An Alternative Synthesis of Alkynyl(phenyl)iodonium Triflates Using (Diacetoxyiodo)benzene and Alkynylsilanes

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Abstract: Phenyl(trimethylsilylethynyl)iodonium triflate (1a) was prepared in high yields (76–88%) by using the PhI(OAc)₂/TfOH or PhI(OAc)₂/Tf₂O reagent systems. This procedure was also applied to the preparation of other alkynyliodonium triflates 1.

Key words: trimethylsilylethynyliodonium triflate, alkynyliodonium triflates, (diacetoxyiodo)benzene, alkynylsilanes, triflic anhydride

Alkynyl(phenyl)iodonium triflates **1** have been recently recognized as versatile compounds in organic synthesis.¹ They act as Michael acceptors, as synthons for alkynyl cations, and as 1,3-dipolarophiles. When alkynyliodonium triflates **1** are reacted with nucleophiles, alkylidenecarbenes are generated as the reactive intermediates and generally undergo 1,5-C–H insertion to give cyclopentene derivatives or 1,2-migration to alkynes. In particular, phenyl(trimethylsilylethynyl)iodonium triflate (**1a**) is expected to have high utility in organic synthesis concerning useful silicon chemistry.² Recently, Bachi et al. have reported the application to the synthesis of functionalized alkynyl- β -lactams.³



Alkynyl(phenyl)iodonium salts have been prepared, so far, from terminal alkynes, alkynylsilanes, and alkynylstannanes. In these preparations, various hypervalent iodine reagents have been used, for example, (dichloroiodo)benzene (PhICl₂),⁴ iodosylbenzene (PhIO),⁵ [hydroxy(tosyloxy)iodo]benzene [Koser's salt, PhI(OH)-OTs],⁶ μ -oxobis[(phenyl)(trifluoromethylsulfonyloxy)iodine] (Zefirov's reagent, PhI(OTf)OI(OTf)Ph],⁷ and [(cyano)(trifluoromethylsulfonyloxy)iodo]benzene [Stang's reagent, PhI(CN)OTf].⁸

Alkynyl(phenyl)iodonium triflates **1** have been prepared by reaction with Zefirov's and Stang's reagents. These reagents are very useful for this purpose, but the preparation of these reagents requires some special precautions because of their instability. (Diacetoxyiodo)benzene, PhI(OAc)₂, is the most stable hypervalent iodine reagent and is commercially available. The use of PhI(OAc)₂ in the preparation of alkynyliodonium triflates **1** is synthetically preferable and convenient. Previously we have found that a hypervalent iodine reagent prepared from PhI(OAc)₂ and triflic acid (TfOH) is highly reactive toward aromatic compounds and is useful for the preparation of diaryliodonium triflates (eq 1).⁹ Thus, we examined the application of the PhI(OAc)₂/TfOH reagent system to the preparation of alkynyliodonium triflates **1**.

The PhI(OAc)₂/TfOH reagent system was prepared by the reaction of PhI(OAc)₂ with TfOH. When a suspension of PhI(OAc)₂ in CH₂Cl₂ was treated with double the molar amount of TfOH, it turned to a clear yellow solution indicating the formation of reactive iodine species. To the solution were added alkynylsilanes at 0 °C and the corresponding alkynyl(phenyl)iodonium triflates **1** were obtained as crystals after evaporation of the solvent and successive crystallization (eq 2). In the case of bis(trimethylsilyl)acetylene, alkynyliodonium triflate **1a** was obtained in high yield (76%) (Table, entry 1) but the reaction of trimethyl(phenylethynyl)silane gave alkynyliodonium triflate **1b** in 40% yield (Table, entry 2).

	PhI(OAc) 2/TfOH (1:2)		
R —C \equiv C —SiMe ₃	CH ₂ CI ₂ , 0 °C	R —C ≡C —I⁺Ph OTf ⁻	(2)
R = Me ₃ Si, Ph		1 a:R=Me ₃Si b:R=Ph	

Next, PhI(OAc)₂ was treated with triflic anhydride (Tf₂O) to make a mild reagent system. We reported that self-condensation occurs on the reaction of PhIO with double the molar quantity of TfOH to give PhI(OH)C₆H₄I(OH)OTf.¹⁰ On the other hand, self-condensation was suppressed by the use of Tf₂O. The reaction of PhIO with half the molar amount of Tf₂O leads to the formation of Zefirov's reagent, PhI(OTf)OI(OTf)Ph.¹¹ These results mean that TfOH activates an iodine reagent more strongly than Tf₂O. This consideration suggests that the replacement of TfOH by Tf₂O leads to the formation of a relatively mild iodine reagent system, PhI(OAc)₂/Tf₂O.

Thus, we conducted the reaction using Tf_2O instead of TfOH. PhI(OAc)₂ was treated with half the molar quantity of Tf₂O at 0 °C in CH₂Cl₂ and reacted with alkynyl(trimethyl)silanes. After evaporation and crystallization, alkynyl(phenyl)iodonium triflates **1** were obtained as crystals (eq 3). The results are given in the Table (entries 3–6). As seen from the Table, the preparation of alkynyliodonium triflate **1a** has been improved by using the PhI(OAc)₂/Tf₂O reagent system. This simple procedure was also applied to the preparation of alkynyliodonium triflates **1b–d**.

$$R - C \equiv C - SiMe_{3} \xrightarrow{Ph(OAc)_{2}/Tf_{2}O(1:0.5)} R - C \equiv C - I^{*}Ph OTf^{-} (3)$$

$$R = Me_{3}Si, Ph, \ 'Bu, \ ''Bu \qquad 1 \ a: R = Me_{3}Si \\ b: R = Ph \\ c: R = \ 'Bu \\ d: R = \ ''Bu$$

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Table. Preparation of Alkynyl(phenyl)iodonium Triflates 1

Entry	Alkynylsilane	Reagent System	Product	Yield (%)
1 2 3 4 5 6	$\label{eq:measurements} \begin{array}{l} Me_3SiC = CSiMe_3\\ PhC = CSiMe_3\\ Me_3SiC = CSiMe_3\\ PhC = CSiMe_3\\ {}^{t}BuC = CSiMe_3\\ {}^{n}BuC = CSiMe_3 \end{array}$	PhI(OAc) ₂ /TfOH PhI(OAc) ₂ /TfOH PhI(OAc) ₂ /Tf ₂ O PhI(OAc) ₂ /Tf ₂ O PhI(OAc) ₂ /Tf ₂ O PhI(OAc) ₂ /Tf ₂ O PhI(OAc) ₂ /Tf ₂ O	1a 1b 1a 1b 1c 1d	76 40 88 56 41 43

In the reaction with the PhI(OAc)₂/Tf₂O reagent system, we assume that a reactive species, such as PhI⁺OAc, is generated and reacts with alkynylsilanes to give alkynyliodonium triflates **1**. When the PhI(OAc)₂/Tf₂O reagent system was treated with hex-1-yne in order to confirm the reactive species, phenyl[2-(trifluoromethylsulfonyloxy)-hex-1-enyl]iodonium triflate (**2**)¹² was obtained in 61% yield (eq 4). This reaction suggests that the reactive species generated in the present reagent system is different from Zefirov's reagent which affords an oxo-bridged product **3** in the reaction with hex-1-yne.¹²



In summary, we have found a simple one-pot synthesis of alkynyliodonium triflates which uses $PhI(OAc)_2$, a stable and commercially available reagent. This method is especially useful for the preparation of trimethylethynyliodonium triflate **1a** which has potential synthetic utility.

Phenyl(trimethylsilylethynyl)iodonium Triflate (1a); Typical Procedure Using the PhI(OAc)₂/TfOH Reagent System:

To a stirred suspension of PhI(OAc)₂ (10.63 g, 33 mmol) in CH₂Cl₂ (50 mL) was added TfOH (5.4 mL, 60 mmol) dropwise at 0°C and the mixture was stirred for 30 min. During this time, the mixture became a clear yellow solution. To the resulting reagent was added bis(trimethylsilyl)acetylene (5.11 g, 30 mmol) at 0°C and the mixture was stirred for 2 h. After evaporation of the solvent, Et₂O was added to crystallize the product. The crystals were collected, washed with Et₂O, and dried in vacuo to give **1a**; yield: 10.33 g (76%); mp 143–146°C (Lit.⁷ mp 138–139°C).

¹H NMR (300 MHz, CDCl₃): δ = 0.22 (s, Me, 9 H), 7.49–7.54 (m, ArH, 2 H), 7.62–7.68 (m, ArH, 1 H), 8.06 (d, *J* = 8.7 Hz, ArH, 2 H). ¹³C NMR (75 Hz, DMSO-*d*₆): δ = -0.96, 53.09, 113.25, 118.62, 132.00, 132.41, 134.72.

$\label{eq:phenyl} Phenyl(trimethylsilylethynyl) iodonium Triflate~(1a); Typical Procedure Using the PhI(OAc)_2/Tf_2O Reagent System:$

To a stirred suspension of PhI(OAc)₂ (16.10 g, 50 mmol) in CH₂Cl₂ (50 mL) was added Tf₂O (4.2 mL, 25 mmol) dropwise at 0°C and the mixture was stirred for 30 min. To the resulting yellow solution of the

reagent was added bis(trimethylsilyl)acetylene (8.60 g, 50 mmol) at 0°C and the mixture was stirred for 2 h. After the same workup of the mixture, **1a** was obtained; yield: 15.57 g (88%). Other alky-nyl(phenyl)iodonium triflates **1b–d**⁷ were obtained in a similar manner.

Phenyl[2-(trifluoromethylsulfonyloxy)hex-1-enyl]iodonium Triflate (2); Reaction of Hex-1-yne with the $PhI(OAc)_2/Tf_2O$ Reagent System:

To a stirred suspension of PhI(OAc)₂ (0.652 g, 2.0 mmol) in CH₂Cl₂ (5 mL) was added Tf₂O (0.282 g, 1.0 mmol) dropwise at 0 °C. After stirring for 30 min, hex-1-yne (0.196 g, 2.0 mmol) was added and the mixture was stirred for 2 h. After evaporation of the solvent, Et₂O was added to crystallize the product. The crystals were collected, washed with Et₂O, and dried in vacuo to give **2**; yield: 0.713 g (61%); mp 124–128 °C (Lit.¹² mp 125–128 °C).

¹H NMR (300 MHz, CDCl₃): δ = 0.91 (t, *J* = 7 Hz, Me, 3 H), 1.30–1.42 (m, CH₂, 2 H), 1.47–1.57 (m, CH₂, 2 H), 2.80 (t, *J* = 7 Hz, CH₂, 2 H), 7.07 (s, =CH, 1 H), 7.48–7.53 (m, ArH, 2 H), 7.63–7.67 (m, ArH, 1 H), 7.94–7.97 (m, ArH, 2 H).

¹³C NMR (75 Hz, CDCl₃): δ = 13.52, 22.00, 27.95, 34.57, 92.31, 113.85, 132.33, 132.64, 134.62, 162.56.

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