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Synthesis of 2*H*-Indazoles via Lewis Acid Promoted Cyclization of 2-(Phenylazo)benzonitriles

Laura D. Shirtcliff, Jazmin Rivers, and Michael M. Haley*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253

haley@uoregon.edu

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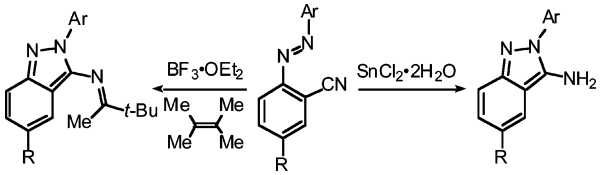
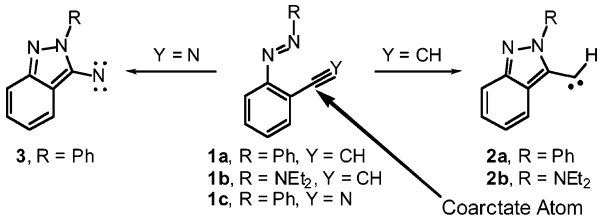


Lewis-acid promoted "coarctate" cyclization of 10 2-(phenylazo)benzonitrile derivatives furnishes the isoindazole ring system in ca. 65−95% yield. A plausible mechanism for this unusual transformation is proposed.

Our laboratory,[1] among others,[2] has been investigating compounds with a conjugated "ene-ene-yne" functionality for the formation of novel five- or six-membered benzo-fused heterocycles. The main body of our research has primarily exploited thermal or Cu-induced cyclization of conjugated azo-ene-yne moieties (**1a**,**b**, Scheme 1) to afford uniquely substituted or previously unknown isoindazoles[1a,b] or bis-isoindazoles.[1c] Typically, these heterocycles are prepared using strong acids in polar solvents to form a diazonium species susceptible to nucleophilic attack by an activated *ortho*-carbon nucleophile.[3] Such vigorous conditions in turn limit the functional group tolerance of these types of reactions. Our cyclizations, however, proceed under neutral conditions by coarctate[4]/pseudocoarctate[5] mechanistic pathways via isoindazolyl carbene intermediates

SCHEME 1. Cyclization of Conjugated "Ene-Ene-Yne" Moieties



2a,**b**. The respective carbenes can then be trapped through the usual carbene trapping methods, i.e., reaction with dioxygen,[6] O−H insertion,[1b] C−H insertion,[7] [2 + 1] cycloaddition with alkenes,[1b] etc. Our interest in isoindazoles not only stems from the unique methodology through which they are attained but also because of their increasing applicability in a variety of fields such as ligands for estrogen receptors,[8] as antiinflammatories,[9] as DNA intercalators for antitumor applications,[10] as chemotherapeutics,[11] and as liquid crystalline materials.[12]

Previous coarctate cyclizations from our laboratory all relied on an alkyne moiety as the triply bonded portion of the conjugated azo-ene-yne system. To fully explore the applicability of the cyclization methodology, we have investigated the effect upon reactivity that changing the C≡CH portion of the conjugated system to C≡N (**1c**) would have, and also have studied the potential for generating nitrene intermediates such as **3**. For clarity, coarctate (Latin for *compressed)* cyclizations are defined by the presence of a coarctate atom where two bonds are being made and two bonds are being broken and that bond making and breaking do not occur in a cyclic array, thus setting them apart from pericyclic reactions. In certain instances, a reaction may be considered not truly coarctate (i.e., pseudocoarctate) based upon the orthogonality of the interacting orbitals in a planar transition state. Previous reports[1b,c,7b] have explicitly outlined the difference between the two; therefore, the dichotomy between coarctate and pseudocoarctate and how it relates to this specific system will not be discussed herein.

Synthetic trials began with the preparation of cyclization precursor **5a**. Iodide **4a**,[1b] readily available in two synthetic steps, was subjected to nucleophilic aromatic substitution with excess CuCN in EtOH.[13] While complete consumption of **4a** required 40 h in refluxing EtOH, switching to higher boiling

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SCHEME 2. Synthesis of Compounds 5−7

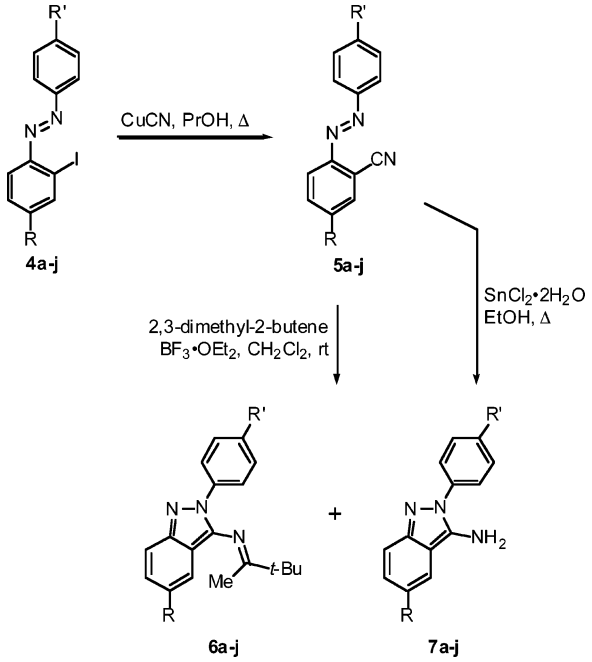

TABLE 1. Effect of Lewis Acid on the Yield of Isoindazole 6a

Lewis acid (equiv)	alkene[a] (equiv)	*T* (°C)	yield of **6a** (%)
CuCl (5)	5	200[b]	NR
$ZnCl_2$ (5)	5	200[b]	dec
$ZnCl_2$ (5)	15	80[b]	65
$ZnCl_2$ (10)	15	80[b]	71
$ZnCl_2$ (10)	15[c]	80[b]	75
$ZnCl_2$[d] (2)	2	80[b]	68
$ZnBr_2$ (10)	15	80[b]	26
$Zn(OTf)_2$ (10)	15	80[b]	NR
$AlCl_3$ (2)	15	rt[e]	57
$AlCl_3$ (2)	5	rt[e]	58
BF_3•OEt_2 (5)	10	rt[e]	83
BF_3•OEt_2 (10)	1	rt[e]	82
BF_3•OEt_2 (5)	2	rt[e]	71
BF_3•OEt_2 (5)	10[c]	rt[e]	94
BF_3•OEt_2 (5)	10	rt[f]	63

[a] 2,3-Dimethyl-1-butene. [b] 1,2-Dichloroethane as solvent. [c] 2,3-Dimethyl-2-butene. [d] Plus 2 mol % of $Rh_2(OAc)_4$. [e] CH_2Cl_2 as solvent. [f] Hexane as solvent.

PrOH afforded nitrile **5a** after 5 h in 98% isolated yield (Scheme 2). Precursor **5a** could be synthesized in multigram quantities with only filtration over a short pad of silica necessary to obtain the desired product in high purity.

Initial cyclization conditions utilized Cu salts as the nitrene stabilizer, analogous to our previous studies. Heating **5a** to 200 °C in the presence of excess CuCl and 2,3-dimethyl-1-butene, however, resulted in no reaction after 48 h. Metal salts that were more Lewis acidic were next explored as it was envisioned that these would facilitate attack at the electron-deficient nitrile carbon atom by the azo linkage. Of the metal salts examined (Table 1), $ZnCl_2$ provided the best results, with a 71% yield of isoindazole **6a** obtained when using 10 equiv of $ZnCl_2$ and 15 equiv of 2,3-dimethyl-1-butene in 1,2-dichloroethane (DCE) at 80 °C for 48 h. The isoindazole could also be synthesized in comparable yields using 2 equiv of $ZnCl_2$ along with catalytic $Rh_2(OAc)_4$ (2 mol %). It should be noted that although an aziridine, resulting from [2 + 1] cycloaddition of the presumed nitrene to the alkene, was the anticipated product, the major isolated product was isoindazole imine **6a** (confirmed by X-ray crystallography; see the Supporting Information). This result is not unsatisfactory as the imine moiety is quite versatile synthetically and can be utilized in additional synthetic steps to form other desirable functionalities.[14]

TABLE 2. Yield of Nitriles 5 and Isoindazoles 6 and 7 in Scheme 2[a]

entry	R	R′	**5**[b] (%)	**6**[c] (%)	**7**[c] (%)	**7**[d] (%)
a	*t*-Bu	H	98	94	NA[e]	87
b	CH_3	H	99	90	5	89
c	H	H	99	84	16	95
d	Cl	H	99	95	NA[e]	94
e	OMe	H	91	72	27	74
f	OMe	Br	99	79	9	76
g	OMe	F	98	70	25	79
h	OMe	CO_2Me	99	89	4	84
i	OMe	CN	92	63	30	94
j	OMe	NO_2	99	78	22	80

[a] Isolated yields. [b] CuCN reaction. [c] BF_3•OEt_2 reaction. [d] $SnCl_2$•H_2O reaction. [e] The amine was not isolated if imine yield was >90%.

Switching to stronger Lewis acids, $AlCl_3$ resulted in a decreased yield of 58%, but also a decrease in the reaction time to a few hours and a reaction temperature down to room temperature. Higher yields were obtained with BF_3•OEt_2 at rt. It should also be noted that complete consumption of **5a** required a minimum of 2 equiv of Lewis acid. If only 1.5 equiv was used, the reaction did not reach completion even after several days. Upon lowering the reaction temperature to ambient and thus suppressing the production of thermally derived degradation products, a second minor product was detected. Isoindazole amine **7** (Scheme 2), which was being formed in 5−30% yield depending on the conditions, can be rationalized as the result of two-electron reduction and addition of two protons (vide infra).

Changing from 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene afforded the highest yields of isoindazole using either $ZnCl_2$ (75%) or BF_3•OEt_2 (94%). Interestingly, the products obtained from either alkene were spectroscopically identical, namely **6a**. Monitored by ^1H NMR spectroscopy, facile isomerization from the less stable terminal alkene to the more stable internal alkene was proven by addition of BF_3•OEt_2 to a solution of 2,3-dimethyl-1-butene in $CDCl_3$ and was complete within 5 min at ambient temperature.

With exemplary yields obtained for the BF_3•OEt_2-promoted cyclization to imine **6a**, we next synthesized a variety of differently functionalized 2-(phenylazo)benzonitriles (Scheme 2). Starting from known iodides **4a**−**j**,[1b] an array of nitrile precursors (**5a**−**j**) was synthesized in yields ranging from 91 to 99% (Table 2). Utilizing the optimized conditions, all of the diazenes were successfully cyclized to the respective isoindazole imines **6a**−**j** in 63−95% isolated yield. In all cases, nearly quantitative isolation of two products was observed, with the remaining percentage of material attributed to 3-aminoisoindazoles **7b**−**j**, with more electroneutral diazenes having a higher ratio of imine:amine. It should be noted that dry solvents were

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crucial for obtaining the highest percentage of **6**, with more **7** being formed when trace amounts of water were present. Also, if LA addition preceded alkene addition, yields of the amine were higher. The cyclization of **5a** with several other alkenes (e.g., cyclopentene, stilbene, vinyl butyrate) was attempted for imine formation but with little success; only modest to low yields of the isoindazole amines were obtained. Based upon these results it appears that only electron-rich alkenes not prone to polymerization are active/stable enough to intercept the LA-stabilized nitrene.

To maximize amine **7**, we determined that $SnCl_2$ in refluxing EtOH effectively gave the 3-aminoisoindazole products in 74−95% yield (Table 2). As has proven typical among these cyclizations, the more electroneutral products tended to form in the highest yields. Although $SnCl_2$-promoted cyclization of 2-cyano-substituted diazenes has been previously reported,[15] the resulting isoindazoles were not completely characterized and only a very small number of diazenes were studied. In these cyclizations, $SnCl_2$ doubles as both Lewis acid and two-electron donor, easily toggling between the Sn(II) and Sn(IV) oxidation states. The anionic intermediates then abstract protons from the solvent media. Interestingly, in the quest to reduce azoarenes such as **5c** to the corresponding hydrazoarenes with Bu_3SnH, Zanardi et al. obtained, in addition to the desired hydrazo compounds, amines such as **7c** as low-yielding side products but did not comment upon their formation.[16]

To shed light on the possible mechanism, we monitored the reaction progress by IR spectroscopy. Lewis acid/base complexes of $HCN{\cdot}BF_3$,[17] $MeCN{\cdot}BF_3$,[17d,18] and $PhCN{\cdot}BF_3$[18c,19] among others[20] are stable at room temperature and have been extensively studied in both the solid state and gas phase, but considerably less so in solution.[18a,c,20f] In our case, however, cyclization appears to be quite facile, which precludes the identification or formation of a stable $RCN{\cdot}BF_3$ complex. Based upon the experimental and theoretical work on these types of systems, Lewis acid coordination most likely occurs to the nitrile N atom; however, it cannot be ruled out under the reaction conditions, i.e., excess BF_3, that there is no coordination to one or both of the N atoms in the azo linkage. Although $BF_3{\cdot}N_2$ complexes have been studied spectroscopically,[21] a literature search did not reveal precedence for these types of azo Lewis acid/base systems.

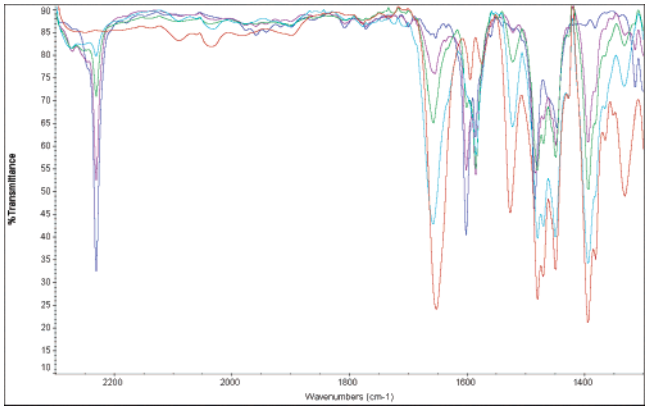

FIGURE 1. FT-IR spectrum of **5b** (dark blue) upon addition of 0.5 equiv of $BF_3{\cdot}OEt_2$ (purple), 1.5 equiv of $BF_3{\cdot}OEt_2$ (green), 2.0 equiv of $BF_3{\cdot}OEt_2$ (light blue), and **7b** with 1.5 equiv of $BF_3{\cdot}OEt_2$ (red).

We examined the cyclization spectroscopically in a qualitative manner. As $BF_3{\cdot}OEt_2$ (0.5 → 4.0 equiv) was added to **5b** in CH_2Cl_2, the sharp nitrile stretch at 2223 cm^{-1} disappeared with concomitant formation of a broader peak at 1652 cm^{-1}, along with distinct changes in the fine structure between the region of 1350−1600 cm^{-1} (Figure 1). The nascent peak was not present in the 3-aminoisoindazole product, although a stretch was present at 1632 cm^{-1}. When $BF_3{\cdot}OEt_2$ was added to a solution of purified isoindazole **7b** in CH_2Cl_2, the 1632 cm^{-1} band disappeared and the 1652 cm^{-1} stretch appeared, thus leading to the conclusion that BF_3 was coordinating to the product and therefore to the educt in a manner that facilitated cyclization. This IR stretch is attributed to the N−H bending mode, as the analogous 3-hydroxymethyl-5-methyl-2-phenyl-2*H*-indazole (replace $-NH_2$ in **7b** with $-CH_2OH$) does not contain a band at that frequency. The FT-IR spectra of **5b**, as increasing amounts of $BF_3{\cdot}OEt_2$ were added, became virtually identical to the **7b**·BF_3 system. In addition, what was attributed to aromatic C═C ring stretching at 1600 cm^{-1} decreased in intensity as BF_3 concentration increased.

Although the intermediacy of free nitrenes such as **3** is highly unlikely under the reaction conditions, the cyclization to generate the isoindazole skeleton nonetheless appears to proceed through what is formally a "coarctate" pathway. One possible mechanism is illustrated in Scheme 3 for the generation of **6**. Nitrile coordination to the LA facilitates attack of one of the diazene nitrogens on the electron deficient "coarctate carbon", furnishing stabilized isoindazolyl nitrene **8**, whether directly from **9** or via intermediate **10**. The LA-stabilized nitrene, which likely possesses appreciable nitrenium ion character, is intercepted by the electron-rich alkene affording zwitterionic species **11**. Facile 1,2-methyl shift on the alkyl chain then gives the imine double bond; subsequent decomplexation of the LA yields free imine **6**. As mentioned earlier, it is likely that a second equivalent of LA is complexed to the other diazene nitrogen during the cyclization, but this is by no means certain.

In conclusion, the coarctate/pseudocoarctate cyclization methodology has proven to be a useful means for successful preparation of the important 2*H*-indazole nucleus while tolerating a wide variety of functional groups under Lewis acidic and/or reducing conditions. The synthetic viability of the cyclization of the conjugated ene-ene-yne moiety has been expanded to

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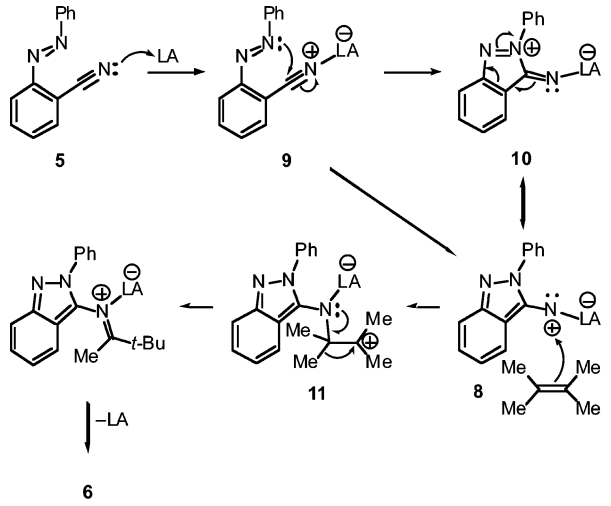
SCHEME 3. Proposed Mechanism for the Formation of Imine 6



include the nitrile functionality. Although the expected [2 + 1] cycloaddition to afford an aziridine was not observed, the reaction proceeded in a manner analogous to the previously reported cyclizations in very good to excellent overall yield with the resulting nitrogen-based functionality at the 3-position allowing for additional synthetic manipulation.

Experimental Section

General Procedure A. The (iodophenyl)diazene was dissolved in PrOH (0.1 M), and CuCN (7.0 equiv) was added to the solution. The reaction was heated to reflux until all starting material was consumed, as visualized by TLC (ca. 5−12 h). The mixture was diluted with CH_2Cl_2/hexanes (1:1), filtered over a short pad of silica, eluting with CH_2Cl_2/hexanes (1:1), and concentrated. If pure (iodophenyl)diazene was used, no additional product purification was typically necessary.

General Procedure B. The 2-(phenylazo)benzonitrile was dissolved in freshly distilled CH_2Cl_2 (0.1 M) followed by addition of alkene (10.0 equiv). $BF_3{\cdot}OEt_2$ (5.0 equiv) was then added and the reaction stirred at rt for 2−8 h. Upon completion, the solution was diluted with CH_2Cl_2/hexanes (1:1) and washed with brine (2×). The organic layer was dried ($MgSO_4$) and filtered over a short pad of silica to afford the isoindazole imine. The combined aqueous washes were basicified with 10% (w/w) NaOH and extracted with Et_2O/CH_2Cl_2 (3×). The combined organic layers were washed with brine (1×), dried ($MgSO_4$), filtered over a short pad of silica, and concentrated in vacuo to afford the isoindazole amine.

General Procedure C. The 2-(phenylazo)benzonitrile and $SnCl_2$ (5.0 equiv) were added to EtOH (0.1 M). The reaction was stirred under reflux until all starting material was consumed, as visualized by TLC (typically 4−24 h). Upon completion, the reaction was cooled to rt, diluted with CH_2Cl_2, and washed with water (7×) to remove excess Sn salts. The combined aqueous washes were neutralized by addition of aq $NaHCO_3$ or aq NH_4Cl and extracted with CH_2Cl_2 (2×). The combined organic layers were dried ($MgSO_4$), filtered over a short pad of silica (eluting with MeCN), and concentrated. Further purification via column chromatography was performed if necessary.

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Supporting Information Available: Synthetic details, spectral data, and copies of ^1H or ^{13}C NMR spectra for **5a**−**j**, **6a**−**j**, and **7a**−**j**; X-ray structure of **6j**, structure refinement details, tables of atomic coordinates, thermal parameters, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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