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Hypervalent Iodine Compounds with Tetrazole Ligands

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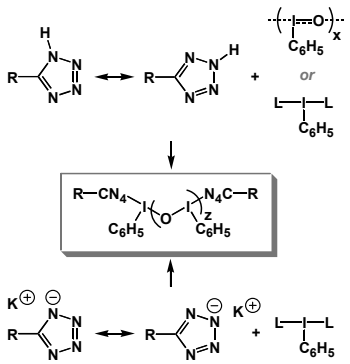


R = CH_3, C_6H_5, 4-CH_3-C_6H_4; L = Cl, CH_3CO_2, CH_3CO_2; z = 0, 1, >2

ABSTRACT

Hypervalent iodine compounds with two I-N bonds, containing 5-substituted tetrazoles as the ligands $PhI(N_4CR)_2$ (R = CH_3, C_6H_5, and 4-$CH_3C_6H_4$), were synthesized from $PhI(O_2CCF_3)_2$ or $PhICl_2$ and the corresponding tetrazole potassium salts. Alternatively, PhIO was reacted with the free tetrazoles, and the reactions afforded either the compounds $PhI(N_4CR)_2$ or, in most cases, μ-oxo- or oligomeric compounds with several I and O atoms in the backbone and two terminal tetrazole groups. The isolated compounds were reasonably stable in the solid state as well as in solution at room temperature but explosive at elevated temperatures (135-180 ^oC depending on the structure). The crystal structure of one representative compound (an oligomer with three I atoms in the backbone and 5-phenyltetrazole end groups) was solved and refined from synchrotron powder X-ray diffraction. The novel compounds were characterized by cyclic voltammetry and were found to be strong oxidants. In addition, they were proved to be useful reagents for the iodotetrazolylation of unsaturated compounds such as styrene and cyclohexene, and for the transfer of tetrazole groups to *N,N*-dimethylaniline.

INTRODUCTION

The organic compounds of polyvalent iodine have been known since 1886 when several (dichloroiodo)arenes $ArICl_2$ were prepared by Willgerodt[1] by the reaction of iodoarenes ArI with chlorine. This discovery was followed, in a swift succession during the following decade, by other organic compounds of iodine(III) such as iodosylarenes $ArIO$[2-4] and (diacyloxyiodo)arenes $ArI(O_2CR)_2$ (and other, e.g., nitric and chromic, acid derivatives),[3,5] as well as some of iodine(V), notably iodylarenes $ArIO_2$.[4-6] By 1914, when the first monograph[7] summarizing the knowledge about organic polyvalent iodine compounds was published, hundreds of them had been reported and studied. The nature of bonding in the molecules of these and in many other compounds containing polyvalent (i.e., exceeding the valency expected from the octet rule) main group elements was a subject of debate for several decades. In 1951, Hach and Rundle,[8] and Pimentel[9] reasoned that in polyhalide anions (and, as it was soon realized, by extension – in the molecules of many of the other aforementioned compounds[10]), delocalized 3-center-4-electron bonds are formed exclusively with the participation of p-orbital(s) of the central polyvalent atom. This idea was applied more broadly to describe theoretically the bonding in many molecules containing polyvalent main group elements in 1969 by Musher[11] who dubbed the bonds in question *hypervalent* (HV). The molecules of $ArIL_2$ compounds (L represents a ligand with electronegative atom(s), such as carboxylate or (pseudo)halide), which are the subject of this work, are T-shaped and contain the almost linear L-I-L fragment. The presence of the relatively weak, compared to the "classical" covalent (2-center-2-electron), and highly polar HV bonds I-L determines the rich reactivity of HV iodine compounds, i.e., their ability to participate in various electron transfer, ionic (e.g., ligand exchange with nucleophiles), and radical reactions. A number of monographs or edited books[7,12-15] and review papers[16-27] deal with all aspects of organic HV iodine compounds, including the methods of their preparation, structures, spectral and other physical as well as chemical properties, and uses in synthetic chemistry and materials science.

HV iodine(III) reagents can serve as efficient electrophiles and have found numerous applications in synthetic organic chemistry in this capacity, for instance in C-H bond functionalization reactions with trifluoromethyl,[28] cyano,[29] azido,[30] and many other functional groups. Radical reactions involving HV iodine(III) compounds have found synthetic utility as well.[22,31,32] Heterocyclic compounds with HV iodine(III) atoms as part of the ring, such as Zhdankin's,[33] Togni's,[28] and other related reagents[34] have gained significant popularity due to their increased stability, compared to their acyclic analogues, at ambient conditions. Acyclic compounds of the type $ArIL_2$ are easily prepared by ligand exchange reactions between commercially available compounds such as $PhI(O_2CCH_3)_2$ or $PhI(O_2CCF_3)_2$ and either sources of the anions L^- (salts) or the silicon compounds Me_3SiL. An alternative approach is to employ the reaction between iodosylarenes ArIO and the acid HL or Me_3SiL. Some $ArIL_2$ compounds are rather unstable (e.g., when L = N_3) and are prepared *in situ* to afford, upon decomposition, the monovalent iodine compound ArI and the radicals $L^\bullet$, which can functionalize substrates (e.g., unsaturated compounds) or initiate radical polymerization, yielding end- and in some cases backbone-functionalized polymers.[35,36] In other words, ligand exchange reactions at HV iodine(III) centers with the nucleophiles L^- followed by homolytic decomposition of the newly-formed compound $ArIL_2$ – a reaction that is formally identical to oxidation of the anion L^- to the radical $L^\bullet$ – is a convenient route to functional radicals from readily accessible precursors.

Out of many oxidative ligand transfer reactions, those that allow for the direct transformation of C-H to C-N bonds are of great interest, as the products of these reactions are often the building blocks of various pharmaceuticals and biologically active natural compounds. Such transformations are often conveniently carried out using HV iodine(III) reagents with I-N bonds but unfortunately, these compounds, especially the acyclic ones, are comparatively unstable and difficult to store, which limits the range of synthetically useful reactions that can be developed. These compounds are also usually hydrolytically unstable, which imposes a further restriction on their utility. The formation of acyclic HV iodine(III) compounds with I-N bonds derived from cyclic imides[19] or azoles[37] was first reported by

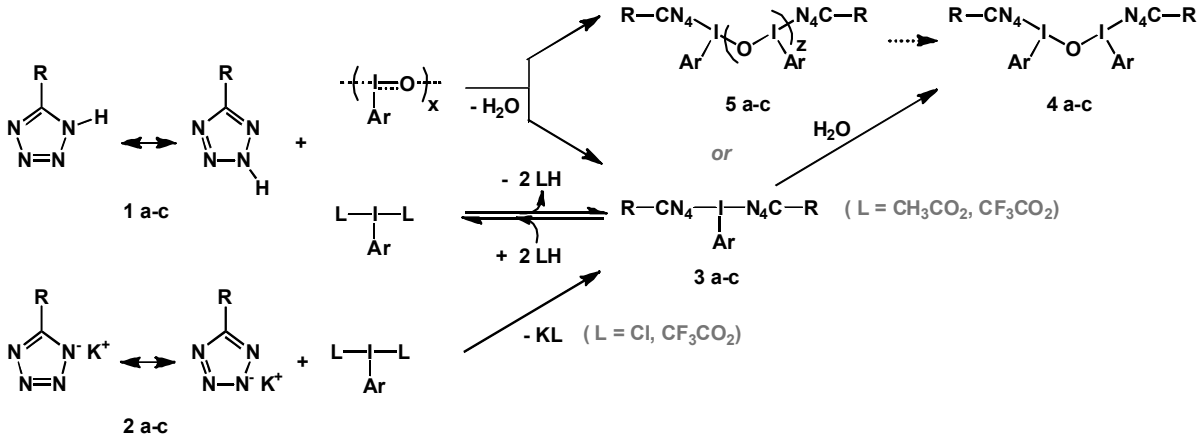
Varvoglis. Over the following years, several other structural classes were demonstrated including heterocyclic and iodonium salts with I-N bonds. For instance, azidoiodanes,[33,34,38,39] benziodazoles,[40,41] and iminoiodanes[42-46] were investigated as efficient reagents for C-N bond-forming reactions. These reagents have been used in direct azidation,[39,47-49] amination,[43,47,50-55] aziridination,[44,45] and C-H insertion reactions.[49,56] The discovery of reactions in which the HV iodine(III) reagents with I-N bonds were formed *in situ* using iodoarenes (typically, iodobenzene) as catalysts,[50,57] was a major advancement due to the relatively inexpensive setup and the markedly reduced negative environmental impact compared to C-H to C-N transformations mediated by transition metal compounds. Nevertheless, the need remains to isolate and characterize structurally and determine the reactivity of more, especially acyclic, HV iodine(III) compounds with N-based ligands, both from fundamental and applied chemistry viewpoint.

Among the many N-based nucleophiles that can potentially serve as ligands in HV iodine compounds, tetrazoles[58-63] are of interest, due to properties such as complex-formation ability, biological activity, and especially their highly positive enthalpy of formation,[64] which makes them attractive as effective propellants and explosives producing molecular nitrogen as the dominating gaseous product of decomposition. C-(5-)substituted tetrazoles RCN_4H resemble structurally carboxylic acids RCO_2H and are often characterized by similar (typically, within an order of magnitude) values of K_a,[65] which is why they are often referred to as tetrazolic acids. For instance, pK_a of 5-methyltetrazole CH_3CN_4H is around 5.6,[65] while pK_a of CH_3CO_2H is 4.8.[66] Likewise, the pKa values of 5-phenyltetrazole and benzoic acid are respectively 4.8[65] and 4.2.[66] It was therefore to be expected that tetrazoles or tetrazolate anions can be used in the place of carboxylic acids or carboxylate anions to prepare the compounds $ArI(N_4CR)_2$, which are formally analogues of the corresponding dicarboxylates $ArI(O_2CR)_2$. Herein, we report the formation, isolation, structural characterization, and reactivity studies of acyclic compounds of the type $ArI(N_4CR)_2$, as well as some oligomers with I-O bonds in the backbone, derived from 5-methyl-, 5-phenyl-, and 5-(p-tolyl)tetrazole.

RESULTS AND DISCUSSION

Synthesis

The reactions between iodosylbenzene PhIO and trimethylsilyl halides TMSX, hydrogen halides or carboxylic acids are convenient routes to various HV iodine(III) compounds such as $PhIF_2$,[67-69] $PhI(O_2CCH_3)_2$,[67,70] $PhI(O_2CCF_3)_2$,[71,72] etc. In our initial efforts, PhIO (2.0 mmol in 2 mL solvent) was reacted with 2 eq. of 5-methyltetrazole **1a** to afford compound **3a** (Scheme 1) in high yield in various solvents such as CH_2Cl_2, $CHCl_3$, and CH_3CN (Table 1, entries 1-3).



Scheme 1. Synthetic routes to HV iodine(III) compounds with tetrazole ligands.

Table 1. Synthesis of HV iodine(III) compounds with tetrazole ligands in different solvents at 25 ºC

Entry	HV iodine(III) precursor	R in RCN_4H (eq.)	Solvent	Time (h)	Yield (%)
1	PhIO	CH_3 (2)	CH_3CN	0.5	70
2	"	,,	DCM	"	85
3	"	,,	$CHCl_3$	"	82
4	"	4-$CH_3C_6H_4$ (2)	CH_3CN	2	28 [a]
5	"	,,	"	20	56 [b]
6	"	4-$CH_3C_6H_4$ (4)	"	2	72 [b]
7	"	,,	"	20	78 [b]
8	"	C_6H_5 (2)	"	2	27 [a]
9	"	,,	"	20	60 [b]
10	$PhI(O_2CCH_3)_2$	CH_3 (2)	"	0.5	12
11	$PhI(O_2CCF_3)_2$	,,	"	"	25

[a] Oligomeric product **5** was obtained.
[b] The main product was μ-oxo compound **4**.

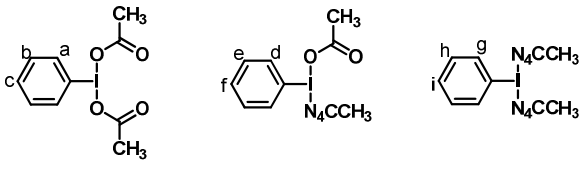
As the reactions proceeded, PhIO dissolved and the reaction mixtures remained homogeneous. Compound **3a** was isolated after vacuum evaporation of the solvent as an oily substance, which turned into a sticky solid upon drying under high vacuum; it was stable at low temperature (ca. -20 ^{o}C) for several weeks. Its chemical identity was confirmed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, HRMS and MALDI-ToF.

The same reaction of PhIO was then conducted using 5-phenyltetrazole (**1b**) and 5-(p-tolyl)tetrazole (**1c**). The reaction mixtures when using 2 eq. of the tetrazoles vs PhIO in MeCN were heterogeneous, and the products, isolated by filtration, were obtained as off-white solids and were found to be insoluble in most organic solvents with the notable exception of MeOH. The reaction between PhIO and carboxylic acids such as CH_3CO_2H and CF_3CO_2H usually generates oligomeric HV iodine(III) compounds with I and O atoms in the backbone.[70] Similarly, it was ascertained that the compounds obtained from the reactions of PhIO and tetrazoles **1b** and **1c** were oligomeric compounds – **5b** and **5c**, respectively (instead of the expected compounds **3b** and **3c**). The structural data (*vide infra*) revealed that **5b** exists as oligomeric HV iodine(III) compound, containing three I atoms linked through two bridging O atoms, and the N2-atoms of 5-phenyl tetrazole were coordinated to the two terminal HV iodine(III) centers. The reason the reactions of PhIO with **1b** and **1c** afforded oligomers could plausibly be attributed to the poor solubility of those oligomers, which, as soon as formed, precipitated, and were not accessible to react with the still present unreacted tetrazole. In contrast, as mentioned, compound **3a** is much more soluble and is formed as the main product (possibly via the reaction of initially formed oligomers **5a** (not observed) with **1a**). The contact time of PhIO and **1b** or **1c** (2 eq.) in CH_3CN was increased to 20 h in order to allow the unreacted tetrazole to cleave the I-O-I bridges in the poorly soluble oligomers (Table 1, entries 5, 7, and 9). The increased reaction time resulted in off-white solids in both cases and the products were found to be soluble in polar solvents such as DMF. ^{1}H NMR analysis in DMF-d_7 revealed that both products were μ-oxo compounds **4b** and **4c**. This suggested that by varying the reaction time between PhIO and **1b** or **1c** (2 eq.) and/or the excess amount of tetrazole, the molecular weights of obtained HV

iodine(III) species could be controlled to some degree. It was observed that compounds **4b** and **4c**, while soluble in DMSO, reacted with it and oxidized it.

Symmetric HV iodine(III) compounds such as $PhI(OMe)_2$,[73] $PhI(O_2CCH_3)_2$,[70,74,75] or $PhI(O_2CCF_3)_2$[76] are often conveniently prepared in high yields (and without the formation of noticeable amounts of oligomers) by the reaction of PhIO with methanol or the corresponding carboxylic acids but in all these cases the reactants are liquids and are employed as the reaction solvents, i.e., in large excess relative to PhIO. Likewise, if large excess of the 5-aryltetrazoles relative to PhIO and longer reaction times were used in the reactions described above, most likely the amount of μ-oxo bridged compounds **4b** and **4c** would decrease and eventually compounds **3b** and **3c** would form in larger yields, but due to the need of using expensive reagents, this route was not pursued further.

Subsequently, alternative methods to prepare symmetric HV iodine(III) compounds containing **1b** and **1c** as the ligands were explored to eliminate the necessity of using excess amounts of tetrazoles. To achieve this goal, ligand exchange reactions between dicarboxylates such as $PhI(O_2CCH_3)_2$ with various tetrazoles were studied (Scheme 1). Varvoglis and coworkers showed that various acidic N-containing ligands can participate in exchange reactions with $PhI(O_2CCH_3)_2$.[37,77] The reaction of $PhI(O_2CCH_3)_2$ with **1a** afforded **3a** in 12 % yield (Table 1, entry 10). The yield did not increase even at longer reaction times, most likely due to the establishment of an equilibrium characterized with a comparatively low equilibrium constant. This observation encouraged us to perform a solution study by ^{1}H NMR spectroscopy to investigate the ability of **1a** to replace the acetoxy groups in $PhI(O_2CCH_3)_2$ (Figure 1a).



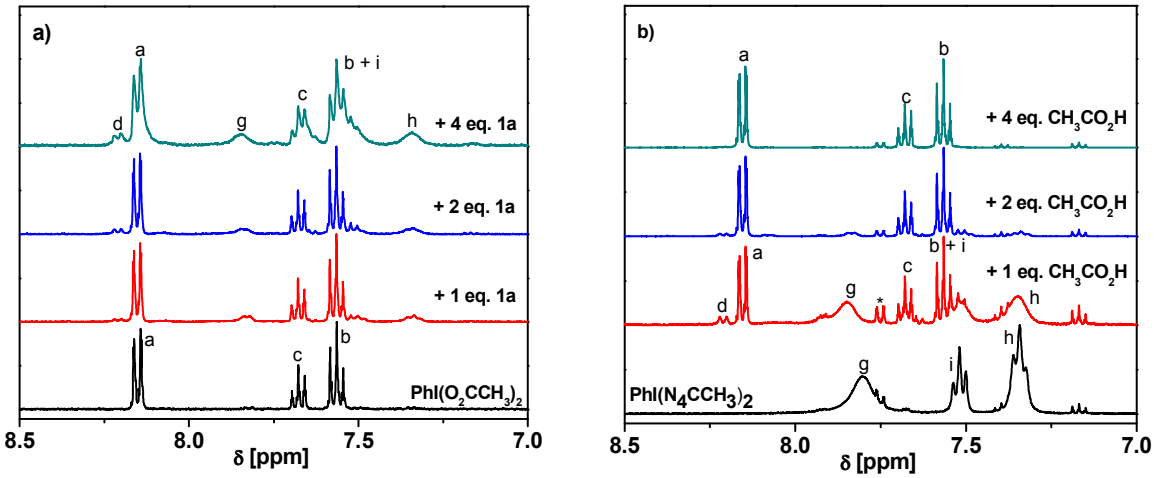
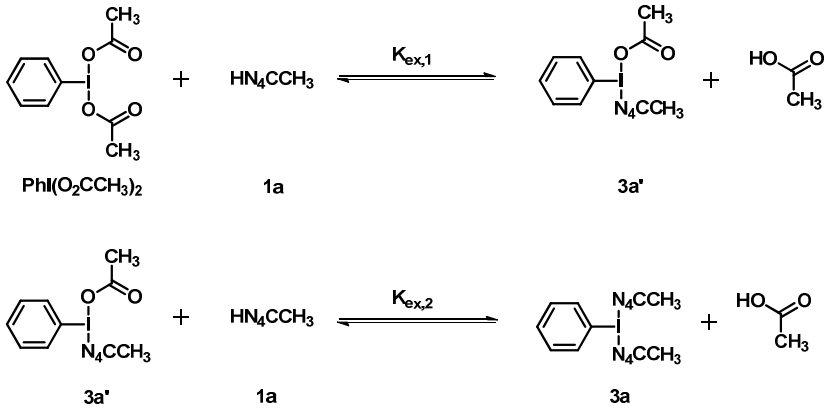


Figure 1. ^{1}H NMR spectra of equilibrated (5 h) reaction mixtures containing (a) $PhI(O_2CCH_3)_2$ (10 mM in CD_3CN) and varying amounts of **1a**, and (b) compound **3a** (10 mM in CD_3CN) with varying amounts of CH_3CO_2H.



Scheme 2. Exchange of the acetoxy groups in $PhI(O_2CCH_3)_2$ with **1a**.

$PhI(O_2CCH_3)_2$ (10 mM in CD_3CN) was mixed with different amounts of **1a** (1, 2, and 4 eq.) and sufficient time (5 h) was allowed for an equilibrium to be reached. With 1 eq. of **1a** vs $PhI(O_2CCH_3)_2$, the formation of **3a** (21 mol % of all HV iodine(III) species) and asymmetric compound **3a'** (6 mol %) was observed (Scheme 2). When **1a** was mixed with $PhI(O_2CCH_3)_2$ (in a molar ratio of 2:1 or even 4:1), the ^{1}H NMR yields of compounds **3a** and **3a'** did not change substantially, suggesting that, as expected (from

the low reaction yields discussed above) the equilibrium constants $K_{ex,1}$ and $K_{ex,2}$ (Scheme 2) were relatively low. Another set of experiments were carried out (Figure 1b) where the isolated compound **3a**, from the reaction of PhIO and **1a**, was mixed with varying amounts of CH_3CO_2H (1, 2, and 4 eq.) in CD_3CN. When 1 eq. of CH_3CO_2H was added, the formation of $PhI(O_2CCH_3)_2$ and mixed compound **3a'** was immediately evident with NMR yields (after equilibrium was established in 5 h) of 28 mol % and 6 mol %, respectively. When 2 eq. of CH_3CO_2H was mixed with the solution of **3a**, the NMR yields of $PhI(O_2CCH_3)_2$ and **3a'** were calculated to be 78 mol % and 7 mol %, respectively. Increasing the amount of CH_3CO_2H to 4 eq. was sufficient to replace all the tetrazole ligands from the symmetric and the asymmetric HV iodine(III) compounds. These ^1H NMR solution studies further proved that, at least in CD_3CN, acetate anions have more pronounced affinity to HV iodine(III) centers than tetrazolate anions. The results also explained why the exchange of acetoxy groups in $PhI(O_2CCH_3)_2$ with **1a** was not an efficient way to synthesize compound **3a**. Even at high concentrations, compound **1a** was incapable of replacing all the acetoxy groups of $PhI(O_2CCH_3)_2$.

Table 2. Synthesis of $PhI(N_4CR)_2$ compounds under different conditions at 25 °C in CH_3CN.

Entry	HV iodine(III) precursor	R in $RCN_4^-K^+$	Yield (%)
1	$PhICl_2$	CH_3	82
2	„	C_6H_5	69
3	„	4-$CH_3C_6H_5$	65
4	$PhI(O_2CCF_3)_2$	CH_3	70
5	„	C_6H_5	80
6	„	4-$CH_3C_6H_4$	82

The goal to obtain symmetric HV iodine(III) species with tetrazole ligands using minimum amount of reactants was yet to be accomplished. Instead of free tetrazoles, efforts were undertaken to accomplish the exchange using tetrazolate anions, in the form of potassium salts (**2a-c**) of the studied tetrazoles and HV iodine(III) precursors such as $PhICl_2$ and $PhI(O_2CCF_3)_2$. These attempts were inspired by the known fact that symmetric HV iodine(III) compounds of the type $ArIL_2$ are efficiently produced by the reaction of $ArICl_2$ and $ArI(O_2CR)_2$ with a sodium or potassium salts with nucleophilic anions L^-.[51-53] First, $PhICl_2$ was prepared by reacting PhI with sulfuryl chloride in CH_3CO_2H.[78] The isolated crystalline

$PhICl_2$ was then reacted with the potassium salts **2a-c** (2 eq.) in dry CH_3CN for 15 h (Scheme 1), affording the compounds **3a-c** in very good to excellent yields (Table 2, entries 1-3). The identity of the isolated compounds **3a-c** was confirmed by ^1H, $^{13}C\{^1H\}$ NMR, and mass spectroscopy. When the same reactions were carried out in CH_3CN, which had not been dried prior to the synthetic procedures, the salt **2a** gave **3a** in similar yields but the salts **2b** or **2c** afforded the μ-oxo bridged compounds **4b** or **4c**. To further prove this, a solution study using ^1H NMR spectroscopy was performed where **3c** (40 mM, 1 eq.) was dissolved in DMF-d_7 (0.9 mL) and D_2O (100 eq.) was added. As shown in Figure S1, the formation of **4c** was evident after several hours. This suggested that the aryl tetrazole-based HV iodine(III) compounds **3b** and **3c** are more hydrolytically unstable than the aliphatic derivative **3a**.

Exchange reactions were also carried out with $PhI(O_2CCF_3)_2$ and the potassium salts **2a-c** in dry CH_3CN for 15 h. The advantage of the reaction involving $PhI(O_2CCF_3)_2$ is that the byproduct, potassium trifluoroacetate, remains dissolved, while the reaction products precipitate, which makes the purification less involved than in the case of reactions employing $PhICl_2$, in which the main product and the byproduct (KCl) are both insoluble and need to be separated. The two studied exchange reactions with potassium salts of tetrazoles proved to be very suitable for the preparation of symmetric HV iodine(III) compounds **3a-c**, with equimolar amounts of tetrazoles to HV iodine(III) precursors being sufficient to obtain the desired products in high yields.

Characterization

After synthesis and isolation of three symmetric HV iodine(III) compounds **3a-c**, they were further characterized by cyclic voltammetry (CV) to examine their oxidizing ability. The CV measurements were performed in dry and deoxygenated DMF (good solvent for all compounds **3a-c**) using glassy carbon electrode. In addition to that, the reduction potential of $PhI(O_2CCH_3)_2$ was measured in the same solvent and it was found that $PhI(O_2CCH_3)_2$ was harder to reduce than the tetrazole-based HV iodine(III) compounds. The cyclic voltammogram of $PhI(O_2CCH_3)_2$ showed an irreversible wave with two-electron reduction peak ranging from -1.223 V to -1.360 V (vs. Fc^+/Fc), depending on the scan rates

(Table S1, entries 10-12 and Figure S4). Compounds **3a-c** were better electron-acceptors with a less negative reduction potential than $PhI(O_2CCH_3)_2$ at any scan rate (Figure 2a). Compound **3b** had the least negative reduction potential ranging from -0.316 V to -0.332 V (vs. Fc^+/Fc) at various scan rates (Table S1, entries 1-3 and Figure S5). The oxidizing power of compounds **3a-c** followed the expected trend based on the electron donating ability of the R group in the tetrazole ligand, i.e., compound **3c** was more oxidizing than compound **3a** but less than **3b** with reduction potential from -0.444 V to -0.412 V (vs. Fc^+/Fc) at different scan rates (Table S1, entries 4-6 and Figure S6). The reduction potential of compound **3a** varied from -0.500 V to -0.588 V (vs. Fc^+/Fc) upon altering the scan rates (Table S1, entries 7-9 and Figure 2b). It was found that the electrolyte used in CV measurements, $(n\text{-Bu})_4NPF_6$, does not interact with the HV iodine(III) compounds (Figure S2).

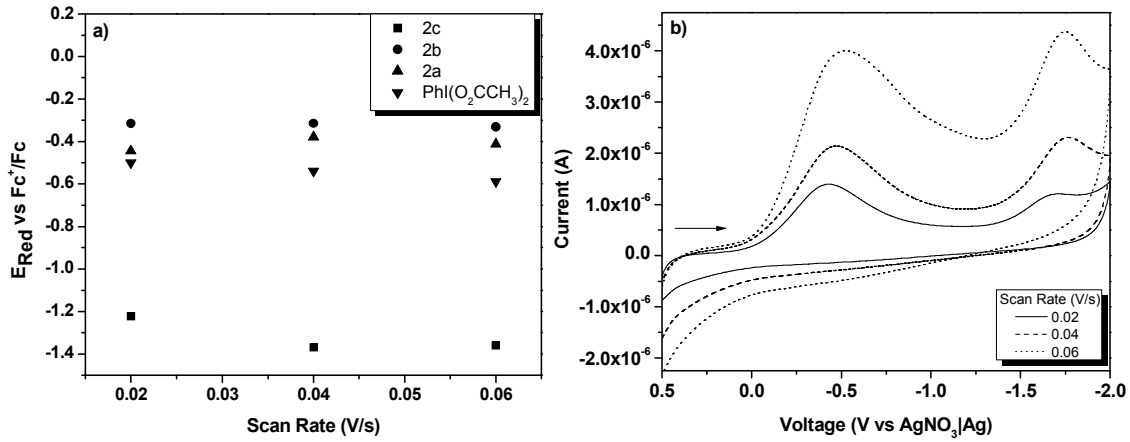


Figure 2. a) Reduction potentials for 1 mM solutions of $PhI(O_2CCH_3)_2$ and tetrazole-containing HV iodine(III) compounds **3a-c** (vs. Fc^+/Fc) in anhydrous DMF containing 0.1 M $(n\text{-Bu})_4NPF_6$, at various scan rates using a glassy carbon electrode, b) Cyclic voltammograms of 1 mM solutions of compound **3a** at different scan rates.

Growing single crystals of the studied compounds, suitable for single crystal X-ray diffraction, proved to be a challenging task. However, **5b** was obtained as a polycrystalline powder with an excellent crystallinity. Therefore, the crystal structure was analyzed using powder X-ray diffraction data, collected

with synchrotron radiation. The structure was solved using the Simulated Annealing algorithm, and refined by the Rietveld method (more information in the SI). The molecule of **5b** consists of three iodine atoms (Figure 3a), linked through bridging oxygen atoms, with I–O distances ranging between 1.95 and 2.08 Å. The two terminal iodine atoms are coordinated by the nitrogen atoms (N2) of the 5-phenyl tetrazole units, with I–N bond distances of 2.443(1) Å and 2.401(1) Å, respectively. The N–I–O–I–O–I–N fragment of the structure adopts a characteristic zigzag geometry, because of the almost linear (with maximum deviation from linearity of 11 ^{o}) arrangement of the structural motif L-I-L, where L is either bridging O atom or the N2 atom of the terminal tetrazole ligands, combined with the valent angles of about 131.7(1)^{o} and 120.7(1)^{o} in the I-O-I fragments. This geometry is similar to other HV iodine(III) compounds.[79] As mentioned, the N–I–O and O–I–O angles were refined to be close to linear. Each iodine atom is coordinated to a phenyl group, with I–C bond distances ranging between 2.00 and 2.12 Å. The three phenyl groups are positioned perpendicularly to the zigzag motif of the oligomer backbone, and aligned in almost parallel fashion one to another, with an average π–π distance of 3.8 Å. The crystal packing of **5b** is made of infinite, one-dimensional molecular chains, connected with relatively strong intermolecular I···N bonds (2.99(1) Å and 3.12(1) Å), as shown in Figure 3b.

We noticed that the lone pair of N3 of the tetrazole groups was not directed exactly as one would expected. However, all attempts to model the orientation resulted in worse fit to the Rietveld plot. Considering that the orientation deviates by only few degrees (and the I…N is relatively weak bonding), we decided to present the structure as freely-refined (as it is customary for solving crystal structures from powder diffraction data). This observation might be a result from local disorder, *i.e.*, it can be assumed that the tetrazole ring is rotationally disordered and the presented structure is an average of all positions. Due to severe limitations of the powder X-ray diffraction method, it is not possible to address this potential disorder issue in much greater detail. Less likely, this observation might be due to steric effects in the solid state, where the crystal packing "forces" the tetrazole ligand in a slightly deviated angle with respect to the I atom. A close inspection of difference Fourier electron density map did not indicate the presence of

solvent molecules. However, we cannot exclude the possibility of disordered solvent molecules in close contacts with the **5b** molecule in the solid-state. Unfortunately, even if present, these solvent molecules would be difficult to detect even with single crystal diffraction, due to (potentially) low occupancies and disorder.

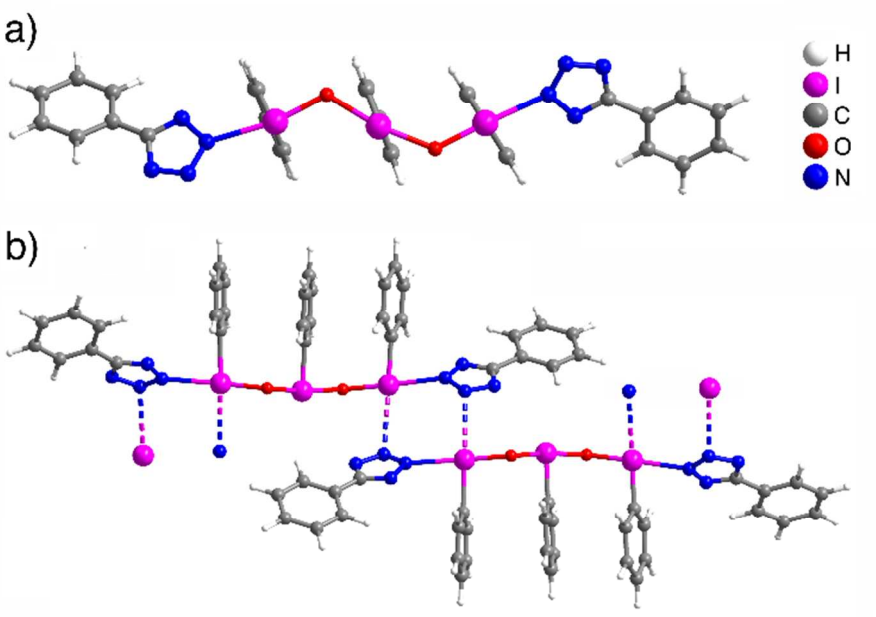


Figure 3. a) One molecule of **5b** featuring three HV iodine (III) atoms, linked by bridging oxygen atoms and terminal nitrogen (N2) atoms of the 5-phenyltetrazole units in a zigzag motif. b) Intermolecular I---N interactions between two neighbouring molecules in the crystal packing of **5b**.

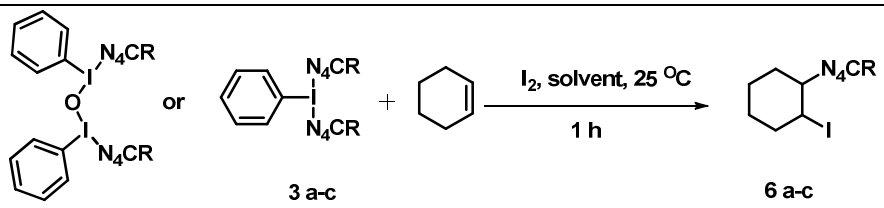
Reactivity

In the above discussion, the preparation of HV iodine(III) compounds with two tetrazole terminal groups, containing only one HV iodine(III) atom (compounds **3a-c**), two HV iodine(III) atoms connected through an oxo-bridge (the μ-oxo compounds **4a-c**), and more than two iodine(III) atoms and several oxo-bridges (the oligomeric compounds **5a-c**) was demonstrated. Tetrazoles are commonly used as propellants and explosives and it was interesting to test and compare the thermal stability of a series of HV iodine(III) compounds with two identical tetrazole ligands at both ends of molecules with different chain lengths. Four compounds (several milligrams) were charged in four test tubes, namely 5-(p-tolyl)tetrazole (**1c**,

placed in test tube No. 1), and compounds with the general formula 4-$CH_3C_6H_4CN_4$-I(Ph)-[O-I(Ph)]$_n$-$N_4CC_6H_4$(4-)CH_3 with n = 0 (i.e., compound **3c** in test tube No. 2), n = 1 (i.e., the μ-oxo compound **4c** in test tube No. 3), and n = 2-3 (mixture of oligomers **5c** in test tube No. 4). The test tubes were immersed in an oil bath, the temperature of which was gradually increased and monitored. The lowest molecular weight HV iodine(III) compound (in test tube No. 2), which contained the largest molar fraction of tetrazole groups, decomposed explosively at ca. 135 ^oC, and it was followed by the next higher molecular weight (μ-oxo) compound at ca. 145 ^oC. Eventually, the oligomer exploded at ca. 178 ^oC, at which point the experiment was stopped. The parent tetrazole was stable up to the end of the heating (i.e., up to ca. 180 ^oC). The experiment was recorded and can be found as a video file in the SI. It can be expected that control over the degree of polymerization in oligomers of type **5** would allow for control over the temperatures of explosive degradation. More detailed studies related to the thermal properties of tetrazole-containing HV iodine(III) compounds are underway.

Suarez and coworkers[80,81] demonstrated the use of $PhI(O_2CCH_3)_2$-I_2 in the acetoxylation of various substrates, and the reaction was further implemented to the iodoacetoxylation of olefins.[82] In this context, compounds **3a-c** were reacted with cyclohexene and styrene in the presence of I_2 in different solvents, leading to the formation to iodotetrazolylation (addition) products. All reactions were performed in dark at 25 ^0C for 1 h as shown in Table 3.

Table 3. Iodotetrazolylation reaction of cyclohexene in different solvents.



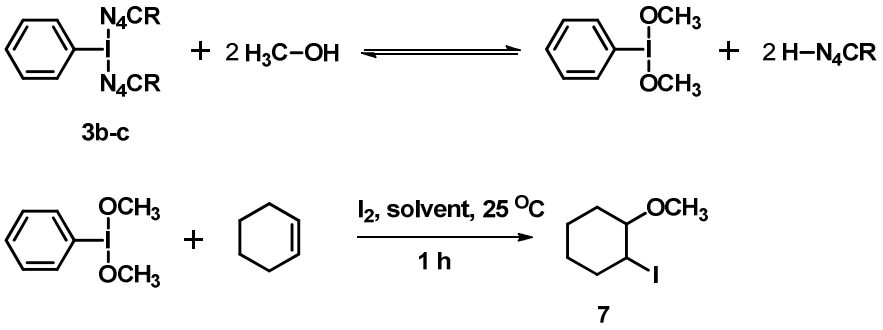
4 b-c 3 a-c 6 a-c

Entry	Reactant	Solvent	Yield (%)
1	**3a**	CH_3CN	75
2	,,	DCM	70
3	,,	$CHCl_3$	69
4	,,	DMF	80
5	,,	MeOH	82

6	**3b**	CH_3CN	85
7	,,	DCM	82
8	,,	MeOH	90[a]
9	**3c**	CH_3CN	80
10	,,	DCM	75
11	,,	MeOH	89[a]
12	**4b**	DCM	82
13	**4c**	DCM	72

[a] The reaction proceeded with the formation of iodomethoxylation product

When the reactions with compounds **3b** and **3c** with cyclohexene were conducted in methanol (Table 3, entries 8 and 11), the product obtained in both cases was compound **7** (Scheme 3). This product could be the result of an exchange reaction between **3b** or **3c** and methanol (yielding $PhI(OCH_3)_2$), followed by reaction of the newly formed compound with iodine and eventually – with cyclohexene. The reaction between **3c** and increasing amounts of MeOH was examined by ^{1}H NMR in DMSO-d_6 and the results suggested that the exchange reaction indeed occured (Figure S8). This product was not observed when compound **3a** (Table 3, entry 5) was reacted with cyclohexene in the presence of iodine in methanol.

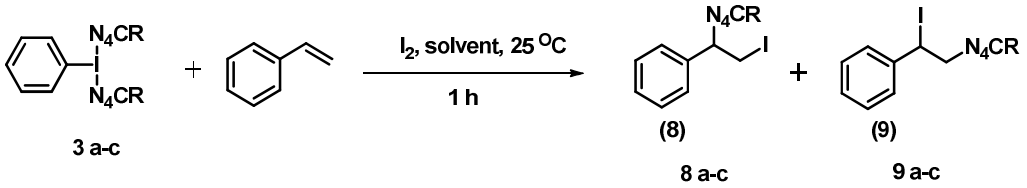


Scheme 3. Exchange reaction of compounds **3b** and **3c** with MeOH and further reaction with cyclohexene in the presence of I_2.

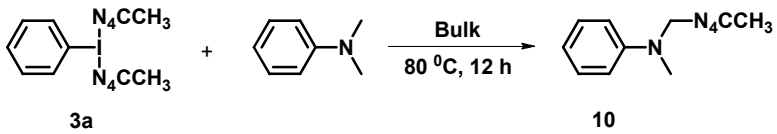
This reaction was extended to styrene. Under similar conditions, two isomers, **8** and **9**, were isolated and characterized spectroscopically, and the former was determined to be the major product

(Table 4). The structures of the isomers were ascertained by comparing their NMR spectra (SI) with the spectra of similar compounds that were products of the reaction between styrene with (diazidoiodo)benzene (generated *in situ*) and iodine,[82] which yielded a mixture of (1-azido-2-iodoethyl)benzene (similar to **8** and dominant) and (2-azido-1-iodoethyl)benzene (analogous to **9**). The higher yield of primary iodide was explained with the stability of the corresponding carbocation intermediate.

Table 4. Iodotetrazolylation of styrene in different solvents.



Entry	R in $PhI(N_4CR)_2$	Solvent	Yield (%)	
			8	**9**
1	CH_3	CH_3CN	75	20
2	,,	DCM	70	15
3	,,	MeOH	82	10
4	C_6H_5	DCM	85	16
5	4-$CH_3C_6H_5$	DCM	80	12



Scheme 4. Oxidative radical tetrazolylation of *N,N*-dimethylaniline at 80 °C in CH_3CN.

In addition to these $PhI(N_4CR)_2$-I_2-mediated reactions, the possibility of radical reactions of compound **3a** in the absence of I_2 was explored. The reaction between **3a** and *N,N*-dimethylaniline (Scheme 4) was performed at 80 °C in bulk for 12 h and the product **10** was isolated using preparative TLC.

In conclusion, novel symmetric HV iodine(III) reagents containing different 5-substituted tetrazoles were prepared and were found to be reasonably stable under ambient conditions in both the solid and

solution states. The compounds proved to be strong oxidants. An oligomer with I-O-based backbone and tetrazole end groups was characterized by X-ray diffraction. The use of these reagents allowed oxidative iodotetrazolylation reactions of styrene and cyclohexene as well as radical transfer of tetrazole groups to *N,N*-dimethylaniline. Further investigations focused on expanding the utility of the HV iodine(III) reagents is currently in progress.

EXPERIMENTAL SECTION

Materials. 5-Methyl-1H-tetrazole (Alfa Aesar, 97 %), 5-phenyl-1H-tetrazole (Alfa Aesar, 99 %), 5-(p-tolyl)-1H-tetrazole (TCI, 98 %), (diacetoxyiodo)benzene ($PhI(O_2CCH_3)_2$, Acros, 98 %), [bis(trifluoroacetoxy)iodo]benzene ($PhI(O_2CCF_3)_2$, Acros, 98 %), cyclohexene (Sigma-Aldrich, 97+ %), styrene (Acros, 99 %), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, TCI, 98 %), NaCl (Sigma-Aldrich, 99.9 %), $NaNO_3$ (Sigma-Aldrich, 99.9 %), $(n\text{-}Bu)_4NPF_6$ (TCI, 98 %), I_2 (Sigma-Aldrich, 99.8 %), $Na_2S_2O_3$ (Acros, 99.8 %), CH_3CO_2H (Sigma-Aldrich, 99 %), Na_2SO_4 (Sigma-Aldrich, 99.8 %), *N,N*-dimethylaniline (Sigma-Aldrich, 99 %) were used as received. Iodosylbenzene (PhIO) was synthesized using a procedure described in the literature,[83] which is based on the hydrolysis of $PhI(O_2CCH_3)_2$ with 3 M aqueous NaOH (pellets, 97+ %, Sigma-Aldrich, were employed to prepare the solution), followed by washing with chloroform (Acros, 99 % extra pure). Dichloroiodobenzene ($PhICl_2$) was synthesized using a procedure described in the literature.[78] The solvents, including anhydrous acetonitrile (Acros, 99.9 %), anhydrous dichloromethane (Acros, 99.9 %), 1,2-dichloroethane (Acros, 99.8 %), diethyl ether (Acros, 99 %), *n*-hexane (Acros, 99.9 %), methanol (Acros, 99.8 %) were used as received.. The deuterated solvents, DMSO-d_6 (Acros, 99.8 % D), DMF-d_7 (Alfa Aesar, 99.5 % D), CD_3CN (Cambridge Isotope Laboratories, 99.8 % D), $CDCl_3$ (Cambridge Isotope Laboratories, 99.8 % D), and CD_3OD (Cambridge Isotope Laboratories, 99.8 % D), contained a small amount of tetramethylsilane (TMS) as a chemical shift reference. All chemicals were used as recieved without further purification.

Analytical procedures. NMR spectra were recorded on a Bruker Avance DRX (400 MHz) spectrometer. Compound **3b-c** and **4b-c** were characterized by MALDI-ToF. MALDI mass spectra were aquired on a Shimadzu Axima Performance MALDI TOF-TOF (Shimadzu Biotech) in both positive and negative ion reflectron modes (100-1000 Da). For each compound, 100 profiles of 10 spectra/profile were collected at repetition rates of either 10 or 50 Hz. Laser power was optimized for each sample based on the intensity and resolution of the peaks in the spectra. Pulsed ion extraction voltages were optimized for the expected molecular weight of each compound. The matrix used was DCTB dissolved in methanol (30 mg/mL) and NaCl and $NaNO_3$ were used as doping agents. All spectra were baseline subtracted and Gaussian filtered for final analysis and compared with the matrix spectrum. The exact mass for compounds **3a, 6a-c, 8a-c, 9a-c**, and **10** was obtained using Shimadzu LCMS-IT-ToF. Standard conditions (electrospray ion source, positive-ion acquisition mode, interface voltage of +4.50 kV, CDL temperature of 200 °C, and block heater temperature of 200 °C) were used to identify all compounds except **3a**. Due to the instability of **3a**, a small peak corresponding to a fragment could only be observed when the analysis conditions were changed as follows: electrospray ion source, positive-ion acquisition mode, interface voltage of +1.00 kV, CDL temperature of 100 °C, and block heater temperature of 100°C. However, the HRMS data for **4b** and **3c** could not be obtained due to fragmentation of the fragile hypervalent I-N bonds. Electrochemical measurements were carried out in an electrochemical cell system controlled with a CHI620E electrochemical station (CH Instruments, Inc., USA) with a Pt wire as the counter electrode, $AgNO_3$/Ag as the reference and glassy carbon (GC) as working electrode while purging dry argon. All potential values are referenced to $AgNO_3$/Ag in 0.1 M $(n\text{-Bu})_4NPF_6$ with 0.01 M $AgNO_3$ in DMF. Samples were prepared by dissolving 10^{-5} mol of the studied HV iodine(III) compounds in 10 mL of 0.1 M solution of $(n\text{-Bu})_4NPF_6$ in dry and deoxygenated DMF. The sample (10 mL) was divided in 3 parts and CV measurements were done on each part only once at a particular scan rate. For comparison, first, the redox potential of 1 mM ferrocene solution in DMF was measured with respect to $AgNO_3$/Ag at the same scan rates. All samples were prepared in glove box to avoid moisture or air. X-ray diffraction setup is described in the SI.

General procedure for the synthesis of HV iodine (III) compounds 3a, 4b, 4c, 5b, and 5c

In a 10 mL dry reaction tube, a magnetic stir bar was placed followed by PhIO (2.0 mmol, 1 eq.) and **1a** (4.0 mmol, 2 eq.). The tube was capped with a rubber septum and wrapped with aluminum foil to prevent exposure of the contents to light. Then, dry solvent (2.0 mL) was injected, the tube was immersed in a water bath at 25 °C, and the mixture was stirred until a clear solution was formed (ca. 30 min). The solvent was then evaporated under reduced pressure and the desired product was isolated. Similar experiments were performed in CH_3CN using tetrazoles **1b** and **1c** for two different time intervals: 2 h and 20 h. When the reaction time between PhIO and **1b** or **1c** was 2 h, the products were **5b** or **5c**, whereas, when contact time was increased to 20 h, mixture of oligomers **4b** or **4c** were obtained. Due to the poor solubility of both **5b** and **5c**, the spectroscopic characterizations were not performed.

*Bis(5-methyltetrazolyl)iodobenzene (**3a**)*. Following the general procedure, PhIO (0.44 g, 2.0 mmol) and 1a (0.34 g, 4.0 mmol) were added in a vial followed by the addition of anhydrous CH_2Cl_2 (2.0 mL) and then removal of CH_2Cl_2 in 30 min yielded 3a (0.63 g, 85 %) as a sticky solid; ^{1}H NMR (400 MHz, CD_3CN): δ 2.43 (s, 6H), 7.28 (t, J = 7.9 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.86 (d, J = 7.9 Hz, 2H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN): δ 9.3, 125.9, 132.0, 132.8, 134.4, 154.9 ppm; HRMS: calculated m/z for $C_8H_8IN_4^+$ $[M\text{-}CH_3CN_4]^+$: 286.9788; found: 286.9756; MALDI-ToF: calculated m/z for $C_{10}H_{11}IN_8Na^+$ $[M+Na]^+$: 393.0038; found: 392.9162.

*μ-Oxo-bis(5-phenyltetrazolyl)iodobenzene (**4b**)*. Following the general procedure, PhIO (0.44 g, 2.0 mmol) and 1b (0.58 g, 4.0 mmol) were added in a vial followed by the addition of anhydrous CH_3CN (20.0 mL) and then removal of solvent in 20 h yielded 4b (0.80 g, 60 %) as an off-white solid; ^{1}H NMR (400 MHz, DMF-d_7): δ 8.00 (s, 8H), 7.47 (dd, J = 36.0, 29.6 Hz, 12H).; ^{13}C{^{1}H}NMR (100.578 MHz, DMF-d_7): δ 126.6, 127.0, 128.0, 130.0, 131.0, 131.1, 133.7, 137.7 ppm; MALDI-ToF: calculated m/z for $C_{19}H_{15}I_2N_4O^+$ $[M\text{-}N_4CC_6H_5]^+$: 568.9335; found: 568.8090.

*μ-Oxo-bis(5-p-tolyltetrazolyl)iodobenzene (**4c**)*. Following the general procedure, PhIO (0.44 g, 2.0 mmol) and 1c (0.64 g, 4.0 mmol) were added in a vial followed by the addition of anhydrous CH_3CN

(20.0 mL) and then removal of solvent in 20 h yielded 4c (0.83 g, 56 %) as an off-white solid; ^{1}H NMR (400 MHz, DMF-d_7): δ 2.35 (s, 6H), 7.31 (d, J = 7.75 Hz, 4H), 7.44 (t, J = 7.5 Hz, 4H), 7.55 (t, J = 7.9 Hz, 2H), 7.92 (d, J = 7.8 Hz, 4H), 8.03 (b, 4H); ^{13}C{^{1}H}NMR (100.578 MHz, DMF-d_7): δ 140.30, 137.68, 133.80, 132.06, 131.22, 130.78, 130.60, 129.74, 127.99, 126.97, 126.66, 20.80 ppm; MALDI-ToF: calculated m/z for $C_{28}H_{23}I_2N_8O^-$ [M-H]$^-$: 741.0084; found: 740.9355.

General procedure for the synthesis of PhI(N_4CR)$_2$ (R = CH_3, C_6H_5, and 4-$CH_3C_6H_4$)

In a 10 mL dry reaction vial, a magnetic stir bar was placed followed by $PhICl_2$ (2.0 mmol) and **2a** (4.0 mmol). The tube was capped with a septum and wrapped with aluminum foil and then dry CH_3CN (4.0 mL) was injected. The tube was immersed in a water bath at 25 °C and the mixture was stirred for 15 h. The white precipitate (KCl) was filtered off and washed with CH_3CN (5×2 mL). The combined solvent was evaporated under reduced pressure to afford **3a** as yellow oil. The oil was dried under high vacuum for 15 h to obtain a sticky solid in 82 % yield. Similar experiments were performed with **2b** and **2c** (to afford **3b** and **3c**, respectively). In these cases, solids were isolated by filtration and washed with a minimum amount of water (2×2 mL) in order to remove the byproduct, KCl, followed by CH_3CN (5×10 mL) and finally with diethyl ether. The products were dried overnight under high vacuum to obtain the pure products with yields indicated in Table 2. The experiments with PhI(O_2CCF_3)$_2$ and **2a-c** were performed under similar conditions but with the change in the purification steps. After the reaction between PhI(O_2CCF_3)$_2$ and **2a**, the CH_3CN was evaporated and the obtained sticky yellow solid was dissolved in CH_2Cl_2. The CH_2Cl_2 dissolves the desired product **3a**, leaving behind the salt, KO_2CCF_3 which was then filtered and further washed with CH_2Cl_2 (4×4 mL). The combined solvent was evaporated under reduced pressure to afford **3a** as yellow oil. The oil was dried under high vacuum for 15 h to obtain a sticky solid in 70 % yield. Similar experiments were performed with **2b** and **2c** (to afford **3b** and **3c**, respectively). In these cases, solids were isolated by filtration and washed with CH_3CN (5×5 mL) in order to remove the byproduct, KO_2CCF_3, followed by diethyl ether and dried under vacuum.

*Bis(5-phenyltetrazolyl)iodobenzene (**3b**)*. $PhICl_2$ (0.55 g, 2.0 mmol) and 2b (0.74 g, 4.0 mmol) were added to a vial, followed by anhydrous CH_3CN (20.0 mL), and the general method yielded 3b (0.68

g, 69 %); ^{1}H NMR (100.578 MHz, DMSO-d_6): δ 8.06 (d, J = 6.6 Hz, 6H), 7.59 (d, J = 7.5 Hz, 9H); ^{13}C{^{1}H}NMR (400 MHz, DMSO-d_6): δ 158.1, 134.1, 132.1, 131.4, 130.8, 129.7, 127.1, 126.5 ppm; MALDI-ToF: calculated m/z for $C_{13}H_{10}IN_4Cl$ [M-PhCN$_4$+Cl]$^-$: 383.9644; found: 383.9654

*Bis(5-(4-tolyltetrazolyl))iodobenzene (**3c**).* $PhICl_2$ (0.55 g, 2.0 mmol) and 2c (0.79 g, 4.0 mmol) were added to a vial, followed by anhydrous CH_3CN (20.0 mL), and the general method yielded **3c** (0.68 g, 65%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08 (d, J = 7.7 Hz, 2H), 7.92 (d, J = 8.1 Hz, 4H), 7.62 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 8.1 Hz, 4H), 2.39 (s, 6H); ^{13}C{^{1}H}NMR (100.578 MHz, DMSO-d_6): δ 158.0, 140.7, 134.0, 132.1, 131.3, 130.2, 127.1, 125.1–124.5, 123.6, 21.3 ppm; MALDI-ToF: calculated m/z for $C_{22}H_{20}IN_8^+$ [M+H]$^+$: 523.0856; found: 523.0084

^{1}H NMR studies of exchange reaction between acetoxy groups of $PhI(O_2CCH_3)_2$ with 1a in CD_3CN

In a 10 mL glass tube, $PhI(O_2CCH_3)_2$ (9.6 mg, 3.0×10^{-5} mol, to reach final concentration of 10 mM) was added in CD_3CN (3 mL) followed by $C_2H_4Cl_2$ (internal standard; 10 μL) and **1a** (2.5 mg, 3.0×10^{-5} mol, to reach final concentration of 10 mM) and the mixture was stirred to dissolve the components. Then, 0.8 mL of this solution was taken in a dark NMR tube and spectra (8 scans) were collected. The equilibrium was determined as the time, at which the ratio of the integrals of the $C_2H_4Cl_2$ protons and aromatic protons of $PhI(O_2CCH_3)_2$ remained constant. It took 5 h to reach equilibrium. Similar experiments were performed where larger amounts of **1a** (2 and 4 eq.) in CD_3CN were used to replace acetoxy groups of $PhI(O_2CCH_3)_2$.

Exchange of CH_3CN_4 groups in $PhI(N_4CCH_3)_2$ with acetoxy groups

In a 10 mL reaction tube, a stir bar was added followed by $PhI(N_4CCH_3)_2$ (11 mg, 3.0×10^{-5} mol; to reach final concentration of 10 mM) and the tube was wrapped with aluminum foil to protect the contents from light. CD_3CN (3.0 mL) was then added. The solution was stirred until it became homogeneous (30 min) at room temperature. Then, CH_3CO_2H (1.72 μL, 3.0×10^{-5} mol, to reach final concentration of 10 mM) was added followed by $C_2H_4Cl_2$ (10 μL, 0.13 mmol) and TMS vapors. Then, 0.8

mL of the solution were transferred into a dark (ambered) NMR tube and ^{1}H NMR spectra (8 scans) were collected. It took 5 h to reach equilibrium. Similar experiments were performed with larger amounts of CH_3CO_2H.

Reaction of $PhI(N_4RC)_2$ and RCN_4-I(Ph)-[O-I(Ph)]$_n$-N_4CR with cyclohexene in the presence of I_2

In a 10 mL reaction tube, a stir bar was placed followed by **3a** (0.37 g, 1.0 mmol) and the tube was wrapped with aluminum foil to protect the contents from light. Then, anhydrous CH_3CN (2.0 mL) was added and the tube was immersed in a water bath at 25 °C and stirred until the solution became clear (ca. 30 min). Then, I_2 (0.26 g, 1.0 mmol) was added and clear solution turned turbid white. This heterogeneous solution was stirred for another 5 min. and cyclohexene (0.11 mL, 1.0 mmol) was added using a micropipette. It was noted that upon the addition of cyclohexene the color turned brown and the solution remained heterogeneous. After 1 h, the reaction was quenched using 10 % $Na_2S_2O_3$ and the contents were extracted with CH_2Cl_2 (5×10 mL). All the CH_2Cl_2 layers were collected and washed with distilled water (3×10 mL), dried over Na_2SO_4, and then the solvent was evaporated using rotovap to obtain a yellow oil as the crude product. The crude product was dissolved in CH_2Cl_2 (1.0 mL) and hexane (20.0 mL) was added. Subsequently, the mixture was left at room temperature for about an hour to obtain crystals of pure **6a** (0.218 g, 74.8 % yield). Similar experiments were carried out with **3a** in different solvents and with **3b** and **3c** under the same conditions, as well as with **4b** and **4c** in DCM. In the later case, the products were identical to those isolated from the reactions involving **3b** and **3c**.

*1-(2-iodocyclohexyl)-5-methyltetrazole (**6a**)*. Following the above procedure, product **6a** was obtained as colorless crystaline compound (0.22 g, 75 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.57 (ddd, J = 12.5,10.9, 4.3 Hz, 1H), 4.27 (td, J = 11.2, 4.2 Hz, 1H), 2.82–2.64 (m, 1H), 2.64 (s, 3H), 2.27–1.93 (m, 4H), 1.71 (dd, J = 7.1, 2.6 Hz, 1H), 1.68–1.41 (m, 2H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN): δ 152.7, 64.4, 40.4, 34.7, 33.9, 28.3, 25.1, 9.4 ppm; GC-MS: calculated m/z for $C_8H_{13}IN_4$: 292.12; found: 292.0. **6a** was reported by Hassner and co-workers but no NMR spectrum was reported.[84]

*1-(2-iodocyclohexyl)-5-phenyltetrazole (**6b**)*. Following the above procedure, product 6b was obtained as colorless crystalline compound (0.30 g, 85 %); ^{1}H NMR (400 MHz, CD_3CN): δ 7.80–7.40 (m, 5H), 4.70 (ddd, J = 12.4, 10.9, 4.2 Hz, 1H), 4.64–4.50 (m, 1H), 2.64–2.55 (m, 1H), 2.39–2.04 (m, 4H), 1.75–1.12 (m, 3H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN): δ 155.6, 132.2, 130.3, 130.3, 125.1, 65.3, 40.2, 35.1, 33.9, 28.2, 25.0 ppm; GC-MS: calculated m/z for $C_{13}H_{15}IN_4$: 354.19; found: 354.0. ^{1}H NMR spectrum is in agreement with that reported for **6b**.[85]

*1-(2-iodocyclohexyl)-5-(p-tolyl)tetrazole (**6c**)*. Following the above procedure, product 6c was obtained as colorless crystalline compound (0.29 g, 80 %); ^{1}H NMR (400 MHz, CD_3CN + DMSO-d_6): δ 7.72 – 7.56 (m, 2H), 7.56 – 7.40 (m, 2H), 4.76 – 4.61 (m, 1H), 4.54 (td, J = 11.3, 4.1 Hz, 1H), 2.55 (ddd, J = 12.8, 5.6, 2.1 Hz, 1H), 2.46 (s, 3H), 2.29 (ddd, J = 6.0, 4.9, 3.1 Hz, 1H), 2.16 – 2.00 (m, 2H), 2.01 – 1.90 (m, 1H), 1.67 – 1.41 (m, 3H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN + DMSO-d_6): δ 141.37, 129.55, 128.78, 120.47, 117.24, 63.83, 33.69, 32.71, 26.82, 23.59, 20.25; HRMS: calculated for $C_{14}H_{17}IN_4$ $[M+H]^+$: 369.0566; found: 369.0571.

*1-iodo-2-methoxy-cyclohexane (**7**)*. ^{1}H NMR (500 MHz, CD_3CN): δ 4.06 (dd, J = 7.6, 5.5 Hz, 1H), 3.41 (s, 3H), 3.31 – 3.16 (m, 1H), 2.40 (d, J = 15.8 Hz, 1H), 2.21 (d, J = 3.3 Hz, 1H), 2.13 – 1.90 (m, 1H), 1.90 – 1.66 (m, 1H), 1.66 – 1.49 (m, 1H), 1.53 – 1.11 (m, 3H); GC-MS: calculated m/z for $C_7H_{13}IO$: 240.08; found: 240.00. The ^{1}H NMR spectrum is in agreement with that reported for **7**.[86]

Reaction of PhI(N_4CR)$_2$ with styrene in the presence of I_2

In a 10 mL reaction tube, a stir bar was added followed by **3a** (0.37 g, 1.0 mmol) and the tube was wrapped with aluminum foil. Anhydrous CH_3CN (2.0 mL) was added and the tube was immersed in a water bath at 25 °C and stirred until the solution became clear (ca. 30 min). Then, I_2 (0.26 g, 1.0 mmol) was added and clear solution turned turbid white. This heterogeneous solution was stirred for another 5 min and then styrene (0.12 mL, 1.0 mmol) was added using a micropipette. After 1 h, the reaction was quenched using 10 % $Na_2S_2O_3$ and then the contents were extracted with CH_2Cl_2 (5×10 mL). All the

CH_2Cl_2 layers were collected and washed with distilled water (3×10 mL), dried over Na_2SO_4, and the solvent was evaporated to afford a yellow oil as the crude product. The crude product (a mixture of isomers) was dissolved in CH_2Cl_2 (2.0 mL) and the isomers were separated using a preparative thin-layered chromatography. The separated isomers were dissolved in CH_2Cl_2 (1.0 mL) and hexane (20.0 mL) was added. Subsequently, the mixtures were left at room temperature for about an hour to obtain crystals of compounds **8a** and **8b** as the pure products. Similar experiments were carried out with **3a** in different solvents and with **3b** and **3c** under the same conditions.

*1-(2-iodo-1-phenylethyl)-5-phenyl-tetrazole (**8a**)*. Following the above procedure, product 8a was obtained as colorless crystalline compound (0.24 g, 75 %); ^{1}H NMR (400 MHz, CD_3CN): δ 7.44–7.37 (m, 5H), 6.20 (dd, J = 10.5, 4.7 Hz, 1H), 4.20 (t, J = 10.6 Hz, 1H), 3.94 (dd, J = 10.7, 4.8 Hz, 1H), 2.48 (d, J = 3.7 Hz, 3H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN): δ 164.1, 137.6, 130.3, 130.0, 129.9, 129.2, 128.7, 127.9, 126.9, 73.8, 69.9, 11.1 ppm; HRMS calculated for $C_{10}H_{11}IN_4$ $[M+H]^+$: 315.0095; found: 315.0101.

*1-(2-iodo-1-phenylethyl)-5-phenyl-tetrazole (**9a**)*. Following the above procedure, product 8a was obtained as colorless crystalline compound (0.24 g, 75 %); ^{1}H NMR (400 MHz, CD_3CN): δ 7.55–7.23 (m, 5H), 5.63 (dd, J = 10.5, 4.7 Hz, 1H), 4.19 (t, J = 10.6 Hz, 1H), 3.85 (dd, J = 10.7, 4.8 Hz, 1H), 2.54 (d, J = 3.7 Hz, 3H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN): δ 153.31, 137.4, 130.05, 129.14, 128.60, 127.95, 126.87, 73.73, 64.14, 6.57; HRMS calculated for $C_{10}H_{11}IN_4$ $[M+H]^+$: 315.0099; found: 315.0101.

*1-(2-iodo-2-phenylethyl)-5-phenyl-tetrazole (**8b**)*. Following the above procedure, product 8b was obtained as colorless crystalline compound (0.32 g, 85 %); ^{1}H NMR (400 MHz, CD_3CN): δ 8.14–8.12 (s, 2H), 7.55–7.54 (m, 5H), 7.54–7.41 (m, 3H), 6.31 (dd, J = 10.4, 5.3 Hz, 1H), 4.27 (t, J = 10.6 Hz, 1H), 2.16 (dd, J = 10.8, 5.3 Hz, 1H); ^{13}C{^{1}H}NMR (100.578 MHz, CD_3CN): δ 165.1, 136.6, 130.6, 129.5, 129.2, 129.1, 127.3, 127.1, 126.6, 69.5, 4.4; HRMS calculated for $C_{15}H_{13}IN_4$ $[M+H]^+$: 377.0261; found: 377.0258.

*1-(2-iodo-1-phenylethyl)-5-phenyl-tetrazole (**9b**)*. Following the above procedure, product 9b was obtained as white solid (60.2 mg, 16 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.50 (m, 5H), 7.48–7.36 (m, 5H), 5.62 (dd, J = 11.1, 4.4 Hz, 1H), 4.23 (t, J = 11.0 Hz, 1H), 3.77 (dd, J = 10.8, 4.4 Hz, 1H);

$^{13}C\{^{1}H\}$NMR (100.578 MHz, $CDCl_3$): δ 155.5, 136.7, 131.6, 129.8, 129.7, 129.4, 126.8, 123.8, 65.2, 6.1 ppm; HRMS calculated for $C_{15}H_{13}IN_4$ $[M+H]^+$: 377.0255; found: 377.0258.

*1-(2-iodo-2-phenylethyl)-5-tolyl-tetrazole (**8c**)*. Following the above procedure, product 8c was obtained as white solid (0.31 g, 80 %); ^1H NMR (400 MHz, $CDCl_3$): δ 8.15–7.99 (m, 2H), 7.53–7.42 (m, 2H), 7.41–7.32 (m, 3H), 7.28 (dd, J = 8.5, 0.6 Hz, 2H), 6.15 (dd, J = 10.3, 5.3 Hz, 1H), 4.31–4.13 (m, 1H), 3.87 (dd, J = 10.8, 5.3 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$NMR (100.578 MHz, $CDCl_3$): δ 165.4, 140.6, 136.2, 129.6, 129.6, 129.2, 126.9, 126.9, 124.5, 70.0, 21.6 ppm; HRMS calculated for $C_{16}H_{15}IN_4$ $[M+H]^+$: 391.0414; found: 391.0414.

*1-(2-iodo-1-phenylethyl)-5-tolyl-tetrazole (**9c**)*. Following the above procedure, product 9c was obtained as white solid (50.0 mg, 12 %); ^1H NMR (400 MHz, CD_3CN): δ 7.36–7.29 (m, 9H), 5.73–5.69 (dt, J = 7.6, 3.8 Hz, 1H), 4.09 (td, J = 10.8, 6.6 Hz, 1H), 3.81 (dt, J = 20.8, 10.4 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$NMR (100.578 MHz, CD_3CN): δ 156.3, 143.0, 137.7, 130.9, 130.6, 130.3, 130.2, 130.1, 130.0, 129.9, 127.9, 127.8, 127.5, 65.0, 21.5 ppm; HRMS calculated for $C_{16}H_{15}IN_4$ $[M+H]^+$: 391.0417; found: 391.0414.

Reaction of $PhI(N_4CCH_3)_2$ with *N,N*-dimethylaniline in CH_3CN

In a 10 mL reaction tube, a stir bar was added followed by **3a** (5.84 g, 15.78 mmol) and the tube was wrapped with aluminum foil in order to protect the contents from light. The tube was carefully purged with nitrogent for 30 min and in a different vial, *N,N*-dimethylaniline (20 mL) was added and purged with nitrogen for 30 min. Then, *N,N*-dimethylaniline (10 mL, 78.9 mmol) was withdrawn using a nitrogen purged syringe and added to the tube containing **3a** immediately turning into a dark solution. The reaction tube was then immersed in an oil bath preheated to 80 °C and stirred there for 12 h. Then, the reaction was quenched using 10 % $Na_2S_2O_3$ (20 mL) and the contents were extracted with ethyl acetate (5×50 mL). All the ethyl acetate layers were collected and washed with distilled water (3×100 mL), dried over Na_2SO_4 and the solvent was evaporated to afford a dark brown oil as the crude product. The crude

product was dissolved in ethyl acetate (10.0 mL) and the products were separated using a preparative thin-layered chromatography. The desired product was isolated as brown solid (0.17 g, 15%).

*N-methyl-N-((5-methyl-1H-tetrazol-1-yl)methyl)aniline (**10**)*. Following the above procedure, product 10 was obtained in the mixture; ^{1}H NMR (400 MHz, CD_3CN): δ 7.14 (d, J = 8.8 Hz, 2H), 6.89-6.61 (m, 3H), 5.36 (s, 2H), 2.90 (s, 3H), 2.45 (s, 3H); $^{13}C\{^{1}H\}$NMR (100.578 MHz, CD_3CN): δ 153.3, 137.4, 130.2, 130.0, 129.1, 127.9, 126.9, 73.7, 64.1; HRMS calculated for $C_{10}H_{13}N_5$ $[M+H]^+$: 204.1243; found: 204.1244.

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SUPPORTING INFORMATION

Supporting information includes spectral studies of the hydrolysis of **3c**, interaction between $(n\text{-Bu})_4NPF_6$ and **3c**, and ligand exchange of **3c** with CH_3OH; CV data for compounds **3a-c** and $PhI(O_2CCH_3)_2$; ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, mass spectra; crystallographic data for **5b** (CIF); and a video comparing the explosive decomposition of **3c**, **4c** and **5c**.

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