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σ-Bond initiated generation of aryl radicals from aryl diazonium salts

Elene Tatunashvili, <sup>a</sup> Bun Chan, <sup>b</sup> Philippe E. Nashar <sup>a</sup> and Christopher S. P. McErlean\*<sup>a</sup>

σ-Bond nucleophiles and molecular oxygen transform aryl diazonium salts into aryl radicals. Experimental and computational studies show that Hantzsch esters transfer hydride to aryl diazonium species, and that oxygen initiates radical fragmentation of the diazene intermediate to produce aryl radicals. The operational simplicity of this addition–fragmentation process for the generation of aryl radicals, by a polar–radical crossover mechanism, has been illustrated in a variety of bond-forming reactions.

## Introduction

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Aryl diazonium salts are a versatile source of aryl radicals, which can be employed to achieve a range of transformations.<sup>1-11</sup> Conceptually, the aryl diazonium species can be reduced to the aryl radical via two distinct pathways: single electron transfer (SET), or addition-fragmentation (Scheme 1). Synthetic chemists have largely adopted SET methods as the pathway of choice, and while the direct electrochemical reduction of the aryl diazonium ion is feasible, the most frequently reported protocols employ ground-state metal reductants (CuCl, SnCl<sub>2</sub>, FeCl<sub>2</sub>, etc.).<sup>1</sup> A small number of organic molecules are also known to participate in ground-state SET processes with diazonium salts.<sup>12-15</sup> In the past decade, the photo-excited states of metal complexes, as well as the photoexcited states of some small organic molecules, have similarly been used in SET processes to give the desired aryl radicals.<sup>16-34</sup> In contrast to SET processes, the addition-fragmentation strategy remains underdeveloped.35

The addition-fragmentation process (Scheme 1) is most commonly performed by weak bases such as carbonates, acetates, or formates, or by hydroxide in heated aqueous solution. Pyridine and triethylamine have been shown to mediate the reaction in organic solvents, but the intermediate adduct required elevated temperatures to decompose.<sup>36-39</sup> Stoichiometric amounts of the inorganic nitrite ion was likewise reported to generate the aryl radical via the addition fragmentation pathway.<sup>40</sup> Recently, Maulide and co-workers have significantly expanded the scope of the process by demonstrating that hydrazines can also perform the additionfragmentation generation of aryl radicals.<sup>41-43</sup> In each of those



Scheme 1. Aryl radical formation from aryl diazonium ions.

instances, non-bonded electrons were utilized as the nucleophiles for the addition step. We wondered whether a nucleophilic  $\sigma$ -bond could similarly be used in the addition step. Our ideas were informed by the prior work described below:

The hydrodediazoniation reaction of aryl diazonium salts in acidic (heated) alcoholic solutions has been intensively studied since at least 1887,<sup>44, 45</sup> and it is unambiguously known that aryl radicals are intermediates in the reaction and that molecular oxygen suppresses radical chain events.<sup>46-50</sup> There has been much controversy regarding the mechanism of aryl radical generation under those acidic reaction conditions.<sup>1</sup> In 1958 Meerwein and Kousge independently invoked a hydride transfer, ultimately giving the aryl radical by an unknown

<sup>&</sup>lt;sup>a.</sup> School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia. E-mail: christopher.mcerlean@sydney.edu.au.

<sup>&</sup>lt;sup>b.</sup> Graduate School of Engineering, Nagasaki University, Bunkyo-machi 1-14, Nagasaki-shi, Nagasaki, 852-8521, Japan.

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mechanism.<sup>39, 46</sup> Indeed, the use of inorganic hydride sources (NaBH<sub>4</sub> and Bu<sub>3</sub>SnH) has been reported for the hydrodediazoniation of aryl diazonium salts 1 (Scheme 2).<sup>51, 52</sup> Although the mechanism of those reactions remained unclear (products resulting from polar mechanisms were isolated and deuterium incorporation was low yielding) aryl radical formation was strongly implicated by the isolation of biphenyls. Kosower and Huang have made extensive studies on the proposed aryldiazene intermediate 2 and reported that it was exquisitely sensitive to oxygen, highlighting the need for rigorously anaerobic reaction conditions.53 Diazene 2 underwent a bimolecular decomposition to yield the hydrodediazo product 3, and again, an aryl radical intermediate was hypothesized. In contrast to the work with metal hydrides, Yasui and co-workers have reported the extensive use of the hydride small molecule organic donor N-benzvl dihydronicotinamide (BNAH) for the reduction of aryl diazonium salts, but their results strongly favoured a SET mechanism.<sup>47, 48</sup> Zhu and co-workers have shown that BNAH can act as a hydride donor at room temperature, and as a single electron donor under photo-induced conditions.54 Since Hantzsch esters (HEs) are more nucleophilic than BNAH,<sup>55</sup> we hypothesized that HEs would engage in hydride addition to diazonium species 1 to give aryldiazene intermediate 2 and that molecular oxygen would initiate fragmentation to give aryl radicals, while simultaneously suppressing radical chain events. The result would be a polar-radical crossover reaction<sup>56-58</sup> initiated by cleavage of a  $\sigma$ -bond in a small organic molecule. The outcomes of our investigations are reported in this article.

## **Results and discussion**

Our work began by assessing the ability of a series of HEs (4-11) to generate aryl radicals in the reaction between diazonium salt 12 and furan (13) in an open reaction vessel at room temperature (Scheme 3). Minicsi and coworkers demonstrated that the major by-products of aryl radical generation from aryl diazonium salts are the corresponding symmetric diazenes.59 These can be avoided by keeping the relative concentration of aryl diazonium salt low, which would also disfavour the bimolecular hydrodediazoniation of the proposed aryldiazene intermediate.53 As shown in the insert in Scheme 2, this was trivial to achieve in practise. Our reaction set-up involved the simultaneous addition of dimethylsulfoxide (DMSO) solutions of the HEs and the diazonium salt to a solution of furan (10 equivalents) that was open to the air. To our delight, each of the HEs facilitated formation of the desired arylated furan 14 with different levels of efficiency (Table 1). Because the process was so rapid (total reaction times of just 3 minutes) and avoided any of the practical complications usually associated, with any radical generation (e.g. anaerobic DConditions, Conditions, the use of expensive metal or organocatalysts, the use of speciality equipment and/or light sources, etc.), we felt



Scheme 3. HE and oxygen mediated arylation of furan. Conditions: 1 equiv.HE in DMSO (3 mL), 1.5 equiv. 12 in DMSO (3 mL), 10 equiv. 13 in DMSO (1 mL).

Table 1. Isolated product yields for reactions shown in Scheme 3.

a. Isolated yield after chromatography; b. Standard conditions: 1 equiv. HE in DMSO (3 mL), 1.5 equiv. 12 in DMSO (3 mL), 10 equiv. 13 in DMSO (1 mL); c. Used 1.25 equiv. 12;
d. used 1 equiv. 12; e. Reaction performed in MeOH; f. Reaction performed in the dark;
g. In the presence of 10 mol% NaNO<sub>2</sub>.

Entry	Hantzsch Ester (HE)	Yield of <b>14</b> (%) <sup>a</sup>	Recovered HE (%)ª
1	-	4	-
2	4	82 <sup>b</sup>	-
3	5	84 <sup>b</sup>	-
4	6	93 <sup><i>b</i></sup>	6
5	6	71°	29
6	6	58 <sup>d</sup>	41
7	7	82 <sup>b</sup>	-
8	8	90 <sup><i>b</i></sup>	-
9	9	8 <sup>b</sup>	-
10	10	32 <sup>e</sup>	_
11	11	65 <sup><i>b</i></sup>	-
12	6	70 <sup>f</sup>	-
13	-	42 <sup>g</sup>	-

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that it held significant advantages over existing methods.

Our first task was to illustrate the practical advantages the process, by using inexpensive, bench-stable Hantzsch esters as nucleophiles for the addition-fragmentation σ-bond generation of aryl radicals in a series of well known and well studied reactions. As depicted in Figure 1, both diethyl HE (4) and dibenzyl HE (6) enabled the Gomberg-Bachmann-Hey (GBH) arylation of oxygen, sulfur, and nitrogen containing heterocycles (14-36), with a total reaction time of just 3 minutes in an open reaction vessel at room temperature. The addition of triflouroacetic acid was tolerated and enabled the in situ activation of pyridine and quinoline substrates (27-30), which obviated the need for protecting groups. Radical addition onto 2-substituted furans proceeded with complete regioselectivity (31-33), and as expected, addition onto 3substituted furans delivered predominantly the 2,3-substituted products (34 and 35) alongside a minor amount of the 2,4regioisomer. The generation of compound 36 in moderate yield demonstrated that heteroaromatic diazonium species were compatible with the addition-fragmentation procedure.

König and co-workers used photo-excited eosin Y to generate aryl radicals from diazonium salt **37** via a SET process, which underwent cascade alkyne addition– $S_{\rm H}$ i reaction to give benzothiaphenes.<sup>20, 60-62</sup> As depicted in Scheme 4, the combination of HEs and molecular oxygen was also capable of effecting that transformation to speedily give **39, 41** and **43** in

an open reaction vessel via an addition-fragmentation pathway.

Scheme 4. Cascade olefin addition-substitution reactions.



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Modified phenanthracene scaffolds (**46** and **48**) could be generated from biphenyl diazonium salt **44** by using dibenzyl HE **6** and oxygen to initiate a radical cascade that terminated with an aromatic substitution (Scheme 5).<sup>63</sup> Similarly, the addition–fragmentation pathway allowed the synthesis of ketones **50** and **52** by reaction of the generated aryl radical onto silyl enol ethers **49** and **51** respectively (Scheme 6).

The outcomes shown in Figure 1 and Schemes 4–6 demonstrate that Hantzsch ester mediated addition–fragmentation protocol is amenable to a wide range of the well-established and synthetically useful transformations that aryl radicals are known to engage in. The major advantage of this metal-free process for the generation of aryl radicals is it's extreme practicality – inexpensive, bench-stable Hantzsch

mixture



Scheme 6. Arylation of silyl enol ethers

esters as  $\sigma$ -bond nucleophiles, open reaction flasks, room temperature conditions, and short reaction times.

Our attention then turned to the more complex task of elucidating the mechanism for the process. After conducting the mechanistic studies described below, we propose that the Hantzsch ester and oxygen mediated generation of aryl radicals from diazonium salts occurs by the polar-radical crossover mechanism depicted in Scheme 7.

The control reaction between diazonium salt **12** and furan, in which no HE was employed, returned a 4% yield of the arylated furan **14** (Table 1, entry 1). It has been suggested that DMSO could act as a nucleophilic reducing agent to give the

Ð DMSO 02 53 (DMSO-d<sub>6</sub>) (53a) 4(4a)R = Et58 6 R = Bn 55 0-N TEMPO 54 (56)12 H(D)(D)ł OH (D)H 0-N 0-N 59 82% in ambient light (59a) 57 77% 70% in the dark \* Reaction occurs in the dark. Reaction is sensitive to O2 concentration. \* Deuterated solvent = no deuterium incorportation into 14. reaction +ve control -ve control 0 0 C-4 Deuterated HE 4a = no deuterium incorportation into 14. KI/starch KI/starch KI/starch \* Recovered 4/4a shows apparent isotope effect of ~1.6. + H202 + reaction

Scheme 7. Proposed mechanism for Hantzsch ester and oxygen mediated generation of aryl radicals from aryl diazonium salts. TEMPO = (2,2,6,6-tetramethylpiperidin-

1-vl)oxvl.

Use of 59/59a shows apparent isotope effect of ~2.4.

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As shown in Scheme 7, the intermediacy of aryl radicals under the reaction conditions was confirmed by performing the standard GBH arylation reaction in the presence of TEMPO (**56**) and isolating the adduct **57** in 77% yield.

The possible intermediacy of the corresponding aryl cation was then investigated (Scheme 8). Zollinger reported that the thermal decomposition of the 4-nitrophenyl diazonium salt 12 at 50 °C or 80 °C gave the phenyl radical by a homolytic process, but that parent phenyl diazonium salt 1 thermally decomposed heterolytically to give (almost exclusively) the phenyl cation.<sup>64</sup> Evidence supporting this view was provided by generating the reactive intermediates in the presence of the known radical scavenger, molecular iodine. Zollinger reported that reaction of 12 provided aryl iodide 60 in moderate yield (33%), but reaction of 1 produced aryl iodide 61 in <2% yield. As shown in Scheme 8, when HE 6 and either 12 or 1 were subjected to the current reaction conditions (open reaction vessel, room temperature, 3 minute reaction time) in the presence of molecular iodine, the corresponding aryl iodides 60 and 61 were produced in yields much greater than Zollinger's outcomes. We reasoned that the difference between the product yields for the two iodination reactions did not reflect aryl radical versus aryl cation reactivity as had been suggested, but reflected the different rates of reaction between aryl radicals and molecular iodine. Indeed, when we used TEMPO (56) as the radical trap (in the absence of furan), both TEMPO adducts 57 and 62 were isolated in good yield, demonstrating that aryl radicals were the reactive intermediates in both instances.

Scheme 8. Aryl radical versus aryl cation reactivity.





Table 2. Effect of solvent on the GBH reaction.



Entry	Solvent	Yield of <b>14</b> (%) <sup>a</sup>
1	DMSO	93
2	DMF	80
3	CH₃CN	62
4	MeOH	trace <sup>a</sup>
5	DCM	0 <sup><i>b</i></sup>
6	5% $H_2O$ in DMSO	30
7	10% $H_2O$ in DMSO	21
8	25% $H_2O$ in DMSO	trace
a Compounds <b>6</b> and	12 were snaringly soluble: h. Com	nound <b>12</b> was insoluble

corresponding aryl radical,<sup>50, 64</sup> and the low product yield of this control reaction may represent that background process. However, as shown in Table 2, the reaction is operable in a range of polar solvents and so the action of DMSO alone cannot account for the observed product yields reported in Figure 1 and Schemes 3-5. It is conceivable that the relatively high yields in all of those instances were the result of radical chain processes. Even though the SET from allylic radical intermediate 58 in Scheme 6 to diazonium salts is well known,<sup>22</sup> the low product yield for the control reaction (no HE) suggests that a radical chain mechanism may not appreciably contribute to product formation. When the control reaction (no HE) was repeated in the presence of 10 mol-% of the known stoichiometric aryl radical generator NaNO<sub>2</sub>,<sup>40</sup> (conditions that favoured radical chain events and ensured the presence of intermediate 58 as the diazonium salt 12 was introduced to the reaction vessel) the product 14 was isolated in 42% yield after the same 3 minute reaction time (Table 1, entry 13). This result demonstrates that the radical chain process is, in principle, feasible. However, in practice the yield of arylated furan 14 correlated with the recovered unreacted HE (Table 1, entries 5-7), even when an excess of diazonium salt was used. This shows that HE was the limiting reagent and that radical chain

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Scheme 9. SET processes from HEs

Having demonstrated the intermediacy of aryl radicals in the Hantzsch ester mediated addition–fragmentation protocol, the question of how they were generated was then investigated.

If the reaction involved SET from a photo-excited of the HE to the diazonium salt **12** to give a transient diazenyl radical **63** (Scheme 9), then extended irradiation of the HE with wavelengths <410 nm would be necessary (see ESI).<sup>24, 26, 27, 65</sup> As shown in Scheme 7 and Table 1 (entry 12), the GBH arylation reaction proceeded in the dark within the same 3 minute reaction time. This outcome discounts a photo-induced mechanism. If the reaction involved SET from the ground state of the HE to the diazonium salt **12**, then the efficiency of the reaction should correlate to the ease of HE oxidation. We utilized Nicewicz's method to record the  $E_{p/2}$  of HEs **4–11** (see ESI),<sup>66</sup> and found that the measured values do not correlate with the yields of the reactions shown in Table 1.

Definitive evidence that neither ground state nor excited state SET from the HE was involved in aryl radical generation, was provided by conducting the GBH reaction with HE 10 (Scheme 10). Fasani and coworkers have demonstrated that photoexcitation of HE 10 leads exclusively to 4-(2nitrosophenyl)pyridine 64.67,68 Similarly, Lu and coworkers have shown that SET from HE 10 to the photoexcited state of Ru(bpy)<sub>3</sub><sup>2+</sup> also leads exclusively to the nitroso compound 64.69 These outcomes result from an intramolecular electron transfer mechanism coupled with the close proximity of the nitro group to the acidic hydrogen atom at C-4 of the dihydropyridine ring. When the GBH arylation of furan was carried out using HE 10 under the present reaction conditions, mass spectroscopic analysis of the reaction mixture showed the oxidized 4-(2nitrophenyl)pyridine 65 and an absence of the corresponding nitroso compound 64.



Having ruled out SET mechanisms for the generation of and radicals under the Hantzsch ester and: 10xyger 00mediated protocol (Scheme 9), left an addition—fragmentation as the only viable mechanism for aryl radical generation. We next had to ascertian which portion of the HE was performing the addition step.

Given that the nitrogen-centred lone pairs on pyridine, triethylamine, and morpholinohydrazine have been shown to add to the terminus of the diazo group,<sup>36-38, 41-43</sup> it is was conceivable that the lone pair on the dihydropridine nitrogen of the Hantzsch esters could react in a similar manner. As reported in Table 1 entries 2–5, methylation of the dihydropridine nitrogen atom had little effect on the reaction outcome. In stark contrast, substituents attached to the C-4 position of the HE had a detrimental impact on the reaction (Table 1, entry 9–11). Together, these outcomes suggested that the nitrogen lone pair was not acting as a nucleophile, but rather, the  $\sigma$ -bonded hydrogen at C-4 was acting as a hydride donor.

If a  $\sigma$ -bonded hydrogen from HE 4 (or 6) is involved in a polar hydride addition to 12 and oxygen mediates the radical fragmentation of diazene 54 (Scheme 7), then hydrogen peroxide would be generated. Adding a few drops of the crude reaction mixture shown in Scheme 7 to a KI-starch solution returned a positive result for peroxide (Scheme 7 insert). Indeed, despite the fact that oxygen cannot be excluded from the simple reaction set-up depicted in Scheme 2, sparging the DMSO solutions of HE 6 and 12 with argon prior to addition, resulted in a 38% yield of product 14 (see ESI). Given that oxygen is much less soluble in DMSO-water mixtures than in pure DMSO,<sup>70</sup> the reaction was repeated with various amounts of added water (see Table 2). The yield decreased with increasing water content, and the reaction in a 25% water in DMSO solution gave only trace product. As depicted in Scheme 7, when the reaction was conducted with C-4 deuterated HE- $d_2$ 4a, no deuterium incorporation was observed in the product 14. Similarly, no deuterium incorporation was observed when DMSO- $d_6$  was used as the reaction solvent. Performing the reaction with a 1:1 mixture of HE 4 and deuterated HE- $d_2$  4a and monitoring the oxidation to pyridinium species 53 and 53a revealed an apparent isotope effect of 1.6,<sup>71, 72</sup> suggesting that cleavage of a bond to hydrogen/deuterium was indeed involved in aryl radical generation.<sup>71, 73, 74</sup> It is known that the magnitude of isotope effects resulting from radical-mediated H-atom abstraction from GBH arylation intermediates such as 58 is dependent on the degree of resonance stabilization of the intermediate.<sup>75</sup> The competition experiment using a 1:1 mixture of furfuryl alcohol (59) and deuterated 59a revealed an apparent isotope effect of 2.4.

To gain further insight into the mechanism of the transformation, DFT calculations were performed to compare the energy changes corresponding to possible reaction pathways. As shown in Figure 2, both addition of the nitrogencentred lone pair of dimethyl HE **66** onto diazonium **1**, and ground state SET from HE **66** to **1** were energetically unfavourable. In striking contrast, hydride addition from the C-4 position<sup>54</sup> of HE **66** onto **1** was strongly exergonic. The product diazene **2** could undergo radical disproportionation to give the

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2 equivalents of aryl radical 71, leading to biphenyl. In practise the concentration of 71 is too low to allow this bimolecular process, and biphenyl by-products were never observed. The competing reaction between diazene 2 and molecular oxygen is only slightly endergonic and the released aryl radical 71 reacts rapidly with furan to give 72. As discussed above, SET from species such as 72 to another diazonium 1 is energetically favourable, but no radical chain process is observed in the reaction performed under air. SET from the stabilized radical intermediate 72 to the peroxyl radical was energetically unfavourable, which accords with the deuterium labelling studies as elimination of deuteron from the cation 74 is predicted to be rapid. Pratt and co-workers have calculated that the aromatization of the related 1,4-cyclohexadienyl radical

Figure 2. Calculated energies of possible reaction intermediates. BF<sub>4</sub> counter-ion omitted for clarity.





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occurs via reaction with molecular oxygen followed by line concerted syn-elimination ( $\Delta G^{\ddagger} = 64.4 \text{ kcaphal}^{39}/\text{ARRBUGRAB}$ analogous mechanism cannot be ruled out for the GBH reaction (and would account for the observed apparent isotope effect), no oxygen-containing by-products were observed in the related reactions shown in Schemes 4 and 5. Instead, our calculations showed that direct conversion of 72 into arylated furan 14 by Hatom abstraction was strongly favoured.

## Conclusions

Bench stable and economical Hantzsch esters act as  $\sigma$ -bond nucleophiles that transfer hydride to aryl diazonium salts. Molecular oxygen subsequently initiates fragmentation to give aryl radicals, which can be engaged in a large number of synthetically important bond-forming events. The major benefits of this process are the high degree of operational simplicity - open reaction flasks, room temperature conditions, short reaction times, metal-free conditions, and no special equipment and/or light sources. The exploration of cascade processes involving aryl radicals generated by this polar-radical crossover method is underway in our laboratory.

Historically, non-bonded electrons have been used to initiate addition-fragmentation generation of aryl radicals from aryl diazonium salts. Nucleophilic  $\sigma$ -bonds from bench-stable small organic molecules now join the list of reagents capable of effecting this transformation.

# **Conflicts of interest**

There are no conflicts to declare.

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