8**

Scheme 7.

A time resolved laser spectroscopic investigation of anilinium radicals, generated by flash excitation of a solution of N,N-dimethylaniline (DMA) and 1,4-dicyanobenzene (DCB), was conducted by Mariano, Falvey and their coworkers [13]. When generated in the absence of added bases, the free ion radical transients, **5** and **6**, undergo diffusion controlled, second order decay by back electron transfer (Scheme 6). Importantly, α-CH deprotonation of anilinium radical **6** (R=H), can be promoted by the weak bases nBu_4NOAc and $nBu_4NO_2CCF_3$. These processes occur with respective second order rate constants of 3.1×10^5 and 8×10^4 $M^{-1}s^{-1}$. Studies with para-OMe, -Me, -CF$_3$ substituted dimethylanilinium radicals showed that substituents have a pronounced effect on the rates of nBu_4NOAc induced deprotonation (k(p-OMe)=2.0×10^4 $M^{-1}s^{-1}$, k(p-Me)=1.1×10^5 $M^{-1}s^{-1}$, k(p-CF$_3$)=2.5×10^6 $M^{-1}s^{-1}$).

The steric and electronic effects of substituents located on the α-carbon center also influence the rates of aminium radical α-CH-deprotonation. Mariano, Falvey and their coworkers [13] by using N-substituted-N,N-diphenylamines **7** (Scheme 7), observed that alkyl substitution at the α-carbon retards deprotonation while conjugating substituents at this position bring about an acceleration in the rate of deprotonation.

Relative Rates of Aminium Radical α-CH Deprotonation Based on Photoproduct Distributions

The relative kinetic acidities of aminium radicals has been evaluated by using product distributions of SET-promoted photoaddition and photocyclization reactions of amines. For example, detailed investigations of the SET photoaddition reactions between tertiary amines and stilbene (Scheme 8) by Lewis and his coworkers [14-16] have demonstrated that steric and electronic effects govern the rates of proton transfer in stilbene anion radical - amine cation radical contact ion radical pairs (CIRP). Lewis proposed that the energy of the transition state for proton transfer in the CIRP is influenced by steric strain associated with internal interactions between alkyl groups in the amine cation radical component [14-15].

The electronic effects on aminium radical α-CH deprotonation rates have also been probed in studies by Mariano and his coworkers [17-18] of the photocyclization reactions of β-aminoethyl -substituted cyclohexenones **9**. These SET-promoted photocyclization reactions, leading to mixtures of regioisomeric products **11**, proceed *via* the intermediacy of zwitterionic biradicals **10**. Intramolecular proton transfer between the aminium and enone anion radical moieties in **10** is followed by radical coupling to give spirocyclic aminoketones **11** (Scheme 9). The relative rates of aminium radical α-deprotonation obtained from analysis of the product ratios, demonstrate that the radical stabilizing ability of α-substituents (C$\equiv$ CH > CH=CH$_2$ > Ph > CO$_2$Me > TMS > Me > H) plays a key role in determining the aminium radical kinetic acidities in these cases.

Desilylation Reactions of α-Trimethylsilylaminium Radicals

α-Silylamines are more easily oxidized than their non-silicon containing counterparts due to an aminium radical stabilizing interaction between a high energy σ-CSi orbital and the half filled p-orbital on nitrogen. This effect also causes kinetic

$$PhCH=CHPh \; + \; R_1CH_2\overset{R_3}{\overset{|}{N}}CH_2R_2 \; \xrightarrow{hv} \; \left[[PhCHCHPh]^{\overset{-}{\bullet}} \; + \; R_1CH_2\overset{R_3}{\underset{+\bullet}{\overset{|}{N}}}CH_2R_2\right]$$

$$\Big\downarrow \sim H^+$$

$$R_1CH_2\overset{R_3}{\overset{|}{N}}\overset{\bullet}{C}HR_2 \; or \; R_1\overset{R_3}{\overset{|}{C}}HNCH_2R_2 \; \longleftarrow \; \left[Ph\overset{\bullet}{C}HCH_2Ph \; + \; R_1CH_2\overset{R_3}{\overset{|}{N}}\overset{\bullet}{C}HR_2 \; or \; R_1\overset{R_3}{\overset{|}{C}}HNCH_2R_2\right]$$
$$|$$
$$Ph\overset{\bullet}{C}HCH_2Ph \quad Ph\overset{\bullet}{C}HCH_2Ph$$
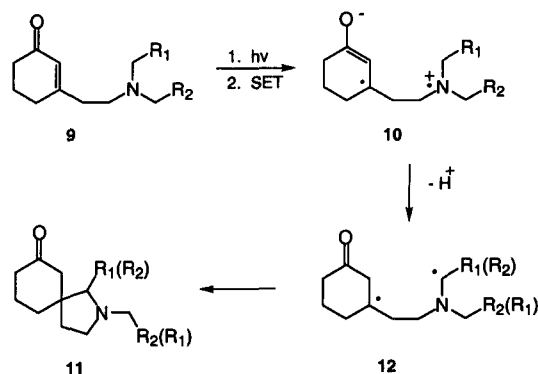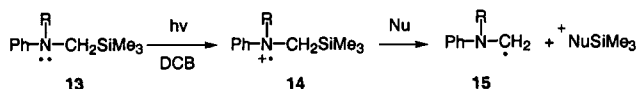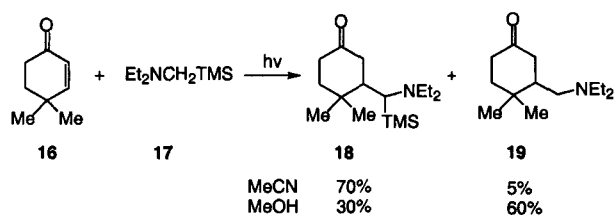
Scheme 8.

Scheme 9.

Scheme 10.

Scheme 11.

instabilty, since the σ-CSi bond is weakened and the silicon is made more electropositive by this orbital interaction. As a consequence, silophile promoted C-Si bond cleavage in α-silylaminium radicals is a common process.

Mariano, Falvey, Yoon and Su [13,19] probed the dynamics of aminium radical desilylation by using time resolved laser flash photolysis studies of SET-photoreactions of 1,4-dicyanobenzene (DCB) and N-silylmethylanilines 13 (Scheme 10). Interestingly, the rate of desilylation of the anilinium radical 14 (R=Me), formed by SET from the corresponding aniline to DCB, is slow and not competitive with back-SET (BSET) when weak silophiles like MeCN are present. However, in the presence of good silophiles, such as MeOH or water, desilylation of 14 (R=Me) occurs more rapidly than either BSET or α-deprotonation. Second order rate constants for the desilylation processes parallel the silophilicity of the silophile (e.g., $8.9 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ for MeOH and $1.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for H_2O, and $3.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for fluoride ion in MeCN).

In a fashion similar to amine cation radical α-CH-deprotonation reactions, the presence of electron withdrawing substituents on nitrogen results in a significant enhancement of the rates of desilylation of α-silylaminium radicals. This is seen in comparisons of the second order rate constants for methanol promoted desilylation of anilinium radicals 14 having N-methyl (R=Me, $9 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$), N-ethoxycarbonyl (R=CO$_2$Et, 2×10^7 M^{-1}s^{-1}), and N-acetyl (R=COMe, 6×10^7 M^{-1}s^{-1}) substituents. Since an N-electron withdrawing group pronouncedly increases the oxidation potential of the silylaniline 13 while having little effect on the stability of the resulting α-amino radical 15, the rate acceleration is attributable to destabilization of the amine cation radical.

The Influence of Aminium Radical α-Heterolytic Fragmentation Rates on SET-Photoreactions of α-Silylamines

The results of early studies by Mariano, Yoon and their coworkers [20-21] demonstrated that SET-promoted photoreactions of α-silylamines are governed by the relative rates of aminium radical desilylation and deprotonation. An example is found in the photoaddition reactions of silylamine 17 and cyclohexenone 16 (Scheme 11). The polarity, protic nature and silophilicity of solvents govern the relative efficiencies for formation of the TMS and non-TMS photoadducts 18 and 19. Production of the TMS-adduct 18 is favored when the photoreaction is conducted in low polarity, aprotic, less silophilic solvents (e.g., MeCN) while the non TMS-adduct predominates in processes occurring in high polarity, protic, highly silophilic media (e.g., MeOH).

These along with additional observations suggest that the nature of photoreactions of cyclohexenone-silylamine systems is controlled by factors that govern the nature and chemical reactivity of the intermediate aminium radicals. The reaction is initiated by SET from the silylamine 17 to triplet excited state of 16, initially generating a solvent separated ion radical pair (SSIRP) 20 and then either a CIRP 21 or free radical ions (Scheme 12). α-Proton transfer from the most kinetically acidic site in the aminium radical to the enone anion radical in the CIRP generates the caged radical pair 24 which undergoes radical coupling to give the TMS-adduct 18. In polar protic solvents, transformation of SSIRP to free radical ions (22 and 23) rather than the CIRP would be more facile due to strong solvation of the radical ions by H-bonding and dipole interactions. Two possible reaction pathways are available to the solvated free α-silylaminium radical 23. When the concentration of amine 17 (a base) is low and the solvent is highly silophilic, desilylation of 23 is expected to predominate over deprotonation. This yields the α-amino radical 25, which can undergo conjugate addition to enone 16 to yield the non-TMS 19.

To further investigate the modes of C-C bond formation in this process (specifically the competition between radical coupling and radical conjugate addition), Mariano and his coworkers [22] designed a system in which intramolecular trapping of the putative α-ketoradical would reveal the operation of the radical conjugate addition mechanism. For this purpose, photoaddition reactions of N,N-dimethylaniline and its silyl analog 26 (Y=H or TMS) were investigated (Scheme 13). The observed formation of the tricyclic adduct 28 in photoreactions of the silyl-aniline in polar-silophilic solvents indicates that the keto-radical 27 is an intermediate in this process and that the
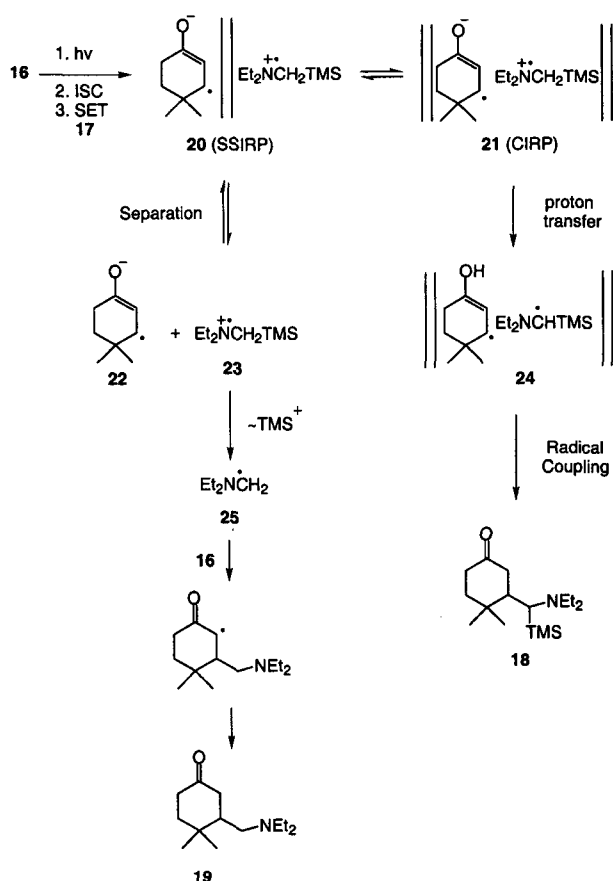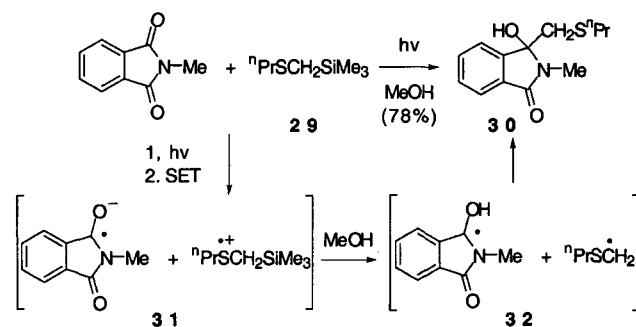
Scheme 12.
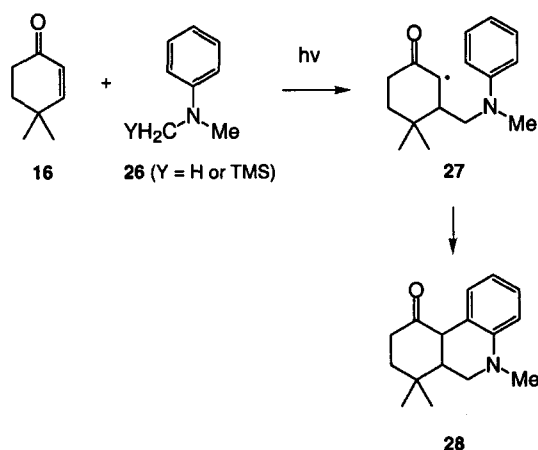
Scheme 13.

radical conjugate addition pathway is operable.

SET-Promoted Photoaddition and Photocyclization Reactions of Silicon Substituted Phthalimides

The ability to control the nature and regiochemistry of fragmentation reactions of silylamine cation radicals by the choice of solvent has served as a key component in the design
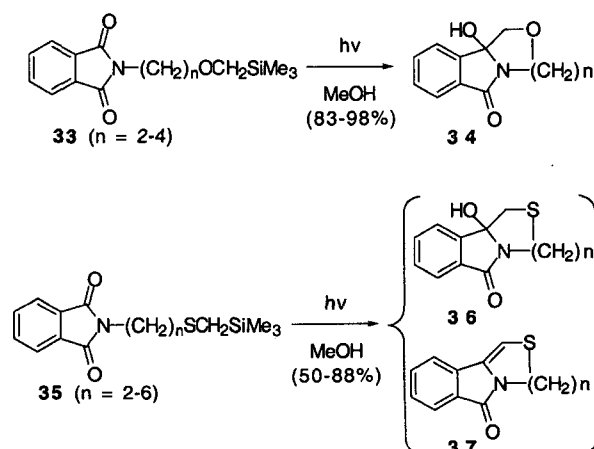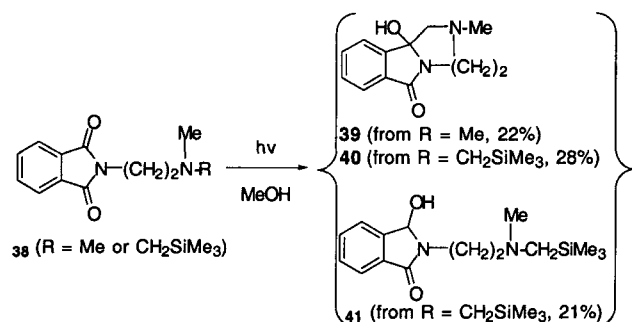

Scheme 14.

of new and highly efficient SET-promoted photocyclization reactions [17,23]. Moreover, studies of SET-induced excited-state reactions of phthalimides with α-trialkylsilyl substituted ethers, thioethers, amines and amides have documented the general nature of photochemical reactions that proceed by pathways involving the generation and desilylation of α-silicon substituted cation radical intermediates. For example, in an early study of phthalimide SET-photochemistry, we observed that simple α-silyl-substituted ethers, thioethers, amines and amides undergo efficient photoadditions to phthalimide and its N-methyl derivative [24] One example is the photoaddition of silylmethylpropylthioether 29 to N-methylphthalimide, which produces the adduct 30 (Scheme 14).

Photocyclization reactions of phthalimides containing N-tethered α-silyl donors proceed with high chemical efficiencies to generate a variety of novel heterocyclic products. For example, irradiation of MeOH solutions of the phthalimido silyl ethers 33 leads to formation of the amidol containing, oxygen heterocycles 34 in excellent yields (Scheme 15) [25]. Analogous photocyclization reactions are observed with the phthalimido thioethers 35 [25].

A parallel investigation of the photochemistry of α-silyl-amine and α-silyl-amide linked phthalimides has provided a greater understanding of the factors that govern both the chemical
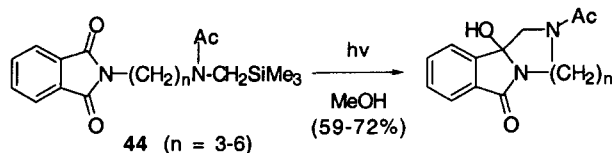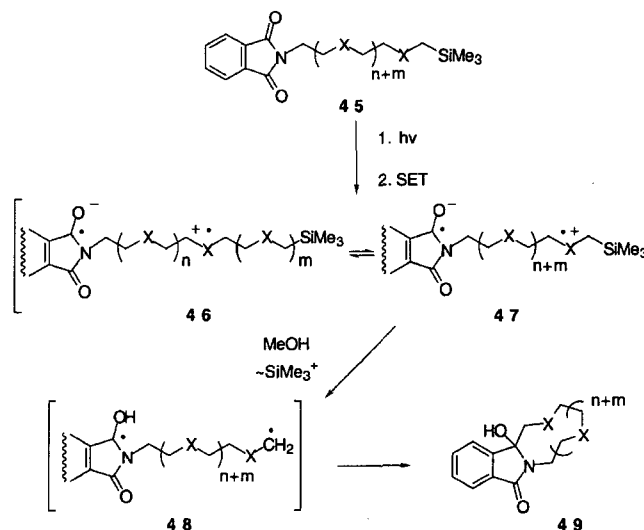

Scheme 15.

Scheme 16.
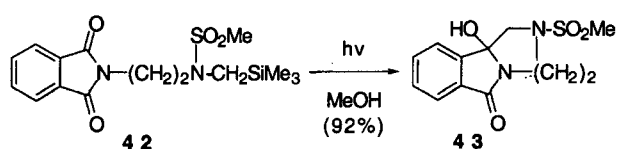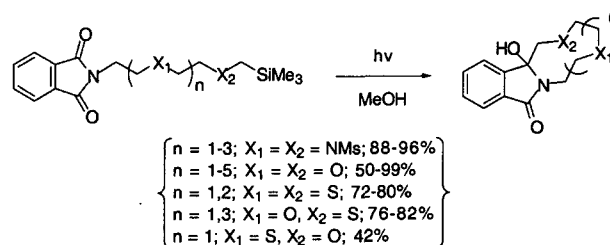
Scheme 17.

Scheme 18.

Scheme 19.

Scheme 20.

and quantum yields of SET-promoted photocyclization reactions [26-28]. Irradiation of a MeOH solutions of the silylamino-phthalimides **38** leads to non-selective formation of a mixture of products including the fused diazines **39** and **40**, and amidol **41** (Scheme 16). In stark contrast, the tricyclic sulfonamide **43** is formed in high yield when the silylamido-phthalimide **42** is irradiated in MeOH (Scheme 17). The results suggest that the preparative utility of photocyclization reactions, operating by sequential SET-desilylation pathways, could be enhanced by using substrates that contain α-silylamide rather than α-silylamine donor sites. Support for this proposal is found in photoinduced cyclization of the acetamide derivatives **44** shown in Scheme 18. Quantitative studies showed that the quantum yields of photocyclization reactions of the linked phthalimides **38** and **42** are also greatly dependent on the nitrogen-substituent with the amide substrate **42** reacting with a greater efficiency ($\phi = 0.12$) than the amine analog **38** ($\phi = 0.04$). Additional studies showed that the quantum yields for photocyclization reactions of the phthalimido-ether **33** (n=2, $\phi = 0.22$) and -thioether **35** (n=2, $\phi = 0.11$) also parallel donor oxidation potentials / cation radical stability [28].

Phthalimide SET-Photochemical Routes for Macrocyclic Polyamide, Polyether and Polythioether Synthesis

The chemical yields of photoaddition and photocyclization

reactions of systems comprised of linked phthalimides and α-silyl heteroatom donors are normally quite high. As a result, these processes can be used as key steps in routes targeted at selected members of polyamide, polyether and polythioether macrocyclic families. As depicted in Scheme 19, photoinduced SET in phthalimides **45**, which have N-linked, silylmethyl terminated, polyheteroatom chains would yield a mixture of rapidly interconverting zwitterionic biradicals **46** and **47**, whose populations would be governed by the relative energies of the cation radicals. Importantly, the rates of α-deprotonation and α-desilylation adjacent to the positively charged odd electron centers in each of the rapidly interconverting zwitterionic biradicals will contribute in determining the relative yields of 1,n-biradicals that will be produced in these processes. Since desilylation at the terminal cation radical sites in **47** should be the most rapid fragmentation process [29-30], selective generation of the ω-diradicals **48** should occur and these intermediates should generate macrocyclic products **49** preferentially. As seen by viewing the photoreactions depicted in Scheme 20, irradiation of the phthalimido-silylpolyamides, polyethers and polythioethers in MeOH solution does indeed result in efficient production of the corresponding macrocyclic products [29-30].

Summary

In this review, several important types of α-heterolytic

fragmentation reactions of aminium radicals have been discussed. In these fragmentation processes, transfer of electrofugal groups from the aminium radicals to either Lowry-Bronsted or Lewis bases produces α-amino radicals. The results of recent studies that provide key information about the dynamics of the important aminium radical fragmentation reactions, deprotonation, desilylation, were summarized. Finally, examples have been provided to demonstrate how knowledge of the relative rates of aminium radical cleavage can be used to design synthetically relevant SET-promoted photocyclization reactions.

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