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Complete List of Authors:	Sunagawa, Shun; Tokyo University of Agriculture and Technology, Division of Applied Chemistry, Institute of Engineering Tezuka, Yoko ; Tokyo University of Agriculture and Technology, Division of Applied Chemistry, Institute of Engineering Tsubouchi, Akira; Tokyo University of Agriculture and Technology, Division of Applied Chemistry, Institute of Engineering Yoshimura, Akira; Aomori Daigaku; University of Minnesota Duluth, Chemistry & Biochemistry Saito, Akio; Tokyo University of Agriculture and Technology, Division of Applied Chemistry, Institute of Engineering

ARTICLE

Synthesis of *N*-triflyl aldimines catalyzed by imino-λ^3-iodane

Shun Sunagawa,[a] Yoko Tezuka,[a] Akira Tsubouchi,[a] Akira Yoshimura [b] and Akio Saito*[a]

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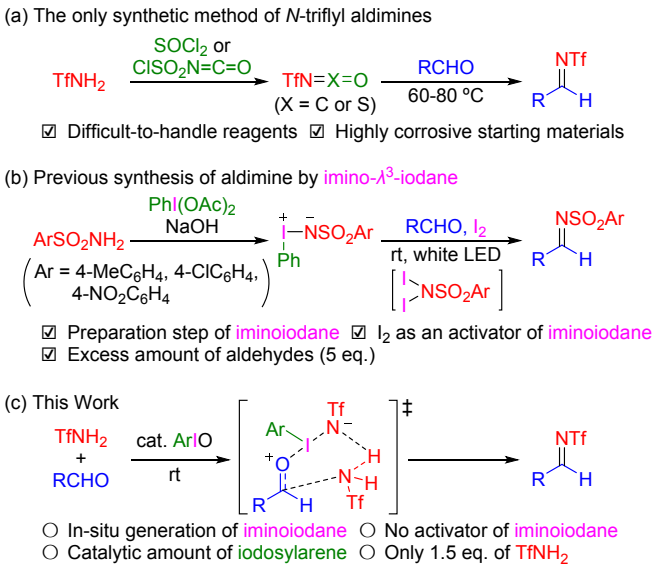
We report a catalytic synthesis of *N*-triflyl aldimines from aldehydes and triflylamide using imino-λ^3-iodane generated in situ from iodosylarene precatalyst and triflylamide. In the present reaction, imino-λ^3-iodane works as acid-base cooperative catalyst to activate aldehydes and triflylamide.

Introduction

Since *N*-sulfonyl imines not only show higher electrophilicity than the corresponding *N*-alkyl and *N*-aryl compounds but also have an easily removable protecting group on the nitrogen,[1] they are often used in various organic transformations such as nucleophilic addition,[2] aza-Friedel-Crafts,[3] imino-aldol,[4] imino-ene reaction,[5] cycloaddition[6] and C-H functionalizations.[7] Among the synthetic methods of these valuable compounds, the condensation of aldehydes and sulfonamides provides a simple and convenient method.[8-13] Generally, sulfonamides have significantly lower nucleophilicity and thus require activation of the carbonyl group of the aldehyde by Lewis or Brønsted acids.[8] However, these acid-activated methods are met with disadvantages including harsh conditions and/or excessive amounts of substrates or additives. Although the two-step synthesis using sulfinic acid[9] and secondary amine-catalyzed reactions[10] have been known as milder methods, the synthesis of *N*-sulfonyl imines with strong electron-withdrawing groups such as triflyl (Tf) and nosyl (Ns) groups has not been achieved. In addition to these dehydration-based methods, aza-Wittig reactions[11] and other deoxygenative methods using isocyanates[12a,b] and their analogues[12c-e] have been reported. In particular, isocyanates[12b] and λ^4-sulfanones[12c] are applicable to the synthesis of *N*-triflyl imines (Scheme 1a). Nevertheless, these reagents are difficult to handle and their preparation also requires highly corrosive reagents and complicated operations.

We have focused on the versatile reactivity of hypervalent iodine compounds[13] and have developed organic synthetic methods using hypervalent iodine reagents.[14] As part of our study, we recently found that imino-λ^3-iodane (ArINTf) generated in situ from iodosylarene (ArIO) and $TfNH_2$ promotes the α-amidation reaction of dicarbonyl compounds under catalyst-free conditions.[14a] The reaction suggests that ArINTf would serve as an acid-base cooperative reagent as well as a nitrene donor. In this work, a catalytic synthesis of *N*-triflyl imines from aldehydes and $TfNH_2$ has been developed using the acid-base cooperative action of ArINTf, which is reported herein (Scheme 1c). Although it has been known that $PhINSO_2Ar$ (Ar = 4-MeC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$) in the presence of molecular iodine promoted the formation of *N*-sulfonyl imines from aldehydes (Scheme 1b),[15] there are no reports on the reaction of ArINTf with aldehydes.



Scheme 1. Synthesis of *N*-sulfonyl imines.

a Division of Applied Chemistry, Institute of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan.
b Faculty of Pharmaceutical Sciences, Aomori University, 2-3-1 Kobata, Aomori 030-0943, Japan..

† Footnotes relating to the title and/or authors should appear here.
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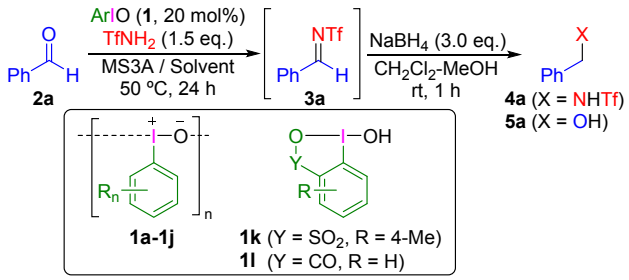
Results and discussion

Initially, the formation of *N*-triflyl imine **3a** from benzaldehyde (2a, 0.4 mmol) was examined in the presence of MS3A (120 mg) in $CHCl_3$ using iminoiodanes catalytically generated from various iodosylarenes **1** (20 mol%) and $TfNH_2$ (1.5 eq.) (Table 1). Note that the yield of the product was calculated as the amide **4a** after reduction with $NaBH_4$, because **3a** is sensitive to moisture.[16] As a result, compared to the unsubstituted **1a** (entry 1) and **1f**-**1i** having electron withdrawing groups (entries 6-9), **1b**-**1e** having electron donating groups were effective on the present reaction (entries 2-5). Especially, when the 2-OMe-substituted **1e** was used at 50 ºC for 24 h, the desired **4a** was obtained in 65% yield (entry 5), probably because the electron-donating ability and the coordination effect of the MeO group at the *ortho*-position facilitate the active monomer structure.[17] However, in the case of the aminocarbonyl substituted **1j** possessing strong coordinating ability and cyclic iodosylarene **1k** and **1l**, **4a** was scarcely obtained (entries 10-12), likely due to the reduced Lewis acidity of iodine.

Table 1. Optimization of conditions.[a]



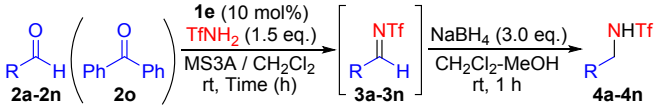
Entry	1	R_n	Solvent	4a[b] (%)	5a[b] (%)
1	**1a**	H	$CHCl_3$	19	65
2	**1b**	4-Me	$CHCl_3$	39	45
3	**1c**	2-Me	$CHCl_3$	22	67
4	**1d**	4-OMe	$CHCl_3$	30	58
5	**1e**	2-OMe	$CHCl_3$	65	35
6	**1f**	4-Cl	$CHCl_3$	24	46
7	**1g**	4-CF_3	$CHCl_3$	20	56
8	**1h**	2-NO_2	$CHCl_3$	18	61
9	**1i**	F_5	$CHCl_3$	18	61
10	**1j**	2-CO_2NMe_2	$CHCl_3$	2	87
11	**1k**	-	$CHCl_3$	trace	84
12	**1l**	-	$CHCl_3$	trace	85
13[c]	**1e**	2-OMe	$CHCl_3$	50	31
14[d]	**1e**	2-OMe	CH_2Cl_2	66	29
15[c,e,f]	**1e**	2-OMe	CH_2Cl_2	94 (86)[g]	6
16[c,e,f,h]	**1e**	2-OMe	CH_2Cl_2	90 (86)[g]	9
17[c,e]	-	-	CH_2Cl_2	0	98

[a] **2a**: 0.4 mmol, MS3A: 120 mg. [b] Determined by ^1H NMR analysis using an internal standard. [c] Conditions: rt, 4 h. [d] Conditions: rt, 2 h. [e] MS3A: 360 mg. [f] **2a**: 10 mol%. [g] Isolated yield. [h] **2a**: 2.0 mmol.

On the other hand, 2-OMe-substituted **1e** promoted the formation of **3a** even at room temperature for 4h (entry 13). Among the tested solvents (MeCN, CH_2Cl_2, hexane, toluene, 1,1,1,3,3,3-hexafluoro-2-propanol, see Table S1 in ESI), CH_2Cl_2 showed the good result (**4a**: 66%, entry 14). Furthermore, even when **1e** was reduced to 10 mol%, increasing the amount of MS3A (360 mg) resulted in the isolation of **4a** at 86% (entry 15). Even when the reaction was scaled up under similar conditions, **4a** was obtained in similar yields (entry 16). It should be mentioned that the absence of iodosylarene (entry 17) and use of $BF_3{\cdot}Et_2O$[8d] or rutile[18] (Table S1 in ESI) did not afford **4a** even under similar conditions.

Based on the above results, the substrate scope of the optimized conditions (Table 1, entry 15) was investigated (Table 2). The electron-rich aromatic aldehydes **2b**, **2c**, **2k** (entries 2, 3 and 11) and the *ortho*-substituted **2e** and **2h** (entries 5 and 8) required increased amount of **1e** (20 mol%), higher reaction temperature (50 ºC) and/or longer reaction time (16-24 h), probably due to their reduced electrophilicity. However, regardless of the substituent position, the present method was applicable to many aromatic aldehydes **2a**-**2i** and **2k** (56-92%, entries 1-9 and 11). On the other hand, the yield of nitro-substituted **4j** was only 32% (entry 10). The increase in reaction temperature and the amount of **1e** rather decreased the yield of **4j**, suggesting that imine **3j** may be relatively unstable. Unfortunately, aliphatic aldehydes **2m** and **2n** having hydrogen at the α-position gave complex mixtures (entries 13 and 14) and the reaction with benzophenone (**2o**) hardly proceeded (entry 15), although aliphatic aldehyde **2l** could be converted into the desired **4l** in 57% yield (entry 12).

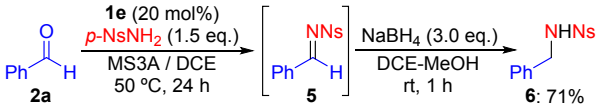
Table 2. Substrate scope.[a]



Entry	2	R	Time (h)	4	(%)[b]
1	**2a**	Ph	4	**4a**	86
2[c,d,e]	**2b**	4-$OMeC_6H_4$	24	**4b**	76
3[c]	**2c**	4-MeC_6H_4	24	**4c**	92
4	**2d**	3-MeC_6H_4	4	**4d**	84
5[c]	**2e**	2-MeC_6H_4	24	**4e**	76
6	**2f**	4-BrC_6H_4	4	**4f**	85
7	**2g**	3-BrC_6H_4	4	**4g**	70
8	**2h**	2-BrC_6H_4	16	**4h**	75
9	**2i**	4-$CF_3C_6H_4$	4	**4i**	67
10	**2j**	4-$NO_2C_6H_4$	4	**4j**	32
11	**2k**	2-thienyl	24	**4k**	56
12	**2l**	CMe_2Ph	48	**4l**	57
13	**2m**	CH(Me)Ph	4	**4m**	0
14	**2n**	$(CH_2)_2Ph$	4	**4n**	0
15[c,d,e]	**2o** (benzophenone)		24	**4o**	0

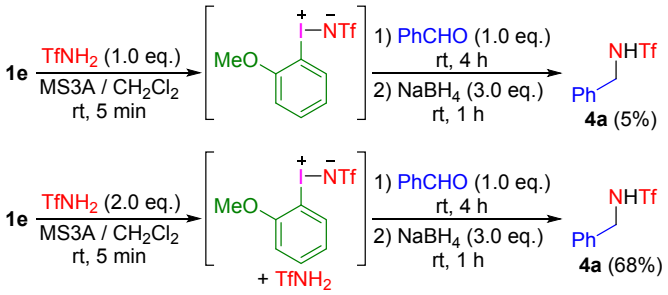
[a] **2a**: 0.4 mmol, MS3A: 360 mg. [b] Isolated yields. [c] **1e**: 20 mol%. [d] Temp.: 50 ºC. [e] Solvent: DCE.

Moreover, the present method could be applied to the synthesis of *N*-*p*-nosyl imine as shown in Scheme 2. When **2a** was treated with *p*-$NsNH_2$ (1.5 eq.) in the presence of **1e** (20 mol%) and MS3A at 50 ºC for 24 h, **6** was obtained in 71% yield after the reduction by $NaBH_4$.



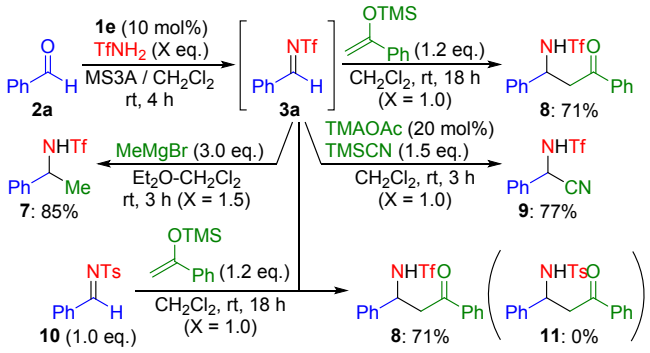
Scheme 2. Synthesis of *N*-*p*-nosyl imine.

To better understand the involvement of imino-λ^3-iodane as the active catalyst, control experiments were performed using stoichiometric amounts of imino-λ^3-iodane (Scheme 3). As a result, the use of imino-λ^3-iodane in situ generated from iodosylarene **1e** (1.0 eq.) and $TfNH_2$ (1.0 eq.) hardly led to the formation of imine **3a** from **2a** (5% as **4a**). On the other hand, when $TfNH_2$ was increased to 2 equivalents under similar conditions, the formation of a significant amount of **3a** was observed (68% as **4a**). These results suggest that the presence of $TfNH_2$ is essential in addition to imino-λ^3-iodane. Therefore, as shown in Scheme 1c, we believe that imino-λ^3-iodane would act as an acid-base cooperative catalyst to promote the addition of $TfNH_2$ to the aldehyde **2**.



Scheme 3. Control experiments.

Finally, we carried out other conversion reactions of imine **3a** obtained by this method (Scheme 4). After treatment of **2a** with $TfNH_2$ (1.5 eq.) in the presence of **1e** (10 mol%) and MS3A at room temperature for 4 h, the addition of MeMgBr (3.0 eq.) gave the corresponding adduct **7** in 85% yield. The use of silyl enol ether instead of Grignard reagent also produced adduct **8** in 71% yield. Note that it was better to reduce $TfNH_2$ to 1 equivalent because silyl enol ether is decomposed by $TfNH_2$. In addition, although the addition of tetramethylammonium acetate (TMAOAc, 20 mol%)[19] was required in the case of TMSCN, the desired adduct **9** was obtained in 77% yield. It should be mentioned that a 1:1 mixture of **3a** and *N*-tosyl imine **10** was exposed to silyl enol ether exclusively giving rise to the adduct **8**.



Scheme 4. Conversion reactions of *N*-triflyl imine **3a**.

Conclusions

We have developed the synthetic method of *N*-triflyl aldimines catalyzed by imino-λ^3-iodane. The imine obtained by this method can be used for nucleophilic addition reactions with various carbon-centered nucleophiles as well as hydrides. Furthermore, it was demonstrated that the imine has a higher electrophilicity than the Ts analogues in the reaction with silyl enol ethers. Since the involvement of hypervalent iodine in dehydrative condensation reactions is rare, these findings not only provide an efficient method for imine synthesis, but also open up new possibilities for hypervalent iodine catalysts.

Experimental

Representative procedure for synthesis of compound 4. To a suspension of 1-iodosyl-2-methoxybenzene (10.0 mg, 0.04 mmol) and MS3A (360 mg) in dichloromethane (DCM, 1.0 mL) was added $TfNH_2$ (89.5 mg, 0.6 mmol) and aldehyde **2a** (40.4 µL, 0.4 mmol) at room temperature. After the reaction mixture was stirred at same temperature for 4 h, $NaBH_4$ (45.4 mg, 1.2 mmol) and methanol (1.0 mL) were added at 0 ºC. The reaction mixture was stirred at room temperature for 1 h and then was filtered through celite pad. The filtrate was quenched with H_2O and extracted with DCM. The organic layer was dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by preparative thin layer chromatography (hexane:AcOEt = 3:1) to give **4a** (82.1 mg, 86%).

Author Contributions

Conceptualization, A.S.; data curation, all; formal analysis, all; funding acquisition, A.S.; investigation, S.S., Y.T. and A.T.; methodology, S.S. and A.T.; project administration, A.S.; resources, A.S.; supervision, A.S.; validation, S.S., Y.T. and A.T.; visualization, S.S., Y.T. and A.T.; writing—original draft preparation, A.S.; writing—review and editing, A.T., A.Y. and A.S.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information.

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Data availability

The data supporting this article have been included as part of the Supplementary Information.