Inorganic Chemistry

Diverse Reactions of Thiophenes, Selenophenes, and Tellurophenes with Strongly Oxidizing I(III) PhI(L)₂ Reagents

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ABSTRACT: We report the outcomes of the reactions of aromatic group 16 thiophene, selenophene, and tellurophene rings with the I(III) oxidants PhI(OAc)(OTf) and $[PhI(Pyr)_2][OTf]_2$ (Pyr = pyridine). In all reactions, oxidative processes take place, with generation of PhI as the reduction product. However, with the exception of tellurophene with PhI(OAc)(OTf), +4 oxidation state complexes are not observed, but rather a variety of other processes occur. In general, where a C-H unit is available on the 5-membered ring, an electrophilic aromatic substitution reaction of either –IPh or pyridine onto the ring occurs. When all positions are blocked, reactions with PhI(OAc)(OTf) give acetic and triflic anhydride as the identifiable oxidative byproducts, while [PhI(Pyr)₂][OTf]₂ gives pyridine electrophilic aromatic substitution onto the peripheral rings. Qualitative mechanistic studies indicate that the presence of the oxidizable heteroatom is required for pyridine to act as an electrophile in a substantial manner.

INTRODUCTION

Recently Seferos and co-workers demonstrated a new type of functionalization to modulate the properties of tellurophene rings: oxidation of the Te center from Te(II) (e.g., 1) to Te(IV) (2) using halogenating oxidizing agents, which was found to be reversible under green light irradiation or heat.¹⁻³ This is an interesting advance in potentially generating switchable organic molecules, as tellurophenes are of increasing interest in the organic electronics field.⁴ Klapötke and coworkers have demonstrated that dihalogenated Se(IV) analogues of Se(II) benzoselenophenes (3 and 4) can be isolated and characterized via oxidation using X₂ sources for X = F, Cl, Br.⁵

Our group has reported that use of the very strong I(III) oxidizing agents PhI(OAc)(OTf) and [PhI(4-DMAP)₂]²⁺ to oxidize 2,5-diphenyltellurophene resulted in unusual reactivity (Scheme 1). Use of $[PhI(4-DMAP)_2]^{2+}$ resulted in a reaction where the oxidation state of Te remained at +2, but an electrophilic aromatic substitution (EAS) reaction occurred at the 3-position of the tellurophene via intermediates 5 and 6, giving 7, where the pyridine nitrogen atom acts as the electrophile. Oxidation with PhI(OAc)(OTf) gave a clean

Te(IV) product 8; addition of pyridine to this species resulted in the same EAS as with $[PhI(4-DMAP)_2]^{2+}$, indicating that the EAS reaction likely proceeds through Te(IV) intermediate 5.6

These I(III) reagents (both PhI(OAc)(OTf) and [PhI- $(Pyr)_2$ ²⁺ (Pyr = pyridine or related pyridine derivative)) are finding increasing use as oxidants in organic chemistry as more reactive analogues of commercially available $PhI(OAc)_2$. $[PhI(Pyr)_2]^{2+}$ was first reported by Weiss,⁷ and later used by Zhdankin for preparation of phosphorane-iodonium reagents.⁸ We reported the first crystal structure of these dications in 2012 and found that they can be used for the oxidative coupling of N-heterocyclic carbenes.⁹ Huber has shown that they are effective reagents for the oxidative coupling of anilines.¹⁰ Very recently Wengryniuk used these reactive dications for the oxidative rearrangement of benzylic alcohols,¹¹ and Liu and Liang demonstrated their use in synthesizing labile I(III) precursors for synthesizing radiofluorinated compounds.¹² Wirth and co-workers used the PhI(OAc)(OTf) reagent (among other related I(III) reagents) for stereoselective

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Scheme 1. Reactions of 2,5-Diphenyltellurophene with PhIL₂ Reagents, Leading to Te Oxidation and Electrophilic Aromatic Substitution of Pyridine onto the 3-Position



oxidations of aryl ene-ones.¹³ DiMagno used PhI(OAc)(OTf) in the formation of aryl iodides.¹⁴ Very recently this highly reactive molecule had its solid state structure confirmed, showing that the triflate is only weakly bound to the iodine center, explaining the powerful nature of this oxidant as essentially a $[PhI(OAc)]^+$ source.¹⁵

In this context, we have investigated the reactivity of $[PhI(pyr)_2]^{2+}$ and PhI(OAc)(OTf), as well as $PhI(OAc)_2$ with selected thiophenes, selenophenes, and tellurophenes, as well as control substrate anisole. The results show that EAS-type reactions dominate, with either –IPh or pyridine acting as the electrophile depending on the substrate. The results indicate that for pyridine to act as the electrophile, the presence of the oxidizable group 16 atom is required, suggesting intermediacy of a Ch(IV) species to turn pyridine into an electrophile.

RESULTS AND DISCUSSION

Reactions with Tetraphenyltellurophene. We began investigating reactions with tetraphenyltellurophene to examine the effect of blocking the 3- and 4-positions on the EAS reaction. The 1:1 stoichiometric reaction of tetraphenyltellurophene and PhI(OAc)(OTf) in CDCl₃ resulted in formation of a brown solution within 10 min. After 30 min an aliquot was removed for NMR analysis. The ¹H NMR spectrum of the mixture indicated the presence of iodobenzene and one other species. The ¹²⁵Te NMR showed a shift from 533 ppm for tetraphenyltellurophene to 992 ppm. Tellurium-125 NMR spectroscopy is useful in detecting changes of Te containing compounds, especially in cases with a change in oxidation state as this will result in a large shift in the signals.¹⁶ The change of the ¹²⁵Te NMR resonance from 533 to 992 indicates that the Te in the tellurophene had likely been oxidized from +2 state to +4 state. This data is consistent with compound 9 (Scheme 2) having a OTf and an OAc attached to the Te(IV) of tetraphenyltellurophene, similar to the Te(IV) compound (8)



from our earlier study.⁶ Consistent with our previous work, attempts to isolate a bulk powder from the reaction mixture resulted in decomposition, and in this case we were unable to grow single crystals from solutions stored at low temperatures to confirm the compound's identity. However, the NMR data is consistent with compound **9**.

The 1:1 stoichiometric reaction of tetraphenyltellurophene and [PhI(Pyr)₂][OTf]₂ in CDCl₃ resulted in a pale yellow solution after stirring overnight. Examination of the ¹H NMR spectrum revealed that the reaction mixture contained iodobenzene, tetraphenyltellurophene, and one other pyridine containing species, with a chemical shift downfield from that of free pyridine. Tellurium-125 NMR spectroscopy confirmed the presence of tetraphenyltellurophene with only one resonance observed at 533 ppm. The presence of iodobenzene in the reaction mixture indicates that an oxidation reaction had occurred, but had apparently left the tetraphenyltellurophene unchanged. The ¹⁹F NMR spectrum of the reaction mixture had only one resonance at -78.1 ppm, indicating that the triflate anion is intact. This leaves the pyridine ligands as the likely oxidation products. To explore this we repeated the reaction where the $[PhI(Pyr)_2][OTf]_2$ had been generated from labeled d-5 pyridine. The ESI mass spectra of the labeled and unlabeled reaction were compared, but unfortunately there were no signals that increased in apparent mass by 2.5, 5, or 10 mass units.

To investigate whether the reaction of tetraphenyltellurophene with $[PhI(Pyr)_2][OTf]_2$ potentially goes through a Te(IV) intermediate, 2 equiv of pyridine was added to 9. This experiment resulted in the ¹²⁵Te NMR chemical shift immediately reverting to 533 ppm from 992 ppm, indicating that 9 is reduced back to tetraphenyltellurophene upon addition of pyridine. The unidentified pyridine byproduct was identical to the direct reaction with $[PhI(Pyr)_2][OTf]_2$. Acetic acid and acetic anhydride could also be observed in the ¹H NMR spectrum, and intact triflate was observed in the ¹⁹F NMR spectrum. Based on the available data, the pyridine is likely oxidized somehow, but we have been unable to identify the fate of the pyridine. Clearly, however, even with the 3- and 4-positions of the tellurophene ring blocked, the target pyridine stabilized dication analogous to 5 is an unviable species.

Reactions with Selenophene and Substituted Selenophene Derivatives. The reaction of the parent selenophene with PhI(OAc)OTf in CD₃CN resulted in a color change to green within 10 min. The ¹H NMR spectrum of the mixture contained a downfield proton at ~11 ppm and a methyl resonance consistent with the presence of acetic acid (HOAc) and one other species, with resonances consistent with a substituted selenophene. The addition of diethyl ether resulted in a green precipitate, which the ¹H NMR spectrum indicated was a substituted selenophene bearing a phenyl group. The ⁷⁷Se NMR shift of the green product was 727 ppm, which is a modest downfield shift from that of selenophene at 605.0 ppm, which given Klapötke's work on compounds 3/4 is ambiguous if an oxidation of Se had taken place. In that study downfield shifts of 150-300 ppm were seen in oxidations of benzoselenophenes from Se(II) to Se(IV).⁵ The ESI mass spectrum of the product in CH₃CN solution had a peak with the very distinctive isotope pattern for selenium at $[m/z]^+ = 335.0$.

X-ray diffraction studies were done on a single crystal obtained from crystals grown in CH₃CN at -35 °C, which confirmed the product as iodonium derivative 10 (Scheme 3,







Figure 1. Solid-state structure of the selenophene dication in compound 10. Thermal ellipsoids are drawn to the 50% probability level; triflate anion and hydrogen atoms are omitted. The major component of the disordered selenophene ring is shown.

Figure 1), an unreported derivative of selenophene. Unfortunately severe disorder between the 3-position carbon and the selenium atom in the crystal structure prevents any interpretation of the structure beyond simple identification. When selenophene was reacted with $PhI(OAc)_2$, it resulted in no reaction.

The treatment of selenophene with $[PhI(Pyr)_2][OTf]_2$ in CD_3CN resulted in a color change to brown within 5 min. The ¹H NMR spectrum of the reaction mixture indicated that there was a complex mixture of products present. The ⁷⁷Se NMR spectrum had several peaks in the 550–750 ppm region, indicating six selenophene containing products in the mixture, all being likely in the Se(II) oxidation state given the result observed for **10** (Scheme 4).

The positive ESI-MS detection had signals with the distinctive isotope pattern for selenium containing complexes that could be identified at $[m/z]^+ = 334.9$ corresponding to 10 and $[m/z]^+ = 210.0$ corresponding to 11.

The reaction of 2,5-diphenylselenophene with PhI(OAc)-(OTf) in CD₃CN resulted in the immediate formation of a brown solution. In the ¹H NMR spectrum, iodobenzene was present (indicating that an oxidation had occurred), but intact 2,5-diphenylselenophene remained, which was confirmed via ⁷⁷Se NMR spectroscopy. The ¹⁹F NMR spectrum displayed peaks at -72.2 and -73.5 ppm, as well as a larger signal at -77

Scheme 4. Reaction of Selenophene with $[PhI(Pyr)_2][OTf]_2$



ppm, all upfield from ionic triflate. The peak at -72.2 ppm was assigned to triflic anhydride based on comparison with the chemical shift of a commercial sample. The region of -72 to -73 ppm is also consistent with the chemical shifts of aryl triflates.¹⁷ In the mass spectrum of the reaction mixture a signal at m/z = 102.1 was present, which is consistent with acetic anhydride, which was also observed in the ¹H NMR spectrum. Triflic anhydride and acetic anhydride are in an oxidized state compared to ionic triflate and acetate; therefore it appears that the Se(IV) intermediate analogous to 8 and 9 is unstable and Se returns to the +2 oxidation state via oxidizing triflate and acetate fragments. Triflic anhydride has also been observed to be generated from high oxidation state triarylphosphorus(V)triflate species in conjunction with the PhI(OAc)(OTf) reagent and other systems.^{9,18}

The reaction of 2,5-diphenylselenophene with one stoichiometric equivalent of [PhI(Pyr)₂][OTf]₂ in CD₃CN resulted in the formation of a brown solution. The ¹H NMR spectrum of the reaction solution showed a mixture of products, with multiple pyridine containing species, as well as starting material. The ¹⁹F NMR spectrum in this case showed largely ionic triflate, with only a trace of triflic anhydride present. A mass spectrum of the reaction mixture revealed a signal associated with starting 2,5-diphenylselenophene, as well as a signal consistent with 7Se, the analogue of compound 7 that is quantitatively generated in the reaction with 2,5-diphenyltellurophene. The presence of this compound was confirmed by performing the reaction with [PhI(Pyr)₂][OTf]₂ generated from d-5 pyridine, which gave a corresponding increase of 5 mass units to the signal arising from 7Se. A small amount of acetic anhydride was also present in the mass spectrum of the reaction mixture. No single compound could be isolated from the reaction mixture.

Tetraphenylselenophene with all four positions of selenophene blocked was reacted with PhI(OAc)OTf in $CDCl_3$, which resulted in a color change to brown within 5 min. The results of the reaction were similar to that found from 2,5-diphenylselenophene, with iodobenzene, tetraphenylselenophene (also observed in the ⁷⁷Se NMR), and acetic anhydride being present in the ¹H NMR spectrum, and triflic anhydride observed in the ¹⁹F NMR spectrum. Again, these results indicate that the Se(IV) analogue of **8** and **9** is likely an unstable species.

The reaction of tetraphenylselenophene and $[PhI(Pyr)_2]$ - $[OTf]_2$ in a 1:1 stoichiometric ratio in CD₃CN resulted in a color change to orange after stirring overnight. The ¹H NMR spectrum of the reaction mixture revealed the presence of tetraphenylselenophene, protonated pyridine, and one other pyridine and one other selenophene containing compound in the reaction mixture. The ⁷⁷Se NMR spectrum had two resonances at 620 and 628 ppm for the starting material and the new compound, respectively.

The cationic ESI mass spectrum had two peaks with the distinctive isotope pattern for selenium containing complexes at

 $[m/z]^+ = 514.1$ as the most abundant peak and $[m/z]^+ = 296.1$. The peak at 296.1 corresponds to a dicationic species as the distance between the isotopic peaks is 0.5 mass unit giving a mass of 592 for the dicationic compound. The difference between 592 and 514 is consistent with loss of a pyridine unit. To investigate the presence of pyridine containing species the experiment was repeated using deuterated pyridine by reacting tetraphenylselenophene and d-5 pyridine labeled $[PhI(Pyr)_2]$ - $[OTf]_2$. The positive ESI-MS had two peaks with the selenium isotope pattern at $[m/z]^+ = 519.1$ and $[m/z]^+ = 301.1$. Both peaks are five mass units higher than the previous peaks. Therefore, the dicationic species would be ten mass units higher, indicating the presence of two pyridine units in this species.

X-ray diffraction studies were performed on a single crystal obtained from yellow crystals grown in $CDCl_3$ solution, at -35 °C, and confirmed the new product as dicationic 12, with pyridines having substituted at the para positions of the phenyl groups at the 2- and 5-positions of the selenophene (Figure 2).



Figure 2. Solid-state structure of the selenophene dication in compound 12. Thermal ellipsoids are drawn to the 50% probability level; triflate anions and hydrogen atoms are omitted.

The reaction was driven to completion when performed using two stoichiometric equivalents of $[PhI(Pyr)_2][OTf]_2$, tracked by having one peak at 628 ppm in the ⁷⁷Se NMR spectrum of the reaction mixture, and **12** could be isolated in an ~80% yield (Scheme 5). It should be noted here that reinspection of the mass spectrum of the reaction mixture generated from tetraphenyltellurophene and $[PhI(Pyr)_2]$ - $[OTf]_2$ did not show any evidence for the presence of a complex analogous to **12**.

Reactions with Thiophenes. The 1:1 stoichiometric reaction of thiophene with PhI(OAc)OTf in $CDCl_3$ resulted in a color change from an initially colorless solution to purple and then on to brown within 10 min. A proton NMR spectrum of the mixture indicated the presence of acetic acid (HOAc) and one other compound. The addition of *n*-hexane resulted in a dark green precipitate. Proton NMR spectroscopy of the filtered, washed, and dried product indicated that the thiophene was substituted at the 2-position with a phenyl group attached to it.

Scheme 5. Synthesis of 12



The positive ESI-MS of the mixture gave $[m/z]^+ = 286.9$ as the base peak. This indicated the presence of 13 with an iodobenzene group attached to the thiophene, consistent with NMR data. Colorless crystals were grown from CH₂Cl₂ solution at -35 °C, and X-ray diffraction studies were done on a single crystal to confirm the product 13. An examination of the literature indicated that this compound was known and in fact had been synthesized via the reaction of thiophene with a related hypervalent I(III) compound, commercially available Koser's reagent PhI(OTs)(OH), arising from direct EAS from the thiophene ring onto the iodine center.¹⁹

The reaction of 2,5-dimethylthiophene, having the 2- and 5positions blocked, with PhI(OAc)(OTf) also resulted in iodobenzene EAS at the 3-position (14), as has also been reported using Koser's reagent (Scheme 6). The reaction of

Scheme 6. Reaction of Thiophene and 2,5-Dimethylthiophene with PhI(OAc)(OTf)



 $PhI(OAc)_2$ with thiophene and 2,5-dimethylthiophene resulted in no reaction, indicating that this reagent is not electrophilic enough to perform the substitution reaction.

The 1:1 stoichiometric reaction of thiophene with [PhI-(Pyr)₂][OTf]₂ in CDCl₃ resulted in a brown solution after overnight stirring at room temperature. The ¹H NMR spectrum of the reaction solution indicated that it contained a mixture of products including protonated pyridine. The positive ESI-MS detection of the mixture indicated the presence of protonated pyridine by $[m/z]^+ = 80.1$ and $[m/z]^+ = 286.9$ corresponding

to the product 13 as the base peak, $[m/z]^+ = 160.0$ for compound 16, with a phenyl substituted, and $[m/z]^+ = 162.0$ for compound 15, with pyridine substituted (Scheme 7). The similar solubilities of these products prevented their isolation.

The 1:1 stoichiometric reaction of 2,5-dimethylthiophene with $[PhI(Pyr)_2][OTf]_2$ in CDCl₃ resulted in an orange solution after overnight stirring at room temperature. The ¹H NMR spectrum of the reaction mixture again showed several species in solution. The positive ESI-MS detection of the mixture indicated the presence of protonated pyridine by $[m/z]^+ = 80.1$, $[m/z]^+ = 315.0$ corresponding to the product 14 as the most abundant peak, $[m/z]^+ = 188.0$ for compound 17, and $[m/z]^+ = 190.0$ for compound 18 in a similar result to the parent thiophene (Scheme 7). The similar solubilities of these products again prevented their isolation as single components.

For tetraphenylthiophene with all four positions blocked, reaction with PhI(OAc)(OTf) gave a similar result to the reaction with the analogous selenophene, with iodobenzene, triflic anhydride, and/or aryl triflates and acetic anhydride being identified through a combination of NMR and mass spectral studies. In this case however free tetraphenylthiophene could not be identified in the ¹H NMR spectrum among the products of a rather messy reaction.

Reaction with $[PhI(Pyr)_2][OTf]_2$ also gave the same result as with the selenium analogue (Scheme 8), with dication **19** being clearly apparent as the major product in the mass spectrum of the reaction if two stoichiometric equivalents of $[PhI-(Pyr)_2[OTf]_2$ was used. Solids isolated from the reaction gave ¹H NMR resonances consistent with **19** via comparison to Se analogue **12**. Single crystals were grown from CH₃CN solution at -35 °C. While the crystals were of relatively poor quality, we were able to obtain an X-ray structural solution confirming the synthesis of **19** (Figure 3).

Qualitative Mechanistic Studies. The results obtained for thiophene and selenophene, with -IPh being substituted onto the rings, raise questions about the mechanism we proposed for the electrophilic aromatic substitution of pyridine onto tellurophenes using $[PhI(Pyr)_2][OTf]_2$, which was hypothe-

Scheme 7. Reaction of Thiophene and 2,5-Dimethylthiophene with [PhI(Pyr)₂][OTf]₂

 $\begin{array}{c} \vdots\\ & \overset{[\mathsf{Phl}(\mathsf{pyr})_2][\mathsf{OTf}]_2}{\longrightarrow} \left[\begin{array}{c} \vdots\\ & \ddots\\ & \ddots\\ & & \mathsf{Ph} \end{array} \right]^{\oplus} + \left[\begin{array}{c} \vdots\\ & & \ddots\\ & & \mathsf{N} \end{array} \right]^{\oplus} + \begin{array}{c} \vdots\\ & & & \vdots\\ & & \mathsf{I5} \end{array} \right]^{\oplus} + \begin{array}{c} \vdots\\ & & & \mathsf{I6} \end{array} \right]^{\oplus} \\ & & \mathsf{I6} \end{array}$ $\begin{array}{c} & & \mathsf{Observed by mass spec} \end{array} \qquad -\mathsf{H} \text{ observed by mass spec} \\ & & \mathsf{H} \text{ observed by mass spec} \end{array}$

17

Scheme 8. Reaction of Tetraphenylthiophene with [PhI(Pyr)₂][OTf]₂ Giving 19





Figure 3. Solid-state structure of the thiophene dication in compound **19**. Thermal ellipsoids are drawn to the 50% probability level; triflate anions and hydrogen atoms are omitted.

sized to go via a Te(IV) intermediate.⁶ The isolation of 10, 13, and 14 suggests an alternate possibility, where the reaction results in a cationic –IPh substituted product via direct EAS, and the liberated pyridine reacts with this product in a subsequent nucleophilic aromatic substitution. To investigate this possibility, pyridine or 4-DMAP was added to samples of 10 and 14 in CH₃CN solvent and monitored via ¹H NMR spectroscopy (Scheme 9). No reaction was observed, indicating

Scheme 9. Null Reaction on Adding Pyridine or 4-DMAP to Compounds 10 and 14



that this alternate nucleophilic substitution pathway is not occurring. For the syntheses of **12** and **19**, if the formation was via a para –IPh substituted cation/dication generated via direct electrophilic aromatic substitution, it would be expected that such a species would be observed as a product in the reactions with PhI(OAc)(OTf), analogous to the isolation of **10**, **13**, and **14**. However, close inspection of the mass spectra shows no evidence of mass of cations or dications consistent with single or double substitution of –IPh onto the tetraphenylthiophene or selenophene in reactions with PhI(OAc)(OTf).

Our key supposition in the EAS reaction where pyridine is turned into an electrophile at nitrogen is the intermediacy of a Ch(IV) species with pyridine bound to the chalcogen center. We hypothesized that the mixture of products observed in the reaction of $[PhI(Pyr)_2][OTf]_2$ with thiophenes and selenophenes arises from competing processes of direct EAS at the iodine and oxidation of the S/Se atoms followed EAS at the pyridine nitrogen. To test the validity of this hypothesis PhI(OAc)(OTf) and [PhI(Pyr)₂][OTf]₂ were reacted with anisole as a model EAS substrate without an oxidizable heteroatom. The reaction of PhI(OAc)(OTf) with anisole in CDCl₃ resulted in an instant color change to blue. The ¹H NMR spectrum of the reaction showed the presence of acetic acid, iodobenzene, and one other species with para substitution on the anisole, and a new phenyl containing product. The ESI-MS of a sample had signals at $[m/z]^+ = 311.1$ and $[m/z]^+ = 184.2$ as the most abundant peak corresponding to product **20** (Scheme 10), which has been previously reported by Kita and co-workers using Koser's reagent.²⁰





The reaction of anisole with $[PhI(Pyr)_2][OTf]_2$ (14) resulted in a yellow solution after stirring overnight. The ¹H NMR spectrum of the reaction showed 20 as the major product, which was also apparent in the mass spectrum. In the mass spectrum a signal consistent with 21 was also observed, but only a very small amount. This result indicates that pyridine substitution is possible, but very suppressed in this case, in contrast to the systems containing potentially oxidizable group 16 atoms.

CONCLUSIONS

Our study sheds light on the reactions of the oxidations of thiophenes, selenophenes, and tellurophenes using the $PhIL_2$ class of oxidants. With the exception of Te(IV) compounds **8** and **9**, generated from PhI(OAc)(OTf), the Ch(IV) species are clearly unstable species and undergo further reactions. The initial target of a pyridine stabilized Ch(IV) dication is clearly unviable for all rings investigated. However, there is evidence for Ch(IV) intermediates in these reactions, indicating that the +4 species can be fleetingly obtained.

In the case of reactions with either the parent or disubstituted thiophenes and selenophenes when using [PhI-(Pyr)₂][OTf]₂, competing reactions are observed, resulting in substitution of either -IPh or pyridine. With PhI(OAc)(OTf), -IPh substitution is observed when there are available C-H positions on the chalcogen containing ring, giving known thiophene derivatives, but a new derivative of selenophene. These -IPh substituted compounds were shown not to be intermediates in the generation of pyridine substituted compounds, as addition of pyridine to these cations does not result in displacement of iodobenzene. We believe that the two competing pathways are direct electrophilic aromatic substitution when -IPh is substituted and Ch(IV) mediated electrophilic aromatic substitution when pyridine is the substrate. This is supported by the generation of 12 and 19, where reactions with PhI(OAc)(OTf) with the tetraphenylthiophene and tetraphenylselenophene return starting material and mixed byproducts including acetic and triflic anhydride with no evidence for –IPh substitution, but [PhI(Pyr)₂][OTf]₂ gives relatively clean substitution onto the para position of the phenyl rings at the 2- and 5-positions. We hypothesize that the observed oxidative byproducts of acetic and triflic anhydride in the reactions with PhI(OAc)(OTf) are generated from unstable Ch(IV) intermediates, which undergo reduction back to the stable aromatic Ch(II) starting compounds.

Also supportive of the hypothesis of Ch(IV) involvement in turning pyridine into an electrophile is the dominant substitution of –IPh onto the para position of anisole, where no oxidizable heteroatom is present, with reactions between anisole and $[PhI(Pyr)_2][OTf]_2$ only giving a trace of pyridine substituted compound.

A key outcome of this study, given the increased use of these oxidants, is that care should be taken when using PhI(OAc)-(OTf) or $[PhI(Pyr)_2]^{2+}$ as these are highly active toward electrophilic aromatic substitution reactions and can give unpredictable results when they do occur. The substrates used in concert with these reagents should be designed so that undesirable EAS side reactions are unlikely.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b02386.

Experimental details, ¹H, ¹³C, ⁷⁷Se, and ¹²⁵Te NMR spectra, and mass spectra (PDF) X-ray crystallographic details (CIF)

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Notes

The authors declare no competing financial interest.

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Article

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