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Metal-Free Synthesis of Polysubstituted Pyrroles by (Diacetoxyiodo)Benzene-Mediated Cascade Reaction of 3-Alkynyl Amines

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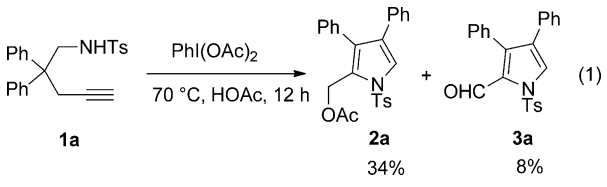
In memory of Emanuel Vogel

Pyrrole has been found extensively as a subunit in pharmacologically active natural and unnatural products.[1] Its derivatives are important building blocks in the syntheses of various heterocyclic compounds.[2] Accordingly, synthetic methods to develop pyrroles have received continuing attention of synthetic chemists since their discovery. Nowadays, a variety of protocols for the construction of pyrroles are available.[3] The classical Hantzsch procedure,[4] Paal–Knorr reaction,[5] various cycloaddition reactions,[6] and aza-Claisen rearrangements,[7] have been widely applied for the syntheses of pyrrole derivatives. Recent developed strategies based upon metal catalysis such as the Buchwald–Hartwig coupling reaction,[8] metal-catalyzed cyclizations,[9] and C–H bond amination[10] provide even more synthetic approaches. However, some of them suffer from either multistep synthetic operations, low chemical yield, low regioselectivity, or the use of toxic or expensive metals. An efficient synthetic procedure for the regioselective construction of pyrroles is still to be explored. Recently, we have developed a hypervalent iodine-mediated oxidation of terminal alkynes to afford α-acyloxy ketones by using OAc (Ac = acetyl) as the nucleophile.[11,12] In this reaction, the key steps involve the formation of the alkynyliodonium salt from terminal alkyne with $PhI(OAc)_2$ and the subsequent Michael-type addition of AcOH to the alkynyliodonium salt. Based on the results, we deduced that the amination product of acetylene would be afforded if amines were used as nucleophiles. Herein, we report our preliminary results of the simple and efficient $PhI(OAc)_2$-mediated reaction for the regioselective synthesis of polysubstituted pyrroles from alkynyl amines under metal-free conditions.[13]

Initially, phenylacetylene was treated with $TsNH_2$, benzylamine, or *N*-Methyl benzylamine, respectively, in the presence of $PhI(OAc)_2$ in AcOH at 70 °C. Unfortunately, only the formation of α-acyloxy ketone, instead of the amination product, was observed. In order to avoid the nucleophilic attack of the OAc anion, we considered that an intramolecular amination of the alkyne could be the solution. To this end, alkynyl amine **1a** was treated with two equivalents of (diacetoxyiodo)benzene in acetic acid at 70 °C for 12 hours under argon. Surprisingly, we did not observe the expected dihydropyrrole, but more appealing 2,3,4-trisubstituted pyrroles **2a** and **3a** were obtained in 34% and 8% yields, respectively [Eq. (1)]. The structure of pyrrole **2a** was determined by NOESY experiments. Interestingly, almost the same yield was afforded when the reaction ran under aerobic conditions.



Encouraged by these promising results, the influence of the reaction parameters was examined (Table 1). A survey of solvents indicated that the reaction is sensitive to the reaction medium. Only the starting material **1a** was recovered using *N*,*N*-dimethylformamide (DMF) or tetrahydrofuran (THF) as solvents (Table 1, entries 1 and 2), while the reaction proceeded sluggish in the solvents such as acetonitrile,

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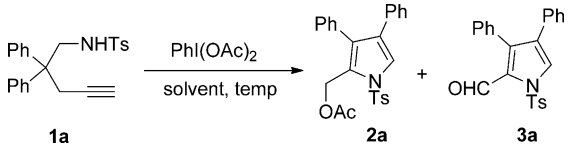
Table 1. Optimization of Reaction Conditions.[a]



1a 2a 3a

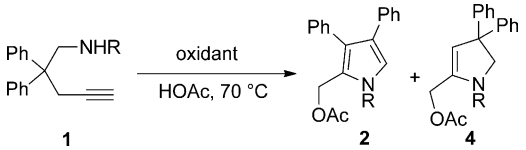
Entry	Equiv. of $PhI(OAc)_2$	Solvent	T [°C]	**2a**:**3a** [%][b]
1	3.0	DMF	70	–
2	3.0	THF	70	–
3	3.0	CH_3CN	70	12:–
4	3.0	DCE	70	25:–
5	3.0	*t*BuOH	70	11:–
6[c]	3.0	DCE	70	49:–
7	3.0	HOAc	70	75:10
8	3.0	HOAc	25	14:–
9	3.0	HOAc	50	36:9
10	3.0	HOAc	100	10:50
11	3.0	HOAc	120	–:64
12	1.0	HOAc	70	16:trace
13	2.0	HOAc	70	34:8
14	4.0	HOAc	70	64:15

[a] Reaction conditions: **1a** (0.2 mmol), solvent (3.0 mL). [b] Yield of isolated product. [c] HOAc (5.0 equiv) was added.

1,2-dichloroethane (DCE), or *t*BuOH (Table 1, entries 3–5). The product **2a** was obtained in 49% yield when five equivalents of HOAc were added to DCE (Table 1, entry 6). Consequently, when HOAc was chosen as the solvent, the yield of trisubstituted pyrrole **2a** increased to 75% and pyrrole **3a** was formed in 10% yield (Table 1, entry 7). The amount of (diacetoxyiodo)benzene also has a significant impact on the yield of pyrroles **2a** and **3a** (Table 1, entry 7, and 12–14). Using three equivalents of (diacetoxyiodo)benzene proved to be optimal for the transformation (Table 1, entry 7). The investigation on the effect of the temperature showed that **2a** was obtained in higher yield at 70°C while pyrrole **3a** became the major product when temperature increased to 100°C (Table 1, entries 7–11).

The substituents on the nitrogen atom of alkynyl amines showed their critical role in the reaction (Table 2). The reaction of alkynyl amine **1** with tosyl (Ts) and triflate (Tf) groups provided **2a** in high yield (Table 2, entries 1 and 2), but no isolable product was detected if alkynyl amine **1** bearing PhCO and PhNHCO groups were used (Table 2, entries 3 and 4). With alkynyl amine **1** having a Ts group as the substituent, different hypervalent iodine compounds were also screened. The employment of $PhI(COO{t}Bu)_2$ and $PhI(COOPh)_2$ as oxidants diminished the yield of pyrrole **2a** (Table 2, entries 5 and 6 vs 1). Other hypervalent iodine sources such as Koser's reagent and phenyliodine bis(trifluoroacetate) (PIFA) gave inferior results (Table 2, entries 7 and 8).

Table 2. Effect of R Group of **1** and Oxidant on the Reaction.[a]



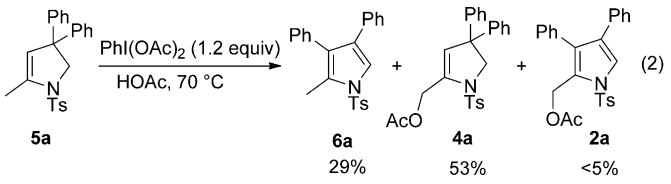
1 2 4

Entry	**1**, R	Oxidant	**2**:**4** [%][b]
1	Ts	$PhI(OAc)_2$	75:–
2	Tf	$PhI(OAc)_2$	69:–
3	C(O)Ph	$PhI(OAc)_2$	–[c]
4	C(O)NHPh	$PhI(OAc)_2$	–[c]
5	Ts	$PhI(COO{t}Bu)_2$	69:–
6	Ts	$PhI(COOPh)_2$	45:8
7	Ts	PhI(OH)OTs	–
8	Ts	PIFA	5:–

[a] Reaction conditions: **1** (0.2 mmol), oxidant (0.6 mmol), HOAc (3.0 mL). [b] Yield of isolated product. [c] Complex mixture.

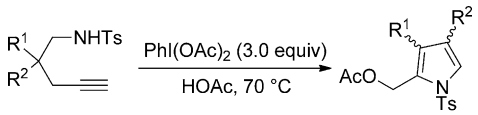
Under the optimized conditions, we explored the substrate scope of the reaction, and the results are summarized in Table 3. Treatment of various 2,2-disubstituted 3-alkynyl amines **1** with $PhI(OAc)_2$ furnished the corresponding 2,3,4-trisubstituted pyrroles **2** regioselectively in good isolated yields (Table 3, entries 1–6 and 10). The protocol is also viable for preparing 2,3-disubstituted pyrroles with high regioselectivity using 2-substituted-3-alkynyl amines **1** (Table 3, entries 7–9). The alkynyl amines **1** with electron-rich aromatic substituents afforded the pyrroles **2** in higher yield than electron-deficient aromatic substituents (Table 3, entries 2 vs 3 and 7 vs 8). Pyrrole **2e** possessing cyclohexane and pyrrole **2j** bearing benzocycloheptane were obtained readily from alkynyl amines **1e** and **1j** in 56% and 65% yields, respectively (Table 3, entries 5 and 10). Two regioisomers were obtained in the case of alkynyl amines **1k** and **1l** with two different substituents at the 2-position (Table 3, entries 11 and 12); these regioisomers are separable by silica-gel column chromatography. When the substrate with disubstituted alkyne was used, no reaction occurred and the substrate was recovered.

During the study of this reaction, we isolated dihydropyrrole **4a** in 8% yield using $PhI(COOPh)_2$ as the oxidant (Table 2, entry 6), which was deduced as a reaction intermediate. To confirm this, the dihydropyrrole **5a** was prepared according to the literature procedure[14] and was subjected to 1.2 equivalents of $PhI(OAc)_2$ in acetic acid at 70°C [Eq. (2)]. Trisubstituted pyrroles **6a** and **2a** were obtained in 29% and 5% yield, respectively, meanwhile the dihydropyrrole **4a** was formed in 53% yield by allylic oxidation of the dihydropyrrole **5a**. Further studies indicated that the dihydropyrrole **4a** can be readily transformed into the trisubstituted pyrrole **2a** in 31% yield, with the formation of three byproducts **3a**, **7a**, and **8a** [Eq. (3)]. These results suggest that the dihydropyrrole **4a** should serve as the precursor of the pyrrole **2a**.



5a 6a 29% 4a 53% 2a <5%

Table 3. Substrate Scope of the $PhI(OAc)_2$-Mediated Reaction of Alkynyl Amines.[a]



1 2

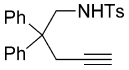
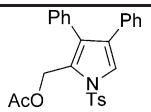
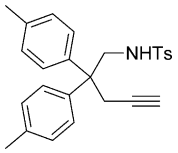
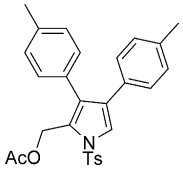
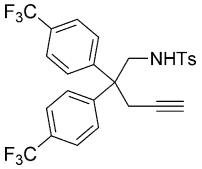
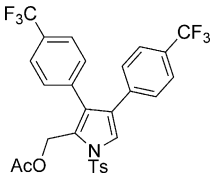
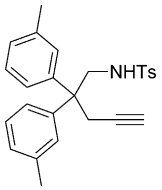
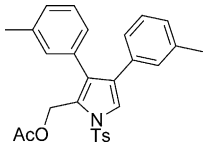
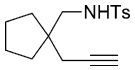
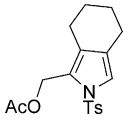
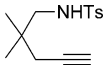
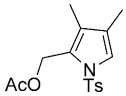
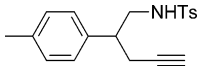
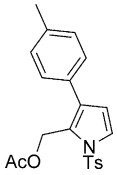
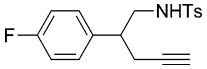
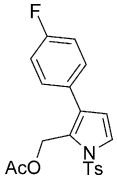
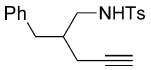
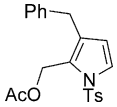
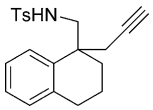
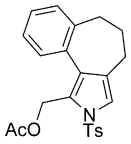
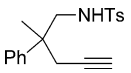
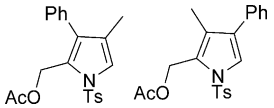
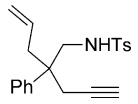
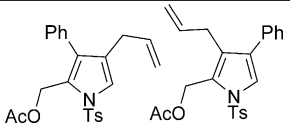
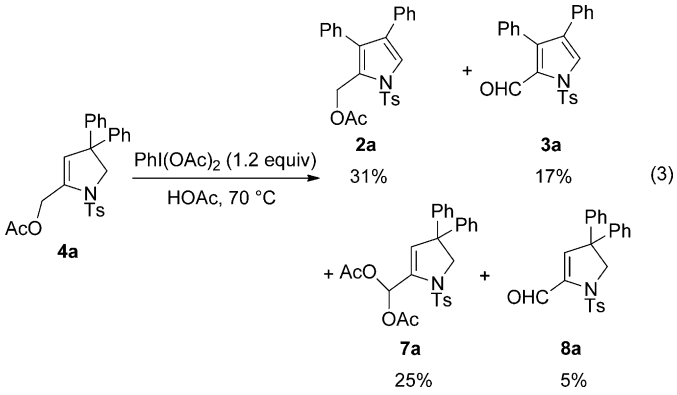
Entry	1		Product		Yield [%][b]
1		**1a**		**2a**	75
2		**1b**		**2b**	82
3		**1c**		**2c**	68
4		**1d**		**2d**	72
5		**1e**		**2e**	56
6		**1f**		**2f**	45
7		**1g**		**2g**	78
8		**1h**		**2h**	68
9		**1i**		**2i**	55
10		**1j**		**2j**	65
11		**1k**		**2k**	71(3:1)[c]

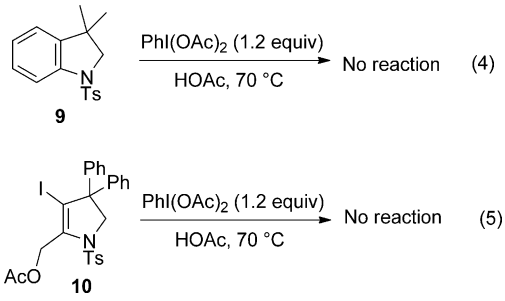
Table 3. (Continued)

Entry	1	Product	Yield [%][b]
12		**11**		**21**	49(1:1)[c]

[a] Reaction conditions: **1** (0.2 mmol), $PhI(OAc)_2$ (0.6 mmol), HOAc (3.0 mL). [b] Yield of isolated product. [c] The ratio of two isomers was determined by ^1H NMR spectroscopy.



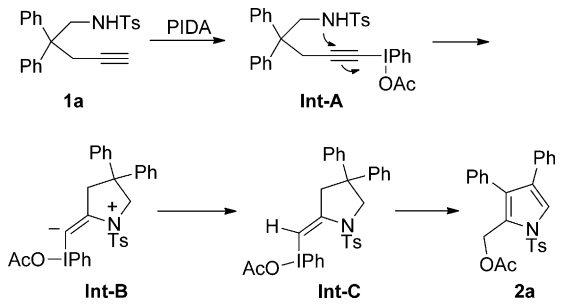
(3)



(4)

(5)

When compounds **9** and **10** were treated with 1.2 equivalents of $PhI(OAc)_2$ under the reaction conditions, as shown in Table 3, no reaction occurred and the starting material was recovered [Eqs. (4) and (5)]. It was suggested that the double bond of the dihydropyrrole **4a** might be initially oxidized by $PhI(OAc)_2$ during the conversion into the pyrrole **2a**. With the above-experimental results and literature reports,[12,15,16] a speculated mechanism was proposed using alkynyl amine **1a** as an example (Scheme 1). Reaction of terminal alkyne **1a** with $PhI(OAc)_2$ forms the alkynyliodonium salts **Int-A**.[12] An intramolecular aza-Michael-type addition affords the **Int-B,**[16] the migration of the proton gives rise to the **Int-C**. The transformation of the **Int-C** into pyrrole **2a** may proceed through a $PhI(OAc)_2$-mediated oxidation process and 1,2-rearrangement.[17] The exact reaction mechanism still needs more experimental evidence.



Scheme 1. Speculated Mechanism for the $PhI(OAc)_2$-Mediated Reaction of Alkynyl Amine **1a**. PIDA = $PhI(OAc)_2$.

In summary, we have developed an efficient metal-free regioselective synthesis of polysubstituted pyrroles in good yields by a $PhI(OAc)_2$-mediated reaction of alkynyl amines, and some complex pyrrole structures can be constructed. A plausible reaction mechanism was proposed. Further investigations on the detailed reaction mechanism and applications of the reactions in organic synthesis are in progress.

Experimental Section

General procedure for preparation of polysubstituted pyrrole ***2***

In a Schlenk tube, alkynyl amine **1** (0.2 mmol) was added to a stirring mixture of $PhI(OAc)_2$ (192 mg, 0.6 mmol), and acetic acid (1.5 mL) under an atmosphere of air. Then, the mixture was heated to 70 °C for 12 h until the substrate **1** disappeared, as monitored by TLC. The mixture was diluted with dichloromethane (5 mL) and water (5 mL) was added. The aqueous solution was extracted with dichloromethane (5 mL × 3) and the organic layer was combined and washed with $NaHCO_3$ (5 mL × 2), dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using petroleum ether/EtOAc (10:1–5:1) as an eluent to give product **2**.

Acknowledgements

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Keywords: amines · cascade reaction · hypervalent compounds · pyrrole · regioselectivity

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