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One-step synthesis of (1-iodovinyl) arenes from trimethylsilyl ethynylarene through iodotrimethylsilane-mediated hydroiodation

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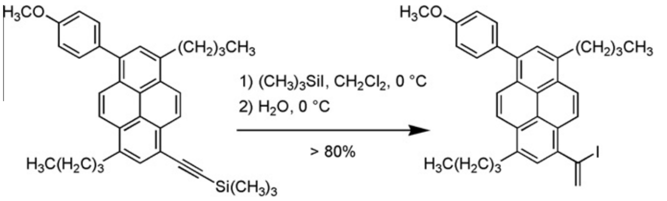
One-step access to (1-iodovinyl) arenes from trimethylsilyl ethynylarenes is described. The method is superior to a conventional multi-step approach, and is enhanced by the Sonogashira reaction that provides ready access to a variety of trimethylsilyl ethynylarenes.

Vinyl halides are important building blocks in organic synthesis.[1] They are readily converted into various functional groups by halogen–metal exchange and are significant for carbon–carbon bond forming reactions by way of transition-metal catalyzed cross-coupling reactions.[2–4] α-Vinyl iodides are especially important[5]; the sterically unhindered terminal-olefin and weakly bonded iodine are highly reactive and incredibly useful toward the synthesized complex molecules.[6] Despite the utility of α-vinyl iodides, their synthetic availability still remains a challenge, because of the inherent difficulty in hydroiodation.[7] The stoichiometric addition of hydrogen iodide (HI) to terminal alkynes is one way to prepare α-vinyl iodides; however, the generation and transfer of hygroscopic and gaseous HI are inconvenient and difficult to perform.[8–10] As an alternative hydrometalation exists, although it requires several reaction steps.[11]

The pioneering work for synthesis of α-vinyl iodides from alkynes via addition of HI was reported by Ishii and co-workers: HI was generated in situ from mixing of chlorotrimethylsilane, sodium iodide, and water in acetonitrile.[12] And continuous efforts have aimed to refine this initial method.[13] More recently, Ogawa and co-workers developed a novel hydroiodation of alkynes using an iodine/hydrophosphine binary system.[14] However, there is still room for improvement, especially in terms of its scale;[15] the system worked using 0.2 mmol of starting alkynes.

Recently we have developed the synthesis of unsymmetrically functionalized pyrene derivatives.[16] In the course of our study, we encountered the unforeseen reaction (Eq. 1). Although we intended the demethylation of the ethereal methyl group, instead α-vinyl iodide was isolated in high yield. We immediately began exploring the scope and utility of this transformation. Herein we report a simple synthesis of (1-iodovinyl)arenes from both ethynylarenes as well as trimethylsilyl ethynylarenes (Scheme 1). Commercially available TMSI was useful for the direct transformation of both of these functional groups into styrene-type α-vinyl iodide units in high yield and in one step. Our synthetic protocol does not require operations for desilylation, which is superior to the conventional step-by-step approach.[6,11,14] To the best of our knowledge, so far such a direct synthesis has not been reported. In addition, the protocol is enhanced by Sonogashira reaction that readily makes trimethylsilyl ethynylarenes from aryl halides.[17] Thus, it provides a rapid access to (1-iodovinyl) arenes.



(1)

The hydroiodation of 1-ethynyl-4-methylbenzene (**1**) is examined in Table 1.[18,19] TMSI was employed as a 1 M CH_2Cl_2 solution, utilization of neat TMSI was not successful.[20] To the mixture of the alkyne (1 mmol) and TMSI (1.2 equiv) was added H_2O (20 equiv) at

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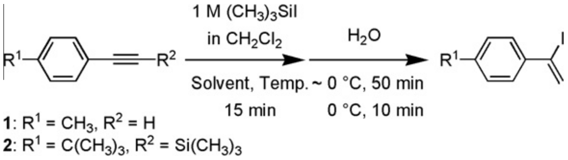


Scheme 1. Synthesis of (1-iodovinyl)arenes from **1** and **2**.

low temperature, the reaction was allowed to warm to 0 °C.[21] Entry 1 illustrates a high yielding transformation when the reaction was carried out at −78 °C. The resulting 1-(1-iodovinyl)-4-methylbenzene was isolated in 88% yield and the Markovnikov addition product's structure was confirmed by ^1H NMR. Over the course of the reaction the starting alkyne completely disappeared in TLC monitoring, additionally the corresponding isomer of β-vinyl iodide was not observed. For entries 2–4, the reaction at −45 °C gave a comparable 87% yield, but decreased at −20 °C and 0 °C.[22] The concentration of the reaction was increased in entries 5 (3.3 mL CH_2Cl_2) and 6 (1 mL) and gave comparable yields to entry 1 (8 mL). For entry 7, use of CH_3OH instead of H_2O resulted in only 20% yield. For entry 8, addition of H_2O (20 equiv) to the solvent in advance gave 70% yield. Other solvents were explored in entries 9–13, the hydroiodation in toluene and hexane properly occurred with 81% and 71% yields, respectively. On the other hand, methanol, acetonitrile, and THF were not successful giving multi-spots on TLC monitoring. In marked contrast to the pioneering work,[12,23] it is presumed that the non-polar and non-coordinated solvents are best for this transformation.

Next, we examined the reaction of ((4-*tert*-butylphenyl)ethynyl)trimethylsilane (**2**) with TMSI to give α-vinyl iodides (Table 2). Alkyne **2** was prepared via Sonogashira reaction. For entries 1–5, the equivalent of TMSI was varied, 1.5 equiv proved appropriate to consume all of **2** and to achieve a high yielding transformation (entry 3). For entry 2, unreacted alkyne was recovered in 3% when 1.2 equiv TMSI was used. For entries 6–8, the elevated temperatures to −45, −20, and 0 °C were not successful. Other solvents were explored in entries 9–11, toluene, hexane, and acetonitrile gave 74%, 70%, and 30%, respectively. Thus, the optimum conditions in Table 2 are close to those in Table 1.

Table 3 illustrates different trialkylsilyl patterns tested. Like trimethylsilyl ethynylarene, triethyl-, and triisopropylsilyl substrates underwent α-vinyl iodation, yet the yields decreased in 80% and 54% (entries 2 and 3); presumably due to the sterically hindered alkyl groups for desilylation process. For entries 2 and 3, unreacted alkynes were recovered in 13% and 45%, and the prolonged reaction time did not increase the yields.

Preliminary mechanistic investigations were performed through deuteration experiments. Deuterioiodation of **1** was carried out with D_2O, and the deuterium was incorporated under several conditions (Table 4). In each case the major product was (*E*)-adduct[5b] (entries 1–3). For entry 4, when D_2O was added in advance, a similar selectivity to entry 1 was observed. As a matter of form, deuterium and iodine add to the alkyne with anti-selectivity. Interestingly, this result is the opposite selectivity to Ishii's pioneering work which reported that DI adds to alkynes with complete syn-selectivity.[12] Sub-

Table 1
Evaluation of the reactivity of **1** conducted via Scheme 1[a]

Entry	Solvent	Temp. (°C)	Yield[b] (%)
1	CH_2Cl_2	−78	88
2	CH_2Cl_2	−45	87
3	CH_2Cl_2	−20	74
4	CH_2Cl_2	0	49
5[c]	CH_2Cl_2	−78	82
6[d]	CH_2Cl_2	−78	74
7[e]	CH_2Cl_2	−78	20
8	CH_2Cl_2/H_2O (4% v/v)	−78	70
9	Toluene	−78	81
10	Hexane	−78	71
11	CH_3CN	−20	24
12	CH_3OH	−78	0
13	THF	−78	0

[a] Reaction conditions: alkyne **1** (1 mmol), solvent (8 mL), 1 M $(CH_3)_3SiI$ in CH_2Cl_2 (1.2 mmol), H_2O (20 mmol). All reactions were performed in accordance with the representative procedure in Ref.[21], unless otherwise stated.
[b] Purified yields after silica gel column chromatography (hexane containing 5% v/v triethylamine).
[c] 3.3 mL of CH_2Cl_2 as a solvent was used.
[d] 1.0 mL of CH_2Cl_2 as a solvent was used.
[e] CH_3OH was added instead of H_2O.

Table 2
Evaluation of the reactivity of **2** via Scheme 1[a]

Entry	Solvent	$(CH_3)_3SiI$ (equiv)	Temp. (°C)	Yield (%)
1	CH_2Cl_2	1.0	−78	58
2[b]	CH_2Cl_2	1.2	−78	88
3	CH_2Cl_2	1.5	−78	88
4	CH_2Cl_2	2.0	−78	64
5	CH_2Cl_2	4.0	−78	60
6	CH_2Cl_2	1.5	−45	66
7	CH_2Cl_2	1.5	−20	63
8	CH_2Cl_2	1.5	0	58
9	Toluene	1.5	−78	74
10	Hexane	1.5	−78	70
11	CH_3CN	1.5	−20	30

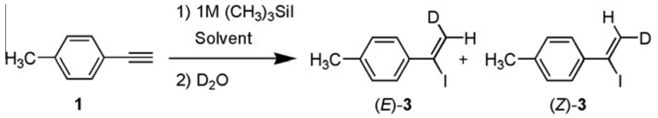
[a] Reaction conditions: alkyne **2** (1 mmol), solvent (8 mL), 1 M $(CH_3)_3SiI$ in CH_2Cl_2, H_2O (20 mmol).
[b] The starting alkyne was recovered in 3%.

Table 3
Effect of the trialkylsilyl groups on the hydroiodation of 2[a]

Entry	R	Yield (%)	Recovered alkyne (%)
1	CH_3	88	0
2	CH_2CH_3	80	13
3[b]	$CH(CH_3)_2$	54	45

[a] Reaction conditions: alkyne (1 mmol), CH_2Cl_2 (8 mL), 1 M $(CH_3)_3SiI$ in CH_2Cl_2 (1.5 mmol), H_2O (20 mmol).
[b] Prolonged reaction time did not increase the yield.

Table 4
Deuterioiodation of 1[a]



Entry	Solvent	Yield[b] (%)		% *D*[b]
		(*E*)-**3**	(*Z*)-**3**	
1	CH_2Cl_2	59	23	87
2	Toluene	62	16	80
3	Hexane	71	2	89
4	CH_2Cl_2/H_2O (4% v/v)	53	12	86

[a] Reaction conditions: alkyne 1 (1 mmol), CH_2Cl_2 as a solvent (8 mL), 1 M $(CH_3)_3SiI$ in CH_2Cl_2 (1.2 mmol), D_2O (20 mmol).
[b] Determined by ^1H NMR in Ref.[12,5b]