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Reactions of Radical Anion and Cations: An Overview

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Abstract
Radical reactions occur through the intermediacy of odd electron species, and are among the key fundamental classes of organic transformations. Such processes play important roles in mechanistic and synthetic organic chemistry and are essential for many biological and materials applications. In this review the cationic and anionic mode of reactions of radicals in organic molecules have been discussed in details with their mechanistic development.

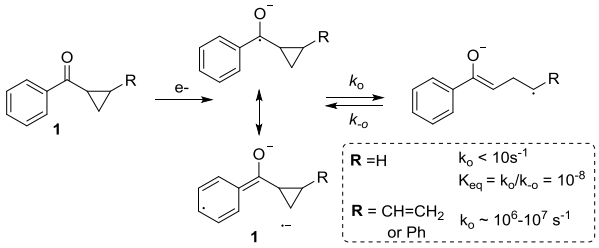
Keywords: *Radical-cations, radical-anions, intermediate, ring closure, electron transfer processes*

1. Introduction

The use of small organic molecules to catalyze asymmetric transformations has been known since the early 1970's (e.g. the Hajos-Parrish-Eder-Sauer-Wiechert Reaction). However, the recognition of this reaction's mechanism as a general mode of carbonyl activation was overlooked. In 2000, general modes of activation using small organic molecules (secondary amines) were introduced, namely enamine and iminium ion catalysis. Recently, catalysis based on single-electron oxidation of transiently produced, electron rich enamines has introduced a new mode of activation termed SOMO organocatalysis. Activation by this method allows for reaction with a variety of weakly nucleophilic substrates incompatible with previous methods. For successful SOMO organocatalysis, an equilibrium population

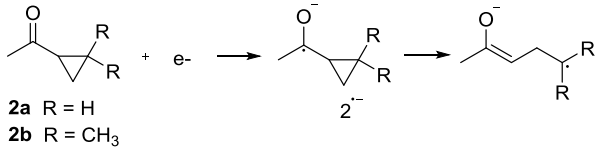
2. Recent Developments and reactions of Radical ions

Over the past several decades, radical ions have emerged as an important class of reactive species. Their role as potential intermediates in numerous organic and bio-organic reactions and development of new synthetic methods based on their chemistry has attracted significant attention. In 1990, the chemistry of radical anions generated from substituted phenyl cyclopropyl ketones was first reported by Tanko and co-workers (**Scheme 1**) [1]. For R = alkyl or hydrogen, ring opening of $1^{\bullet-}$ is very slow and reversible with an equilibrium constant favoring the ring-closed radical anion (ko < 10s-1 and Keq = ko/k-o = 10-8 for R =H). Placement of radical-stabilizing substituents (R = phenyl or vinyl) on the cyclopropyl group partially compensates for this loss of resonance energy, and ring opening becomes more favorable (ko ~ 106-107 s-1 for R = CH=CH2 or Ph).



Scheme 1. Phenyl cyclopropyl ketones radical anion ring opening.

Radical anions can also be generated from aliphatic ketones. Radical anions derived from 2a and 2b undergo cyclopropane ring opening, slightly favoring the 3° distonic radical anion (**Scheme 2**). Electron transfer was found to be the rate limiting step regardless of whether the reduction was carried out directly (CV) or indirectly (homogeneous redox catalysis) suggesting a rate constant for ring opening > 107 s-1. Because the kinetics of reduction of 2a and 2b involve rate limiting electron transfer, the rate constant for ring opening could not be determined.



Scheme 2. Ketyl radical anions ring opening

An important reaction involving radical anion intermediates of is the unimolecular radical nucleophilic substitution ($S_{RN}1$) reaction. The $S_{RN}1$ mechanism was first proposed for the substitution of

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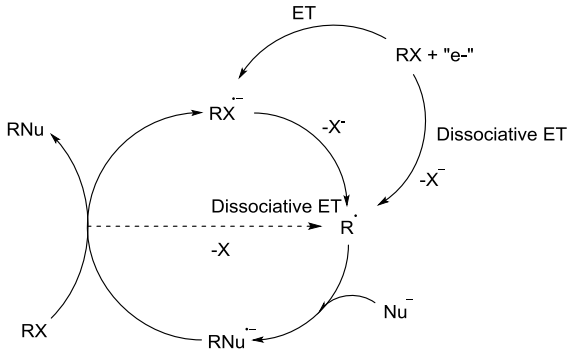
alkyl halides bearing electron-withdrawing groups (EWGs) in the α position and a suitable leaving group [2]. In 1970, Bunnett applied this mechanism to unactivated aromatic halides [3]. Later on, other substrates such as vinyl halides, perfluoroalkyl halides, alkylmercury chlorides, as well as cycloalkyl, bridgehead, and neopentyl halides were reported to react by this mechanism. The process has a considerably wide scope. Many substituents, such as alkyl groups, OR, OAr, SAr, CF_3, CO_2R, NH_2, NHCOR, NHBoc, SO_2R, CN, COAr, NR_2, and F are compatible with the reaction. In addition to halides, many other leaving groups are known for this reaction including $(EtO)_2P(O)O^-$, RS^-, $ArOS^-$, ArO_2S^-, $PhSe^-$, Ph_2S, RSN_2 (R = t-Bu, Ph), BF_4N_2, R_3N, N_2, N_3^-, NO_2^-, and HgX^-. Thus, ArOH and $ArNH_2$ are ultimately the leaving groups through phosphate esters and ammonium salts.

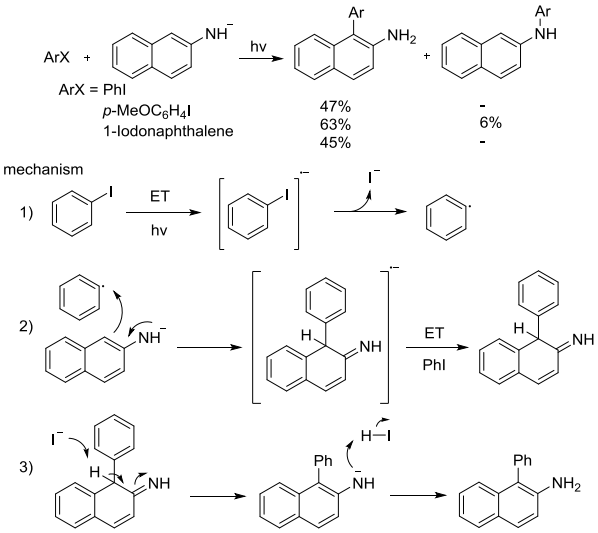
The $S_{RN}1$ mechanism has proved to be an important route to ring-closure reactions, mainly in aromatic systems. The synthesis of indoles, carbazoles, isoquinolones, and other heterocycles, as well as a large number of natural products, has been achieved by this process. Several reviews have been published on the $S_{RN}1$ mechanism for substitution at sp^3 and sp^2 carbons [4]. Aromatic photo-initiated substitutions [5] as well as reactions performed under electrochemical catalysis [6, 7], convey the scope and the synthetic applications of this process [8]. In the initiation step of the $S_{RN}1$ mechanism, the radical anion of substrate $RX^{\cdot-}$ can be formed upon ET from the nucleophile or from a suitable electron source; the ET to unsubstituted alkyl halides is proposed to be a dissociative reaction [9]. $RX^{\cdot-}$ fragments to afford the radical $R^{\cdot}$ and the anion of the leaving group. The radical thus formed can react with the nucleophile to give the radical anion of the substitution product $RNu^{\cdot-}$, which by ET to the substrate forms the intermediates required to propagate the cycle. The termination steps depend on the substrate, the nucleophile, and the experimental conditions (**Scheme 3**) [10].



Scheme 3. Representation of the mechanism of the $S_{RN}1$ reaction

Nitrogen anion is a common nucleophile in the $S_{RN}1$ reaction. The first example of an $S_{RN}1$ type process was the reaction of ArX with the $NH2^-$ ion [11]. Thus, $ArNH_2$ products can be obtained by reaction with 1-chloro-2,4,5-trimethylbenzene and 1-chloro-2,3,5-trimethylbenzene, o-$MeOC_6H_4X$ (X = Br or I), 2-iodo-1,3-dimethylbenzene, PhOPh, 3-bromothiophene, and $ArOP(O)(OEt)_2$, under K metal reduction in liquid ammonia [11]. NH_2^- ions react under photoinitiation with 2-bromo-1,3,5-trimethylbenzene with good substitution yields (70%) [12].

$PhNH^-$ ions reacts in the presence of K metal with PhI, and substitution occurs not only at nitrogen but also at ortho and para carbons of the phenyl ring. On the other hand, the 2-naphthylamide ion reacts under photoinitiation with PhI, p-$MeOC_6H4I$, and 1-iodonaphthalene in liquid ammonia to give 1-aryl-2-naphthylamines in good yields [13]. The $S_{RN}1$ reaction is quite versatile in that other nucleophiles for this reaction can be derived from P [14], As [15], S [16], Se [17], and Te [18].



Scheme 4. The first example of an $S_{RN}1$ type process with the mechanism below

Reactions of carboanions to afford a new C-C bond constitutes one of the more representative examples of $S_{RN}1$ reactions with aromatic substrates. Carbanions derived from hydrocarbons, such as 1,3-pentadienyl, 1-(4-anisyl)propenyl, fluorenyl, and indenyl anions, have been studied along this line [19]. The regiochemistry of the coupling favors the formation of the more stable radical anion intermediate. When aromatic substrates with two leaving groups such as 3 react with enolates, mono and disubstituted products can be obtained, depending on the nature and the position of the leaving group and on the nucleophile. Upon receiving an electron, substrate 3 forms the radical anion $3^{\cdot-}$, which fragments at the more labile C-X bond to give radical 4. Then, this radical intermediate 4 reacts with the nucleophile to form

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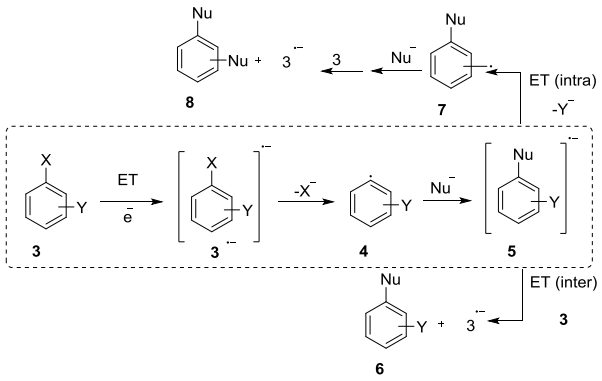
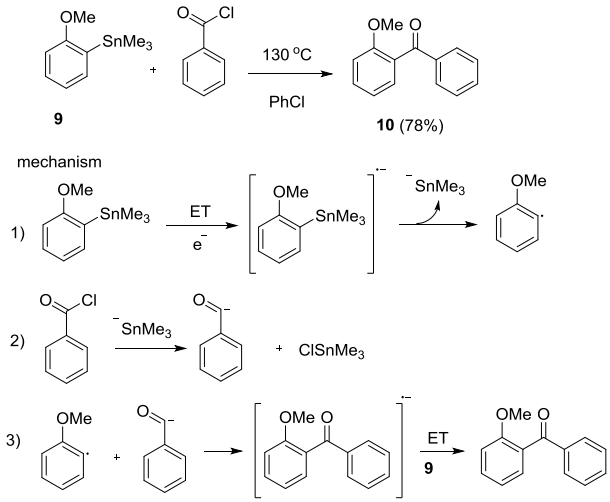
the radical anion 5. This radical anion can transfer the extra electron to another molecule of 124 (ETinter) to furnish product 6, or to the second C-Y bond by an intramolecular ET (ETintra). If ETintra occurs, 5 fragments to afford radical 7, which by coupling with the nucleophile followed by an ET reaction, generates the disubstitution product 8 (**Scheme 5**). This behavior is observed with dihalo substrates, not only with anions derived from ketones but with other nucleophiles as well [20].



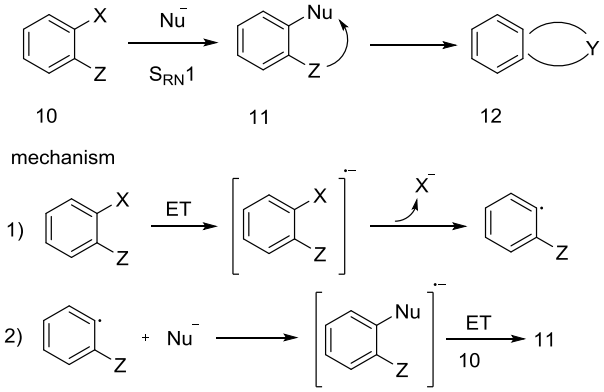
Scheme 5. Two possible pathways in $S_{RN}1$ reactions with two leaving groups

Transition metals such as Sn can help in generating the nucleophile in the $S_{RN}1$ reaction. For example, the leaving group ability of the Me_3Sn group in nucleophilic substitutions allows the synthesis of asymmetric diaryl ketones in good yields (40-78%) through the reaction of Me_3SnAr with acyl chloride. These reactions are completely regioselective, allowing the synthesis of diarylketones not usually available under Friedel-Crafts reactions. The reaction of stannane 9 with PhCOCl in PhCl as solvent, for instance, furnished diarylketone 10 in 78% yield [21]. Specific di- and triketones are obtained in good to excellent yields (45-83%, **Scheme 6**) [22].



Scheme 6. The leaving group ability of Me_3Sn allows efficient formation of diarly ketones upon reaction with acylchloride.

There has been much study into the use of ring closing $S_{RN}1$ reactions. These reactions work through the $S_{RN}1$ substitution of aromatic compounds that have an appropriate substituent (Z) ortho to the leaving group, such as 10, which reacts with a nucleophile to afford product 11. The ring-closure product 12 is obtained by the reaction between the (Nu) and (Z) groups.



Scheme 7. Dual role of aromatic substituents as directing groups and reactive pendants for cyclization.

For example the $S_{RN}1$ approach can be used as a route to isoquinoline rings and derivatives by reaction of o-iodobenzylamines with enolate ions under irradiation. The substitution product 13 reacts further by ring closure to give product 14. If 14 is treated with $NaBH_4$, tetrahydroisoquinolines 15 are obtained. On the other hand, treatment with Pd/C provides isoquinoline derivatives 16 (**Scheme 8**) [23]. For more examples of the $S_{RN}1$ reaction see "The $S_{RN}1$ Reaction" [24]. The atomic oxygen radical anion plays a key role in a number of biological reactions [25]. The carbonate radical anion ($CO_3^{\bullet-}$) is an important oxidant in cellular environments[26].

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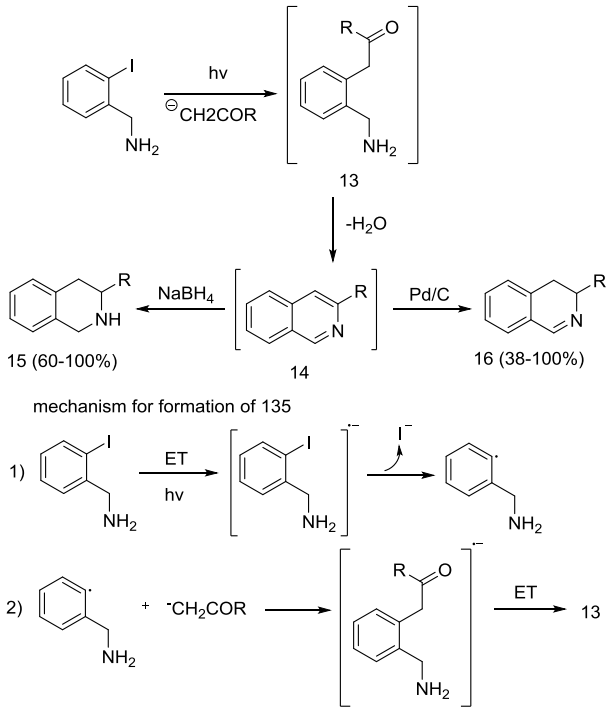


Scheme 8. Synthesis of tetrahydroisoquinolines (15) and isoquinolines (16) from o-iodobenzylamines and $^{-}CH_2COR$ anions by $S_{RN}1$-ring-closure sequence.

Reactions that proceed through radical cations have not garnered as much attention as the other radical processes. Currently, only a small fraction of preparative reactions is based on electron transfer processes [27]. Examples include the Birch reduction [28], acyloin condensation [29], Ullman coupling [30], formation of Grignard reagents [31], the radical cation catalyzed Diels-Alder reaction [32], and the above mentioned $S_{RN}1$ reaction [33]. As mentioned before, the major reason for the scarcity of radical cation ET reactions in synthesis is due to the difficulty in controlling the various reaction events involving odd-electron species, regardless of whether a catalytic (**Figure 1a**) or stoichiometric transformation is considered (**Figure 1b**). This section will briefly outline select examples of radical cations in synthesis.

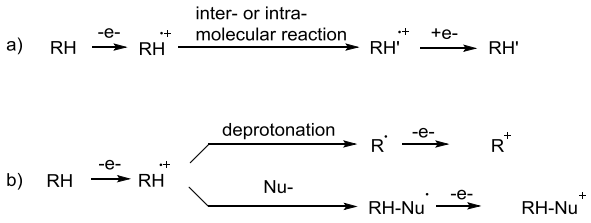
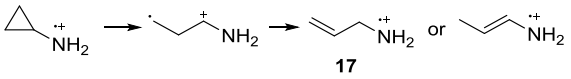


Figure 1. Reaction of odd-radical species in catalytic (a) and stoichiometric amounts (b)

Similar to the cyclopropane ring opening reactions involving radical anions, radical cation ring openings have been studied as well. Ring opening reactions of this nature are still in infancy though, as kinetic data is virtually non-existent for aliphatic amine radical cations. Theoretical and experimental studies demonstrate that the cyclopropylamine radical cation undergoes barrier-less ring openings in both gas and solution (Freon) phase [34]. The distonic ring-opened radical-cation isomerizes via successive 1,2-hydride migration (**Scheme 9**) [35]. Ring-opened cyclopropylamine radical cations preferentially form the radical cation of allylamine 17.



Scheme 9. Ring openings of aliphatic cyclopropylamine radical cation and subsequent 1,2-hydride migration.

Rings opening through radical cation intermediates can also be used for ring expansion. Siloxy cyclopropane radical cations are key intermediates in synthesis of larger ring systems wherein the radical cation ring opens. Without nucleophilic assistance to a distonic radical cation, subsequent loss of the silane group forms a β-keto radical [36]. These β-keto radicals can undergo further intramolecular addition to π systems. Transition state calculations by Mattay and coworkers on (bicyclo[4.1.0]heptan-1-yloxy)trimethylsilane determined that endocyclic bond cleavage of the cyclopropane ring occurs predominantly [37]. Experimental work with analogous compounds is supported by Hasegawa [38]. Further study of the regioselectivity of the cleavage of the bonds in these bicyclic compounds (**Scheme 10**) revealed that (i) photochemically induced electron transfer and chemically induced oxidation (by tri-bromophenylaminyl radical cation) caused ring opening to occur via different pathways, as evidenced by observed products and (ii) the presence of a nucleophile in chemically oxidized systems enhances the ability of the radical cation to undergo desilylation thus increasing reaction efficiency. In addition to utility in synthesis, N-cyclopropyl substituted radical cations have been interesting target molecules for use as mechanistic probes and radical clocks.

N-alkyl-N-cyclopropylaniline radical cations have also been investigated in ring opening processes. N-alkyl-N-cyclopropylanilines have been employed previously as mechanistic probes in nitrosations of aromatic amines where ring opening is an indicator of radical cation intermediates. Nitrosation of N-

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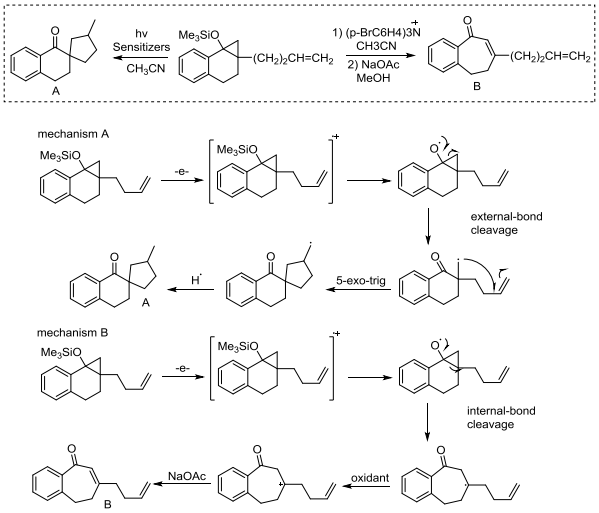
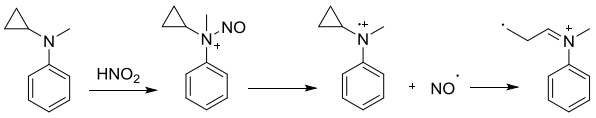


Scheme 10. Spirocyclic cyclopropane radical cation exhibits regioselectivity during ring opening as determined by mode of radical cation generation

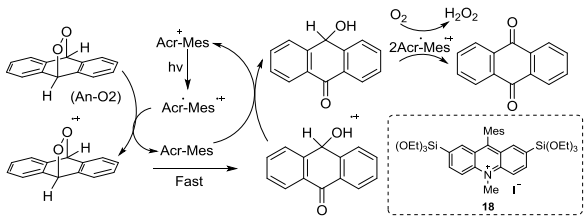
alkyl-N-cyclopropylanilines in acidic media (**Scheme 11**) proceeds through an aminyl radical cation intermediate. This intermediate undergoes regioselective ring opening and reacts further to form N-alkyl-N-nitroanilines [39].



Scheme 11. Nitrosation mechanism for N, N-dialkylanilines

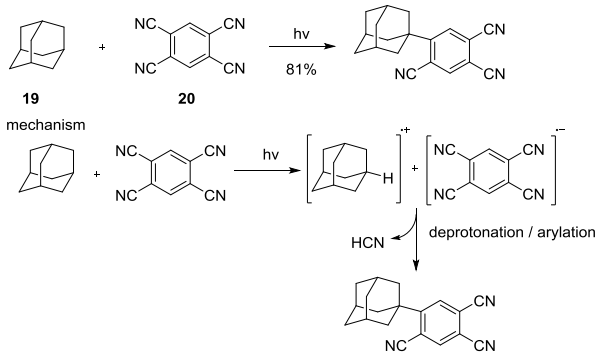
Photoirradiation is another common method of inducing radical transformations that go through radical cation intermediates. For example the photocatalytic oxygenation of anthracene by O_2 with Acr+-Mes complex 18 (**Scheme 12**) to form anthraquinone [40]. The photo-catalytic oxygenation of anthracenes is initiated by photoexcitation of Acr+-Mes, which results in the formation of the electron-transfer state ($Acr^{\cdot}$-$Mes^{\cdot+}$), followed by electron transfer from anthracenes to the $Mes^{\cdot+}$ moiety together with electron transfer from the $Acr^{\cdot}$ moiety to O_2 [41]. The resulting anthracene radical cation undergoes radical coupling reactions with $O_2^{\cdot-}$ to produce the epidioxyanthracene (An-O_2). The mechanism of the photocatalytic conversion of An-O_2 to 10-hydroxyanthrone is shown in **Scheme 12**.

Photochemistry is useful in reactions that proceed through radical cations. Evidence for σ C-$H^{\cdot+}$ cleavage was deduced from pulse radiolysis studies [42]. From ESR investigations, it was suggested that deprotonation preferentially occurs at the C-H bond with the highest unpaired electron density [43].



Scheme 12. Photocatalytic oxygenation of anthracene by O_2 with Acr+-Mes

A couple of decades ago it was observed that σ C-$H^{\cdot+}$ deprotonations occurred through the arylation of alkanes upon PET with TCB 20 or CA (**Scheme 13**) [44, 45]. In $19^{\cdot+}$ deprotonation at the tertiary carbon atom is always favored. For more examples on the mechanistic insights of reactions involving radical cations see review by Schmittel and Burghart [46]. For more photochemical reactions involving radical cations see "Photoinduced Reactions of Radical Ions via Charge Separation"[47].



Scheme 13. σ C-$H^{\cdot+}$ deprotonation in arylation of adamantine

The use of small organic molecules to catalyze asymmetric transformations has been known since the early 1970's (e.g. the Hajos-Parrish-Eder-Sauer-Wiechert Reaction). However, the recognition of this reaction's mechanism as a general mode of carbonyl activation was overlooked. In 2000, general modes of activation using small organic molecules (secondary amines) were introduced, namely enamine and iminium ion catalysis. Recently, MacMillan and Sibi have developed catalysis based on single-electron oxidation of transiently produced, electron rich enamines has introduced a new mode of activation termed SOMO organocatalysis. Activation by this method allows for reaction with a variety of weakly nucleophilic substrates incompatible with previous methods. For successful SOMO organocatalysis, an equilibrium population of enamine must undergo preferential oxidation, the amine catalyst must enforce high levels of enantiocontrol in the coupling of the radical cation with nucleophiles, and the general reactivity mode must be useful in other enantioselective reaction.

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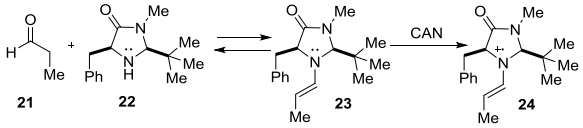
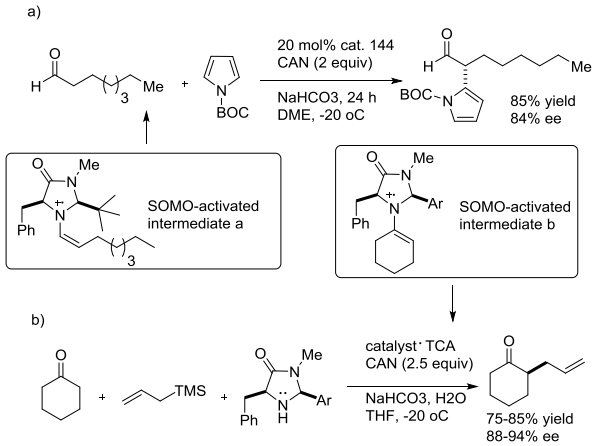
As of recent, enantioselective oganocatalysis to form carbon-carbon bonds has received much attention. MacMillan and Sibi have developed in the realm of organocatalysis, in which singly occupied molecular orbital (SOMO) activation is used for enantioselective α-allylation [48, 49], α-vinylation [50], α-oxygenation of aldehydes [51], and α-allylation of ketones [52]. The SOMO catalysis proceeds by single-electron oxidation of a transiently formed enamine to give the radical cation (SOMO of activated species). For example, propanal 21 reacts with imidazolidinone catalyst 22 to form eneamine 23. This can then go through a one-electron oxidation, using a reagent such as ceric ammonium nitrate (CAN), to form the radical cation 24 (**Scheme 14**).



Scheme 14. Catalytic chemical steps leading to formation of SOMO-activated intermediate

Reaction of octanal and N-tert-butyl carbamoyl pyrrole under the SOMO activation conditions enables formyl α-arylation with enantioselectivity and in excellent yields (**Scheme 15a**). It has also been found that unsaturated aldehydes rapidly undergo enantioselective cyclization with trapping of an exogenous halide. α-Allylation of ketones via a similar reaction design was developed later (**Scheme 15b**).



Scheme 15. α-Allylation of aldehydes (a) and ketone (b) through SOMO catalysis with high yields and ee

3. Conclusions

Radical reactions have proven themselves to be among the most powerful and adaptable tools in the synthetic chemists arsenal.

The chemistry of radical reactions has a long history but continues to grow. The synthetic utility of radical reactions is enhanced by their functional group tolerance as well as by the relatively mild conditions (no need for strong acids and bases) under which radicals can be generated and it is further expanded by the ability of radicals to carry on multiple sequential bond-forming reactions in intramolecular cascades. The combination of these features allowed for the synthesis of many complex natural products with remarkable efficiencies. The future development of this area benefits strongly from the abundance of high quality kinetic data and modern computational techniques capable of accurate description of potential energy profiles for radical transformations.

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