Bi(OTf)₃-CATALYZED INTRAMOLECULAR AMINATION OF TRIAZENYLARYL ALLYLIC ALCOHOLS: A STEREOSELECTIVE, HIGH-YIELD SYNTHESIS OF (E)-3-ALKENYL 2H-INDAZOLES

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GRAPHICAL ABSTRACT

Abstract An efficient Bi(OTf)₃-catalyzed synthesis of 3-alkenyl-2-pyrrolidine-2H-indazoles from triazenylaryl allylic alcohols via the intramolecular direct amination process is reported. Compared with the dodecyl benzenesulfonic acid (DBSA)-catalyzed method, the new method is more efficient and gives greater yields and functionality tolerance. Additionally, the 3-alkenyl-2-pyrrolidine-2H-indazoles can be transformed to a series of new products under different reaction conditions.

Keywords Alkenyl 2H-indazole; amination; bismuth triflate; triazenylaryl allylic alcohols

INTRODUCTION

Recently there has been a surge of renewed interest in the construction of indazoles, especially 2H-indazoles, because these compounds have been reported to have diverse applications[1] including antifungal agents,[2] anthelmintic agents,[3] estrogen receptor β ligands,[4] γ-secretase modulators,[5] and liver X receptor modulators.[6] Compared with the thermodynamically favored 1H-indazoles, 2H-indazoles

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are much less explored. Recently, we reported a dodecyl benzenesulfonic acid (DBSA)-catalyzed route to the efficient synthesis of trans-3-alkenyl 2H-indazoles from triazenylaryl allylic alcohols in water. A variety of triazenylaryl allylic alcohols were converted into the corresponding 2H-indazoles, but the substrates with the nonsubstituted benzyl alcohol and with Cl or Br on the aryl triazene motif are not adaptive (Scheme 1). Although various reaction conditions including increase of the DBSA concentration, extension of reaction time, and elevation of temperature were tested, the yield could not be improved. Thus, to overcome this problem a brand new and more compatible reaction system is needed.

Recently, with increasing environmental concerns, the need for more efficient, sustainable, and environmentally friendly organic synthesis has gained increased importance. Bismuth(III) salts, as typical green reagents and catalysts, have been widely applied to the synthesis of natural products or important pharmaceuticals. Catalytic quantities of Bi(III) compounds are effective in promoting different type of transformations including epoxide opening, Claisen rearrangement, protection/deprotection, Mannich-type reactions, Mukaiyama aldol reaction, and Diels–Alder reaction. Among them, bismuth-catalyzed direct substitution of alcohols has emerged as a desirable area of research because this approach does not need preactivation of the alcohols. Recent elegant examples include tandem ene-reaction/hydroamination of amino-olefin and amino-allene compounds with some enophiles, intramolecular alkynylocyclopropanation of olefins by Takaki and coworkers, benzylaition of arenes or 2,4-pentanediones, allylic alkylation of 2,4-pentanediones by Rueping, and bismuth-catalyzed direct amination of allylic, propargylic, and benzylic alcohols with amides by Shibasaki and coworkers. In addition, the intramolecular 1,3-chirality transfer reaction catalyzed by Bi(OTf)$_3$ for the formation of chiral 1-substituted tetrahydroisoquinolines from the corresponding chiral allylic alcohols was also developed. As a new approach to direct substitution of alcohols, herein we present a useful Bi(OTf)$_3$-catalyzed intramolecular amination strategy for the direct formation of 3-alkenyl-2-pyrrolidine-2H-indazoles from triazenylaryl allylic alcohols.

Scheme 1. DBSA-catalyzed amination and limitation.
RESULTS AND DISCUSSION

Initially, we treated the substrate 1a with BF₃·OEt₂ (5 mol%) in CH₂Cl₂, leading to the formation of the desired 2H-indazoles 2a in 64% yield (Table 1, entry 1). Upon treating the substrate 1a with CuBr (5 mol%) in CH₂Cl₂, the starting material was recovered in 95% yield and a trace of the desired 2H-indazole compound was obtained (entry 2). To our delight, further examination on InCl₃ and FeCl₃ resulted in improved yields of 71% and 74%, respectively (entries 3 and 4). Using BiCl₃ as the Lewis acid catalyst, the yield of the desired product 2a decreased to 13% (entry 5). When the reaction was carried out using Bi(OTf)₃ as the catalyst in CH₂Cl₂, the yield increased to 94%. Thus the best result was obtained when the reaction was carried out in CH₂Cl₂ at room temperature using Bi(OTf)₃ as the catalyst (entry 6).

With the optimized conditions in hand, a variety of triazenylaryl allylic alcohols 1 were examined, and the results are summarized in Table 2. Compared with catalyst DBSA, Bi(OTf)₃ gave greater yields in most cases, as indicated by the last two columns of Table 2. Particularly, the formerly inadaptable substrates 1c and 1d were successfully converted to the corresponding 2H-indazoles (Table 2, 66–68%, entries 2 and 3). The electron property at the aryl triazene moiety significantly influenced the outcome of the reaction: The yields of the 2H-indazoles increased sharply from trace to 95% as stronger electron-withdrawing groups (entries 1–4, Table 2) were directed to the aryl triazene motif. The electronic identity of the benzyl alcohol substituents also influenced the yield of the transformation: The yield surged to 90%, when using OCH₃ (entry 5) instead of H (entry 4) on the benzyl alcohol moiety for the substrates 1e and 1f. Substrates with electron-donating substituents such as CH₃ (90%, entry 12), OCH₃ (92–96%, entries 13 and 14), and dimethyl

Table 1. Optimization of the reaction conditions

| Entry | Cat. (mol%) | Yield (%) |
|-------|-------------|-----------|
| 1     | BF₃·OEt₂ (5)| 64        |
| 2     | CuBr (5)    | 4         |
| 3     | InCl₃ (5)   | 71        |
| 4     | FeCl₃ (5)   | 74        |
| 5     | BiCl₃ (5)   | 13        |
| 6     | Bi(OTf)₃ (5)| 94        |

*aAll reactions were carried out with 3-aryl triazenylaryl allylic alcohol 1a (0.5 mmol) and catalyst in DCM (2 mL) at room temperature for 12 h.

*bYield of the isolated product after flash column chromatography.
Table 2. Scope of synthesis of the functionalized 3-alkenyl-2-pyrrolidine-2H-indazoles from triazenylaryl allylic alcohol 1a

| Entry | Substrate | Product | Yield (%)<sup>a,b</sup> | Yield (%)<sup>c,d</sup> |
|-------|-----------|---------|--------------------------|--------------------------|
| 1     | 1b: R=CN  | 2b: R=CN | 95                       | 99                       |
| 2     | 1c: R=Cl  | 2c: R=Cl | 68                       | Trace                    |
| 3     | 1d: R=Br  | 2d: R=Br | 66                       | Trace                    |
| 4     | 1e: R=CH<sub>3</sub> | 2e: R=CH<sub>3</sub> | Trace | Trace |
| 5     | 1f: R=CH<sub>3</sub> | 2f: R=CH<sub>3</sub> | 90                       | 52                       |
| 6     | 1g: R=H   | 2g: R=H | 91                       | 78                       |
| 7     | 1h        | 2h      | 74                       | 79                       |
| 8     | 1i: R=F   | 2i: R=F | 85                       | 83                       |
| 9     | 1j: R=Cl  | 2j: R=Cl | 86                       | 77                       |
| 10    | 1k: R=Br  | 2k: R=Br | 90                       | 59                       |
| 11    | 1l: R=I   | 2l: R=I | 81                       | 57                       |
| 12    | 1m: R=CH<sub>3</sub> | 2m: R=CH<sub>3</sub> | 90                       | 92                       |
| 13    | 1n: R=OCH<sub>3</sub> | 2n: R=OCH<sub>3</sub> | 92                       | 95                       |
| 14    | 1o        | 2o      | 96                       | 83                       |
| 15    | 1p        | 2p      | 94                       | 79                       |

(Continued)
groups (94–99%, entries 15 and 16) on the benzyl alcohol moiety showed greater reactivity than electron-withdrawing ones (81–90%, entries 8–11) for the substrates 1i–q. All of these results suggest that enhancement of either the electron-withdrawing ability on triazene moiety or the electron-donating ability on the benzyl alcohol unit may facilitate the cyclization progress. Aromatic motifs including naphthyl and biphenyl groups and cyclopropyl group were successfully incorporated into the 3-alkenyl-2-pyrrolidine-2H-indazole products in 88–95% yield, as shown in the formation of the products 2r–t (entries 17–19).

Under the same conditions, the substrates 1-aryl triazene cinnamyl alcohols were further investigated. Upon treating the 1-aryl triazene cinnamyl alcohols 3 with

| Entry | Substrate | Product | Yield (%)<sup>a</sup> | Yield (%)<sup>b</sup> |
|-------|-----------|---------|----------------------|----------------------|
| 16    | 1q        | 2q      | 99                   | 99                   |
| 17    | 1r        | 2r      | 88                   | 84                   |
| 18    | 1s        | 2s      | 95                   | 98                   |
| 19    | 1t        | 2t      | 92                   | 92                   |

<sup>a</sup>Bi(OTf)<sub>3</sub>-catalyzed reaction: All reactions were carried out with triazenylaryl allylic alcohol 1 (0.5 mmol), and Bi(OTf)<sub>3</sub> (0.025 mmol, 5 mol%) in DCM (2 mL) at room temperature for 12 h.

<sup>b</sup>Yield of the isolated product of Bi(OTf)<sub>3</sub>-catalyzed reaction after flash column chromatography.

<sup>c</sup>DBSA-catalyzed reaction: All reactions were carried out with triazenylaryl allylic alcohol 1 (0.5 mmol) and DBSA (0.1 mmol, 20 mol%) in water (2 mL) at 35 °C for 24 h to 4 d.

<sup>d</sup>Yield of the isolated product of DBSA-catalyzed reaction after flash column chromatography from Ref. 7.
Bi(OTf)₃ in dichloromethane (DCM) for 12 h, substrates with ester, cyano, and naphthyl groups were all converted to the corresponding 3-alkenyl-2-pyrrolidine-2H-indazoles in good to excellent yields (Scheme 2).

On the basis of these mentioned results, a plausible reaction mechanism for this process is depicted in Scheme 3. The interaction between the hydroxy group of triazenearyl allylic alcohol \( \text{1} \) and the Lewis acid Bi(OTf)₃ led to the activation of the hydroxy and formed the intermediate cation \( \text{4/5} \), which lost HOBi(OTf)₂ to form allylic carbocation \( \text{6} \). Intramolecular nucleophilic attack of allylic carbocation \( \text{6} \) by nitrogen on the triazene motif provided the intermediate cation \( \text{7} \), which underwent deprotonation to generate the product 3-alkenyl-2-pyrrolidine-2H-indazole \( \text{2} \).

The 3-alkenyl-2-pyrrolidine-2H-indazole \( \text{2a} \) can be converted to various products under different reaction conditions (Scheme 4). Upon cleavage of pyrrolidine from 3-alkenyl-2-pyrrolidine-2H-indazole \( \text{2a} \) with Zn in CH₃COOH, 3-alkenyl-1H-indazole \( \text{8a} \) was obtained in 75% yield. By treating pyrrolidine-substituted 2H-indazole \( \text{2a} \) with Pd/C-H₂ in EtOH at room temperature, the alkene reduction product \( \text{8b} \) was formed in 99% yield. Further cleavage pyrrolidine from \( \text{8b} \) with Zn/CH₃COOH led to the 1H-indazole \( \text{8e} \) in 91% yield. Selective oxidation can also be achieved by switching oxidants. When KMnO₄ was used, the 3-alkenyl-2-pyrrolidine-2H-indazole \( \text{2a} \) could be oxidized to 3-formyl-2-pyrrolidine-2H-indazole (\( \text{8d} \)) in 60% yield, while dihydroxylation product \( \text{8e} \) was obtained in 90% yield with OsO₄ and 4-methylmorpholine N-oxide.

In conclusion, a convenient and facile protocol for the synthesis of 3-alkenyl-2-pyrrolidine-2H-indazoles from 3-aryl triazene allylic alcohols via the
intramolecular direct amination process using Bi(OTf)₃ catalysis in DCM has been developed. Additionally, the 3-alkenyl-2-pyrrolidine-2H-indazoles can be further transformed to a series of new products under different reaction conditions.

Scheme 3. Plausible reaction mechanism for this reaction.

Scheme 4. Transformations of the 3-alkenyl-2-pyrrolidine-2H-indazole 2a.
Further investigations of the reaction mechanism and synthetic applications are under way.

**EXPERIMENTAL**

**Typical Procedure for the Synthesis of 3-Alkenyl-2-pyrrolidine-2H-indazoles 2 from Triazenylaryl Allylic Alcohols 1**

Bi(OTf)₃ (17 mg, 0.025 mmol) was added to a solution of triazenylaryl allylic alcohol 1 (0.5 mmol) in DCM (2 mL). The reaction mixture was stirred at room temperature for 12 h. Ethyl acetate and water were added, and the resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na₂SO₄, concentrated in vacuo, and purified by silica-gel chromatography to provide the 3-alkenyl-2-pyrrolidine-2H-indazoles 2.

**Representative Analytical Data**

**(E)-5-Chloro-2-(pyrrolidin-1-yl)-3-styryl-2H-indazole (2c).** R₆= 0.44 (10:1 petroleum ether/EtOAc); mp = 128–130°C; ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, J = 1.2 Hz, 1 H), 7.64–7.59 (m, 3 H), 7.56 (d, J = 17.2 Hz, 1 H), 7.45–7.23 (m, 5 H), 3.51–3.38 (m, 4 H), 2.15–2.02 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 144.2, 137.0, 131.6, 131.0, 128.8, 128.2, 127.6, 127.5, 126.6, 119.6, 119.1, 115.5, 55.2, 23.1; IR (ATR-FTIR): 1942, 1394, 1211, 1110, 956, 805, 685 cm⁻¹; MS (EI): m/z (%): 325 (M⁺, Cl³⁻, 18), 323 (M⁺, Cl³⁻, 45), 253 (100), 218 (75), 189 (58), 163 (12), 91 (14), 70 (40). HRMS (EI-TOF) calcd. for C₁₉H₁₈ClN₃(M⁺): 323.1189; found: 323.1187.

**(E)-5-Bromo-2-(pyrrolidin-1-yl)-3-styryl-2H-indazole (2d).** R₆= 0.45 (10:1 petroleum ether/EtOAc); mp = 134–136°C; ¹H NMR (400 MHz, CDCl₃): δ 8.10 (s, 1 H), 7.60 (d, J = 7.2 Hz, 2 H), 7.58–7.50 (m, 2 H), 7.50–7.23 (m, 5 H), 3.55–3.33 (m, 4 H), 2.15–2.00 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃): δ 144.2, 137.0, 131.4, 131.1, 129.7, 128.8, 128.2, 126.6, 122.9, 119.3, 118.8, 115.4, 55.2, 23.1; IR (ATR-FTIR): 1206, 1106, 948, 807, 739, 681 cm⁻¹; MS (EI): m/z (%): 369 (M⁺, Br⁸⁻, 6), 367 (M⁺, Br⁷⁻, 6), 300 (100), 218 (45), 189 (49), 70 (10). HRMS (EI-TOF) calcd. for C₁₉H₁₈BrN₃(M⁺): 367.0684; found: 367.0681.

**(E)-Ethyl 3-(2-Cyclopropylvinyl)-2-(pyrrolidin-1-yl)-2H-indazole-5-carboxylate (2t).** R₆= 0.60 (5:1 petroleum ether/EtOAc); mp = 72–74°C; ¹H NMR (400 MHz, CDCl₃): δ 8.55 (s, 1 H), 7.89 (dd, J = 9.2, 1.2 Hz, 1 H), 7.58 (d, J = 9.2 Hz, 1 H), 6.97 (d, J = 16.4 Hz, 1 H), 6.22 (dd, J = 16.0, 1.2 Hz, 1 H), 4.39 (q, J = 7.1 Hz, 2 H), 3.49–3.30 (m, 4 H), 2.14–1.96 (m, 4 H), 1.76–1.61 (m, 1 H), 1.40 (t, J = 7.2 Hz, 3 H), 0.97–0.92 (m, 2 H), 0.69–0.65 (m, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 147.2, 140.3, 134.4, 125.9, 125.3, 123.2, 116.81, 116.77, 114.6, 60.7, 54.9, 23.1, 15.7, 14.4, 8.1; IR (ATR-FTIR): 1698, 1277, 1230, 950, 771 cm⁻¹; MS (EI): m/z (%): 325 (M⁺, 18), 280 (10), 256 (100), 241 (86), 227 (50), 213 (45), 183 (45), 168 (30), 153 (29), 70 (84). HRMS (EI-TOF) calcd. for C₁₉H₂₃N₃O₂ (M⁺): 325.1790; found: 325.1790.
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SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher’s website.

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Bi(OTf)3-CATALYZED SYNTHESIS OF 2H-INDAZOLES

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