REVIEW ARTICLE

UPI JOURNAL OF CHEMICAL AND LIFE SCIENCES (UPI-JCLS)

ISSN: 2581-4648 (An International online Peer Reviewed, Open Access Journal)

www.uniquepubinternational.com Published by Unique Pub International (UPI)

HYPERVALENT IODINE (III) VERSUS SULFONIUM SALTS AS ELECTROPHILIC GROUP-TRANSFER REAGENTS: A COMPARATIVE REVIEW OF STABILITY, REACTIVITY, SAFETY AND SUSTAINABILITY

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Received: 24 08 2026 Revised: 06 10 2026 Accepted: 18 10 2026

Abstract
Many modern methods install a group by reversing its usual polarity: a trifluoromethyl, alkynyl, cyano, aryl or vinyl unit is handed to a nucleophile as if it were a cation. Two reagent families carry most of this chemistry, hypervalent iodine (III) compounds (λ^3-iodanes) and sulfonium salts. In both, the group sits on a heavy main-group atom that leaves in reduced form, as an iodoarene or a neutral sulfide. The two families are rarely judged side by side, and this review does so on four practical axes. For stability, we contrast the three-centre, four-electron bond of iodine (III) with the octet sulfonium cation. For reactivity, we follow polar, single-electron and metal-catalysed pathways and collect the few studies that tested both classes on the same bond. The available calorimetric and impact data are collected for safety. Several benziodoxol(on)e reagents are energetic decompositions but at least one alkynyl sulfonium salt is also high-energy. Data on sulfonium salts is scant. For sustainability, we combine element supply estimates with a mass partition of fifteen reagents estimated from their formulae. 7 to 42% of the mass of each reagent ends up in the result, hence the waste balance depends on the recovery of the carrier. We read the evidence straightforwardly. Iodine (III) reagents are still the top choice for quick polar transfers on a small scale, but sulfonium salts become desirable when therma margins, site-selective arene activation or recycling of the carrier matter more. We end with data gaps that nevertheless prevent a fair, quantitative choice.

Keywords: Hypervalent iodine; λ3-iodanes; sulfonium salts; thianthrenium salts; electrophilic group transfer; trifluoromethylation; process safety; green chemistry.

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1. INTRODUCTION

Most bond-forming reactions pair a nucleophile with an electrophile, and for most groups a partner of the right polarity is easy to find. Some groups resist this. A free trifluoromethyl anion falls apart to difluorocarbene and fluoride, cyanide and acetylides are nucleophiles by nature, and aryl cations are far too unstable to handle. Chemists solved the problem by loading such groups onto a leaving atom and delivering them as formal cations, a polarity reversal often called umpolung [1]. The idea is old. It became routine only when shelf-stable reagents appeared. Two families now do most of this work. One is hypervalent iodine(III): diaryliodonium salts and the cyclic benziodoxol(on)es linked with the names of Togni, Waser and Zhdankin [1–5]. The other is sulfonium salts, from the S-(trifluoromethyl)diarylsulfonium salts of Yagupolskii and the dibenzothiophenium salts of Umemoto to the thianthrenium salts that now allow site-selective arene functionalisation [6–10]. In each case the departing atom takes two electrons with it and leaves as a stable neutral molecule, an iodoarene or a sulfide. The two families are usually reviewed separately [2, 4, 5, 10–12]. But a working chemist is frequently faced with the choice between them for the same bond, and then the questions that matter are seldom answered. "Will the reagent stand up to being heated in a big reactor?" How much of it goes to waste? Where does the iodine come from? Is the sulphide reusable? The questions become more significant as these reagents move into pharmaceutical chemistry, radiochemistry and process work. This review we directly compare the two classes. We first outline the bonding which governs their behaviour and then compare them stability, reactivity, safety and sustainability, using public data where available and simple calculations where not. We don't strive to pick a winner. The purpose is to provide a clear basis for choice of reagent, and an honest map of where data is still thin.

2. STRUCTURE AND BONDING: WHY THE GROUP LEAVES

2.1. The iodine(III) centre

Iodine(III) reagents are hypervalent in Musher's sense, because the central atom formally holds more than eight valence electrons [13]. A λ^3-iodane of the type $ArIL_2$ is T-shaped (Figure 01a). The aryl group occupies an equatorial position and is held by an ordinary two-centre bond, while the two apical ligands share one 5p orbital of iodine through a three-centre, four-electron bond [2, 3]. This bond is longer and weaker than a normal covalent bond. It is also polarised, with negative charge on the apical ligands and positive charge on iodine, so the iodine atom is electrophilic and ligand exchange is easy.

The real driving force lies in the leaving group. When an apical ligand is transferred, iodine(III) is reduced to iodine(I) and an iodoarene departs. From the solvolysis of a cyclohexenyl iodonium salt, Okuyama, Ochiai and co-workers estimated that the phenyliodonio group leaves about 10^6 times faster than triflate, which is why it is often called a hypernucleofuge [14]. Diaryliodonium ions are also strong Lewis acids. Mayr, Legault and co-workers placed seventeen of them on a quantitative Lewis acidity scale towards oxygen, nitrogen and halogen bases, with binding constants that span about six orders of magnitude [15]. Iodine(III) cations of this kind are now also used as halogen-bond donors in catalysis [16].

2.2. The sulfonium centre

Sulfonium ions do something else. Sulphur has a complete octet with three sigma bonds and one lone pair in a trigonal pyramid (Figure 01b), hence there is nothing hypervalent here. The group leaves because the C–S bond is polarised toward a cationic, electron deficient sulphur and because the neutral sulphide that exits is a good leaving group [10]. Formally, sulphur is reduced from S(IV) to S(II) which follows fairly well the two-electron logic of iodine [10]. The incoming nucleophile or electron is accepted by the C–S σ* orbitals. Sulphur also participates in chalcogen bonds, for the same reason. Cockroft and co-workers attributed these interactions mostly to lone-pair donation into σ* orbitals, not to electrostatics alone [17].

The practical difference is tunability. Umemoto and Ishihara showed that the strength of S-(trifluoromethyl)dibenzothiophenium salts as CF3 donors is enhanced by the introduction of nitro groups into the ring and diminished by replacement of sulphur with selenium and then tellurium [7, 18]. Ring fusion is also the deciding factor in who leaves. In dibenzothiophenium and thianthrenium salts the cyclic sulphide remains intact and exocyclic group is transferred. Iodine(III) chemistry addresses the same selectivity problem in two ways: by employing auxiliary ("dummy") aryl groups such as 2,4,6-trimethoxyphenyl in unsymmetrical iodonium salts [19] or by embedding the carrier in a benziodoxole ring [1].

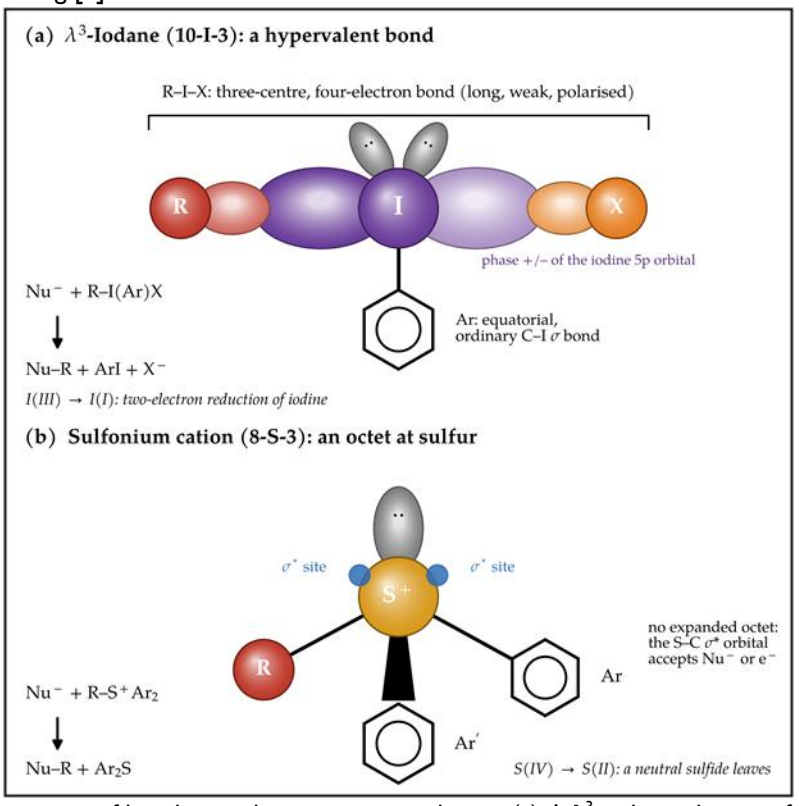


Figure 01: Pictorial comparison of bonding in the two reagent classes. (a) A λ^3-iodane: the transferable group R and the ligand X share one iodine 5p orbital through a three-centre, four-electron bond, while the aryl ring sits in the equatorial position; transfer releases ArI and reduces iodine(III) to iodine(I). (b) A sulfonium cation: octet sulfur with three σ bonds, one lone pair and σ* acceptor sites opposite the S–C bonds; transfer releases a neutral sulfide and reduces S(IV) to S(II).

3. THE REAGENT FAMILIES AND HOW THEY ARE MADE

3.1. Iodine(III) reagents

Diaryliodonium salts are the oldest members of the group, and for decades they were mostly curiosities. One-pot syntheses from arenes and iodine or iodoarenes, with m-CPBA as oxidant and triflic acid, made them easy to obtain [4, 20], and updated protocols now cover combinations of electron-rich and electron-poor rings that the first methods could not make [21]. They transfer aryl groups to carbon, nitrogen, oxygen, sulfur and phosphorus nucleophiles, with or without a metal catalyst [4].

Cyclic λ^3-iodanes changed the field after 2006, when Togni and co-workers introduced the 1-trifluoromethyl-1,2-benziodoxoles now called Togni reagents I and II [22]. Under mild conditions these trifluoromethylate β-keto esters, thiols and many other nucleophiles [5, 23]. The same frame carries alkynyl (EBX), cyano (CBX) and azido (ABX) groups [24–26]. For example, TIPS-EBX alkynylates thiols in minutes at ambient temperature and does not react with most other functional groups [27]. These compounds are practicable due to the 5-membered ring. Cyclic benziodoxol(on)es are known to be more stable than their acyclic equivalents, some of which are too unstable even for metal catalysis [1]. One cautionary tale here is an electrophilic SCF3 reagent that was originally designated as a benziodoxole but later proved by X-ray research to be a thioperoxide [28, 29]. The assignments of structures in this area are worth checking.

3.2. Sulfonium reagents

For trifluoromethylation, sulfonium salts actually came first. Yagupolskii and co-workers reported S-(trifluoromethyl)diarylsulfonium salts in 1984 [6, 30], and Umemoto followed with S-(trifluoromethyl)dibenzothiophenium salts and their selenium and tellurium relatives [7, 8, 18]. Shibata's group later added fluorinated Johnson-type sulfoximinium salts and extended Yagupolskii–Umemoto-type salts made by acid-catalysed cyclisation [31, 32]. Umemoto's 2,8-difluoro and 2,3,7,8-tetrafluoro analogues, reported in 2017, combine high reactivity with thermal stability, a one-pot synthesis and a recyclable sulfide [33].

Beyond CF_3, the platform grew quickly in the last decade. Alcarazo's group used dihalo(imidazolium)sulfuranes as a starting point for new transfer reagents [34] and then prepared 5-(alkynyl)- and 5-(cyano)dibenzothiophenium triflates for electrophilic alkynylation and cyanation [35, 36]. Aryl sulfonium salts had long been used as arylating agents [37], and Procter and co-workers made aryl dibenzothiophenium salts directly from arene C–H bonds by interrupted Pummerer activation of the S-oxide, then coupled them under photoredox conditions [38, 39]. The biggest step came from Ritter's thianthrenation, which converts an arene C–H bond into an aryl thianthrenium salt with very high para selectivity [9, 40]. Even toluene gives para/ortho and para/meta ratios above 100 [40]. The same chemistry gave vinyl thianthrenium tetrafluoroborate from ethylene gas [41] and alkenyl thianthrenium salts from olefins [42]. Figure 02 shows representative structures and Table 01 lists the landmark reports.

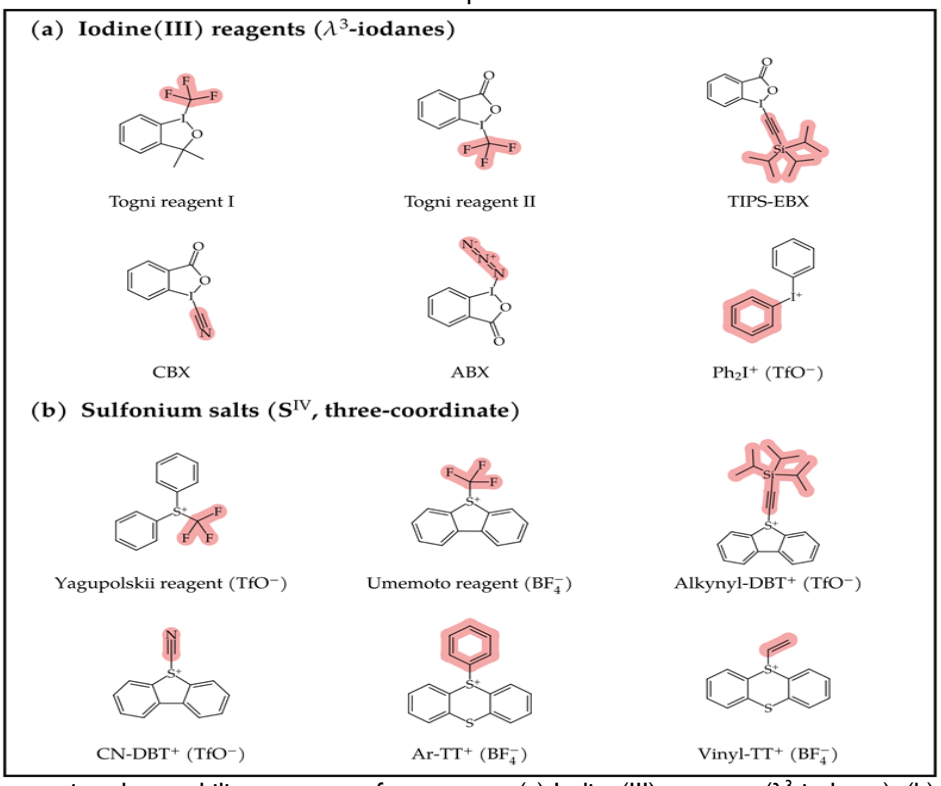


Figure 02: Representative electrophilic group-transfer reagents. (a) Iodine(III) reagents (λ^3-iodanes). (b) Sulfonium salts. The shaded fragment is the group delivered to the nucleophile; the unshaded part is the carrier released as an iodoarene or a sulfide. Counter-anions are given in parentheses. DBT, dibenzothiophenium; TT, thianthrenium.

Table 01: Landmark electrophilic group-transfer reagents and the studies that introduced or defined them.

Reagent (class)	Group	Key study	Main finding
Diaryliodonium triflates, I(III)	Ar	Bielawski and Olofsson, 2007 [20]	One-pot synthesis from arenes and iodine or iodoarenes with m-CPBA and TfOH
Togni reagents I and II, I(III)	CF_3	Eisenberger, Gischig and Togni, 2006 [22]	First 10-I-3 compounds with CF_3 bound to iodine; T-shaped; formal CF_3 umpolung
Togni reagent II, I(III)	CF_3	Kieltsch, Eisenberger and Togni, 2007 [23]	Mild CF_3 transfer to β-keto esters, α-nitro esters and thiols; recyclable reagent
TIPS-EBX, I(III)	alkynyl	Frei and Waser, 2013 [27]	Fast, chemoselective alkynylation of thiols
CBX, I(III)	CN	Le Vaillant, Wodrich and Waser, 2017 [25]	Photoredox decarboxylative cyanation; mechanism differs from alkynylation
ABX, then tBu-ABX and ABZ, I(III)	N_3	Zhdankin et al., 1996 [26]; Alazet et al., 2018 [43]	Crystalline azidoiodinanes; later shown hazardous and replaced by safer analogues
Aryl(TMP)iodonium salts, I(III)	Ar	Seidl et al., 2016 [19]	2,4,6-Trimethoxyphenyl as a dummy ligand; one-pot synthesis and stability study
S-CF_3 diarylsulfonium salts (Yagupolskii)	CF_3	Yagupolskii et al., 1984 [6]	First electrophilic CF_3-transfer reagent
S-CF_3 dibenzothiophenium salts (Umemoto)	CF_3	Umemoto and Ishihara, 1990, 1993 [7, 18]	Power-variable CF_3^+ reagents tuned by heteroatom and ring substituents
Fluorinated S-CF_3 dibenzothiophenium salts	CF_3	Umemoto et al., 2017 [33]	More powerful, thermally stable, one-pot and recyclable
5-(Alkynyl)dibenzothiophenium triflates	alkynyl	Waldecker et al., 2018 [35]	Sulfur-based electrophilic alkynylation from DBT S-oxide
5-(Cyano)dibenzothiophenium triflate	CN	Li, Golz and Alcarazo, 2019 [36]	Cyanation without Lewis acid; biomimetic cyanocyclisations
Aryl thianthrenium salts (Ritter)	Ar	Berger et al., 2019 [9]	Site-selective C–H thianthrenation of arenes and broad follow-up chemistry
Vinyl thianthrenium BF_4^-	vinyl	Juliá et al., 2021 [41]	Practical vinylating reagent made from ethylene
Aryl dibenzothiophenium salts (Procter)	Ar	Aukland et al., 2020 [38]	Interrupted Pummerer activation; metal-free photoredox C–H/C–H coupling

4. STABILITY: SHELF, SOLUTION AND HEAT

Stability has three layers here: shelf life, behaviour in solution, and the temperature at which decomposition begins. The two families do not rank the same way on all three.

On the shelf, most reagents in Figure 02 are crystalline solids that can be weighed in air. Diaryliodonium salts are generally easy to store and handle [4], and the benziodoxole ring gives the Togni, EBX and CBX reagents much better stability than their acyclic relatives [1]. Sulfonium salts are, as a rule, just as easy to store. Umemoto described his fluorinated dibenzothiophenium reagents as thermally stable [33], and aryl and vinyl thianthrenium salts are bench-stable solids [9, 41]. Vinyl thianthrenium tetrafluoroborate, for instance, was unchanged after a year in air and showed no decomposition below 280 °C [41].

In solution the picture is different. Iodine(III) reagents are turned on by acids. Strong activation of the Togni reagent by a Lewis acid, e.g. Zn(NTf2)2, results in trifluoromethylation on oxygen of even aliphatic alcohols [44]. The same activation can also open paths to breakdown and so acid additions need some care. Sulfonium salts are highly tolerated to acid. Thianthrenation itself utilises thianthrene S-oxide with trifluoroacetic anhydride and HBF4·OEt2 [40]. Their weaknesses are elsewhere. Soft nucleophiles can target the incorrect carbon. Salts bearing α-hydrogens can lose a proton to produce ylides under basic circumstances [10].

Families truly do diverge at thermal limits, but not as cleanly as is frequently supposed. The weak hypervalent bond of a cyclic iodane is an energy storage . The typical benziodoxol(on)es in Table 02 breakdown exothermically in the range of roughly 80–150 °C [45–47]. Pseudocyclic, N-heterocycle-stabilised iodanes, a class related to the diaryliodonium salts, show breakdown maxima in the range 120–270 °C [48]. The typical Umemoto reagent decomposes at ca. 153 °C with a weak endothermic signal [49]. Table 02 contains the published numbers, to which we come back from the safety side in section 6.

Table 02: Published thermal and sensitivity data for representative reagents. Positive energies are exothermic.

Reagent	Group	Onset or decomposition (°C)	Energy (J g^{-1})	Impact or friction	Ref.
Togni reagent II	CF_3	≈149	502 (415–652 with purity)	explosive properties found on scale-up; transport class revised	[45, 49]
Togni reagent II	CF_3	110	574	n.r.	[46, 47]
Togni reagent I	CF_3	78	740	n.r.	[46, 47]
TIPS-EBX	alkynyl	135	497	no shock sensitivity; impurities lower stability	[47, 50]
CBX	CN	135	571	no shock sensitivity observed	[47]
ABX	N_3	90	1770	impact and friction sensitive; explosions in routine use	[43, 47]
tBu-ABX	N_3	98	1440	fall hammer > 2 J; friction negative	[43, 47]
ABZ	N_3	143; 268	965; 380	fall hammer > 5 J; friction negative	[43, 47]
Umemoto reagent	CF_3	≈153	−67 (endothermic)	n.r.	[49]
TIPS-ethynyl-DBT$^+$ TfO^-	alkynyl	> 155 (on melting)	> 600	no reaction at 30 J (BAM fall hammer)	[51]
Vinyl-TT$^+$ BF_4^-	vinyl	> 280 (none below)	n.r.	unchanged after 1 year in air	[41]
DBT S-oxide (precursor)	–	≈294	≈544	n.r.	[51]

n.r., not reported. Values come from different laboratories, heating rates and sample purities, so they are not strictly comparable; the two entries for Togni reagent II show the spread. For thianthrenium salts only the DSC–TGA result for the vinyl reagent was found.

5. REACTIVITY: THREE WAYS TO HAND OVER A GROUP

Figure 03 summarises the three main manifolds. Each is discussed below, followed by the studies that compared the two families directly.

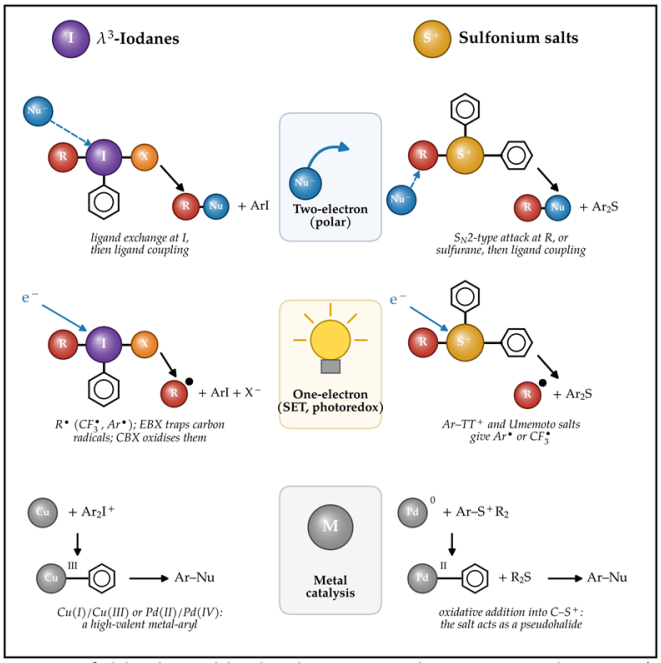


Figure 03: The three activation manifolds shared by both reagent classes: two-electron (polar) transfer, one-electron reduction (single-electron transfer, often photoredox), and transition-metal catalysis. A reduced carrier (ArI or Ar_2S) leaves in every case. The metal manifolds differ: diaryliodonium salts transfer an aryl group oxidatively to Cu(I) or Pd(II), whereas Pd(0) or Ni(0) adds oxidatively into the C–S^+ bond of aryl sulfonium salts.

5.1. Polar transfer

Under polar conditions iodine(III) reagents usually react by ligand exchange followed by ligand coupling. The nucleophile first binds iodine, the new ligand and the transferable group then couple, and the iodoarene leaves [2, 4]. For the Togni reagent, DFT work describes two competing modes. A substrate that is a good reductant triggers single-electron transfer and $CF_3^{\bullet}$ release, while a Zn(II)-activated reagent undergoes S_N2-type attack of a nucleophile at CF_3; which mode wins depends on the partner [52]. The thiol alkynylation with TIPS-EBX mentioned above shows how fast such transfers can be [27].

Sulfonium salts are less uniform. A nucleophile may attack the carbon bound to sulfur directly, in an S_N2-like step, or add to sulfur first to give a four-coordinate sulfurane that collapses by ligand coupling [10, 11]. With alkynyl dibenzothiophenium salts, labelling studies showed both α- and β-attack at the alkyne, the latter followed by a 1,2-shift [35]. In everyday use, Alcarazo describes the reactivity of dibenzothiophenium salts as close to that of iodine(III) reagents [11, 49].

How strong are the two families as CF_3^+ donors? Cheng, Xue and co-workers tackled this with computed heterolytic X–CF_3 bond dissociation enthalpies, which they called trifluoromethyl cation-donor abilities [53]. Their values for 99 reagents span 27 to 89 kcal mol^{-1}, and the scale follows the reactivity seen in the laboratory across the Umemoto, Yagupolskii–Umemoto and Togni families. A companion study ranked the same reagents as CF_3 radical donors and showed that adding one electron weakens the X–CF_3 bond so much that $CF_3^{\bullet}$ release becomes easy [54, 55].

5.2. Single-electron pathways

Both families accept electrons readily. One-electron reduction breaks the weak bond to the transferable group and releases it as a radical, together with the iodoarene or the sulfide. $Ru(bpy)_3^{2+}$ and *fac*-$Ir(ppy)_3$ reduce Umemoto, Yagupolskii–Umemoto and Togni reagents alike in redox-neutral cycles, which is why both families serve as CF_3 radical sources in photoredox catalysis [56]. For aryl transfer the gap is wider. A computational study placed the reduction potential of the diphenyliodonium ion near −0.68 V vs SCE in acetonitrile, and argued that the often-quoted −0.2 V is wrong [57], whereas aryl thianthrenium salts are reduced near −1.5 V vs SCE [58]. Iodonium salts can therefore be reduced by weaker photoreductants. With radicals made in other ways, the two benziodoxolone relatives part company. An alkyl radical adds to the alkyne of EBX and the benziodoxolone unit leaves, whereas CBX first oxidises the radical to a cation, which then captures cyanide [1, 25]. On the sulfur side, light-driven radical chemistry of aryl and alkyl sulfonium salts has grown fast [39], and aryl sulfonium salts made by interrupted Pummerer chemistry or by thianthrenation now take part in many photoredox couplings, including late-stage trifluoromethylation with a copper–CF_3 reagent [38, 59].

5.3. Metal-catalysed pathways

With metals the two families are somewhat different. λ_3-Iodanes react with both Pd(0) and Pd(II), and can substitute aryl halides in cross-coupling and act as oxidants in Pd-catalysed C–H functionalisation [60]. Diaryliodonium salts arylate indoles at C3 at mild circumstances in the presence of copper through a hypothesised electrophilic Cu(III)-aryl intermediate [61]. Aryl sulfonium salts behave more like aryl halides or triflates. Pd(0) or Ni(0) inserts into the C–S^+ bond, and the aryl–metal species then enters ordinary cross-coupling cycles [9, 62, 63]. One detail favours sulfur here: the iodoarene released by an iodine(III) reagent can itself react in a Pd cycle, whereas the sulfide by-product stays inert [11]. In practice, thianthrenation followed by cross-coupling gives a two-step route from an arene C–H bond to C–C, C–N, C–O or C–halogen bonds, usually at a single position [9, 63].

5.4. Head-to-head comparisons

Studies that test both families on the same reaction are still rare, and they do not point to a single winner (Table 03). For trifluoromethylation, Alcarazo describes the Umemoto and Togni reagents as broadly similar in reactivity [49]. An early exception, summarised by Shibata and co-workers, is a Pd-catalysed *ortho*-trifluoromethylation in which Umemoto salts gave good yields and the Togni reagent as little as 11% [30]. For cyanation, 5-(cyano)dibenzothiophenium triflate matched CBX with anilines, thiols, silyl enol ethers and activated methylene compounds, and it achieved the cyanoamination, a cyanative cyclisation, of *N*-tosyltryptamine that CBX did not give under the same conditions [36, 49]. It is, however, the weaker oxidant, and it does not cyanate the *N*-alkyl groups of dialkylanilines [49]. For alkynylation, the alkynyl dibenzothiophenium salts were offered as alternatives to EBX mainly because they are easy to make and have a broad scope [35]; their thermal profile is not clearly better (Table 02). For alkenyl groups the advantage lies with sulfur, since alkenyl sulfonium salts form directly from unfunctionalised alkenes, whereas alkenyl iodine(III) reagents normally need silyl-, tin-, boron- or zirconium-substituted alkenes [11, 42]. In photocatalytic arylation the sulfide is the poorer leaving group, which can lower reactivity compared with iodonium salts [49], but thianthrenation wins clearly on site selectivity [9, 40]. Radiofluorination gives a last, practical comparison. Spirocyclic iodonium ylides and aryl sulfonium salts both deliver [^{18}F]arenes, including drug-like molecules labelled at a late stage [64–67].

Table 03: Previous studies that compared iodine (III) and sulfonium reagents for the same transformation, directly or within one review.

Transformation	Iodine(III) reagent	Sulfonium reagent	Comparative finding	Ref.
CF_3 transfer (thermodynamics)	Togni I, Togni II	Umemoto, Yagupolskii and related salts	Computed X–CF_3 heterolysis enthalpies for 99 reagents (27–89 kcal	[53, 55]

			mol^{-1}) put both families on one scale that follows observed reactivity	
CF_3 transfer (synthesis)	Togni reagents	Umemoto reagents	Broadly similar reactivity in general use	[49]
Pd-catalysed *ortho*-C–H trifluoromethylation	Togni reagent	Umemoto salts	Umemoto salts gave good yields; the Togni reagent as little as 11%	[30]
Electrophilic cyanation	CBX	5-(Cyano)dibenzothiophenium triflate	Comparable yields with anilines, thiols, silyl enol ethers and activated methylenes; only the sulfonium reagent gave the cyanoamination of *N*-tosyltryptamine; CBX is the stronger oxidant	[36, 49]
Electrophilic alkynylation	EBX reagents	5-(Alkynyl)dibenzothiophenium triflates	Sulfonium salts proposed as easy-to-make alternatives with broad scope; both release > 450 J g^{-1} on decomposition	[35, 47, 51]
Alkenyl transfer	Alkenyl-λ^3-iodanes	Alkenyl thianthrenium salts	Sulfonium salts form directly from unactivated alkenes; iodine analogues need metallated or silylated alkenes	[11, 42]
Pd-catalysed coupling	Diaryliodonium salts	Aryl sulfonium salts	Released ArI can enter the Pd cycle; released sulfide stays inert	[11]
Photocatalytic arylation	Diaryliodonium salts	Aryl sulfonium salts	Lower nucleofugality of the sulfide can lower reactivity	[49]
Aromatic [^{18}F]fluorination	Spirocyclic iodonium ylides	Aryl sulfonium salts	Both give [^{18}F]arenes from non-activated precursors	[64–67]

6. SAFETY: WHEN STORED ENERGY BECOMES A HAZARD

Safety is the axis with the most at stake and the most uneven literature. The first warning came from iodine(V): 2-iodoxybenzoic acid (IBX) was reported to explode on impact or on heating above 200 °C [68]. Among iodine(III) reagents, Togni reagent II is the best-known case. During scale-up at Novasep it proved to be explosive, and its transport classification had to be revised [45]. Its decomposition releases about 502 J g^{-1} from roughly 149 °C, and the energy grows with purity, from 415 J g^{-1} at 60% to 652 J g^{-1} at 90% [45, 49]. A later survey by Obermüller, Waser and co-workers combined DSC data for many cyclic λ^3-iodanes with an OREOS+ explosive-hazard assessment and derived maximum safe storage temperatures [46]. The onset listed for Togni reagent II in that data set (110 °C) is lower than the older value [47], which shows how much such numbers depend on sample and method (Table 02).

The azide reagents give a sharper lesson. Zhdankin's azidobenziodoxolone (ABX) was described in 1996 as a stable crystalline solid [26]. Two decades later Waser and co-workers showed that it is sensitive to impact and friction, and they introduced tBu-ABX and the azidobenziodazolone ABZ as safer alternatives [43, 47]. Their stability data list an onset near 90 °C and about 1770 J g^{-1} for ABX, and record several explosions during routine use, one of them with injury [47]. EBX and CBX are less dramatic. Both still release roughly 500 to 600 J g^{-1} on decomposition [47], and DSC had already shown strong exothermic decomposition across the EBX family when these reagents were first developed [69]. A process study of TIPS-EBX found only weak exotherms during its one-pot synthesis and no shock sensitivity in the product, but it also showed that tosylate impurities lower its thermal stability [50]. The parent EBX cannot even be isolated and is generated in situ from a silyl-protected precursor [47, 70].

Sulfonium salts look better on paper, but their data are thinner. The Umemoto reagent decomposes near 153 °C with a slightly endothermic signal (−67 J g^{-1}) [49]. Alcarazo's TIPS-ethynyl dibenzothiophenium triflate behaves differently: it releases more than 600 J g^{-1} on melting above about 155 °C. It showed no reaction in fall-hammer tests at 30 J, and a modified Yoshida correlation, which combines DSC onset and energy, placed it in the safe zone [51]. The authors treated it as a high-energy compound and advised against heating the solid above 100 °C [51]. So a sulfonium core is not a guarantee of safety. Alkynyl and azido groups bring their own energy, whatever atom carries them.

Two practical measures lower the risk in both families. The first is to keep hazardous inventories small. The exothermic synthesis of diaryliodonium triflates has been moved into continuous flow for exactly this reason [71], and electrochemical flow cells can generate iodine(III) reagents on demand [72]. The second is routine screening: a DSC trace and, when the energy is high, an impact test cost little compared with an incident [46, 73]. Toxicity data are missing for most reagents of both classes. Since all of them are reactive electrophiles, we would handle them as potential alkylating or arylating agents until better data exist.

7. SUSTAINABILITY: ELEMENTS, MASS AND THE FATE OF THE CARRIER

7.1. Where the iodine and the sulfur come from

The two heteroatoms have very different supply chains. World iodine production, leaving out the United States, was about 34,000 t in 2025. Chile and Japan supplied about 23,000 t and 9,000 t of it, from nitrate deposits in the Chilean desert and from brines of gas and oil fields, and only small amounts are recycled [74]. Sulfur works on another scale altogether: about 84 million t in 2025, most of it an unavoidable by-product of fossil-fuel processing [75]. Prices follow. In 2025, crude iodine imported into the United States averaged about US$68 per kg, while sulfur sold for about US$180 per tonne [74, 75]. A kilogram of iodine thus costs a few hundred times more than a kilogram of sulfur, and its supply rests largely on two countries. For a reagent used once and discarded, this matters little in a research laboratory, but a great deal in production.

7.2. How much of the reagent reaches the product

Atom economy and the E factor are the usual yardsticks for waste [76–78], and group-transfer reagents fare poorly on both for a structural reason. To compare them on the same footing, we split the molar mass of fifteen common reagents into the transferred group, the carrier released after transfer, and the counter-anion (Figure 04, Table 04). The numbers come straight from the formulas and ignore yield, excess reagent, solvent and work-up, so real waste is always higher. The pattern is clear all the same. The transferred group is only 7.2% of CN-DBT$^+$ TfO$^-$ and 8.2% of vinyl-TT$^+$ BF_4^-, but 42.3% of TIPS-EBX, where the bulky silyl group inflates the figure (and is usually removed later). Most CF_3 reagents sit between 17 and 22%. Neutral benziodoxoles carry no counter-anion, so their waste is almost entirely the iodoarene. In the salts, 23 to 42% of the mass is counter-anion, and that part is simply lost.

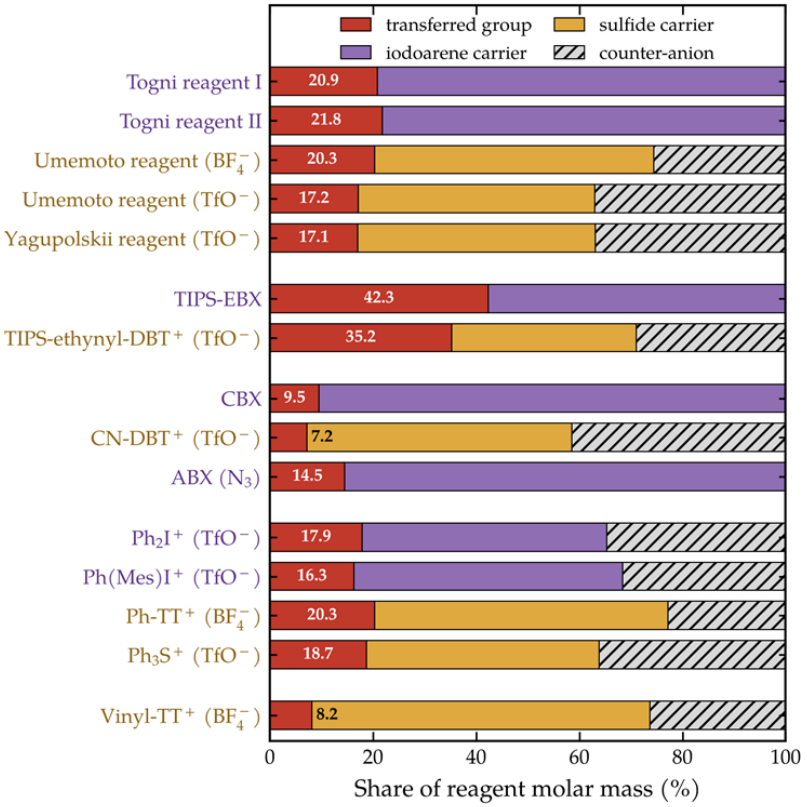


Figure 04: Mass partition of fifteen electrophilic group-transfer reagents, calculated in this work from molecular formulas and standard atomic weights. Each bar is the molar mass of one reagent split into the transferred group (red, value printed), the carrier released after transfer (iodoarene, purple; sulfide, amber) and the counter-anion (hatched). Labels in purple are iodine(III) reagents; labels in brown are sulfonium salts.

Table 04: Mass partition of fifteen common reagents, calculated in this work from molecular formulas with standard atomic weights. *M*, molar mass (g mol^{-1}); w_R, w_C and w_X, mass percentages of the transferred group, the carrier and the counter-anion; Lost, molar mass not delivered to the product (g mol^{-1}).

Reagent	Formula	*M*	Group	w_R	Carrier released	w_C	w_X	Lost
Togni reagent I	$C_{10}H_{10}F_3IO$	330.09	CF_3	20.9	2-(2-iodophenyl)-propan-2-ol	79.1	0	261
Togni reagent II	$C_8H_4F_3IO_2$	316.02	CF_3	21.8	2-iodobenzoic acid	78.2	0	247

Umemoto reagent (BF_4^-)	$C_{13}H_8BF_7S$	340.07	CF_3	20.3	dibenzothiophene	54.2	25.5	271
Umemoto reagent (TfO^-)	$C_{14}H_8F_6O_3S_2$	402.34	CF_3	17.2	dibenzothiophene	45.8	37.1	333
Yagupolskii reagent (TfO^-)	$C_{14}H_{10}F_6O_3S_2$	404.35	CF_3	17.1	diphenyl sulfide	46.1	36.9	335
TIPS-EBX	$C_{18}H_{25}IO_2Si$	428.39	TIPS–C≡C	42.3	2-iodobenzoic acid	57.7	0	247
TIPS-ethynyl-DBT$^+$ (TfO^-)	$C_{24}H_{29}F_3O_3S_2Si$	514.71	TIPS–C≡C	35.2	dibenzothiophene	35.8	29.0	333
CBX	$C_8H_4INO_2$	273.03	CN	9.5	2-iodobenzoic acid	90.5	0	247
CN-DBT$^+$ (TfO^-)	$C_{14}H_8F_3NO_3S_2$	359.35	CN	7.2	dibenzothiophene	51.3	41.5	333
ABX	$C_7H_4IN_3O_2$	289.03	N_3	14.5	2-iodobenzoic acid	85.5	0	247
Ph_2I^+ (TfO^-)	$C_{13}H_{10}F_3IO_3S$	430.19	C_6H_5	17.9	iodobenzene	47.4	34.7	353
Ph(Mes)I$^+$ (TfO^-)	$C_{16}H_{16}F_3IO_3S$	472.27	C_6H_5	16.3	2-iodomesitylene	52.1	31.6	395
Ph-TT$^+$ (BF_4^-)	$C_{18}H_{13}BF_4S_2$	380.24	C_6H_5	20.3	thianthrene	56.9	22.8	303
Ph_3S^+ (TfO^-)	$C_{19}H_{15}F_3O_3S_2$	412.45	C_6H_5	18.7	diphenyl sulfide	45.2	36.1	335
Vinyl-TT$^+$ (BF_4^-)	$C_{14}H_{11}BF_4S_2$	330.18	$CH{=}CH_2$	8.2	thianthrene	65.5	26.3	303

Abbreviations: DBT, dibenzothiophenium; TT, thianthrenium; Mes, mesityl; TIPS, triisopropylsilyl. Values ignore yield, excess reagent, solvents and work-up, so they set a lower bound on waste.

7.3. Recovering the carrier, and what else is lost

The obvious target for recovery is the carrier and both families have examples (Figure 05). On the iodine side, Togni said that his CF3 reagent was recyclable from the very beginning [23]. A recyclable iodine(III) reagent is defined in a recent study as one where the reduced iodoarene is isolated virtually quantitatively and re-oxidised without loss of activity [79] and recoveries of 91-95% have been observed for m-iodobenzoic acid [80]. Catalytic use of iodine(III) goes further: H_2O_2, Oxone or a peracid regenerates the active species, so the iodoarene is never wasted in stoichiometric amounts, and polymer-supported iodoarenes can simply be filtered off and reused [81, 82]. Anodic oxidation removes the chemical oxidant as well [83], and flow cells can make even unstable iodine(III) species on demand [72]. Olofsson's group has also shown cascades in which both aryl groups of a single diaryliodonium salt end up in the product [84]. On the sulfur side, Umemoto designed his fluorinated dibenzothiophenium salts with reuse in mind: the paper describes them as recyclable [33], and the related patent recovers the dibenzothiophene by-product and returns it to the synthesis after desulfurisation [85]. Thianthrene has likewise been recovered after couplings of aryl thianthrenium salts, in one case quantitatively [12].

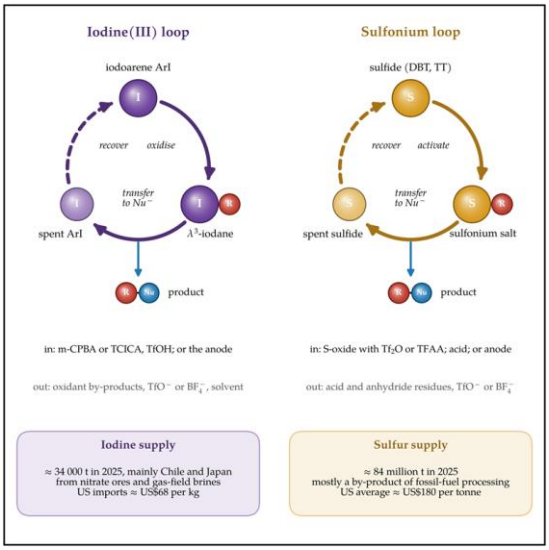


Figure 05: Material loops for the two reagent classes. The reduced carrier (iodoarene or sulfide) can in principle be recovered and re-activated (dashed arrows), but in most published work it is discarded. Inputs and outputs show what each loop consumes and loses besides the carrier. Supply figures are U.S. Geological Survey estimates for 2025; the

world iodine total excludes U.S. production, which is withheld [74, 75]. TCICA, trichloroisocyanuric acid; TFAA, trifluoroacetic anhydride.

There are a couple other notable losses. Fluorine is the first . The counter-anions are usually triflate and tetrafluoroborate and all CF3 reagents are fluorinated by design. A chemical containing a completely fluorinated methyl or methylene carbon counts as a PFAS according to the OECD definition [86]. This includes the CF3 group and the triflate anion. Triflic acid has already been measured in Swedish waterways in the vicinity of known and suspected point sources [87]. The second is the activator employed to form the reagent: m-CPBA or trichloroisocyanuric acid for iodine(III) [20, 88], and triflic or trifluoroacetic anhydride with strong acids for sulfonium salts [36, 40]. Neither family is clean on this count. Electrochemical routes look like the best way out for both. They are well developed for iodine(III) [72, 83], whereas electrochemical C–H thianthrenation has so far been shown mainly on polymers [89].

8. Choosing a reagent in practice

For a quick polar transfer on a milligram-to-gram scale, an iodine(III) reagent is usually the first thing to try. Togni reagents, TIPS-EBX and many diaryliodonium salts are commercial, they react under mild conditions, and their scope is well documented [4, 5, 27]. Their limits show up on scale, where thermal data must be checked before anything is heated [43, 45, 46], and in purification, where the iodoarene by-product still has to be separated from the product.

Sulfonium salts are the superior choice in four scenarios. The first is late-stage arene functionalisation, as thianthrenation dictates the location before the selection of the group [9, 40]. The second is metal-catalyzed cross-coupling where aryl sulfonium ions are used as pseudohalides [62, 63]. Thirdly, in any procedure where the reagents run heated, the dibenzothiophenium reagents often give a greater thermal margin [33, 49]. The fourth is a method in which the recovery of the carrier is intended from the very beginning [12, 33, 85]. Radiofluorination is a particular situation where both families compete as labelling precursors. Spirocyclic iodonium ylides on the one side and aryl sulfonium salts on the other both generate [18F]arenes and the decision tends to follow the substrate [64–67]. Figure 06 summarises these ideas in a basic decision map.

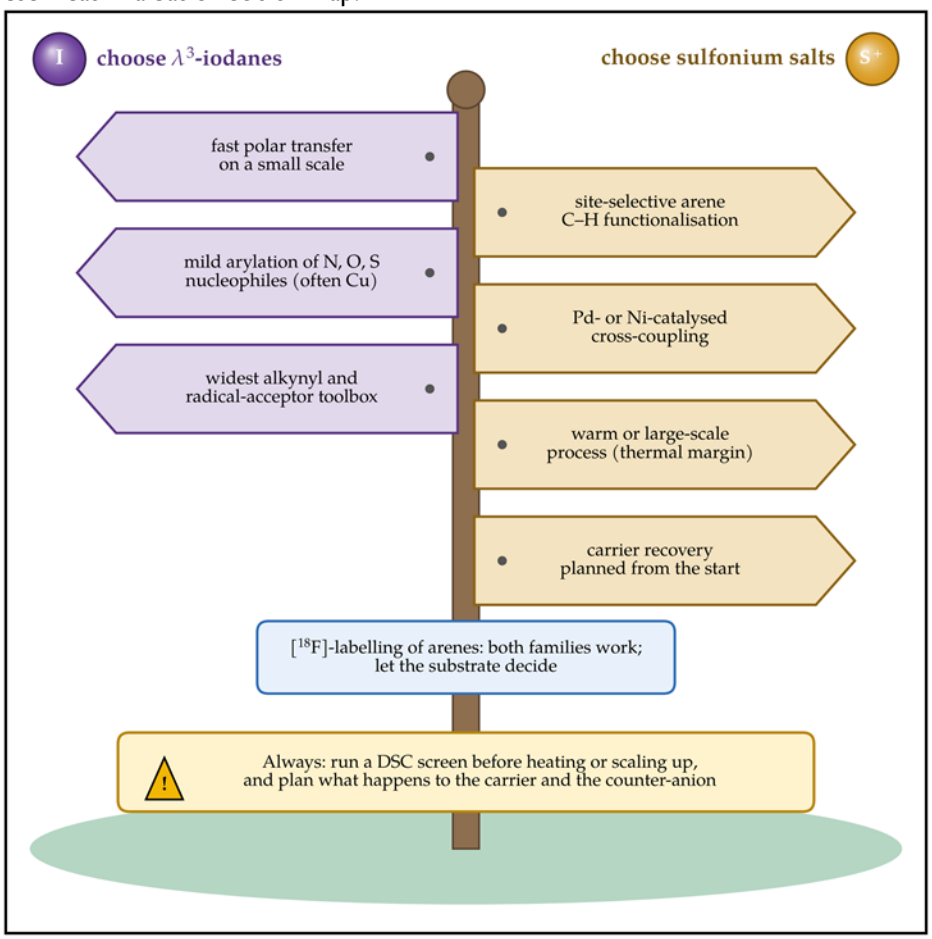


Figure 06: A practical decision map for choosing between iodine (III) and sulfonium reagents. The map summarises the evidence discussed in Sections 4 to 7 and is meant as a starting point, not a rule; thermal screening is recommended for any reagent before scale-up.

9. OPEN QUESTIONS

Three gaps are evident. The first is thermal information. As screening by these values is inexpensive and well established [46, 73], each new transfer agent should be accompanied by a DSC trace, a decomposition energy, and impact and friction data when applicable as part of its supporting material. The second is kinetic. Mayr-type and

calculated donor scales are available for various chemicals [15, 53, 54], however a common experimental scale for alkynyl, cyano and aryl transfer from both families is still missing. Most comparisons use yields achieved under different conditions without one. The third is life cycle data. We are not aware of any cradle-to-gate assessments for any of the reagents in Figure 02 and hence assertions of greenness on either side are qualitative. We found no report of recycling on a scale that would impact cost or waste, although the carrier has been recycled on the bench and patented [33, 85].

10. CONCLUSION

Iodine (III) reagents and sulfonium salts do the same task, although in distinct ways. Both transfer an electrophilic group to a nucleophile and release a reduced carrier, an iodoarene or a sulphide. The iodine reagents are fast owing to a weak, polarised hypervalent bond and a good leaving group, however the same weak bond is also associated with their heat dangers. Octet species are sulfonium cations. They are generally more acidic and often heat tolerant, although alkynyl salts are high energy too. They can be regulated by the core, and in the form of thianthrenium salts they can be created directly from arene C–H bonds. Neither family is efficient in mass terms: most of each reagent ends up as carrier and counter-anion so that recovery of the carrier is more important than any slight gain in yield. Iodine (III) reagents remain the reagent of choice for rapid small-scale polar transfers, while sulfonium salts are the more powerful choice for site-selective arene chemistry, cross-coupling, higher temperature operations, and when recycling is envisaged. Routine thermal measurements, shared kinetic scales and life-cycle studies will be required for both families to allow a fair quantitative choice.

11. ACKNOWLEDGEMENTS

Not Declared.

12. CONFLICT OF INTEREST STATEMENT

Not Applicable.

13. INFORM CONSENT AND ETHICAL STATMNET

Not Applicable.

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