Simple and facile method for the preparation of vinyl azides

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ARTICLE INFO

Article history:
Accepted 30 May 2009
Revised 17 June 2009
Available online 30 June 2009

Keywords:
[bis(trifluoroacetoxy)iodo]benzene
Sodium azide
Carboxylic acids
Vinyl azides

Vinyl azides have found wide applications in organic transformations such as conversions to azirine,1 indole,2 triazole,3 and many other cyclic compounds.4 Although vinyl azides have shown increasing importance in many aspects, synthetic studies toward these compounds are rare. There are only a few methods reported for the preparation of vinyl azides. A commonly used preparation method is the elimination of vinyl azide from the corresponding 3-phenylprop-2-enoyl azides.5 This is the first example of preparation of vinyl azide using α,β-unsaturated carboxylic acids directly by using hypervalent iodine reagent. The advantage of this protocol is characterized with non-toxicity of starting material and shorter reaction times to obtain good preparative yields. The method is also useful for the preparation of acyl azides.

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Available online 25 June 2009

ABSTRACT

A synthetic utility of [bis(trifluoroacetoxy)iodo]benzene on α,β-unsaturated carboxylic acid is described. This is the first example of preparation of vinyl azide using α,β-unsaturated carboxylic acids directly by using hypervalent iodine reagent. The advantage of this protocol is characterized with non-toxicity of starting material and shorter reaction times to obtain good preparative yields. The method is also useful for the preparation of acyl azides.

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During the course of our previous unpublished studies, we found that treatment of α,β-unsaturated carboxylic acids with NaN₃ and tetraethylammonium bromide (TEAB) in dichloromethane gave vinyl azides. Initially, we carried out the reaction with cinnamic acid as a model to explore the suitable reaction conditions with sodium azide and TEAB in dichloromethane at room temperature (Scheme 1; Table 1, entry 1). In this case, the reaction afforded the corresponding 3-phenylprop-2-enoyl azide as a major product in absence of TEAB instead of desired vinyl azide (Scheme 2; Table 1, entry 11). We have also found that chloroform and dichloromethane are the best solvents. As we are working on hypervalent iodine system, to explore the possibility of other trivalent iodine reagents for conversion of α,β-unsaturated carboxylic acids to vinyl azide, we carried out the reaction with cinnamic acid under similar as well as different reaction conditions with hypervalent iodine reagents such as IBX and 4,4'-bis-(dichloriodo)-biphenyl instead of [bis(trifluoroacetoxy) iodo]benzene, no formation of vinyl azide was observed even after 48 h.

In order to explore the reaction scope, a variety of α,β-unsaturated carboxylic acids, prepared by standard reported procedures,

Scheme 1. Cinnamic acid converted into vinyl azide using [bis(trifluoroacetoxy)iodo]benzene and sodium azide and TEAB.


doi:10.1016/j.tetlet.2009.06.097
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*a Reaction conditions (entries 1–10): substrate (1.0 equiv), [bis(trifluoroacetoxy)iodo]benzene (1.2 equiv), TEAB (1.2 equiv), anhyd CH2Cl2, rt, and sodium azide (1.2 equiv).

*b Starting compounds were prepared by standard reported procedures.

*c Isolated yields after column chromatography and structures were confirmed by comparison of the IR and 1H NMR spectra with those of authentic materials.

*d No reaction.

*e Reaction conditions (entries 11 and 12): substrate (1.0 equiv), [bis(trifluoroacetoxy)iodo]benzene (1.2 equiv), sodium azide (1.2 equiv), anhyd CH2Cl2, rt.
that either electron-rich or electron-deficient \( \pi,\beta \)-unsaturated carboxylic acids were suitable for this reaction, giving desired vinyl azide in moderate to good yields in short reaction times (Table 1, entries 2–4). It was noted that a variety of functional groups tolerated these reaction conditions (Table 1, entries 3–7). This feature would allow the use of the present method in the synthesis of wide range of vinyl azides. A lower reaction rate was observed with aliphatic \( \pi,\beta \)-unsaturated carboxylic acids (Table 1, entries 7 and 8).

Further investigations indicated that in the absence of double bond reaction does not take place (Table 1, entries 9 and 10). In the absence of TEAB under similar reaction conditions cinnamic acid readily converted into corresponding acyl azides (Table 1, entries 11 and 12) without affecting the double bond.

In conclusion, a new reaction system using trivalent iodine reagents, [bis(trifluoroacetoxy)iodo]benzene, in combination with TEAB and sodium azide has been developed, which is capable of converting various \( \pi,\beta \)-unsaturated carboxylic acids into corresponding vinyl azides, at room temperature. The method developed is mild and gives moderate to good yields of vinyl azides and acyl azides for both aliphatic and aromatic substrates.

**Acknowledgment**

V.N.T. thanks All India Council for Technical Education (AICTE) for financial support under Research Promotion Scheme (RPS).

**References and notes**

15. **General procedure:** To a stirred solution of [bis(trifluoroacetoxy)iodo]benzene (1.2 equiv) in anhyd CH\(_2\)Cl\(_2\) (15 mL) was added TEAB (1.2 equiv) in one portion. The resultant reaction mixture was stirred for 5 min followed by addition of sodium azide (1.2 equiv) in anhyd CH\(_2\)Cl\(_2\) (15 mL) and washed successively with 10% sodium bisulfate solution (2 x 20 mL), 10% sodium bicarbonate (2 x 15 mL), and water (2 x 20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give crude product. Purification was obtained after silica gel column chromatography (10% EOA-hexane). [Acyl azides were prepared using similar procedure without the addition of TEAB.]