Imido transfer of sulfonylimino-λ^3-bromane makes possible the synthesis of sulfonylimino-λ^3-iodanes†

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Sulfonylimino-λ^3-bromane functions as a reactive nitrenoid, because of the hyperleaving group ability of aryl-λ^3-bromanyl groups, and undergoes transimidations to iodobenzenes at room temperature under metal-free conditions probably *via* an S_N2-type nitrenoid transition state, yielding sulfonylimino-λ^3-iodanes.

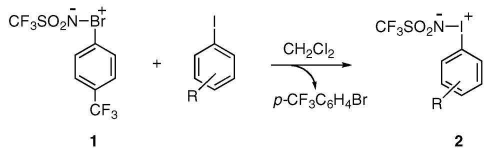
Phenyl(sulfonylimino)-λ^3-iodanes serve as excellent nitrene (or nitrenoid) progenitors either in the aziridination of alkenes or in the C–H amidation of alkanes, arenes, and aldehydes using Cu, Rh, Ru, or Ag catalysts.[1–5] Under thermal or catalytic conditions, they transfer the imido groups to a range of heteroatom nucleophiles.[6] The hyperleaving group ability of aryl-λ^3-iodanyl groups will be responsible for these nitrogen atom transfer reactions[7] and, in most cases, metal imido species are proposed to be crucial intermediates. These methods of introducing nitrogen functionalities are highly reliable, leading to a surge in interest in the research activity of the areas, especially in the last decade.

The methodology for synthesis of the compounds of this important class is limited and all of the methods so far reported rely on ligand exchange on iodine(III) of aryl-λ^3-iodanes with sulfonamides in the presence or the absence of a base:[1] for instance, the most widely used phenyl(*N*-tosylimino)-λ^3-iodane was prepared by the reaction of (diacetoxyiodo)benzene with *p*-toluenesulfonamide in the presence of KOH.[6a] (Dimethoxyiodo)-, (difluoroiodo)-, and iodosylbenzene serve as reactive λ^3-iodanes in the ligand exchange reactions.[8] However, it has been pointed out by Dauban and Dodd in their excellent review that preparation of sulfonylimino-λ^3-iodanes by the ligand exchange method is often difficult to reproduce and that conflicting results are found in the literature.[1a] They also mentioned that their synthesis of *p*-$MeOC_6H_4SO_2N^-I^+Ph$ fails 50% of the time even after several years of experience in this field.

In 1985, Moriarty and coworkers evaluated an entirely different strategy for the synthesis of sulfonylimino-λ^3-iodanes, involving the nucleophilic attack of iodobenzenes on sulfonylnitrenes:[9] however, in their attempted thermolysis of *p*-toluenesulfonyl azide in iodobenzene solution at 120 °C no formation of the desired iminoiodane was detected at all. They found that under these conditions the tosylimino-λ^3-iodane itself decomposes. Transition metal-catalyzed low temperature decompositions of the sulfonyl azide were also found to be fruitless. Thus, this type of ingenious approach to the synthesis of imino-λ^3-iodanes remains to be established.

We have reported that trifluoromethanesulfonylimino-λ^3-bromane **1** functions as an efficient imido group donor and directly undergoes aziridination of olefins stereospecifically with retention of original stereochemistry.[10] Importantly, the aziridination proceeds at room temperature using limiting amounts of alkenes under transition metal-free conditions. The fact that the observed rate constants for aziridination of *cis*-cyclooctene are proportional to concentration of the olefin suggests the involvement of a bimolecular transition state, in which an olefin attacks the σ* N–Br orbital of the iminobromane **1** in the nitrenoid transfer process. It occurred to us that the highly active sulfonylimino-λ^3-bromane **1** probably serves as an efficient nitrenoid source in the Moriarty's approach to the synthesis of imino-λ^3-iodanes. We report herein the first example of transimidations yielding imino-λ^3-iodanes **2**, which involves an imido group transfer from the iminobromane **1** to the iodine atom of iodobenzenes at room temperature under metal-free conditions (Scheme 1).

To a dichloromethane solution of the bromane **1** was added a stoichiometric amount of iodobenzene at room temperature under argon. White precipitates of *N*-triflylimino(phenyl)-λ^3-iodane (**2a**)[8b] appeared within a few minutes with reductive elimination of *p*-(trifluoromethyl)bromobenzene and the reaction afforded a high yield of **2a** (Table 1, Entry 1). Similarly to *N*-tosylimino-λ^3-iodanes, triflyliminoiodane **2a** is sparingly soluble in unreactive organic media such as dichloromethane, chloroform, diethyl ether, *etc.*, presumably due to the aggregated polymeric nature.[11] Substituted iodobenzenes with an electron-donating (Me or MeO) and an electron-withdrawing group (F, Cl, Br, CF_3, CN, CO_2Et, or COMe) produced iminoiodanes **2** efficiently under the conditions (Table 1, Entries 2–11). The imido transfer reaction of imino-λ^3-bromane



Scheme 1 Transylidation between imino-λ^3-bromane **1** and -iodanes **2**.

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Table 1 Transimidation of imino-λ^3-bromane **1** with iodobenzenes[a]

Entry	ArI	**2**	Yield (%)[b]
1	PhI	**2a**	97
2	o-MeC$_6$H$_4$I	**2b**	94
3	p-MeC$_6$H$_4$I	**2c**	90
4	p-MeOC$_6$H$_4$I	**2d**	84
5	p-FC$_6$H$_4$I	**2e**	86
6	p-ClC$_6$H$_4$I	**2f**	96
7	p-BrC$_6$H$_4$I	**2g**	82
8	p-CF$_3$C$_6$H$_4$I	**2h**	86
9	p-NCC$_6$H$_4$I	**2i**	100
10	p-EtO$_2$CC$_6$H$_4$I	**2j**	96
11	o-MeCOC$_6$H$_4$I	**2k**	87

[a] Reaction conditions: iminobromane **1** (0.075 M), ArI (1.2 equiv.), CH_2Cl_2, room temperature, 1 h, Ar. [b] Isolated yields.

1 makes it possible to synthesize a hitherto unknown kind of alkyl(sulfonylimino)-λ^3-iodane; thus, transimidation to 2,2,2-trifluoroethyl iodide afforded a labile imino(trifluoroethyl)-iodane **3** ($CF_3CH_2I^+N^-Tf$) in 76% yield.[12]

Compared with other iminoiodanes **2**, the *ortho*-acyl derivative **2k** is readily soluble in dichloromethane and acetonitrile. This is in line with the observation reported by Protasiewicz *et al.* that replacement of the intermolecular I···N secondary bonding in PhI^+N^-Ts with intramolecular I···O secondary bonding by introducing a sulfonyl group at the *ortho* position impressively increases the solubility in organic media.[14] In fact, the solid state structure of **2k** (Fig. 1) disclosed the formation of intramolecular hypervalent N(1)–I(1)···O(1) bonding with a close I(1)···O(1) contact (2.527(1) Å) and with a near linear triad (165.80(5)°).‡ This intramolecular hypervalent bonding will result in a partial disruption of the polymeric network, and hence enhances the solubility. Interestingly, *ortho*-methyl iminoiodane **2b** exhibits an increased solubility in dichloromethane, compared to the *para*-isomer **2c**. The non-coordinating *ortho*-methyl group probably disrupts the formation of the well-arranged polymeric structure to some extent by its sterically demanding nature.

Rates of the imido group transfer to iodobenzene are dependent upon the concentration of the iodide. The time-course of the reaction in acetonitrile-d_3 at 23 °C clearly demonstrates that the rates of disappearance of the bromane **1** increase with the increasing concentration of iodobenzene (see ESI†). These results are compatible with a bimolecular nitrenoid transition state such as **4**, involving a rate-limiting nucleophilic attack of iodobenzene on the negatively charged nitrogen atom of **1** (Scheme 2), but not with a mechanism that yields a free nitrene by a rate-determining unimolecular decomposition of **1**.

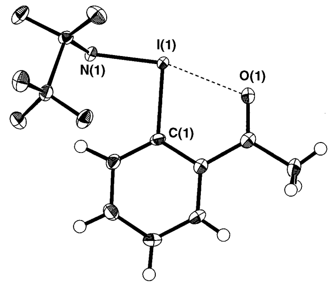
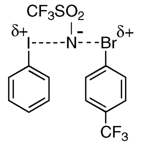


Fig. 1 ORTEP drawing of the imino-λ^3-iodane **2k** with 50% thermal ellipsoids.



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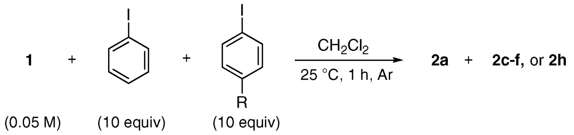
Scheme 2 Bimolecular nitrenoid transition state.

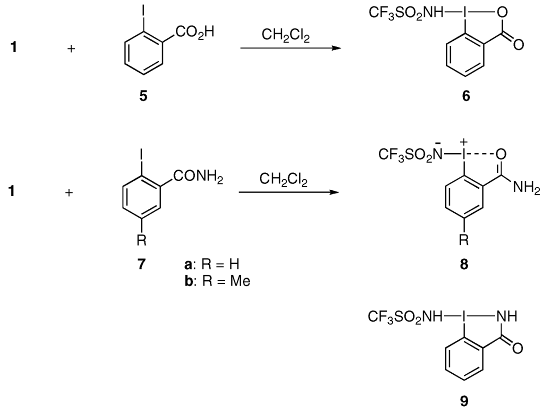
In order to gain further insight into the mechanism, relative rates of the imido transfer for a series of substituted iodobenzenes were measured in dichloromethane by competitive reactions, in which a mixture of each 10-fold excess of two competing substrates was used (Table 2). Table 1 shows that iminoiodanes **2** were formed in high yields irrespective of the substituents on benzene ring. Ratios of the products **2** were determined by ^{1}H NMR of the crude reaction mixture. Electron-releasing p-MeO and p-Me groups remarkably increase the relative rate k_{rel} of the imido group transfer: Hammett plot showed a good correlation of the relative rate factors with the σ_p constants of substituents[15] and afforded the reaction constant $\rho = -2.79$ ($r = 0.96$). The absolute ρ value obtained here is greater than that ($\rho = -0.54$) reported for free carbene [:C(SO$_2$CF$_3$)$_2$] transfer to iodobenzenes at 140 °C and that ($\rho = -0.91$) in rhodium carbenoid [Rh = C(SO$_2$CF$_3$)$_2$] transfer to iodobenzenes at 40 °C.[16] This larger negative ρ value evaluated in the imido group transfer of λ^3-bromane **1** indicates greater buildup of positive charge on the iodine atom of iodobenzenes in the transition state, and probably suggests a later transition state in the nitrenoid transfer compared with that in the carbene (or carbenoid) transfer. The hyperleaving group ability of aryl-λ^3-bromanyl groups will be responsible for the facile imido group transfer of λ^3-bromane **1** to iodobenzenes.[16]

Transimidation between *ortho*-iodobenzoic acid (**5**) and bromane **1** directly afforded cyclic λ^3-iodane **6** with a sulfonamido ligand on the iodine(III) in high yield (93%, Scheme 3). The cyclic *I*-(sulfonamido)benziodoxolone structure was determined by IR absorption of the carbonyl group at 1666 cm^{-1}.[17] Initial formation of the corresponding imino-λ^3-iodane *via* the imido group transfer, followed by an intramolecular coordination of the nearby *ortho*-carboxy group to the iodine(III) and a proton transfer, will produce the benziodoxolone **6**.

Table 2 Relative reactivity of ArI evaluated by competitive reactions



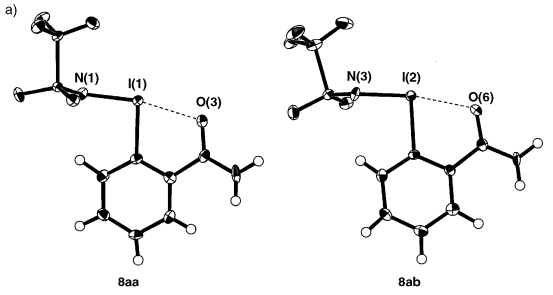
Entry	ArI	k_{rel}	σ_p
1	p-MeOC$_6$H$_4$I	9.8	−0.27
2	p-MeC$_6$H$_4$I	4.9	−0.17
3	PhI	1.0	0
4	p-FC$_6$H$_4$I	0.33	0.06
5	p-ClC$_6$H$_4$I	0.18	0.23
6	p-CF$_3$C$_6$H$_4$I	0.06	0.54



Scheme 3 Transimidation of benzoic acid **5** and benzamides **7**.

Imido group transfer to *ortho*-iodobenzamides **7** does take place efficiently under our conditions; very interestingly, however, no formation of the cyclic λ^3-iodane **9** was detected. Thus, transimidation with iodobenzamide **7a** afforded imino-λ^3-iodane **8a** quantitatively. Similarly, *p*-methyl imino-λ^3-iodane **8b** was prepared in 97% yield. These results are in marked contrast to the reaction with iodobenzoic acid **5**. Fig. 2 illustrates the solid-state structure of imino-λ^3-iodane **8a**, in which two independent but closely related molecules **8aa** and **8ab** that are almost in a mirror image relationship exist.‡ Both imino-λ^3-iodanes **8aa** and **8ab** are stabilized by more powerful intramolecular hypervalent bonding between iodine(III) and oxygen atoms compared to **2k**, which was suggested by their shorter distances (Fig. 2b). These stronger close contacts in **8a** will result in a greater weakening of the *trans* N–I bonds by structural *trans* influence of the ligands and, therefore, N–I bond distances in **8a** are appreciably longer than that in **2k**.[18]

Why does imino-λ^3-iodane **8a** not adopt the cyclic benziodazolone structure **9**? Mutual ligand influence on hypervalent bonding of aryl-λ^3-iodanes will probably determine these structural preferences. The benziodoxolyl unit in **6**, associated with a moderate *trans* influence, accommodates a *trans* ligand with various degrees of *trans* influence, such as Ph, OH, OMe, OAc, Cl, OTs, OTf, *etc*., whereas the benziodazolyl unit in **9**, with a significantly greater *trans* influence, is applicable only to *trans* ligands with weak or moderate influence, such as OAc, Cl, OTs, OTf, *etc*. It seems reasonable to assume that the NHTf group with a relatively large *trans* influence prefers to bind to benziodoxolyl units, but not to benziodazolyl units, on the basis of a preferred combination of *trans* influences.[18]



b)

	2k	8aa	8ab
N–I	2.0055(16)	2.034(2)	2.022(2)
I···O	2.5165(16)	2.398(2)	2.385(2)

Fig. 2 (a) ORTEP structures of imino-λ^3-iodanes **8aa** and **8ab** with 50% thermal ellipsoids. (b) Distances [Å] of hypervalent N–I···O bonding interactions.

Notes and references

‡ Crystal data. For **2k**. $C_9H_7F_3INO_3S$: M = 393.12, orthorhombic, space group $Pna2_1$ (No. 33), a = 10.1845(3), b = 19.9169(5), c = 5.9157(2) Å, V = 1199.96(6) Å^3, Z = 4, μ(Mo Kα) = 28.814 cm^{-1}, T = 93 K, 10 881 reflections measured, 10 360 unique; R(int) = 0.023, final R_1 = 0.0154 ($I > 2\sigma$), R_w = 0.0379. CCDC 692568. For **8a**: $C_8H_6F_3IN_2O_3S$: M = 394.11, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 11.1853(4), b = 14.2294(4), c = 14.5837(4) Å, V = 2321.14(12) Å^3, Z = 8, μ(Mo Kα) = 29.818 cm^{-1}, T = 93 K, 22 608 reflections measured, 22 562 unique; R(int) = 0.030, final R_1 = 0.0215 ($I > 2\sigma$), R_w = 0.052. CCDC 692567.

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