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UPDATE

Development of Imino- λ^3 -iodanes with Improved Reactivity for Metal-Free [2+2+1] Cycloaddition-Type Reactions

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Abstract. Directed toward-Aiming at the enhancement of electrophilicity of imino- λ^3 -iodanes, we have developed (tosylimino)pentafluorophenyl- λ^3 -iodane, which shows the superior reactivity compared to the commonly used (tosylimino)phenyl- λ^3 -iodane for our previously reported-in the [2+2+1]-type synthesis of imidazoles.

Keywords: alkynes; cycloaddition; iminoiodanes; metalfree; imidazoles

In late-recent years, hypervalent iodine reagents have found a broad range of applications to-in organic syntheses because of their low-toxicities toxicity, oxidizing-abilities ability similar to heavy metal oxidants, transition metal-like-reactivities reactivity and so on other beneficial features.^[1] Among them, *N*-sulfonyl-iminophenyl- λ^3 -iodanes reagents (PhINSO₂R) have been well recognized as $\frac{1}{2}$ -useful nitrene precursors in the aziridination of alkenes and the amidation reactions of various organic substrates under metal-catalyzed^[2,3] or metal-free conditions.^[4] Although the catalyst-free aziridination of alkenes was has also been achieved by the modification of substituents on nitrogen atoms of iminophenyl- λ^3 iodane reagents,^[5] the investigation on the synthetic methods utilizing the cationic property of iodonium ion in the iminoiodanes makes little progress have not been explored.^[6]

On the other hand, we have developed the a metalfree method for the synthesis of heterocycles through the activation of alkynes by hypervalent iodine(III) reagents,^[7] and recently found the [2+2+1] cycloaddition-type reactions of alkynes, nitriles and nitrogen from PhINTs (Scheme 1),^[7] Unfortunately, PhINTs has which have a three-dimensional polymeric structure and thereby therefore is characterized by a very low solubility due to

bonds.^[2a,b,d,8] $I \cdots N$ intermolecular secondary Therefore, the addition of BF₃•nitrile complexes, which would disassociate the I···N secondary bonds leading to monomeric iodonium species, is effective has strong effect on the [2+2+1] cycloaddition-type reactions. However, PhINTs/-BF₃•nitrile systems cannot be applied to the bulky substrates and low nucleophilic nitriles, and therefore there is still room for improvement of the [2+2+1] cycloaddition-type reactions. Herein, we report the preparation and the improved reactivity of *N*-tosyliminoaryl- λ^3 -iodanes (ArINTs) having electron-withdrawing--group substituents on their aromatic rings for the metal-free [2+2+1] cycloaddition-type reactions (Scheme 1). Although Protasiewicz's, Zhdankin's and other group succeeded to in developing ArINTs as highly soluble and reactive nitrene precursors by means of the introduction of coordinating group such as alkoxy and sulfonyl group to iodine at ortho-position,^[9] to the best of our knowledge, such a chemical modification was not examined for the enhancement of electrophilicity of ArINTs.



Scheme 1. Iminoiodane-mediated [2+2+1] cycloaddition.

The preparation of the employed iminoiodanes **1a**- **1f**-was is summarized in Scheme 2. Initially, According to Zhdankin's method,^[9f] oalkoxyphenyliminoiodane **1a** was prepared in two

steps starting from 2a (Scheme 2a). Thus In the first step, aryl iodide 2a was oxidized by peracetic acid to form diacetate 3a, which was then converted to iminoiodanes 1a by treatment with TsNH2 under basic conditions in methanol.^[10] On the other hand, when we attempted a similar-although the oxidation of 2b-by with peracetic acid-was attempted for the -(alkoxycarbonyl)preparation of *o*-(alkoxycarbonyl)-phenyliminoiodane, 2-iodosylbenzoic acid (5) was obtained as a main product instead of the expected o-(alkoxycarbonyl)-phenyliminoiodane (Scheme 2b). However-Therefore, we prepared the iodane **1b** from 5-was exposed to Ae₂O and then the obtained via initial conversion to acetate 6 followed by the reaction reacted with TsNH₂ in the presence of TMSOT f-to-afford 1b, [11a] Treatment of 1b which would be treated with BF₃ would be expected to afford-generate the iodonium species **1b**•BF₃, which is similar to the complex of o-(alkoxycarbonyl)phenyliminoiodane^[12] with BF₃. Since the oxidation of o-nitro-iodobenzene (2c)-by with peracetic acid also did not give diacetate 3c, the diacetate 3c was synthesized in-by a similar manner-method to the Nikiforov's-method one [11b] and then converted to iminoiodane 1c (Scheme 2c). Other nitro-substituted iminoiodanes $\mathbf{1d}$, $\mathbf{1e}^{[13a]}$ and pentafluorophenyl derivative 1f^[13b,c] were prepared from 4d-f, which were formed by the oxidation of 2d-f with oxone in the presence of trifluoroacetic acid (TFA, Scheme 2a).^[11c] Novel-The new iminoiodanes 1c-f were identified by elemental analysis and NMR spectroscopy, and the structures of 1c and 1d were characterized by single crystal X-ray analysis (Figures 1 and 2).^[14]



Scheme 2. Preparation of ArINTs.

Similar to the *o-tert*-butylsulfonyl analogue reported by Protasiewicz,^[9b] **1c** has a centrosymmetric

dimer-like structure formed by two I...N secondary bonds (3.020 Å, Figure 1). Also, one of the oxygen atoms in the nitro group (I···O: 2.689 Å) is located to trans-of relative to the intramolecular NTs ligand around-across the iodine center (C-I-N: 96.73°, C-I···O: 68.46°), and $\frac{\text{thus}}{\text{the nitrogen atom in the}}$ intermolecular NTs ligand is located to trans of to the aryl ligand (C–I···N: 168.13°). However, unlike the o-tert-butylsulfonyl analogue,^[9b] intramolecular I...O contacts $(3.168 \text{ Å})^{[15]}$ are formed between the iodine center and one of the oxygen atoms in the NTs ligand. On the other hand, 1d has a polymeric, asymmetrically bridged structure (C-I-N: 98.15°, N-I...N: 87.92°, Figure 2) like PhINTs^[8b] and the oalkoxy analogue such as **1a**.^[9f] Surprisingly, the nitro groups do not participate in the formation of the polymeric structure of 1d, which dependscreated by the I...N secondary bonds (2.951 Å) by involving the nitrogen atom in NTs ligand and $I \cdots O$ secondary bonds (2.943 Å) by the oxygen atom in the other NTs ligand. However, in contrast to PhINTs^[8b] and the *o*-alkoxy analogue,^[9f] the nitrogen atom in the intermolecular NTs ligand is also located to-in trans of position to the aryl group (C-I...N: 162.52°). Furthermore, the intermolecular I...N bond distance of 1d (2.951 Å) is longer than those of PhINTs (2.482 Å)^[8b] and the *o*-alkoxy analogue (2.735 Å).^[9f] The A similar elongation of intermolecular I...N bond^[8c]-of **1e** (3.020 Å) is observed for structure of **1c** (Figure 1). This would be probably due to trans influences of aryl ligand^[1615] along with distortion of C–I···N bond angles. Therefore, -these weak intermolecular interactions in 1e, d would be expected to lead to the enhancement of their reactivities and olubilitio albeit a slight lack of their stabilities.



Figure 1. X-ray crystal structures of 1c.



Figure 2. X-ray crystal structures of 1d. Hydrogen atoms have been omitted for clarity.

Next, we focused on =have evaluated iminoiodanes **1a-f** (1.5 equiv) as reagents for the [2+2+1] cycloaddition-type reactions of alkyne 7a and acetonitrile as a solvent in the presence of BF₃•MeCN (2.0 equiv) at room temperature-for 4-h (Table 1). Compared with PhINTs (entry 1), osubstituted iminoiodanes 1a, b, and even nitrosubstituted 1c drastically reduced the yields of 2a (entries 2-4). Taking the results of X-ray structure analysis (Figure 1)^[9f,12] into consideration, the electrophilicities of o-substituted **1a-c** may be decreased by the secondary bonding of o-substituents such as alkoxy, carboxyl and nitro groups to positive iodine center, even in the presence of BF₃•MeCN. These results suggest that the electrophilicities of osubstituted **1a-e** would be decreased by the secondary bonding of o-substituents such as alkoxy, carboxy and nitro groups to positive iodine center. This is upported by the results of X-ray structure analysis (Figure 1).^(pi, 12) On the other hand, the use of m- or p-</sup>nitro derivative 1d or 1e led to the improved yields of 2a up to ca. 70% (entry 5 or 6). Furthermore, the use of pentafluorophenyl derivative 1f gave 2a in 83% yield (entry 7). When the amounts of 1f and BF₃•MeCN were increased up to 1.8 and 2.4 equiv, respectively, the formation of oxazole 9 as a byproduct was suppressed and 8a was isolated in 76% yield (entry 8). Unfortunately, the diminution in the amounts of BF₃•MeCN and MeCN brought about the reduced yields of 2a even in cases of prolongation of reaction time and/or under the temperature-rising conditions (entries 9-11).

Table 1. Optimization of the reaction conditions.



entry	ArINTs (X _n)	Y (equiv)	8a (%) ^[a]	9 (%) ^[a]
1	PhINTs	2.0	60	6
2	1a (o-PrO)	2.0	20	14
3	1b	2.0	17	13
4	1c (<i>o</i> -NO ₂)	2.0	27	3
5	1d (<i>m</i> -NO ₂)	2.0	68	8
6	1e (<i>p</i> -NO ₂)	2.0	72	21
7	1f (F ₅)	2.0	83	11
8 ^[b]	1f (F ₅)	2.4	85 (76)	3
9 ^[c]	1f (F ₅)	0.3	2	5
10 ^[c]	1f (F ₅)	0	0	0
11 ^[d]	1f (F ₅)	2.0	47	21

^[a] Yields were determined by ¹H NMR analysis. Value in parenthesis is isolated yield.

^[b] **1f**: 1.8equiv.

^[c] Reaction conditions: 80 °C, 24 h.

^[d] CH₂Cl₂ in the presence of 40 equiv MeCN was employed instead of MeCN (corresponds to ca. 210 equiv) as a solvent at rt for 24h.

Subsequently, the reaction scope of various alkynes 7 and nitriles was investigated under the optimal conditions (Method A, Table 2). Thus, in the presence of BF₃•MeCN (2.4 equiv), terminal and internal alkynes 7a-e, to which our previous method using PhINTs (Method B)^[7f] can be applied, reacted with C_6F_5INTs (1f, 1.8 equiv) in MeCN to give the corresponding 2,4-disubstitued and 2.4.5trisubstituted imidazoles 8a-e in 60-76% yield with complete regioselectivities (entries 1-5). To our delight, the yields of 8c, d were improved as well as that of 8a (entries 1, 3, 4). Furthermore, method A promoted the reactions of bulky alkynes **7f**, **g** with MeCN, although method **B** hardly yielded the corresponding products 8f, g (entries 6, 7). Also, in cases of 7h-j having bulky and/or electronwithdrawing halogens (entries 8-10) or in cases of bulky and lower nucleophilic BuCN or PhCN (entries 11-15), method A gave the desired products in ca. 10-30% higher yields than method B. In addition, method A was more effective on the conversion of mono-imidazole 8k (Scheme 3).

Table 2. Reaction scope.



				pr	product (%) ^[a]		
entry	7	\mathbb{R}^1	\mathbb{R}^2		Α	В	
1	7a	Ph	Η	8 a	76	61	
2	7b	phenethyl	Η	8b	62	71	
3	7c	hexyl	Η	8c	75	70	
4	7d	Ph	Me	8d	60	52	
5	7e	Pr	Pr	8 e	63	72	
6	7f	^t Bu	Η	8f	33	trace	
7	7g	mesityl	Н	8g	16	trace	

8	7h	2-BrC ₆ H ₄	Н	8h	56	41	
9	7i	$4-ClC_6H_4$	Н	8i	53	33	
10	7j	$4-BrC_6H_4$	pentyl	8j	52	41	
11	7a	Ph	Н	10a	43	21	
12	7d	Ph	Me	10d	42	14	
13	7a	Ph	Н	11a	36	18	
14	7b	phenethyl	Н	11b	49	20	
15	7d	Ph	Me	11d	47	22	
^[a] Isolated yields.							



Scheme 3. Conversion of mono-imidazole 8k.

On the basis of these results and our previous reports on the [2+2+1] cycloaddition-type reactions using iodine (III) reagents,^[7e-g] the proposed formation-mechanism for the formation of imidazoles is shown in Scheme 4. That is, iodonium species A (and/or A'), in situ generated from ArINTs and BF₃, would activate alkyne 7 to form the intermediate *trans*-B via the the Ritter-type addition of R³CN. And then, the *trans*-B is converted to *trans*-C by the formal reductive elimination of ArI. Finally, after the isomerization to cis-C through the enamine-imine tautomerization, the cyclization of *cis*-C gives imidazoles. Considering the presence of **a** large excess amount of nitrile and the leaving ability of a unilateral nitrile of bis-nitrilium intermediate, the trans-B serve as the highly reactive Michaelacceptor^[17+6] to form cis-B by the addition and elimination of R³CN. Subsequently, the cyclization of cis-B followed by the reductive elimination of PhI in intermediate **D** yields the imidazoles. Therefore, the regiochemistry of imidazoles depends on the outcome of the Ritter-type addition step, in which the bulky iodonium ion would bind to the less sterically hindered R^2 side of the alkyne carbon. Also, the enhancement of electrophilicity of iodonium species A by the strong electron-withdrawing property of pentafluorophenyl group would lead to the more powerful activation of alkynes, and thus the Rittertype processes of bulky and/or low nucleophilic substrates proceeded more smoothly.



Scheme 4. Proposed mechanism.

In summary, we have developed some-new imino- λ^3 -iodanes with the aim to improve electrophilicity of these reagents. Among these reagents, C₆F₅INTs led to demonstrated the excellent results for reactivity in the [2+2+1] cycloadditiontype reaction of alkyne, nitriles and N-atom in the presence of BF₃•nitrile complexes. Thus, compared to our previous method using PhINTs, the present procedure could be applied to the-even bulky and/or low nucleophilic substrates and expand the scope of substrates. Furthermore, the structures of o- and m-NO₂C₆H₄INTs were characterized by single crystal X-ray analysis. Since the chemical modification was not examined for the enhancement of electrophilicity of iminoiodanes, our findings not only provide an attractive procedure for the access to highly substituted oxazoles but also open a new possibility for the use of iminoiodanes in organic syntheses.

Experimental Section

Representative procedure for the formation of imidazole 8a from alkyne 7a with MeCN and C_6F_5INTs

BF₃•MeCN (0.43 mL, 0.96 mmol) was added to a suspension of 7a (44 μ L, 0.40 mmol) and 1f (334 mg, 0.72 mmol) in MeCN (4.0 mL) at 0 °C under an argon atmosphere. After being stirred at ambient temperature for 4 h, the mixture was quenched with sat. NaHCO₃ (0.5 mL), diluted with ether and filtered through a short alumina column. Concentration of the filtrate to dryness and the subsequent purification of the residue by silica gel column chromatography (hexane/AcOEt = 85/15) gave 8a (95.8 mg, 76%) as a white solid.

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