

# Photochemical Nucleophile–Olefin Combination, Aromatic Substitution Reaction. Its Synthetic Development and Mechanistic Exploration

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## ABSTRACT

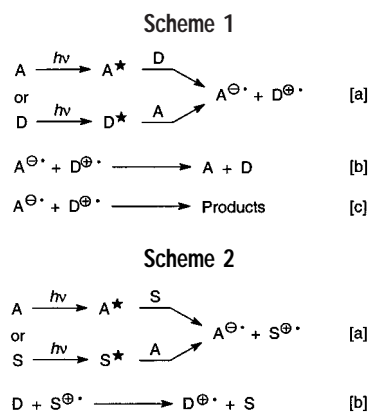
The photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction has been a cornerstone of research in our laboratory for several years. In this Account we present an overview of the mechanistic exploration and rationalization of this photoinduced electron transfer reaction. We have investigated the mechanism and defined the synthetic scope and limitations by variations in reaction conditions and structural modification of the substrates. During our studies, we have come across several other pathways in competition with the photo-NOCAS reaction that dominate once specific conditions are altered. These alternative reactions are also discussed briefly.

## Introduction

One of the rapidly growing areas of research in organic chemistry is the discovery, characterization, and ultimate utilization of reactions involving radical ions as intermediates.<sup>1</sup> These reactive intermediates are commonly generated by photoinduced electron transfer (PET).<sup>2</sup> Photoelectronic excitation facilitates electron transfer by enhancing both the oxidizing and reducing properties of a chemical species by an amount equal to its excitation energy.<sup>3</sup> In the presence of a suitable redox partner, electron transfer will occur to generate the radical anion of the electron acceptor A and the radical cation of the electron donor D (Scheme 1a).

Dino Mangion was born on the Mediterranean island of Malta. He received his B.Sc. in chemistry and physics with highest honors from the University of Malta in 1993 and his M.Sc. in chemistry with distinction from the same university in 1996. He completed his Ph.D. at Dalhousie University under the mentorship of Professor Donald R. Arnold in 2001. He is currently a postdoctoral fellow at McMaster University, working with Professor William J. Leigh. His research interests include organic photochemistry, with a special emphasis on electron-transfer processes.

Donald R. Arnold was born in Buffalo, NY. He received his B.Sc. degree in mathematics and chemistry from Bethany College, WV (1957), and his Ph.D. from the University of Rochester (1961), working under the direction of Marshall Gates. After 10 years of industrial research experience at the Union Carbide Research Institute, he immigrated to Canada and joined the Photochemistry Unit, Department of Chemistry, at the University of Western Ontario (1971–9). He then took up the Killam Research Professorship at the Department of Chemistry, Dalhousie University, and subsequently the Alexander McLeod Professorship (1991). He has received numerous awards and honors, including the Alfred Bader Lecture award in Organic Chemistry (1995) and the Bethany College Alumni Achievement Award (2000). His research interests involve the areas of organic photochemistry and electrochemistry and reactions of free radicals and radical ions.



Once formed, the radical ions may undergo back-electron transfer (BET) to regenerate the neutral starting materials (Scheme 1b). This latter process is essentially an energy-wasting step and the main reason behind the low quantum yields of product formation in many PET reactions. Alternatively, if the photochemical system has been properly selected, the radical ions may either react with each other within the geminate radical ion pair or else diffuse apart and undergo reaction within the bulk of the solvent medium (Scheme 1c).<sup>4</sup>

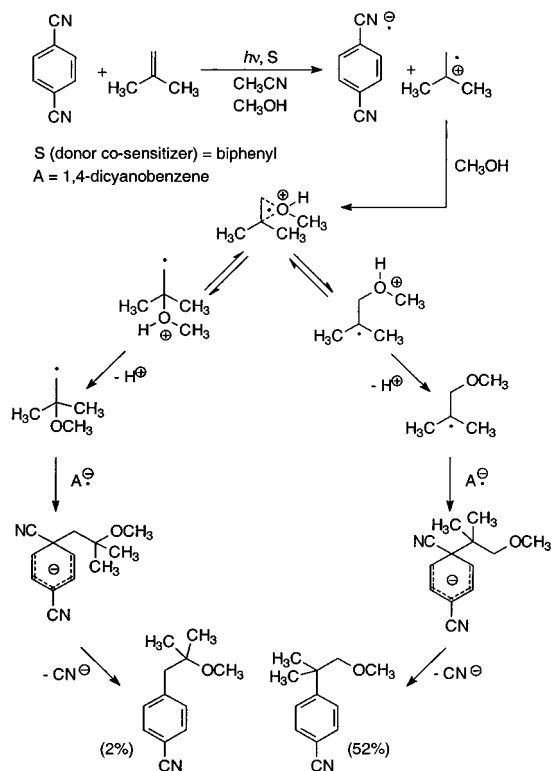
## Co-Sensitization

One of the most successful techniques for reducing BET is co-sensitization.<sup>2a,5</sup> This involves the utilization of a third species, in addition to the fundamental donor–acceptor pair, which acts as an intermediate in the PET process. The co-sensitizer can either be an electron acceptor or an electron donor, although in most cases it is the latter (typically an unreactive aromatic hydrocarbon such as biphenyl or phenanthrene). It can act as the principal light absorber or just partake in the PET step from the ground state.<sup>6</sup> Scheme 2 illustrates a PET mechanism for a donor–acceptor (D–A) pair mediated by a donor co-sensitizer (S).

Rather than occurring directly between A and D, the primary electron-transfer step takes place between the acceptor A and the co-sensitizer S (with either A or S in its excited state, A\* or S\*), generating the radical ions A<sup>•−</sup> and S<sup>•+</sup>, respectively (Scheme 2a). Once these diffuse apart, the co-sensitizer radical cation S<sup>•+</sup> can undergo a secondary electron transfer with the donor D, regenerating the neutral co-sensitizer molecule S and the donor radical cation D<sup>•+</sup> (Scheme 2b). The net result is the generation of the donor and acceptor radical ions, A<sup>•−</sup> and D<sup>•+</sup>, in separate stages.

If the choice of co-sensitizer is appropriate, the quantum yield of formation of the radical ions in the co-sensitized mode should be increased relative to the unsensitized PET reaction. This typically requires the co-sensitizer to have a higher oxidation potential than the electron donor. The enhancement is a consequence of a slower rate of BET for the A<sup>•−</sup>–S<sup>•+</sup> pair as opposed to the A<sup>•−</sup>–D<sup>•+</sup> pair, a phenomenon attributed to the inverse

Scheme 3



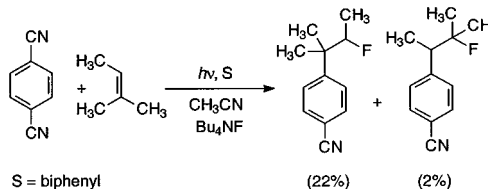
relationship between the rate of BET and its associated free energy in the Marcus inverted region in which BET typically operates.<sup>4,5</sup> We have often observed successful co-sensitization even by species possessing oxidation potentials lower than those of the donors. In these cases, reaction enhancement is attributed to the longer lifetime of  $S^+$  as compared to  $A^*$ , facilitating the formation of  $D^+$ .<sup>2a</sup>

## Photo-NOCAS Reaction

We have dedicated a considerable research effort to the synthetic development and mechanistic exploration of a wide variety of PET reactions. Over the past 20 years we have placed a major emphasis on the understanding of the photochemical nucleophile–olefin combination, aromatic substitution reaction, conveniently referred to as photo-NOCAS. Apart from our interest in defining its synthetic potential, the photo-NOCAS reaction and its mechanistic variants serve as a useful framework in which to investigate the behavior of photogenerated radical ions.

The reaction has been examined in detail and is now well-understood. It involves the co-reactivity of an aromatic electron acceptor, an olefinic electron donor, and a nucleophile in a distinct mechanistic sequence. This is illustrated in Scheme 3 for the archetypical example involving 1,4-dicyanobenzene, 2-methylpropene, and methanol.<sup>7</sup> The first step in the mechanism involves the photochemical excitation of 1,4-dicyanobenzene to its first excited singlet state. This enhances its oxidizing properties so that it undergoes electron transfer from the olefin to give the corresponding olefin radical cation and cyanoarene radical anion. In the majority of cases, including the present example, donor co-sensitization using aro-

Scheme 4



matic hydrocarbons has been demonstrated to have a beneficial effect.

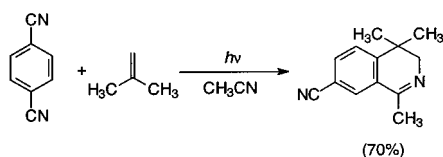
The contact radical ion pairs formed upon electron transfer may diffuse apart to give free, solvated radical ions or undergo BET to regenerate the starting materials. In those cases where BET is circumvented, the alkene radical cation is attacked by methanol to give a nonclassical, bridged radical cation complex in equilibrium with the two possible distonic radical cations. Subsequent deprotonation from the oxygen of the distonic radical cations, giving the corresponding  $\beta$ -methoxyalkyl radicals, determines the regiochemistry of addition. The resulting radicals add on to the 1,4-dicyanobenzene radical anion at the *ipso* position (site of highest spin density). Rearomatization follows via expulsion of cyanide anion to give the final photo-NOCAS products.

In reactions involving methanol as nucleophile, the regiochemistry of nucleophilic addition is determined by the stability of the respective  $\beta$ -methoxyalkyl radicals. This is possible as a result of the involvement of distonic radical cations that provide an opportunity for regiochemical equilibration through the bridged species.<sup>8</sup> This hypothesis is supported by *ab initio* calculations that indicate that the reaction regiochemistry is in closer agreement with the relative stabilities of the radicals rather than those of the corresponding radical cations. In cases involving charged nucleophiles (cyanide and fluoride anions), no such bridged species are possible and product ratios are not a reflection of the relative stability of the radical intermediates.<sup>9</sup> Instead, addition is kinetically controlled and the product ratio is determined before the relative stability of the resulting radicals becomes important. In such a situation, steric and polar factors dominate, so that the nucleophile adds to the less substituted side. This, however, does not necessarily give the more stable intermediate radical. In fact, the more substituted  $\beta$ -fluoroalkyl and  $\beta$ -isocyanoalkyl radicals have been shown by *ab initio* calculations to be the *less* stable of the two possible intermediate radicals despite being responsible for the major products (Scheme 4).

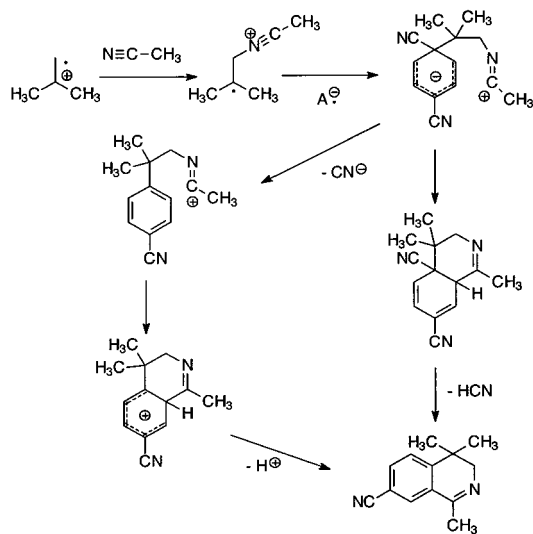
The reaction takes a different course when a neutral, nonprotic nucleophile such as acetonitrile is involved.<sup>10</sup> In this case, the distonic radical cation formed upon nucleophilic trapping of the olefin radical cation is incapable of deprotonation. Consequently, addition to the arene radical anion results in the formation of a zwitterionic intermediate. This species cyclizes to eventually give the observed isoquinoline product (Scheme 5).

Two possible pathways have been proposed (Scheme 6). In the first pathway, the zwitterionic intermediate may eliminate a cyanide anion prior to cyclization. This is

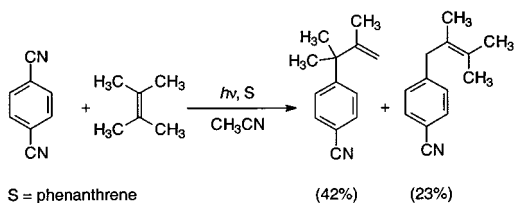
Scheme 5



Scheme 6



Scheme 7

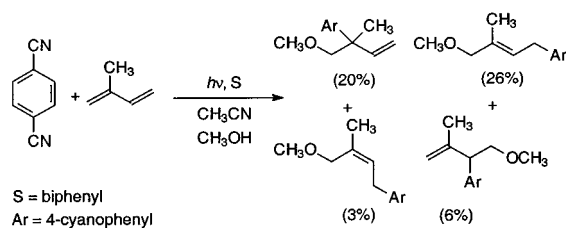


followed by electrophilic attack of the cationic moiety onto the aromatic ring and subsequent deprotonation with concomitant rearomatization. Alternatively, the cyclization may occur at the cation-anion stage before the cyanide anion dissociates and is followed by concerted loss of hydrogen cyanide.

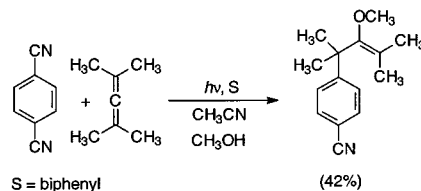
The reaction, however, was found to be limited to highly reactive alkene radical cations, having localized charge and low steric hindrance. Acetonitrile is generally too weakly nucleophilic, so that the olefin radical cations usually tend to deprotonate before they can be trapped. Alkene radical cations are remarkably acidic. Deprotonation of the alkene radical cation generates an allylic radical that subsequently follows a pathway similar to that of the  $\beta$ -methoxyalkyl radical in the corresponding photo-NOCAS reaction. In this case, however, the reaction yields 1:1 alkene-arene substitution products (Scheme 7).<sup>7a,11</sup>

A critical question raised in early studies on the mechanism of the photo-NOCAS and related reactions was whether the radical cation combines first with the radical anion or with the nucleophile. This dilemma was addressed in a study involving conjugated dienes as the electron donors, in which the sequence of these mechanistic steps was particularly evident from the regiochemistry of the adducts (Scheme 8).<sup>12</sup> The results of this work

Scheme 8



Scheme 9



indicate that the nucleophile is always attached to the terminal carbon, implying an initial addition of the nucleophile to the radical cation in order to generate an allylic radical. Subsequent coupling of the arene radical anion with the allylic radical could (and frequently did) occur at both ambident ends of the allylic radical with 1,2-addition placing the aryl group (never the nucleophile) at the 2-position. If the sequence of events were inverted, initial coupling of the radical ions would always bond the aryl group to a terminal position.

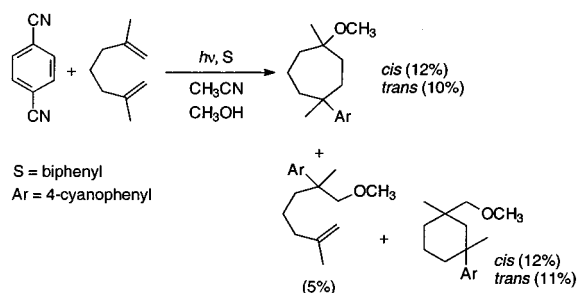
Further unambiguous confirmation comes from a recent study involving allenes as the electron donors (Scheme 9).<sup>13</sup> In all the cases examined, the nucleophile is always attached to the central allenyl carbon; once again this suggests initial trapping of the allene radical cation by the nucleophile (to give an allylic radical) prior to substitution on the arene radical anion.

This particular sequence of events is also suggested upon consideration of the reaction enhancement due to co-sensitization. Co-sensitized reactions tend to inhibit geminate radical ion pair reactions simply because the reactants are generated in separate stages. Coupling of the radical ions prior to nucleophilic trapping would only be possible if the radical ions were formed simultaneously as a geminate pair. The distinct reaction enhancement in the co-sensitized mode clearly excludes reactivity within the geminate radical ion pair. Therefore, with the exception of a few special cases involving intramolecular reactivity,<sup>14</sup> it is now well-established that nucleophilic trapping is favored over radical ion coupling.

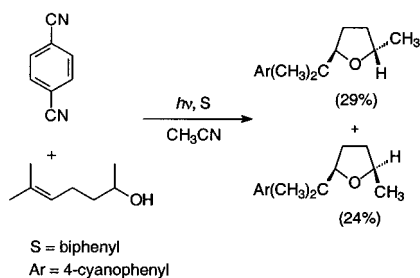
Further diversification of the photo-NOCAS mechanism was attained with nonconjugated dienes as the electron donors.<sup>15</sup> With these species, the initially formed alkene radical cation has the option to cyclize to a 1,*n*-distonic radical cation. For example, the radical cation of 2,6-dimethyl-1,6-heptadiene cyclizes to the 1,4-dimethyl-1,4-cycloheptyl distonic radical cation via a 1,7-*endo,endo* cyclization.<sup>15b</sup> Nucleophilic trapping of the cationic site and substitution on the arene radical anion complete the sequence to yield a cycloheptane derivative (Scheme 10).

Nucleophilic trapping of the initially formed alkene radical cation, prior to cyclization, is a competing path-

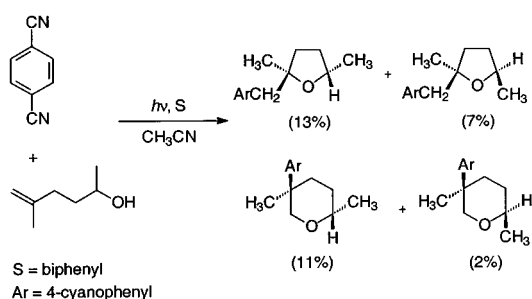
Scheme 10



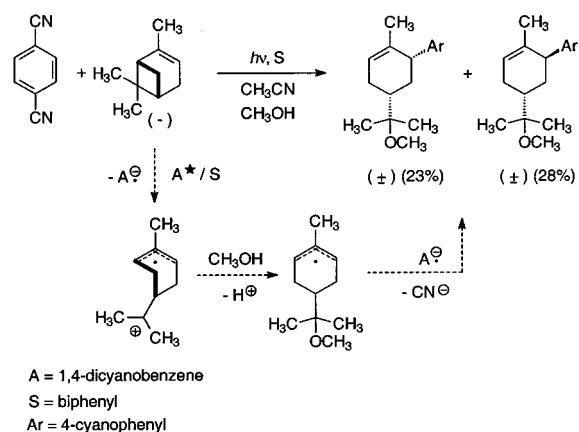
Scheme 11



Scheme 12



Scheme 13



way. This route is responsible for the formation of the open-chain product and the cyclohexane derivative and is favored when the irradiation is performed without the addition of the donor co-sensitizer and at high concentrations of the nucleophile. Under these conditions, initial nucleophilic addition to the alkene radical cation gives a tertiary alkyl radical. This adduct radical has the option of undergoing substitution on the arene radical anion directly, behaving like an isolated alkene unit. Alternatively, the initial radical may react via a 1,6-*endo* cyclization to generate a second tertiary radical. This then substitutes on the arene radical anion to yield the cyclohexane.

Involvement of the donor co-sensitizer and decreased methanol concentration increase the lifetime of the radical cation, and cyclization to the distonic radical cation is favored over nucleophilic trapping. The co-sensitizer probably complexes with the olefin radical cation, reducing the availability of the cationic charge for nucleophilic attack.

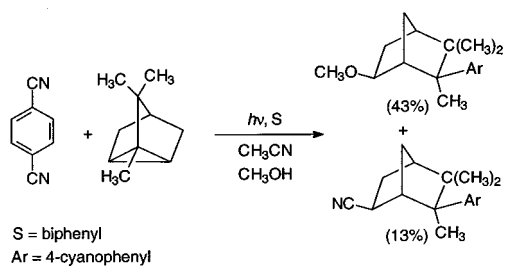
Similar cyclizations have also been achieved with alkenols serving as donors.<sup>16</sup> In these cases, the initially formed alkene radical cation may cyclize via an intramolecular nucleophile addition of the hydroxyl terminus. These reactions exhibit a distinct preference for 1,5-*exo* over 1,6-*endo* cyclization. This selectivity can be rationalized by means of the approach vector analysis model developed by Baldwin and expanded to radical cyclization by Beckwith.<sup>17</sup> For example, the intramolecular cyclization of 6-methyl-5-hepten-2-ol occurs exclusively via a 1,5-*exo* mode, and no products having a tetrahydropyran ring were detected (Scheme 11).<sup>16a</sup> This, perhaps, is of little surprise when one considers that 1,5-*exo* cyclization leads to a tertiary radical in contrast to the secondary radical obtained from a 1,6-*endo* cyclization. However, the preference for 1,5-*exo* cyclization is even more evident in the reactivity of 5-methyl-5-hexen-2-ol (Scheme 12). The

normal intermolecular preference for nucleophilic attack at the primary over tertiary carbon (26:1, as observed in the reaction of 2-methylpropene, Scheme 3) is now dominated by the preference (1.5:1) for 1,5-*exo* over 1,6-*endo* cyclization.

Another mechanistic variation when the initially formed olefinic radical cation may cleave.<sup>18</sup> Cleavage is generally observed to occur selectively, giving the carbocation of that fragment with the lower radical oxidation potential. The radical cation of  $\alpha$ -pinene has been observed to behave in this manner (Scheme 13).<sup>18a</sup> Irradiation of an acetonitrile–methanol (3:1) solution of 1,4-dicyanobenzene, (-)- $\alpha$ -pinene, and biphenyl gave the 1:1:1 *cis* and *trans* photo-NOCAS adducts. The radical cation of  $\alpha$ -pinene cleaves to the achiral, distonic radical cation, with the charge residing on the tertiary alkyl moiety while the spin is located on the allylic moiety. This selectivity is confirmed by *ab initio* spin and charge density calculations for the optimized distonic radical cation. The subsequent association step occurs on both the *cis* and *trans* faces to give racemic, diastereomeric adducts, indicating that there are no bonding interactions between the radical and cationic centers that might maintain chirality. Once again, *ab initio* calculations confirm this, giving interatomic distances between the two centers that are too large for appreciable interaction.

In an attempt to generate this distonic radical cation via an alternative route, an investigation using tricyclene (1,7,7-trimethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane) was conducted (Scheme 14).<sup>18a</sup> Although tricyclene did cleave, it did so at the more substituted bond to give a distinctly different radical cation. The different reaction outcomes clearly

Scheme 14



indicate that these two isomeric distonic radical cations do not interconvert. The observed regiochemistry (*exo* face, less hindered site) suggests that the cyclopropyl ring cleavage is actually assisted by nucleophilic attack. This is supported by the high yield of cyanide-incorporated product, even though the only cyanide ion present is that generated in the final rearomatization step. Cyanide ion is significantly more nucleophilic than methanol, although generally cyanide products are present only in trace amounts.

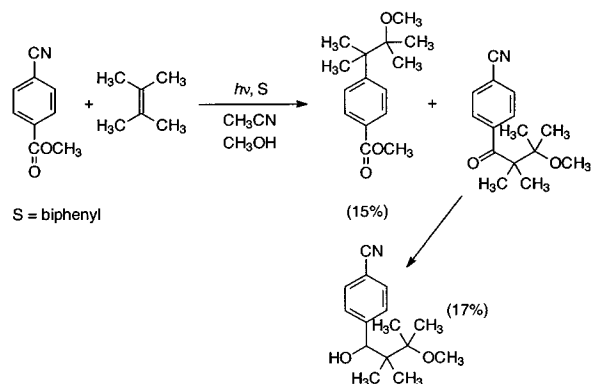
## Varying the Electron Acceptor

All the reactions described so far have involved cyanoarenes, notably 1,4-dicyanobenzene, as the electron acceptors. The reasons for this are various. The cyano function is strongly electron withdrawing, imparting low reduction potentials to these compounds and thus making them good electron acceptors for the PET process. Unlike most other electron withdrawing groups (such as carbonyl, carboxyl, and nitro), the cyano group has no low-energy excited state of its own, and, therefore, it does not exhibit its own photochemistry. Typically, these cyanoarenes have relatively long-lived singlet  $\pi, \pi^*$  excited states. Furthermore, the cyanoarene radical anions resulting from the PET process are relatively stable, making these cyanoarenes suitable both as photosensitizers and co-reactants. Finally, when incorporated in the product, the cyano group is a versatile function that can be readily converted into various other useful substituents.

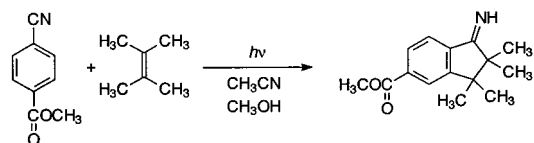
Introducing different substituents will often markedly modify the sequence of events in these electron-transfer reactions. For example, using methyl 4-cyanobenzoate as the electron acceptor under photo-NOCAS conditions leads to a reaction at the carboxyl carbon in addition to the expected photo-NOCAS product (Scheme 15).<sup>19</sup> The  $\beta$ -methoxyalkyl radical resulting from the nucleophilic trapping of the alkene radical cation has the option of coupling with the carboxyl group carbon and eliminating methoxide, in addition to substituting on the aromatic ring in photo-NOCAS fashion.

Removal of the co-sensitizer diverts the reaction, favoring a geminate radical ion pair reaction involving a [3 + 2] cycloaddition that generates a cyclic imine (Scheme 16). A similar reaction was achieved by irradiating 1,4-dicyanobenzene and 2,3-dimethyl-2-butene in acetone.<sup>20</sup> Presumably, the reduced polarity of this solvent prevents the formation of solvent-separated radical ions,

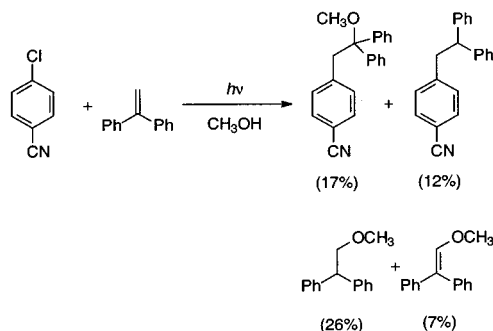
Scheme 15



Scheme 16



Scheme 17



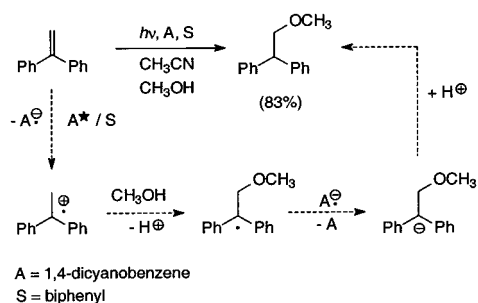
thereby enhancing exciplex-mediated or geminate radical ion pair reactions.

Recently we have shown that by modifying the electron acceptor so that it generates a readily cleavable radical anion, we are able to alter the sequence of events in the mechanism.<sup>21</sup> 4-Chlorobenzonitrile produces an unstable radical anion that cleaves upon formation to generate a highly reactive 4-cyanophenyl radical. This couples with the alkene radical cation while still within the solvent cage, to give an adduct cation that is subsequently trapped by methanol. The overall result is a 1:1:1 arene-olefin-nucleophile product, exhibiting a Markovnikov regiochemistry that complements the photo-NOCAS reaction (Scheme 17). The inverted regiochemistry is a direct consequence of the olefin being trapped by the aryl radical prior to nucleophilic attack.

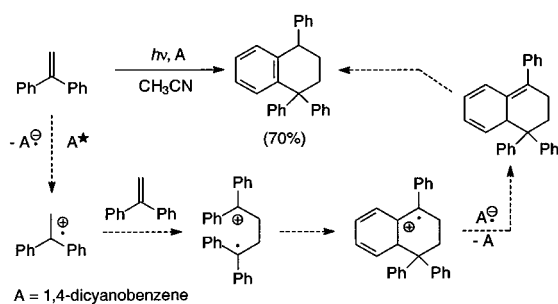
## Aryl-Substituted Alkenes

The photo-NOCAS reaction is generally diverted when aryl-substituted alkenes are involved. Addition of the olefin-nucleophile adduct radical to the cyanoarene radical anion is now less favorable than an alternative mechanistic route involving reduction of the radical to the anion, with subsequent protonation. This electron-transfer step is energetically unfeasible for alkyl-substituted radi-

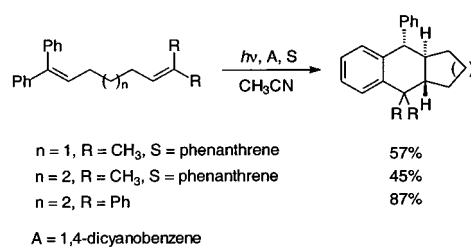
Scheme 18



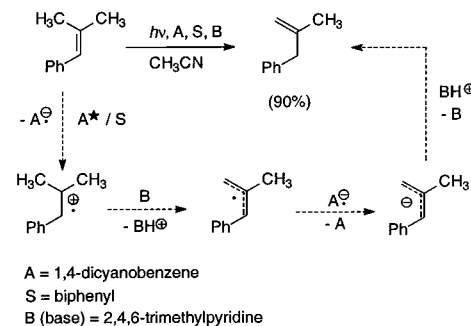
Scheme 19



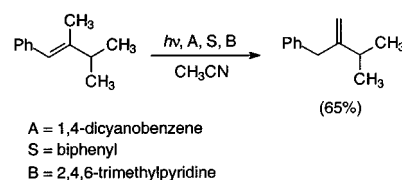
Scheme 20



Scheme 21



Scheme 22



cals, but becomes the dominant pathway when benzylic and bisbenzylic radicals are involved, as a result of their lower reduction potentials.<sup>22</sup> The net result is the *anti*-Markovnikov addition of the nucleophile to the alkene.<sup>23</sup> An early example of this reaction was the formation of 1-methoxy-2,2-diphenylethane from 1,1-diphenylethene (Scheme 18).<sup>23a</sup> Co-sensitization by biphenyl exerts an important role in improving the reaction efficiency, not only by directly enhancing the formation of the ether but also by quenching photochemical degradation side reactions of the product.<sup>21,24</sup> This nucleophilic addition reaction has been shown to have a wide synthetic scope, and has been applied successfully to a large number of olefinic substrates and nucleophiles.<sup>25</sup> If the reaction is carried out in the absence of an added nucleophile, a different pathway becomes available (Scheme 19).<sup>23a,26</sup> The initially formed alkene radical cation may now attack a second neutral alkene molecule. The resulting 1,4-distonic radical cation then cyclizes. Reduction of the cyclized species generates an intermediate triene<sup>26a</sup> that rearomatizes via a proton shift, to give an overall  $[4\pi + 2\pi]$  cycloadduct.

An intramolecular analogue of this cyclization has also been developed using two alkene units tethered by a methylene chain of varying length.<sup>27</sup> In these cases, the initial cyclization to the 1,4-distonic radical cation occurred with remarkable stereospecificity, as a consequence of the imposed steric restrictions (Scheme 20).

The introduction of a base (2,4,6-trimethylpyridine,  $pK_a = 16.8$ ) that is substantially stronger than acetonitrile ( $pK_a \approx -11$ ) favors an alternative route involving deprotonation of the olefin radical cation, over dimerization (Scheme 21).<sup>28</sup> In a manner similar to previous aryl alkene reactions, the allylic radical resulting from deprotonation can be reduced to the corresponding anion. Protonation at the alkyl position regenerates the starting material while protonation at the benzylic position gives a deconjugated

tautomer. The driving force for this transformation takes advantage of the considerably lower oxidation potential of the conjugated tautomer.

This reaction was shown to be synthetically promising for a large variety of aryl alkene systems. 2,3-Dimethyl-1-phenyl-1-butene, in particular, behaved quite interestingly (Scheme 22).<sup>28b</sup> The exclusive formation of 3-methyl-2-phenylmethyl-1-butene, despite a thermodynamic preference for the more heavily substituted isomer, was attributed to stereoelectronic effects involving the extent of  $\pi-\sigma$  orbital overlap. Effective deprotonation requires overlap of the SOMO with the allylic carbon-hydrogen  $\sigma$  bond. The distinct regioselectivity observed in this case is a consequence of poor overlap between the SOMO and the sterically inhibited methine carbon-hydrogen  $\sigma$  bond.

## Conclusion

Several of the reactions developed in our laboratory during the past years and described in this Account exhibit potential as one-step synthetic routes to the products described, bearing in mind that the studies involved very minor reaction optimization. More importantly, however, our work has contributed to the better mechanistic understanding of photoinduced radical ion chemistry. We have observed, rationalized, and manipulated steric, electronic, and stereoelectronic influences in our reactions with the intent of elucidating new reaction pathways. Whenever possible, the inferences and conclusions result-

ing from our experimental work are supported by ab initio theoretical calculations. Through our efforts we have, hopefully, provided the interested chemist with more precise tools for harnessing and unraveling the potential of electron-transfer photochemistry.

We would like to express our deepest gratitude to the numerous graduate and undergraduate students, postdoctoral fellows, and collaborators that have made this work possible and whose names appear as co-authors in the publications listed herein. Most of this work was financially supported by the Natural Sciences and Engineering Research Council of Canada.

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