Rapid access to 1-methyleneindenes *via* palladium-catalyzed tandem reactions of 1-(2,2-dibromovinyl)-2-alkynylbenzenes with arylboronic acids†‡

Shengqing Ye,[a] Xiaodi Yang[c] and Jie Wu*[ab]

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A novel and efficient route for the synthesis of 1-methyleneindenes *via* palladium-catalyzed tandem reactions of 1-(2,2-dibromovinyl)-2-alkynylbenzene with arylboronic acids is described. This reaction proceeded under mild conditions with high efficiency and excellent selectivity.

It is well recognized that compounds with an indene core are found abundantly in many drug candidates with remarkable biological activities.[1] The function of indene-related compounds has been discovered in the field of materials science as well.[2] In addition, metallocene complexes with an indene core structure have been utilized in olefin polymerization as catalysts.[3] Thus, a significant effort continues to be given to the development of new indene-based structures and new approaches for their construction.[4–7] Among the family of indenes, 1-methyleneindenes have attracted much attention recently since they can be easily transferred to functionalized indenes. Although several methods have appeared for the formation of 1-methyleneindene derivatives,[8] development of novel and efficient routes for the generation of functionalized 1-methyleneindenes under mild conditions is still of high interest.

[a] *Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China. E-mail: jie_wu@fudan.edu.cn; Fax: 86 21 6564 1740; Tel: 86 21 6510 2412*
[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China*
[c] *Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai 200433, China*

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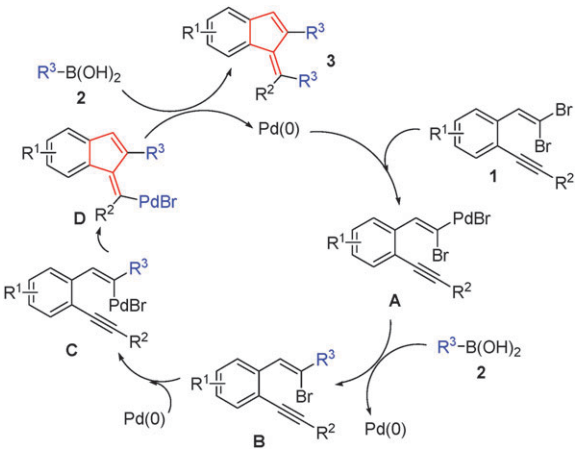
‡ General procedure for palladium-catalyzed tandem reaction of 1-(2,2-dibromovinyl)-2-alkynylbenzene **1** with arylboronic acid **2**: 1-(2,2-Dibromovinyl)-2-alkynylbenzene **1** (0.2 mmol, 1 equiv.) was added to a solution of $Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), $K_3PO_4 \cdot H_2O$ (1.2 mmol, 6 equiv.) and arylboronic acid **2** (0.6 mmol, 3 equiv.) in THF (2.0 mL). The solution was then stirred at room temperature. After completion of reaction as indicated by TLC, the reaction was quenched with water (5.0 mL), extracted with EtOAc (2 × 10 mL), dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel provided the product **3**. Data of selected example: Compound **3a**. Yield: 86%; red solid, melting point: 177–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 3H), 2.18 (s, 3H), 6.35 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 7.8 Hz, 2H), 6.72 (d, J = 7.8 Hz, 2H), 6.76–6.80 (m, 3H), 6.87 (d, J = 7.8 Hz, 2H), 6.89 (s, 1H), 7.09 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.38–7.46 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.0, 120.4, 123.3, 124.5, 126.9, 127.5, 127.8, 128.5, 128.7, 130.9, 132.3, 133.1, 134.8, 135.2, 136.9, 137.9, 138.2, 138.5, 142.2, 143.0, 144.0, 149.5; HRMS (ESI) calc. for $C_{30}H_{25}$ $(M + H)^+$ 385.1956, found 385.1938. Anal. Calc. for $C_{30}H_{24}$: C, 93.71; H, 6.29; Found: C, 93.65; H, 6.42%.

Recently, we have witnessed the important progress of using *gem*-dihaloolefins as electrophiles in metal-catalyzed reactions.[9] These *gem*-dihaloolefins can be easily accessible from an aldehyde (or activated ketone) using CBr_4/PPh_3[10] or the ylide CCl_2PPh_3.[11] So far, polysubstituted alkenes,[12] enynes,[13] polyynes,[14] carboxamide,[15] and carbo- or heterocycles[16,17] could be obtained starting from *gem*-dihaloolefins. Usually, good stereoselectivity could be observed for stepwise functionalization of *gem*-dihaloolefin systems[12,18] and less attention has been paid to potentially more efficient tandem reactions.[19] Recently, tandem carbon–carbon bond and carbon–heteroatom bond formation was reported for the reaction of *gem*-dihaloolefins.[16,17] For instance, Lautens and co-workers described several efficient routes for indole synthesis *via* a transition metal-catalyzed C–N/C–N or C–N/C–C coupling sequence from *gem*-dihaloolefins.[17] Meanwhile, we have developed efficient routes for construction of nitrogen-containing heterocycles starting from 2-alkynylbenzaldoxime or *N*′-(2-alkynylbenzylidene)hydrazide.[20] Prompted by these results and the advancement of *gem*-dihaloolefin chemistry, we conceived that 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1** might be a versatile building block for further transformations due to the structural similarity. Herein, we would like to disclose its useful application, namely reaction with arylboronic acids under mild conditions giving rise to the 1-methyleneindenes in good to excellent yields. This reaction proceeded with high efficiency and excellent selectivity.

1-(2,2-Dibromovinyl)-2-alkynylbenzene could be easily accessed *via* condensation of 2-alkynylbenzaldehyde with carbon tetrabromide. As mentioned above, 1-(2,2-dibromovinyl)-benzene has been found in several applications for the synthesis of *N*-heterocycles.[16,17] Since the two vinyl bromides would undergo cascade coupling reactions, we anticipated that the presence of a coupling partner such as arylboronic acid in the reaction of 1-(2,2-dibromovinyl)-2-alkynylbenzene, could provide access to functionalized 1-methyleneindenes after subsequent reaction processes (Scheme 1). We reasoned that after oxidative addition of Pd(0) to 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1**, the subsequent transmetallation of arylboronic acid and reductive elimination would occur to generate intermediate **B**, with the release of Pd(0). The presence of Pd(0) would react with vinyl bromide **B** by oxidative addition, leading to the intermediate **C**. Intramolecular insertion of Pd(II) to the alkynyl group gave rise to the intermediate **D**, which then reacted with arylboronic acid *via* transmetallation. Subsequently reductive elimination occurred to give rise to the desired product **3** and Pd(0), which

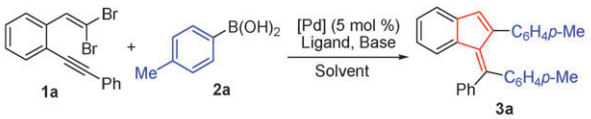


Scheme 1 Proposed route for the palladium-catalyzed tandem reactions of 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1** with arylboronic acids **2**.

would re-enter the catalytic cycle. However, there are several questions associated with the proposed synthetic route, such as selectivity, compatibility, and relative rates. Thus, to verify the practicability of the projected route as shown in Scheme 1, we started to explore the possibility of this palladium-catalyzed reaction of 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1** with arylboronic acids **2**.

To identify suitable conditions for this proposed transformation, we first evaluated the tandem reaction of 1-(2,2-dibromovinyl)-2-alkynylbenzene **1a** with 4-methylphenylboronic acid **2a** (Scheme 2). Different conditions including palladium catalysts, phosphine ligands, bases, and solvents using a combinatorial approach were screened. At the outset, the reaction catalyzed by $Pd(OAc)_2$ (5 mol%) was carried out in the presence of $K_3PO_4{\cdot}H_2O$ (6.0 equiv.) and PPh_3 (20 mol%) in toluene at room temperature. However, only a trace amount of product was detected. Similar results were obtained when the solvent was changed to CH_3CN or DMAc. To our delight, we observed the formation of a product when 1,4-dioxane was utilized as a replacement, with 65% isolated yield. Further screening of solvents led to the identification of THF as the most effective condition for the transformation (86% yield). Structural identification using ^1H and ^{13}C NMR, MS and X-ray diffraction analysis (see ESI†) revealed that the compound obtained was the 1-methyleneindene **3a**. Subsequent reaction optimization of palladium catalysts revealed that $Pd(OAc)_2$ was the best choice. Decreasing the amount of palladium catalyst diminished the product yield (65%). Other phosphine ligands and bases were screened as well, however, no better results were observed (for details see ESI†). In the transformation, 3.0 equiv. of arylboronic acid is essential in order to obtain a respectable yield of product **3a**. Only vinyl bromide **B** was generated when 1.0 equiv. of arylboronic acid was employed in the reaction.

Using the palladium-catalyzed conditions ($Pd(OAc)_2$ (5 mol%), PPh_3 (20 mol%), $K_3PO_4{\cdot}H_2O$ (6.0 equiv.), THF, rt), 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1** reacted with various arylboronic acids **2** to generate a number of 1-methyleneindenes **3** in good to excellent yields (Table 1). When 1-(2,2-dibromovinyl)-2-alkynylbenzene **1a** was employed as



[Pd] catalyst: $Pd(OAc)_2$, $Pd(PPh_3)_4$, $PdCl_2$, $Pd_2(dba)_3$, $PdCl_2(PPh_3)_2$, $PdCl_2$(dppf)

Ligand: PPh_3, BINAP, PCy_3, DPPF, DPPP, JohnPhos, XPhos, CyJohnPhos, $(2\text{-furyl})_3P$, $P(o\text{-tolyl})_3$, S-Phos, Xantphos

Base: K_3PO_4, $K_3PO_4{\bullet}H_2O$, K_2CO_3, Cs_2CO_3, $NaHCO_3$, KOH, LiOH, NaOAc, *t*-BuOK

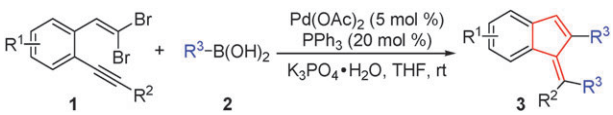
Solvent: toluene, MeCN, DMAc, 1,4-dioxane, THF, DCE, DMF

Scheme 2 Initial studies for palladium-catalyzed reaction of 1-(2,2-dibromovinyl)-2-alkynylbenzene **1a** with 4-methylphenylboronic acid **2a**.

the substrate, this palladium-catalyzed 1-methyleneindene formation was found to be workable with arylboronic acids **2a–2g** with electron-withdrawing and -donating substituents on the aromatic backbone (Table 1, entries 1–7). For example, reaction of substrate **1a** with 4-methoxyphenylboronic acid **2b** afforded the desired product **3b** in 75% yield (entry 2). Other arylboronic acids bearing trifluoromethyl, cyano, carbonyl and nitro functional groups were all tolerated under the reaction conditions (entries 4–7). In addition to the aromatic groups attached to the C≡C triple bond, alkyl groups such as *n*-butyl were found suitable as well to generate the desired product **3h** cleanly in good yield (62% yield, entry 8). Furthermore, the conditions have proven to be useful for other substrates. For instance, fluoro- or methoxy-substituted 1-(2,2-dibromovinyl)-2-alkynylbenzene **1c** or **1d** reacted with arylboronic acids leading to the expected products in good yields (entries 9–13).

In conclusion, we have described a novel and efficient route for the synthesis of 1-methyleneindenes *via* palladium-catalyzed tandem reactions of 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1** with arylboronic acids **2**. This reaction proceeded under mild conditions with high efficiency and excellent selectivity. Further studies by adaptation of the method described herein for the synthesis of functionalized indenes

Table 1 Palladium-catalyzed tandem reactions of 1-(2,2-dibromovinyl)-2-alkynylbenzenes **1** with arylboronic acids **2**



Entry	R^1, R^2	R^3	Yield[a] (%)
1	H, Ph (**1a**)	4-MeC_6H_4 (**2a**)	86 (**3a**)
2	H, Ph (**1a**)	4-$MeOC_6H_4$ (**2b**)	75 (**3b**)
3	H, Ph (**1a**)	C_6H_5 (**2c**)	80 (**3c**)
4	H, Ph (**1a**)	4-$CF_3C_6H_4$ (**2d**)	70 (**3d**)
5	H, Ph (**1a**)	4-NCC_6H_4 (**2e**)	72 (**3e**)
6	H, Ph (**1a**)	4-$MeO_2CC_6H_4$ (**2f**)	74 (**3f**)
7	H, Ph (**1a**)	3-$NO_2C_6H_4$ (**2g**)	88 (**3g**)
8	H, *n*-Bu (**1b**)	C_6H_5 (**2c**)	62 (**3h**)
9	4-F, Ph (**1c**)	C_6H_5 (**2c**)	82 (**3i**)
10	4-F, Ph (**1c**)	4-NCC_6H_4 (**2e**)	74 (**3j**)
11	4-F, Ph (**1c**)	4-$MeO_2CC_6H_4$ (**2f**)	75 (**3k**)
12	4,5-$(OMe)_2$, Ph (**1d**)	C_6H_5 (**2c**)	95 (**3l**)
13	4,5-$(OMe)_2$, Ph (**1d**)	4-$MeO_2CC_6H_4$ (**2f**)	72 (**3m**)

[a] Isolated yield based on 1-(2,2-dibromovinyl)-2-alkynylbenzene **1**.

are currently in progress, and the results will be reported in due course.

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