

Poly{[4-(hydroxyl)(tosyloxy)iodo]styrene} Promoted Halotosyloxylation Reaction of Alkynes

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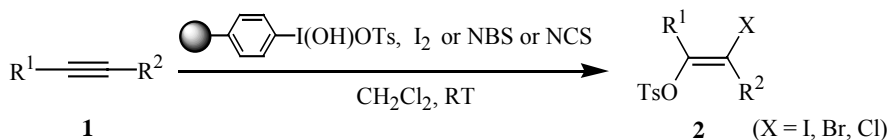
Abstract: Halotosyloxylation reaction of alkynes with iodine or NBS or NCS was efficiently promoted by the poly{[4-(hydroxyl)(tosyloxy)iodo]styrene}.

Keywords: Poly{[4-(hydroxyl)(tosyloxy)iodo]styrene}, halotosyloxylation reaction, alkynes.

Trap of a hypoiodite species with carbon-carbon double bonds and use of its functionalized adducts as synthetic intermediates have been carried out in organic synthesis¹. Recently, it was reported the first trap the arenesulfonyl hypoiodite species with alkynes with 1-(arenesulfonyloxy)benziodoxones or Koser's reagent/iodine system². However, it was failed in bromotosyloxylation and chlorotosyloxylation of the alkynes. Polymer-supported hypervalent iodine reagents have enjoyed an increasing popularity in organic synthesis with the advantages of easy operation, low toxicity and the reuse of the recovered polymer-supported reagents³. On continuing our efforts in the application of poly{[4-(hydroxyl)(tosyloxy)iodo]styrene}⁴, herein, we reported a simple and efficient halotosyloxylation reaction of alkynes (**Scheme 1**). The present method has many advantages such as mild reaction conditions, convenient manipulation and good yields. And the polymer reagent could be regenerated and reused.

Alkynes **1** (1.0 mmol) reacted with poly{[4-(hydroxyl)(tosyloxy)iodo]styrene} (2.0 mmol) and iodine or NBS or NCS (1.1 mmol) in anhydrous CH₂Cl₂ at room temperature overnight and (*E*)-β-halo-α-(*p*-toluenesulfonyloxy)alkenes **2** were obtained in good yields (**Table 1**).

Scheme 1

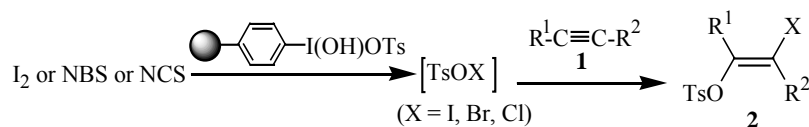


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Table 1 Halotosyloxylation reaction of alkynes

Entry	R ¹	R ²	X	Yield ^a %	Entry	R ¹	R ²	X	Yield ^a %
1	C ₆ H ₅	H	I	95	6	<i>n</i> -C ₄ H ₉	H	Br	83
2	<i>n</i> -C ₄ H ₉	H	I	92	7	C ₆ H ₅	C ₆ H ₅	Br	88
3	C ₆ H ₅	C ₆ H ₅	I	97	8	CH ₃ OCH ₂	H	Br	79
4	H	CO ₂ CH ₃	I	81	9	C ₆ H ₅	H	Cl	60
5	C ₆ H ₅	H	Br	87	10	C ₆ H ₅	H	I	94 ^b

a. The yields are based on the alkynes. b. Using regenerated resin.

Scheme 2

Possible reaction pathway forming the 1,2-halotosyloxyated adducts was proposed as shown in **Scheme 2**. The arenesulfonyl hypohalorite species, which is formed *in situ* by the reaction of poly{[4-(hydroxyl)(tosyloxy)iodo]styrene} and iodine or NBS or NCS, reacts with alkynes **1** to give the corresponding 1,2-halotosyloxyated adducts **2** in good yields.

In conclusion, we have developed a simple and efficient method for the halotosyloxylation reaction of alkynes with iodine or NBS or NCS and poly{[4-(hydroxyl)(tosyloxy)iodo]styrene} to prepare multifunctional olefins in good yields. The polymer reagent could be regenerated and reused.

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