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SYNTHESIS OF 2-(3′BROMO-3′-PHENYLALLYL)INDOLES VIA $ZnBr_2$-MEDIATED ADDITION OF BROMOMETHYLINDOLES/ INDOLYLMETHYLACETATES WITH PHENYLACETYLENE

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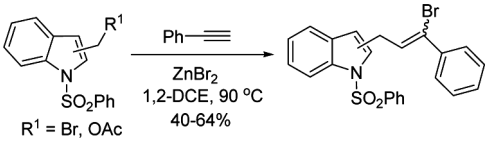
GRAPHICAL ABSTRACT



Abstract *An efficient synthesis of 2-(3′-bromo-3′-phenylallyl)indoles has been developed via direct carbon–carbon bond formation between bromomethylindoles/indolylmethylacetates and phenylacetylene.*

Keywords Allylindoles; bromomethylindole; coupling reaction; indolylmethylacetate

INTRODUCTION

In past decades, Lewis acid–promoted C-C bond-formation reactions by addition of carbenium ions to alkenes have been extensively explored.[1] However, compared with alkenes, the use of alkynes as electron-rich substrates to be attacked by carbenium ions seems limited. Recently, iron-catalyzed reactions have been explored for carbon–carbon couplings.[2] Kabalka et al. have synthesized stereo-defined alkenyl halides using direct C-C bond formation of benzyl alcohols.[3] In organic synthetic reactions, the scope and applications of alkenyl and aryl halides have increased tremendously, because they can be easily converted into other valuable compounds. Moreover, halides play an important role in organic synthesis for C-C and C-N bond formation by coupling using transition-metal catalysts.[4] Particularly, alkenyl halides are very useful substrates in a variety of chemical transformations.[5] Traditionally, vinyl halides are prepared from the corresponding carbonyl

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compounds with halogenated reagents,[6] under reflux or by Wittig[7] and Julia[8] olefination reactions and other related reactions.[9] Kropp et al.[10] reported the synthesis of alkenyl halides by the addition of hydrogen halide and alkyl halides to alkynes in the presence of an excess amount of $ZnCl_2$. Very recently Liu et al.[11] and Jana et al.[12] reported an efficient and mild iron-mediated synthesis of alkenyl halides via direct C-C bond formation of benzyl alcohols and aryl alkynes.

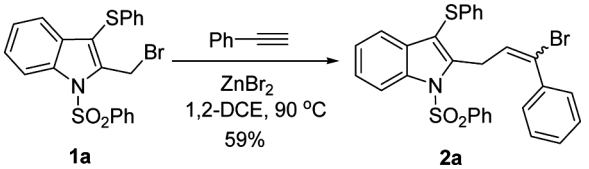
RESULTS AND DISCUSSION

In continuation of our work on studies related to the synthetic elaboration of *N*-protected bromomethylindoles,[13] we herein report a simple and efficient method for the preparation of phenylallylindoles by means of coupling of bromomethylindoles or indolylmethylacetates with phenylacetylene in the presence of $ZnBr_2$. Easy availability of various types of bromomethylindoles prompted us to explore allylation of these compounds using phenylacetylene. Initially, the reaction of 2-(bromomethyl)-3-(phenylthio)-1-(phenylsulfonyl)-1*H*-indole **1a** with phenylacetylene using 0.2 eq. of $ZnBr_2$ in dry 1,2-dichloroethane at reflux for 12 h afforded the expected allylbromo compound **2a** as a mixture of ***E*** and ***Z*** (3:1) isomers in 59% yield (Scheme 1).

A list of various types of bromomethylindoles **1a–f** employed for zinc bromide–mediated phenylallylation with phenylacetylene, the respective allylindoles **2a–f**, and the yields obtained are summarized in Table 1.

3-Phenylthio-2-methylacetate **1a′** underwent a facile phenylallylation reaction with phenylacetylene to afford the respective allyl indole **2a** in comparatively lesser yield as a mixture of ***E*** and ***Z*** isomers (entry 1). Similarly, the interaction of 3-bromo-2-bromomethyl/methylacetate indole **1b**/**1b′** with phenylacetylene furnished the respective allylbromo compound **2b** in moderate yield as an isomeric mixture (entry 2). Surprisingly, when the same reaction was performed with **1b** in the presence of K_2CO_3, a single isomer of allylbromo compound **2b″** was obtained in good yield (entry 3). The isomeric bromo compound **1c** gave the corresponding allylindole **2c** in 57% yield as an isomeric mixture (entry 4).

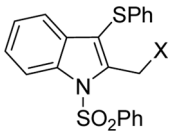
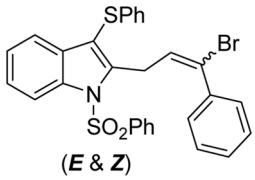
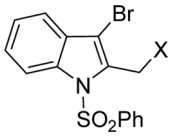
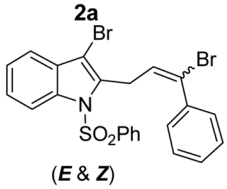
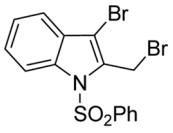
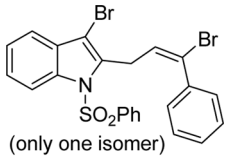
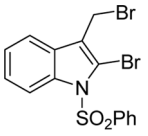
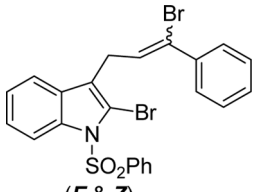
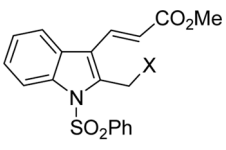
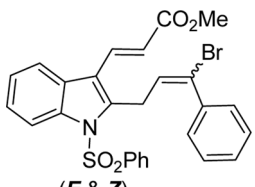
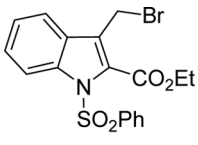
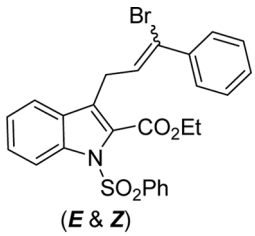
The reaction of 3-vinylester-2-bromomethylindole/indolylmethylacetate **1d**/**1d′** with phenylacetylene gave the bromo compound **2d** as ***E*** and ***Z*** isomers (entry 5). Interaction of phenylacetylene with 3-bromomethylindole **1e** led to the respective allyl compound **2e** in 51% yield (entry 6). It should be mentioned that the yields of the allylated products **2a**/**2b**/**2d** obtained from the corresponding bromo compounds **1a**/**1b**/**1d** are always better than the yields obtained from the respective methyl acetates **1a′**/**1b′**/**1d′.** Surprisingly, the isomeric bromo compound **1f** upon reaction with phenyl acetylene did not give the expected allylindole, but instead the cyclized product **2f**



1a **2a**

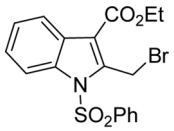
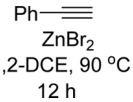
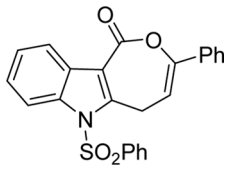
Scheme 1. Preparation of allyl indole **2a**.

Table 1. Synthesis of 3-bromo-3-phenylallylindoles

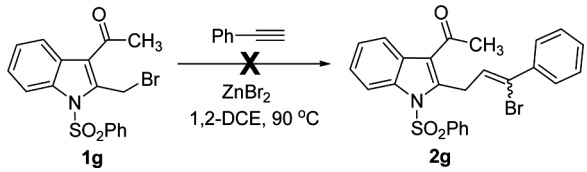
Entry	Substrate	Condition	Allyl indole	Yield (%)[a]
1	 X = Br, OAc **1a, a'**	Ph—≡ $ZnBr_2$ 1,2-DCE, 90 °C 12 h	 (***E*** & ***Z***) **2a**	59 (3:1) 51 (2:1)
2	 X = Br, OAc **1b, b'**	Ph—≡ $ZnBr_2$ 1,2-DCE, 90 °C 12 h	 (***E*** & ***Z***) **2b**	64 (5:1) 57 (2:1)
3	 **1b**	Ph—≡ $ZnBr_2$ / K_2CO_3 1,2-DCE, 90 °C 12 h	 (only one isomer) **2b''**	61
4	 **1c**	Ph—≡ $ZnBr_2$ 1,2-DCE, 90 °C 12 h	 (***E*** & ***Z***) **2c**	57 (4:1)
5	 X = Br, OAc **1d, d'**	Ph—≡ $ZnBr_2$ 1,2-DCE, 90 °C 12 h	 (***E*** & ***Z***) **2d**	54 (5:1) 40 (2:1)
6	 **1e**	Ph—≡ $ZnBr_2$ 1,2-DCE, 90 °C 12 h	 (***E*** & ***Z***) **2e**	51 (3:1)

(*Continued*)

Table 1. Continued

Entry	Substrate	Condition	Allyl indole	Yield (%)[a]
7	 **1f**		 **2f**	50

[a]Isolated yield of the E/Z mixture; the E/Z ratios were determined using ^{1}H NMR.



Scheme 2. Attempted preparation of allylindole **2g**.

was isolated in 50% yield (entry 7). Obviously, the bromo compound **1f** underwent a smooth alkenylation reaction with phenylacetylene followed by intramolecular cyclization involving an elimination of ethyl bromide to afford the seven-member lactone **2f**. Finally, an attempt to form the corresponding allylindole **2g** with indolylbromo compound **1g** having ketone functionality at the indole-3-position was unsuccessful; the starting material was always recovered unchanged (Scheme 2).

In conclusion, we have achieved an efficient synthesis of 2-(3′-bromo-3′-phenylallyl)indoles via direct C-C bond formation of bromomethylindoles/indolylmethyl acetates and phenylacetylene using catalytic amount of $ZnBr_2$. Further studies to explore the synthetic utility of this reaction as well as allyindoles are in progress in our laboratory.

EXPERIMENTAL

All melting points were uncorrected. Reagents were purchased from commercial sources and used as received without purification. Solvents were dried by standard procedures. Column chromatography was carried out on silica gel (grade 60, mesh size 230–400, Merck). Infrared (IR) spectra were recorded on a Shimadzu Fourier transform (FT)–IR 8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard on a Bruker-300 spectrometer. Chemical shift values were quoted in parts per million (ppm), and coupling constants were quoted in hertz (Hz). Chemical shift multiplicities were reported as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were recorded on a Jeol DX 303 HF spectrometer. Elemental analyses were carried out on Perkin-Elmer series II 2400 (IIT Madras) equipment. The required bromomethylindoles **1a**–**h** were prepared from the corresponding 2/3-methyl-*N*-phenylsulfonylindoles following the published procedure.[14]

Representative Procedure for the Phenylallylation of Bromomethyl Indoles 1a–f

A mixture of substrate **1a–f** (1.09 mmol), $ZnBr_2$ (0.21 mmol), and phenylacetylene (1.3 mmol) in dry 1,2-dichloroethane (10 mL) were refluxed under a nitrogen atmosphere for 12 h. It was then poured into crushed ice (100 g) containing few drops of concentrated HCl and extracted with $CHCl_3$ (2×20 mL). The combined extracts were washed with water (10 mL) and dried (Na_2SO_4). Removal of solvent followed by column chromatographic purification (silica gel, EtOAc-hexane 1:5) afforded the allylated indoles **2a–f**.

2-(3-Bromo-3-phenylallyl)-1-(phenylsulfonyl)-3-(phenylthio)-1*H*-indole (2a)

Yield: 0.36 g (59%). IR (KBr): 1351 & 1176 (SO_2Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.19 (d, $J = 8.4$ Hz, 1 H), 7.69 (d, $J = 7.5$ Hz, 2 H), 7.58 (d, $J = 7.8$ Hz, 1 H), 7.43–7.37 (m, 2 H), 7.31–7.24 (m, 4 H), 7.18–7.12 (m, 3 H), 7.01–6.94 (m, 3 H), 6.86–6.83 (m, 2 H), 6.69 (d, $J = 6.9$ Hz, 1 H), 6.14 (t, $J = 6.9$ Hz, 1 H), 4.23 (d, $J = 6$ Hz, 1 H), 3.92 (d, $J = 6.9$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 143.1, 142.9, 139.3, 138.6, 138.5, 138.3, 136.9, 136.8, 136.4, 136.2, 134.1, 130.8, 130.6, 129.8, 129.4, 129.1, 129.0, 128.9, 128.6, 128.5, 128.2, 128.1, 128.0, 127.7, 127.5, 127.0, 126.7, 126.6, 126.5, 126.4, 126.2, 126.0, 125.6, 125.5, 125.4, 124.5 (2C), 122.4, 120.1, 120.0, 115.2 (2C), 112.9, 112.3, 31.0, 28.8. MS (EI) m/z: 582 & 584 [$M^+ + Na$]. Anal. calcd. for $C_{29}H_{22}BrNO_2S_2$: C, 62.14; H, 3.96; N, 2.50; S, 11.44%. Found: C, 62.39; H, 3.65; N, 2.76; S, 11.16%.

3-Bromo-2-(3-bromo-3-phenylallyl)-1-(phenylsulfonyl)-1*H*-indole (2b)

Yield: 0.79 g (64%). Mp: 86–88 °C. IR (KBr): 1360 & 1172 (SO_2Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.12 (dd, $J = 8.4$ Hz, $J = 8.4$ Hz, 1 H), 7.66 (d, $J = 8.1$ Hz, 1 H), 7.55 (d, $J = 8.1$ Hz, 1 H), 7.40–7.17 (m, 11 H), 6.23–6.16 (m, 1 H), 4.10 (d, $J = 6.0$ Hz, 1 H) 3.78 (d, $J = 6.9$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 138.2, 137.5, 137.4, 137.3, 135.0, 134.9, 133.9, 133.6, 133.0, 128.3 (2C), 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.2, 127.1, 126.5, 126.3, 125.3 (2C), 124.8, 123.4, 123.3, 121.4, 118.6, 118.5, 114.0, 113.9, 102.2, 102.0, 30.1, 27.9. MS (EI) m/z: 553 & 555 [$M^+ + Na$]. Anal. calcd. for $C_{23}H_{17}Br_2NO_2S$: C, 52.00; H, 3.23; N, 2.64; S, 6.04%. Found: C, 51.71; H, 3.50; N, 2.39; S, 6.35%.

3-Bromo-2-(3-bromo-3-phenylallyl)-1-(phenylsulfonyl)-1*H*-indole (2b″)

Yield: 0.75 g (61%). Mp: 124–126 °C. IR (KBr): 1360 & 1172 (SO_2Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.18 (d, $J = 8.7$ Hz, 1 H), 7.65 (d, $J = 8.1$ Hz, 2 H), 7.54–7.49 (m, 4 H), 7.46–7.34 (m, 5 H), 7.32–7.27 (m, 2 H), 6.30 (t, $J = 6.9$ Hz, 1 H), 3.87 (d, $J = 6.6$ Hz, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 138.4, 135.9, 134.6, 134.0, 129.2, 128.9, 128.7, 128.2, 127.6, 127.3, 125.8, 124.4, 122.4, 119.6, 115.0, 103.1, 31.1, 29.0. MS (EI) m/z: 553 & 555 [M^++Na]. Anal. calcd. for

$C_{23}H_{17}Br_2NO_2S$: C, 52.00; H, 3.23; N, 2.64; S, 6.04%. Found: C, 51.72; H, 3.50; N, 2.38; S, 6.35%.

2-Bromo-3-(3-bromo-3-phenylallyl)-1-(phenylsulfonyl)-1*H*-indole (2c)

Yield: 0.35 g (57%). Mp: 112–114 °C. IR (KBr): 1362 & 1176 (SO_2Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.26 (d, $J = 7.5$ Hz, 1 H), 7.83 (d, $J = 7.5$ Hz, 2 H), 7.51 (d, $J = 7.5$ Hz, 1 H), 7.42–7.11 (m, 10 H), 6.14 (t, $J = 7.35$ Hz, 1 H), 3.43 (d, $J = 7.5$ Hz, 1 H) 3.36 (d, $J = 7.5$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 138.2 (2C), 138.1, 137.4, 136.7, 134.1, 133.9, 132.4, 130.9, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 127.6, 127.4, 127.1, 127.0, 126.4, 125.5, 125.2, 124.1, 124.0, 122.9, 122.6, 122.1, 118.9, 118.5, 115.4, 109.3, 109.2, 27.1, 26.1. MS (EI) m/z: 553 & 555 [$M^+ + Na$]. Anal. calcd. for $C_{23}H_{17}Br_2NO_2S$: C, 52.00; H, 3.23; N, 2.64; S, 6.04%. Found: C, 51.70; H, 3.51; N, 2.39; S, 6.33%.

(2*E*)-Methyl 3-(2-(3-Bromo-3-phenylallyl)-1-(phenylsulfonyl)-1*H*-indol-3-yl)acrylate (2d)

Yield: 0.67 g (54%). IR (KBr): 1700 (CO_2Me), 1363 & 1172 (SO_2Ph) cm^{-1}. ^1H-NMR ($CDCl_3$, 300 MHz): δ 8.22 (d, $J = 7.8$ Hz, 1 H), 7.91 (d, $J = 16.2$ Hz, 1 H), 7.72 (d, $J = 7.5$ Hz, 3 H), 7.48–7.18 (m, 10 H), 6.46 (d, $J = 16.2$ Hz, 1 H), 6.22 (t, $J = 6.1$ Hz, 1 H), 4.18 (d, $J = 6$ Hz, 2 H), 3.73 (s, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 167.5, 139.9, 139.1, 138.7, 137.0, 135.4, 134.1, 129.5, 128.7, 128.2, 127.6, 127.5, 127.4, 126.5, 126.4, 125.4, 124.5, 120.2, 119.4, 117.5, 115.1, 51.7, 30.2. MS (EI) m/z: 558 & 560 [$M^+ + Na$]. Anal. calcd. for $C_{27}H_{22}BrNO_4S$: C, 60.45; H, 4.13; N, 2.61; S, 5.98%. Found: C, 60.72; H, 3.87; N, 2.92; S, 5.74%.

Ethyl 3-(3-Bromo-3-phenylallyl)-1-(phenylsulfonyl)-1*H*-indole-2-carboxylate (2e)

Yield: 0.56 g (51%). IR (KBr): 1710 (CO_2Me), 1372 & 1186 (SO_2Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.95–7.91 (m, 1 H), 7.84–7.78 (m, 2 H), 7.54–7.40 (m, 3 H), 7.37–7.31 (m, 5 H), 7.22–7.17 (m, 3 H), 6.16–6.12 (m, 1 H), 4.40–4.29 (m, 2 H), 3.78 (d, $J = 6.6$ Hz, 1 H), 3.44 (d, $J = 7.5$ Hz, 1 H), 1.35–1.25 (m, 3 H). ^{13}C NMR ($CDCl_3$, 75 MHz): 162.2, 162.1, 139.3, 138.1, 137.6, 137.4, 137.0, 136.9, 133.8 (2C), 130.1, 129.6, 129.3, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2 (2C), 128.1, 127.6, 127.2 (2C), 127.1, 127.0, 126.9, 126.5, 125.9, 125.7, 124.3, 124.2, 124.1, 122.1, 120.9, 120.5, 120.4, 115.5 (2C), 62.3, 28.3, 26.1, 14.1, 14.0. MS (EI) m/z: 546 & 548 [$M^+ + Na$]. Anal. calcd. for $C_{26}H_{22}BrNO_4S$: C, 59.55; H, 4.23; N, 2.67; S, 6.11%. Found: C, 59.27; H, 4.49; N, 2.37; S, 6.42%.

(*Z*)-6-phenylsulfonyl-3-phenyl-5*H*-oxepino[4,3,-*b*]indol-1(6*H*)-one (2f)

Yield: 0.56 g (51%). Mp: 214–216 °C. IR (KBr): 1661 (C=O), 1180 (C-O), 1378 & 1170 (SO_2Ph) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.15 (d, $J = 8.7$ Hz, 1 H), 8.02 (d, $J = 9$ Hz, 1 H), 7.75 (d, $J = 8.1$ Hz, 2 H), 7.56–7.50 (m, 3 H), 7.40 (t, $J = 7.8$ Hz, 2 H), 7.31–7.24 (m, 5 H), 6.01 (t, $J = 7.0$ Hz, 1 H), 4.08 (d, $J = 6.9$ Hz, 2 H). ^{13}C

NMR ($CDCl_3$, 75 MHz): 160.3, 151.9, 145.8, 137.3, 134.6, 133.7, 132.8, 128.7, 128.0, 127.5, 126.6, 125.3, 124.7, 124.1, 120.2, 113.5, 110.1, 106.8, 28.6, 21.0. MS (EI) m/z: 438 [$M^+ + Na$]. Anal. calcd. for $C_{24}H_{17}NO_4S$: C, 69.38; H, 4.12; N, 3.37; S, 7.72%. Found: C, 69.65; H, 3.86; N, 3.67; S, 7.47%.

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