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Indium-Catalyzed Reductive Alkylation of Pyrroles with Alkynes and Hydrosilanes: Selective Synthesis of β-Alkylpyrroles

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ABSTRACT

Mixing readily available alkynes, pyrroles, and triethylsilane along with an indium catalyst was found to be an efficient procedure to introduce alkyl groups onto a β-position of pyrroles in a complete regioselective manner. This is the first demonstration of catalytic β-alkylation of pyrroles in a single step.

Pyrroles having alkyl chains at the β-positions are key units found in many natural products[1] and functional organic materials.[2] Due to the sufficient aromaticity and π-excessive nature of pyrroles,[3] direct introduction of alkyl groups onto pyrroles by electrophilic aromatic substitution appears to be a straightforward route to access β-alkylpyrroles.[4] However, preferential α-nucleophilicity of pyrroles actually makes the β-alkylation considerably difficult.[5] Despite such characteristics of pyrroles, two strategies are available to alter the

(1) For selected examples, see: (a) de Leon, C. Y.; Ganem, B. *Tetrahedron* **1997**, *53*, 7731–7752. (b) Adamczyk, M.; Johnson, D. D.; Reddy, R. E. *J. Org. Chem.* **2001**, *66*, 11–19. (c) Grag, N. K.; Caspi, D. D.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 9552–9553. (d) Murtagh, J. E.; McCooey, S. H.; Connon, S. J. *Chem. Commun.* **2005**, 227–229. (e) Fürstner, A.; Radkowski, K.; Peters, H.; Seidel, G.; Wirtz, C.; Mynott, R.; Lehmann, C. W. *Chem. Eur. J.* **2007**, *13*, 1929–1945. (f) O'Neal, W. G.; Jacobi, P. A. *J. Am. Chem. Soc.* **2008**, *130*, 1102–1108. (g) Oberhuber, M.; Berghold, J.; Kräutler, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 3057–3061. (h) Kawasaki, T.; Sakurai, F.; Hayakawa, Y. *J. Nat. Prod.* **2008**, *71*, 1265–1267. See also recent reviews: (i) Fürstner, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3582–3603. (j) Banwell, M. G.; Goodwin, T. E.; Ng, S.; Smith, J. A.; Wong, D. J. *Eur. J. Org. Chem.* **2006**, 3043–3060.

(2) For selected recent examples, see: (a) Meltola, N. J.; Wahlroos, R.; Soini, A. E. *J. Fluoresc.* **2004**, *14*, 635–647. (b) Zotti, G.; Zecchin, S.; Schiavon, G.; Vercelli, B.; Berlin, A.; Grimoldi, S. *Macromol. Chem. Phys.* **2004**, *205*, 2026–2031. (c) Xu, H.; Yu, G.; Xu, W.; Xu, Y.; Cui, G.; Zhang, D.; Liu, Y.; Zhu, D. *Langmuir* **2005**, *21*, 5391–5395. (d) Foitzik, R. C.; Kaynak, A.; Beckmann, J.; Pfeffer, F. M. *Synth. Met.* **2005**, *155*, 185–190. (e) Zhao, W.; Carreira, E. M. *Chem. Eur. J.* **2006**, *12*, 7254–7263. (f) Foitzik, R. C.; Kaynak, A.; Pfeffer, F. M. *Synth. Met.* **2006**, *156*, 637–642. (g) Foitzik, R. C.; Kaynak, A.; Pfeffer, F. M.; Beckmann, J. *Synth. Met.* **2006**, *156*, 1333–1340. (h) Jiao, L.; Hao, E.; Vicente, G. H.; Smith, K. M. *J. Org. Chem.* **2007**, *72*, 8119–8122. (i) King, R. C. Y.; Boussoualem, M.; Roussel, F. *Polymer* **2007**, *48*, 4047–4054. (j) Zotti, G.; Vercelli, B.; Berlin, A. *Chem. Mater.* **2008**, *20*, 397–412.

(3) Jones, G. B.; Chapman, B. J. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Bird, C. W., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 1−38.

(4) Intra- and Intermolecular ring closing reactions are alternative direct or indirect ways to access β-alkylpyrroles, see: (a) Sundberg, R. J. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Bird, C. W., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 119−206.

(5) For recent reports on selective α-alkylation of pyrroles with the following alkylating agents by electrophilic aromatic substitution. For alkenes: (a) Yadav, J. S.; Reddy, B. V. S.; Reddy, P. S. R.; Reddy, K. S.; Reddy, P. N. *Synlett* **2003**, 417–419. (b) Zhan, Z.-P.; Yang, W.-Z.; Yang, R.-F. *Synlett* **2005**, 2425–2428. (c) Zhang, C.-X.; Wang, Y.-Q.; Duan, Y.-S.; Ge, Z.-M.; Cheng, T.-M.; Li, R.-T. *Catal. Commun.* **2006**, *7*, 534–537. (d) An, L.-T.; Zou, J.-P.; Zhang, L.-L.; Zhang, Y. *Tetrahedron Lett.* **2007**, *48*, 4297–4300. (e) Unaleroglu, C.; Yazici, A. *Tetrahedron* **2007**, *63*, 5608–5613. (f) Hashmi, A. S. K.; Salathé, R.; Frey, W. *Eur. J. Org. Chem.* **2007**, 1648–1652. (g) Trost, B. M.; Müller, C. *J. Am. Chem. Soc.* **2008**, *130*, 2438–2439. For allylic acetates: (h) Yadav, J. S.; Reddy, B. V. S.; Rao, K. V.; Rao, P. P.; Raj, K. S.; Prasad, A. R.; Prabhakar, A.; Jagadeesh, B. *Synlett* **2006**, 3447–3450. For alcohols: (i) Liu, J.; Muth, E.; Flörke, U.; Henkel, G.; Merz, K.; Sauvageau, J.; Schwake, E.; Dyker, G. *Adv. Synth. Catal.* **2006**, *348*, 456–462. For epoxides and aziridines: (j) Yadav, J. S.; Reddy, B. V. S.; Parimala, G. *Synlett* **2003**, 1143–1145. For diazo compounds: (k) Yadav, J. S.; Reddy, B. V. S.; Satheesh, G. *Tetrahedron Lett.* **2003**, *44*, 8331–8334. See also a review: (l) Schmuck, C.; Rupprecht, D. *Synlett* **2007**, 3095–3110.

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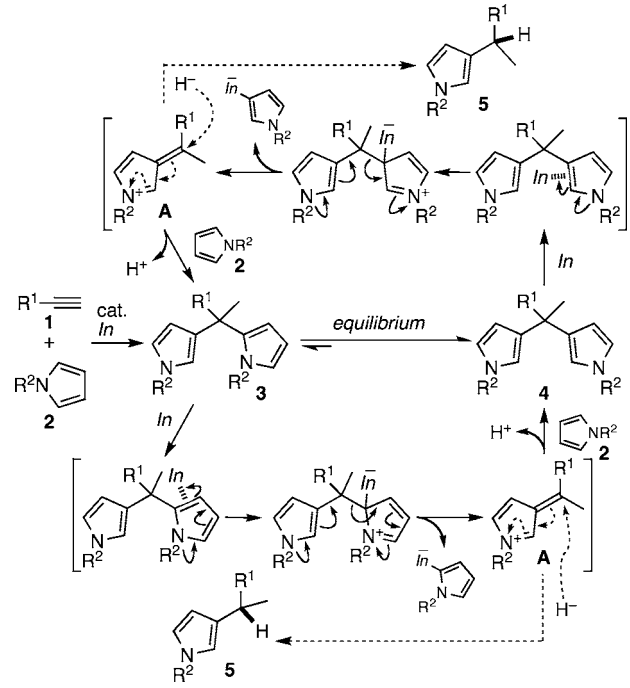
α-orientation to β-orientation:[6] (1) use of pyrrole−metal complexes[7] and (2) use of pyrroles bearing an electron-withdrawing group at the α-position.[8] Some of these have achieved high β-selectivities, but catalytic β-alkylation of pyrroles proceeding in one-step has no precedent. At present, a three-step process, introduced by Rühe and colleagues, seems to have been the most reliable strategy to synthesize β-alkylpyrroles.[9,10]

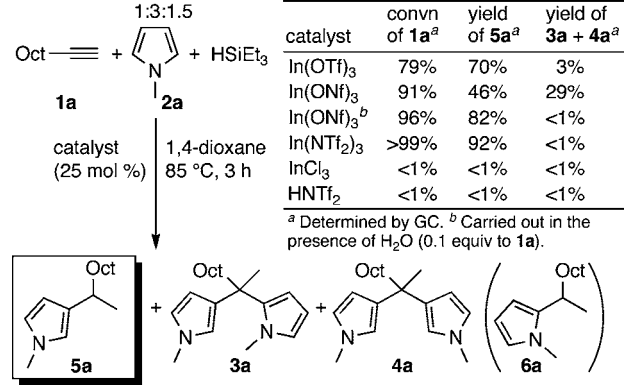
We have reported that indium triflate [$In(OTf)_3$, Tf = SO_2CF_3] catalyzes double addition of *N*-substituted pyrroles **2** to alkynes **1**, giving isomeric mixtures of *gem*-dipyrrolylalkanes **3** and **4** (Scheme 1, $In(OTf)_3$ = *In*).[11,12] The noticeable aspect is that β,β′-adducts **4** are produced selectively due to their thermodynamic stability. During the course of the mechanistic studies on the isomerization between **3** and **4**, we proposed the formation of cationic species **A**[11,13] and envisaged that *in situ* trapping of **A** with hydride would offer a conceptually new synthetic route to β-alkylpyrroles **5**. Herein we disclose the first catalytic regioselective β-alkylation of pyrroles in a single step, by a simple assembly of alkynes, pyrroles and hydrosilanes.

Scheme 1. Working Hypothesis for β-Alkylation of Pyrroles



Because of the potent activity of $In(OTf)_3$ in the double addition of pyrroles to alkynes,[11] we first tested its catalytic activity in the reaction of 1-decyne (**1a**) and *N*-methylpyrrole (**2a**) with $HSiEt_3$ as a hydride donor (Scheme 2). Thus, the reaction with 25 mol % of $In(OTf)_3$ in 1,4-dioxane at 85 °C for 3 h proceeded with 79% conversion of **1a** to give 3-(2-decyl)-*N*-methylpyrrole (**5a**) in 70% yield, along with 3% yield of the isomeric double addition products **3a** and **4a**. Noteworthy is that no α-isomer **6a** was formed. The use of the nonaflate salt [$In(ONf)_3$, Nf = $SO_2C_4F_9$] enhanced the conversion of **1a**, while a considerable amount of **3a** and **4a** remained unconsumed. The addition of H_2O (0.1 equiv)

Scheme 2. Indium-Catalyzed Reductive β-2-Decylation of **2a**



catalyst	convn of **1a**[a]	yield of **5a**[a]	yield of **3a** + **4a**[a]
$In(OTf)_3$	79%	70%	3%
$In(ONf)_3$	91%	46%	29%
$In(ONf)_3$[b]	96%	82%	<1%
$In(NTf_2)_3$	>99%	92%	<1%
$InCl_3$	<1%	<1%	<1%
$HNTf_2$	<1%	<1%	<1%

[a] Determined by GC. [b] Carried out in the presence of H_2O (0.1 equiv to **1a**).

(6) For a review, see: Anderson, H. J.; Loader, C. E. *Synthesis* **1985**, 353–364.

(7) For pyrrolyl−*N*-MgCl: (a) Castro, A. J.; Duncan, W. G.; Leong, A. K. *J. Am. Chem. Soc.* **1969**, *91*, 4304. For pyrrolyl−*N*-ZnBr: (b) Yadav, J. S.; Reddy, B. V. S.; Reddy, P. M.; Srinivas, C. *Tetrahedron Lett.* **2002**, *43*, 5185–5187. For pyrrolyl−*N*-[Re]: (c) DuBois, M. R.; Vasquez, L. D.; Peslherbe, L.; Noll, B. C. *Organometallics* **1999**, *18*, 2230–2240. For pyrrole−η^2-[Os]: (d) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684–5692. (e) Hodges, L. M.; Gonzalez, J.; Koontz, J. I.; Myers, W. H.; Harman, W. D. *J. Org. Chem.* **1995**, *60*, 2125–2146. (f) Valahovic, M. T.; Myers, W. H.; Harman, W. D. *Organometallics* **2002**, *21*, 4581–4589. See also the following reviews on pyrrole−η^2-[Os]: (g) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953–1978. (h) Brooks, B. C.; Gunnoe, T. B.; Harman, W. D. *Coord. Chem. Rev.* **2000**, *206*−*207*, 3–61.

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(9) The strategy consists of the following three steps: β-acylation of *N*-(arylsulfonyl)pyrroles followed by de-arylsulfonylation and reduction of the carbonyl moiety: (a) Rühe, J.; Ezquerra, T.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 103–108. (b) Rühe, J.; Ezquerra, T. A.; Wegner, G. *Synth. Met.* **1989**, *28*, C177−C181.

(10) For examples making use of the Rühe strategy, see: (a) Sigmund, W. M.; Bailey, T. S.; Hara, M.; Sasabe, H.; Knoll, W.; Duran, R. S. *Langmuir* **1995**, *11*, 3153–3160. (b) Barr, G. E.; Sayre, C. N.; Connor, D. M.; Collard, D. M. *Langmuir* **1996**, *12*, 1395–1398. (c) Ashraf, S. A.; Chen, F.; Too, C. O.; Wallace, G. G. *Polymer* **1996**, *37*, 2811–2819. (d) Ng, S.-C.; Chan, H. S. O.; Xia, J.-F.; Yu, W. *J. Mater. Chem.* **1998**, *8*, 2347–2352. (e) Zelikin, A.; Shastri, V. R.; Langer, R. *J. Org. Chem.* **1999**, *64*, 3379–3380. (f) de Lacy Costello, B. P. J.; Evans, P.; Guernion, N.; Ratcliffe, N. M.; Sivanand, P. S.; Teare, G. C. *Synth. Met.* **2000**, *114*, 181–188. (g) Freitas, J. M.; Abrantes, L. M.; Darbre, T. *Helv. Chim. Acta* **2005**, *88*, 2470–2478. See also references 2d, 2f and 2g.

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(13) Cleavage of carbon−pyrrolyl bonds of bis(pyrrol-2-yl)alkanes has been suggested to occur as an undesired process during acid-catalyzed synthesis of porphyrins: (a) Geier, G. R., III.; Littler, B. J.; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 701–711. (b) Auger, A.; Muller, A. J.; Swarts, J. C. *Dalton Trans.* **2007**, 3623–3633, and references cited therein.

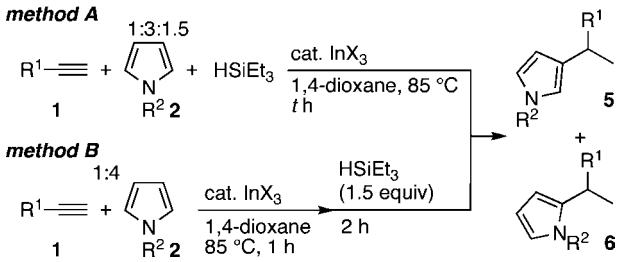
(14) With 20 mol % of $In(NTf_2)_3$, **5a** was obtained in a comparable yield (91%). However, further lower loading of $In(NTf_2)_3$ (15 mol %) resulted in 59% conversion of **1a**, giving **5a** in 50% yield.

(15) Although some hydrosilanes other than $HSiEt_3$ were tested in the reaction using $In(NTf_2)_3$ as a catalyst, their use considerably lowered the yield of **5a** as follows: H_2SiEt_2 (2% yield), $H_2SiMePh$ (1% yield), $H_3Si(CH_2)_7CH_3$ (<1% yield).

affected their complete consumption, showing that H_2O could act as an activator enhancing nucleophilicity of a hydride reagent by its coordination. $In(NTf_2)_3$ recorded the highest yield of **5a** without the aid of H_2O,[14,15] but $InCl_3$ and a Brϕnsted acid, $HNTf_2$, were totally inactive. As a result, $In(NTf_2)_3$ and $In(ONf)_3$ in combination with using H_2O turned out to be promising for the present reaction.

We next surveyed the substrate scope of the reductive β-alkylation (Table 1). Besides **1a**, 4-phenyl-1-butyne, which

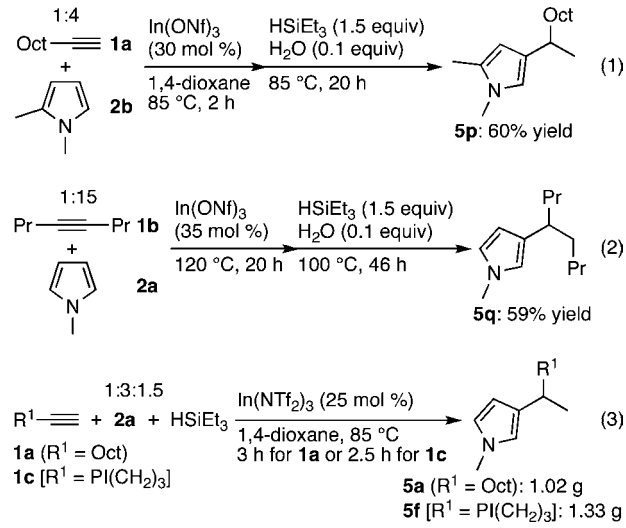
Table 1. Indium-Catalyzed Reductive β-Alkylation of Pyrroles[a]



entry	R^1	R^2	X in InX_3	method (t)	yield (%),[b] product(s)	ratio of **5**:**6**[c]
1	Oct	Me	NTf_2	A (3)	91, **5a**	>99:<1
2	$Ph(CH_2)_2$	Me	NTf_2	A (8)	79, **5b**	>99:<1
3	$Cl(CH_2)_4$	Me	NTf_2	A (20)	53, **5c**	>99:<1
4	$AcO(CH_2)_3$	Me	NTf_2	A (12)	78, **5d**	>99:<1
5[d]	$HO(CH_2)_4$	Me	NTf_2	A (4)	71, **5e**[e]	>99:<1
6	$PI(CH_2)_3$[f]	Me	NTf_2	A (2.5)	92, **5f**	>99:<1
7	*c*-Hex	Me	NTf_2	A (24)	9, **5g**, **6g**	81:19
8[g]	*c*-Hex	Me	ONf	B	76, **5g**	>99:<1
9	*c*-Hex	Me	ONf	B	51, **5g**	>99:<1
10	Ph	Me	NTf_2	B	76, **5h**	>99:<1
11	3-thienyl	Me	NTf_2	B	75, **5i**	>99:<1
12[g]	Oct	Bn	ONf	A (2)	81, **5j**	>99:<1
13[g]	*c*-$PenCH_2$[h]	Bn	ONf	A (15)	85, **5k**	>99:<1
14[g]	$PI(CH_2)_3$[f]	Bn	ONf	A (5)	76, **5l**	>99:<1
15[g]	Ph	Bn	ONf	B	84, **5m**	>99:<1
16	Oct	^{t}Bu	NTf_2	B	89, **5n**	>99:<1
17[g]	Oct	Ph[i]	ONf	B	87, **5o**	>99:<1

[a] Reagents (unless otherwise specified): **1** (0.500 mmol), **2** (1.50 mmol for method A or 2.00 mmol for method B), $HSiEt_3$ (0.750 mmol), $In(NTf_2)_3$ or $In(ONf)_3$ (0.125−0.150 mmol), 1,4-dioxane (1.0 mL). See Supporting Information for further details. [b] Isolated yield based on **1**. [c] Determined by GC. [d] At 70 °C. [e] Product **5e′** having $-OSiEt_3$ instead of −OH also was formed in 2% yield. [f] PI = phthalimidoyl. [g] Performed in the presence of H_2O (0.1 equiv). For method B, H_2O was added successively after the addition of $HSiEt_3$. [h] *c*-Pen = cyclopentyl. [i] *N*-Phenylpyrrole (3.0 equiv) was used.

is capable of cyclizing independently,[16] reacted with **2a** and $HSiEt_3$ to provide **5b** exclusively, by the procedure shown as method A (entries 1 and 2). The functional groups, −Cl, −OAc (Ac = acetyl) and −OH are compatible with the strategy (entries 3−5). The C≡C bond of *N*-(4-pentynyl)phthalimide also accepted the β-position of **2a** exclusively (entry 6). In contrast to these results, the reaction of *c*-HexC≡CH, which has the branched structure adjacent to the C≡C bond, resulted in a poor yield and β-selectivity (entry 7). After re-examination of the reaction conditions and procedure, both the yield and selectivity were markedly improved by the alteration of method A to method B and of $In(NTf_2)_3$ to $In(ONf)_3$. Thus, pretreatment of *c*-HexC≡CH, **2a** and $In(ONf)_3$ at 85 °C for 1 h, followed by the addition of $HSiEt_3$ and H_2O, and further stirring for 2 h gave **5g** as the sole product in 76% yield (entry 8). Here again, the $In(ONf)_3$-catalyzed reaction in the absence of H_2O resulted in a lower yield, as the case shown in Scheme 2 (entry 9). Method B is valid also for the reactions of aryl- and heteroarylalkynes having similar branched structures as *c*-HexC≡CH (entries 10 and 11). Pyrroles with −Bn (Bn = benzyl), −*t*-Bu or −Ph on the nitrogen atom (entries 12−17) as well as 1,2-dimethylpyrrole (**2b**) (eq 1) accepted a certain range of alkynes **1**, together with $HSiEt_3$, in a complete β-selective manner, by the proper choices of methods and indium catalysts. The reaction of internal alkyne **1b** with **2a** also gave only **5q**, while higher loadings of **2a** and $In(ONf)_3$ at higher temperature without solvent 1,4-dioxane were required (eq 2). Utility of the strategy can be demonstrated by performance of preparative scale synthesis. For example, **5a** and **5f** were prepared in 5.0 and 5.4 mmol scale, respectively, and thus 1.02 g (85% yield) of **5a** and 1.33 g (89% yield) of **5f** were obtained (eq 3).



Unfortunately, the strategy cannot be applied well to pyrrole (**2**, R^2 = H),[17] but instead we secured a reliable two-step synthetic route for β-alkylpyrrole **5** (R^2 = H). Thus,

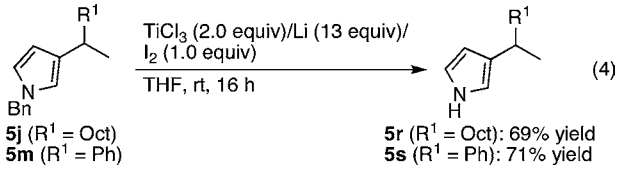
(16) For reviews, see: (a) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167–182. (b) Bandini, M.; Emer, E.; Tommasi, S.; Umani-Ronchi, A. *Eur. J. Org. Chem.* **2006**, 3527–3544.

(17) On treatment of **1a**, pyrrole, $HSiEt_3$ (1:3:1.5) and 25 mol % of $In(NTf_2)_3$ at 85 °C for 24 h using method A, a 54:46 mixture of β- and α-(2-decyl)pyrroles was obtained in 17% yield.

(18) Talukdar, S.; Nayak, S. K.; Banerji, A. *J. Org. Chem.* **1998**, *63*, 4925–4929.

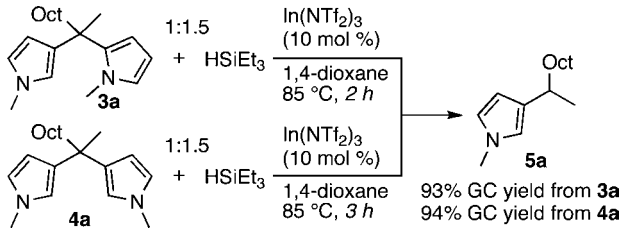
(19) Baba, Shibata and co-workers as well as Miura, Hosomi and co-workers have proposed that treatment of indium salts (InX_3; X = Cl, Br, OAc) with hydrosilanes brings about *in situ* generation of indium hydrides (*In*−H). Therefore, an *In*−H might be formed also in the present reaction: (a) Shibata, I.; Kato, H.; Ishida, T.; Yasuda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 711–714. (b) Hayashi, N.; Shibata, I.; Baba, A. *Org. Lett.* **2004**, *6*, 4981–4983. (c) Hayashi, N.; Shibata, I.; Baba, A. *Org. Lett.* **2005**, *7*, 3093–3096. (d) Miura, K.; Tomita, M.; Ichikawa, J.; Hosomi, A. *Org. Lett.* **2008**, *10*, 133–136.

debenzylation of **5j** or **5m**, each of which has been prepared in entry 12 or 15 of Table 1, upon treatment with a low-valent titanium reagent gave **5r** or **5s**, respectively (eq 4).[18] Importantly, the benzyl group, $-CH(CH_3)Ph$, on the β-carbon atom of the pyrrole ring of **5m** remained untouched.



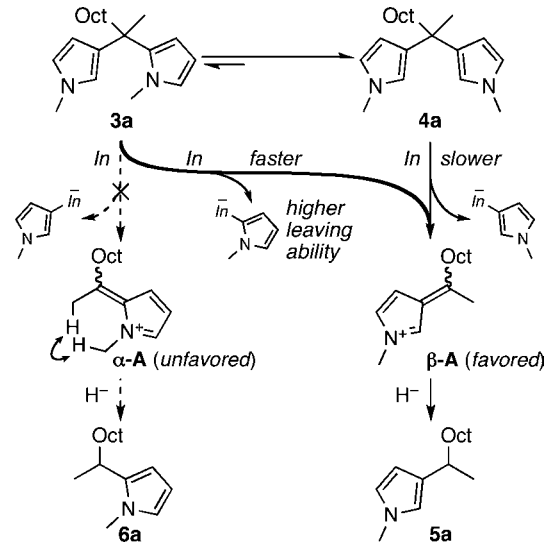
Some pieces of experimental observations are available for the mechanistic studies. First, α,β'-dipyrrolyldecane **3a** and its β,β'-isomer (**4a**) were prepared simultaneously by indium-catalyzed double addition of *N*-methylpyrrole (**2a**) to 1-decyne (**1a**).[11] On treatment of **3a** or **4a** with $HSiEt_3$ and 10 mol % of $In(NTf_2)_3$, both reactions gave only β-(2-decyl)pyrrole **5a** in high yields, in which the reaction of **3a** proceeded faster (Scheme 3). The results suggest that the

Scheme 3. Indium-Catalyzed Reaction of **3a** or **4a** with $HSiEt_3$



reductive β-alkylation using **1a**, **2a** and $HSiEt_3$ proceeds through the formation of **3a** and **4a**. Scheme 4 illustrates possible routes from **3a** and **4a** to the products. In the case of **3a**, both **α-A** and ***β*-A**, which result in **6a** and **5a**, respectively, are possible intermediates. In practice, **5a** was formed exclusively, suggesting that ***β*-A** is much more stable than **α-A**, which has serious steric repulsion between the two hydrogen atoms. The reaction of **4a**, whose intermediate is limited to ***β*-A**, also gives only **5a**. Considering that the difference between **3a** and **4a** is the leaving group, the result on the faster reaction of **3a** compared with that of **4a** indicates that the α-pyrrolyl group has a superior leaving ability to the β-pyrrolyl group. Therefore, the perfect β-selectivities observed in this study are most likely the results of the selective generation of ***β*-A** over **α-A** and the higher leaving ability of the α-pyrrolyl groups over the β-pyrrolyl groups. Consequently, though details of catalyst

Scheme 4. Possible Routes from **3a** and **4a** to Products



active species remain unclear at present,[19] the working hypothesis shown in Scheme 1 surely indicates the outline of the present process.[20]

In conclusion, we have demonstrated the first example of the catalytic regioselective β-alkylation of pyrroles in one-step, by the assembly of readily available alkynes, pyrroles and $HSiEt_3$ with the aid of an indium catalyst. The highlight of the strategy is the achievement of the exclusive synthesis of β-alkylpyrroles **5**. Studies on catalyst active species as well as lowering the catalyst loading, including further investigation of other catalysts, are currently underway.

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Supporting Information Available: Detailed experimental procedures, and characterization data and ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) In the absence of $HSiEt_3$, $In(NTf_2)_3$-catalyzed reaction of 1-decyne (**1a**) and *N*-methylpyrrole (**2a**) in 1,4-dioxane at 85 °C for 2 h gives a 85:14:1 mixture of **4a**, **3a** and α,α′-isomer almost quantitatively. No α-alkylpyrrole **6a** is formed in the corresponding reductive β-alkylation reaction despite that the α,α′-isomer is an inevitable precursor of **6a** (Scheme 2), implying that the contribution of the α,α′-isomer to the reductive β-alkylation reaction is negligible.