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Transition Metal-Catalyzed Synthesis of Pyrroles from Dienyl Azides

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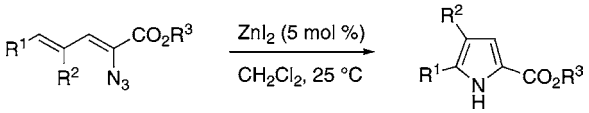
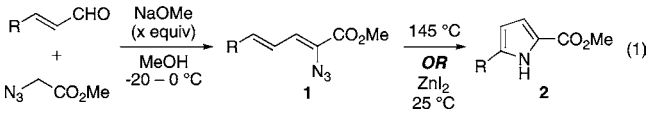
ABSTRACT



A range of 2,5-disubstituted and 2,4,5-trisubstituted pyrroles can be synthesized from dienyl azides at room temperature using catalytic amounts of ZnI_2 or $Rh_2(O_2CC_3F_7)_4$.

Pyrroles[1] are an important moiety in many pharmaceuticals,[2,3] natural products,[4] and materials.[5] As such, the development of new methods that access these molecules has remained a goal of organic synthesis for over 100 years.[6−8] The thermolysis of azidoacrylates, a common method for indole synthesis,[9,10] has seldom been employed for the construction of pyrroles despite the ready availability of dienyl azides (eq 1).[11,12]



In the course of our investigations into the reaction of azidoacrylates with transition metals, we discovered that zinc iodide could efficiently catalyze the formation of pyrroles at room temperature (eq 1). Despite the use of catalytic quantities of zinc(II) salts as Lewis acids in a diverse range of reactions,[13,14] their use with azides is surprisingly rare.[15]

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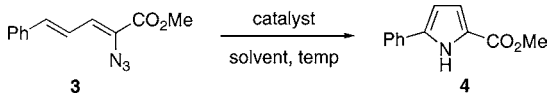
In this Letter, we demonstrate that the zinc-mediated decomposition of dienyl azides provides a general method for the synthesis of pyrroles.

We recently reported that rhodium(II) catalyzed the construction of indoles from azidoacrylates.[16] We wanted to extend this chemistry to the formation of pyrroles from dienyl azides (Table 1) and found that rhodium(II) perfluorobutyrate efficiently promoted this process (entry 2). As before,[16] increasing the electron-donating nature of the carboxylate ligand significantly reduced the reactivity of the catalyst (entry 3). While rhodium(II) perfluorobutyrate is the only efficient catalyst for indole formation,[16] a range of metal salts smoothly catalyzed pyrrole **4** from dienyl azide **3** (entries 4−7).[17] *Both copper(II) triflate and zinc iodide transformed **3** into pyrrole **4** at room temperature (entries 5 and 7).* Diminished yields were observed with other Lewis acids, including mercury(II) triflate (entry 8),[18] gold(I) triflate (entry 9),[19] rhodium(II,III) caprolactamate (entry 10),[20] or triflic acid (entry 11).[21] Optimization of the solvent revealed that methylene chloride was superior to ethereal or aromatic solvents.

The most reactive catalysts were compared by examining the reaction progress after 3 h (Table 2). Both copper(II) triflate and zinc iodide were found to be more reactive than $Rh_2(O_2CC_3F_7)_4$ (entries 2 and 3). Changing the oxidation state of copper or the counterion of the zinc salt inhibited the reaction progress (entries 4 and 5). While copper(II) triflate and zinc iodide exhibited similar activities, we chose to focus method development on the less expensive zinc salt ($0.40/g versus $10/g).[22,23]

The scope and limitations of the method were subsequently investigated (Table 3).[24] The reaction tolerated both electron-rich and electron-poor aryl substituents (entries 1−12). As

Table 1. Optimization of Pyrrole Formation

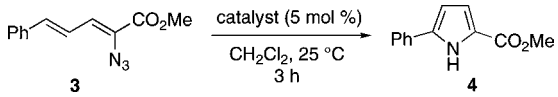


3 **4**

entry	catalyst	mol %	temp (°C)	solvent	yield[a] (%)
1	none	n.a.	40	PhMe	14
2	$Rh_2(O_2CC_3F_7)_4$	2	40	PhMe	>95
3	$Rh_2(OAc)_4$	10	40	PhMe	11
4	$(CuOTf)_2$·PhH	5	25	CH_2Cl_2	90
5	$Cu(OTf)_2$	5	25	CH_2Cl_2	>95
6	$ZnCl_2$	5	25	CH_2Cl_2	86
7	ZnI_2	5	25	CH_2Cl_2	>95
8	$Hg(OTf)_2$	5	25	CH_2Cl_2	39[b]
9	AuOTf	10	25	CH_2Cl_2	n.r.
10	$Rh_2(cap)_4Br$[c]	10	25	PhMe	n.r.
11	HOTf	2	25	CH_2Cl_2	dec.[b]

[a] As determined using ^{1}H NMR spectroscopy. [b] Complete consumption of **1** was observed. [c] cap = caprolactamate.

Table 2. Examination of Catalyst Reactivity



3 **4**

entry	catalyst	conversion[a] (%)
1	$Rh_2(O_2CC_3F_7)_4$	40
2	ZnI_2	53
3	$Cu(OTf)_2$	64
4	$(CuOTf)_2$·PhH	30
5	$ZnCl_2$	34

[a] As determined using ^{1}H NMR spectroscopy.

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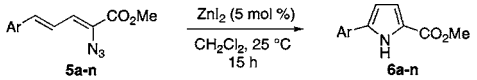
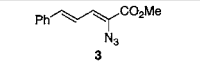
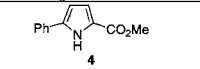
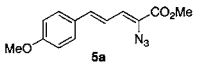
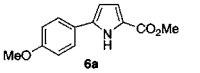
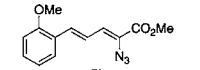
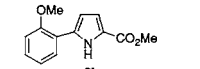
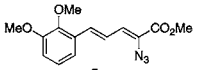
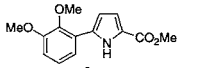
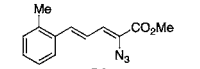
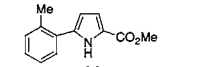
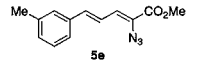
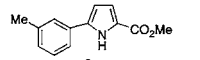
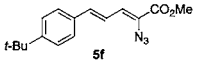
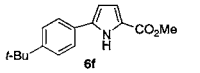
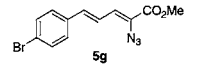
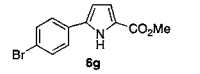
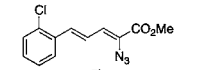
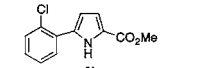
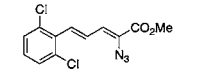
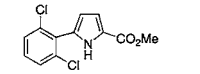
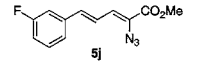
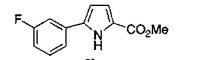
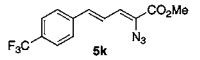
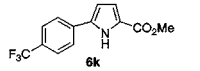
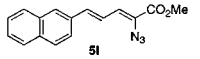
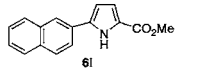
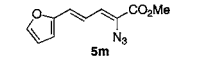
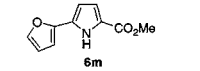
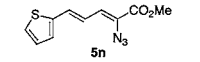
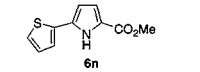
(22) From Sigma-Aldrich: 98% $Cu(OTf)_2$, 5 g, $51.40 (283673); ≥98% ZnI_2, 50 g, $19.90 (223883).

(23) Refer to the Supporting Information for a tabular comparison of the reactivities of the dienyl azides with $Cu(OTf)_2$ and $Rh_2(O_2CC_3F_7)_4$ catalysts.

Table 3. Scope of Pyrrole Formation



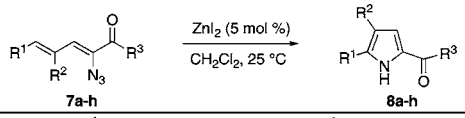
entry	substrate	product	yield (%)
1	 3	 4	>95[a] (93)[b]
2	 5a	 6a	>95 (83)
3	 5b	 6b	>95 (96)
4	 5c	 6c	>95 (92)
5	 5d	 6d	>95 (90)
6	 5e	 6e	>95 (77)
7	 5f	 6f	>95 (90)
8	 5g	 6g	>95 (82) >95 (97)[d]
9	 5h	 6h	89 (80) >95 (97)[d]
10	 5i	 6i	>95 (70) >95 (98)[d]
11	 5j	 6j	83 (70)[c] >95 (98)[d]
12	 5k	 6k	38 (37) >95 (85)[d]
13	 5l	 6l	85 (71)[c]
14	 5m	 6m	21 (n.a.)
15	 5n	 6n	47 (41)[e]

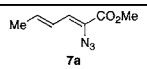
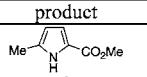
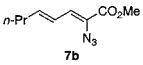
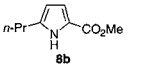
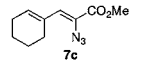
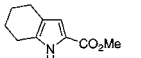
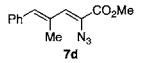
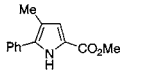
[a] As determined using ^{1}H NMR spectroscopy. [b] Isolated yield after flash chromatography over SiO_2. [c] ZnI_2 (10 mol %) employed. [d] $Rh_2(O_2CC_3F_7)_4$ (3 mol %) employed. [e] ZnI_2 (10 mol %), 40 °C.

the aryl substituents became more electron-deficient, the reaction progress diminished, and more forcing conditions were required (entries 8−12). For these substrates, rhodium(II) perfluorobutyrate was a superior catalyst. Some heteroaromatic substituents were also investigated (entries 13−15). While a naphthyl-substituted dienyl azide reacted well (entry 13), lower conversions and yields are obtained with furan or thiophene substituents (entries 14 and 15). In these cases, increasing the catalyst loading and reaction temperature only modestly improved the yield of the reaction.[25]

In addition to aryl-substituted dienyl azides, substrates containing alkyl substituents at the δ- or γ-position or different carbonyl functional groups were examined (Table 4).[24] While diminished yields were observed with methyl- and *n*-propyl-substituted dienyl azides (entries 1 and 2), these substrates were consumed in minutes—significantly faster than dienyl azides **5**. Dienyl azides with δ- and γ-substitution could be smoothly transformed into 2,4,5-trisubstituted pyrroles (entries 3−5) with faster conversions observed for substrates with δ-alkyl substituents (entries 3 and 4). Changing the nature of the carbonyl substituent also influenced the efficiency of the reaction (entries 6 and 7). While increasing the steric nature of the ester did not negatively affect reactivity (entry 6), ketone **7g** required more stringent conditions (entry 7). When diphenyl-substituted dienyl azide **7h** was subjected to reaction conditions, no pyrrole formation was observed (entry 8).[26]

Table 4. Scope of the Pyrrole Formation



entry	substrate	product	yield (%)
1	 7a	 8a	60[a] (59)[b] >95 (99)[c]
2	 7b	 8b	85 (72)
3	 7c	 8c	73 (71)
4	 7d	 8d	>95 (86)
5	7e	8e	94 (75)
6	7f	8f	93 (89)
7	7g	8g	43 (n.a.) 93 (72)[d]
8	7h	8h	0 (n.a.)

[a] As determined using ^{1}H NMR spectroscopy. [b] Isolated yield after flash chromatography over SiO_2. [c] SiO_2 (200 wt %) employed. [d] $Cu(OTf)_2$ (5 mol %) employed.

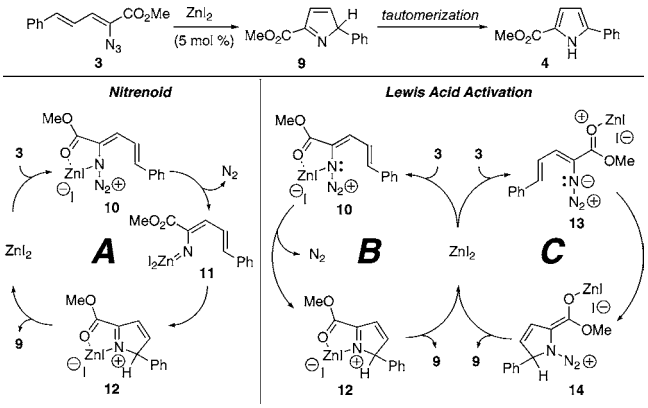
The ZnI_2-catalyzed reaction is sensitive to the isomeric purity of the substrate. When an *E*/*Z* mixture of **7a** (5:95)

(24) Several of the substances reported here were previously described. (a) **3**, **7h**: Geist B.; Knittel D. *Monatsh. Chem.* **1988**, *119*, 571. (b) **4**, **6m**, **8b**: Knight D. W.; Redfern A. L.; Gilmore J. *J. Chem. Soc., Perkin Trans. 1* **2001**, *21*, 2874. (c) **8a**: Yoshida, M.; Uchiyama, K.; Narasaka, K. *Heterocycles* **2000**, *52*, 681. (d) **8c**: May D. A.; Lash T. D., *J. Org. Chem.* **1992**, *57*, 4820. (e) **8d**: Lakhlifi, T.; Sedqui, A.; Fathi, T.; Laude, B.; Robert, J.-F. *Can. J. Chem.* **1994**, *72*, 1417. (f) **8g**: Pale-Grosdemange C.; Chuche, J. *Tetrahedron* **1989**, *45*, 3397.

(25) For the inhibition of zinc-catalyzed Lewis acid reactions by superstoichiometric amounts of Lewis basic solvents, see: Mayr, H.; Striepe, W. *J. Org. Chem.* **1985**, *50*, 2995.

(26) 1,2-Alkyl shifts were observed in the thermal nitrene variant of this reaction; see ref 11c.

Scheme 1. Possible Mechanisms for Pyrrole Formation



was subjected to the ZnI_2 conditions, only the *Z*-isomer reacted (Table 4, entry 1). While the yield of this transformation was moderate, we found that it could be increased if SiO_2 or trace acid[27] was employed. In contrast to zinc catalysis, both stereoisomers of **7a** were transformed into pyrrole **8a** when SiO_2 was employed.

Several mechanisms are possible for the transformation of dienyl azides into pyrroles. Thermal and photolytic reactions are believed to occur via nitrene insertion into the vinylic C−H bond.[11,26,28] In addition to nitrogen atom transfer through nitrenoid **11** (mechanism A),[29−31] Lewis acid activation mechanisms are also possible (Scheme 1).[13,14] In mechanism B, initial coordination of zinc to the azide (and ester) provides complex **10**.[32] Attack of the olefin expels N_2 to directly produce the C−N bond in **12** (without formation of nitrenoid **11**).[17,21] Loss of zinc iodide forms 2*H*-pyrrole **9**, which tautomerizes to 1*H*-pyrrole **4**. Alternatively, in mechanism C, coordination of zinc iodide[33,34] to the carbonyl increases the electrophilicity of the pendant olefin (**13**). Intramolecular attack of the azide would form **14**.[35] Loss of nitrogen, followed by tautomerization, would generate pyrrole **4**.

The reactivity trends of our substrates suggest that the reaction proceeds through the Schmidt-like mechanism B. We observed that, as the aryl-γ-substituent became more electron-deficient, the reactivity of the substrate was reduced. Increasing the electron-donating nature of the substrate through alkyl substitution at the δ- or γ-positions substantially increased the reaction rate.

In conclusion, we have developed a new, mild way to access di- and trisubstituted pyrroles from readily available azides. Presently, we are working to elucidate the relationship between the mechanism and transition metal catalyst and to apply our conclusions to develop new methods that form functionalized *N*-heterocycles from azides.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for the products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Concentration of NMR samples of dienyl azides (**7a**−**e**) in untreated $CDCl_3$ produced pyrroles (**8a**−**e**) quantitatively.

(28) For a study of the mechanism of the intramolecular C−H bond insertion of aryl nitrenes, see: Murata, S.; Tsubone, Y.; Kawai, R.; Eguchi, D.; Tomioka, H. *J. Phys. Org. Chem.* **2005**, *18*, 9.

(29) For recent reviews on the formation and reactivity of metal nitrenoids formed from the reaction of metal complexes and azides, see: (a) Katsuki, T. *Chem. Lett.* **2005**, *34*, 1304. (b) Cenini, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Fantauzzi, S.; Piangiolino, C. *Coord. Chem. Rev.* **2006**, *250*, 1234.

(30) We believe that rhodium-mediated indole formation from azidoacrylates occurs via a rhodium nitrenoid; see ref 16.

(31) For recent, related work on indole formation from azirines through nitrene insertion, see: (a) Taber, D. F.; Tian, W. *J. Am. Chem. Soc.* **2006**, *128*, 1058. (b) Chiba, S.; Hattori, G.; Narasaka, K. *Chem. Lett.* **2007**, *36*, 52.

(32) For leading mechanistic studies on the related Schmidt reaction, see: (a) Newman, M. S.; Gilderhorn, H. L. *J. Am. Chem. Soc.* **1948**, *70*, 317. (b) Bach, R. D.; Wolber, G. J. *J. Org. Chem.* **1982**, *47*, 239. (c) Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1867. (d) Kaye, P. T.; Mphahlele, M. J.; Brown, M. E. *J. Chem. Soc., Perkin Trans. 2* **1995**, 835.

(33) For examples where σ-O-coordination has enhanced the reactivity of Zn(II) salts, see: (a) ref 24. (b) Hayashi, E.; Takahashi, Y.; Itoh, H.; Yoneda, N. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3520.

(34) For related electrophilic azide cyclizations initiated by the activation of epoxides by oxophilic Lewis acids, see: (a) Reddy, P. G.; Varghese, B.; Baskaran, S. *Org. Lett.* **2003**, *5*, 583. (b) Gu, P.; Zhao, Y. M.; Tu, Y. Q.; Ma, Y.; Zhang, F. *Org. Lett.* **2006**, *8*, 5271.

(35) For recent examples of the conjugate addition of azides, see: (a) Couladouros, E. A.; Plyta, Z. F.; Haroutounian, S. A.; Papageorgiou, V. P. *J. Org. Chem.* **1997**, *62*, 6. (b) Lakshmipathi, P.; Rama Rao, A. V. *Tetrahedron Lett.* **1997**, *38*, 2551. (c) Guerin, D. J.; Horstmann, T. E.; Miller, S. J. *Org. Lett.* **1999**, *1*, 1107. (d) Xu, L.-W.; Xia, C.-G.; Li, J.-W.; Zhou, S.-L. *Synlett* **2003**, 2246. (e) Ref 21d.