



Cobalt-catalyzed stereoselective iodosulfonylation and diiodination of alkynes via oxidation of potassium iodide in air

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ARTICLE INFO

Article history:

Received 5 November 2017

Received in revised form

29 January 2018

Accepted 1 February 2018

Available online 3 February 2018

Keywords:

Cobalt catalyst
Iodosulfonylation
Diiodination
Sodium sulfinate
Potassium iodide

ABSTRACT

Cobalt-catalyzed iodosulfonylation of alkynes can be achieved using sodium sulfinates in the presence of KI. This procedure produces numerous stereoselective (*E*)- β -iodoalkenyl sulfones with good yields and suppresses the formation of diiodoalkenes. Furthermore, when this reaction is performed in the absence of sodium sulfinates, the expected (*E*)-diiodoalkenes are obtained.

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1. Introduction

Transition metal-catalyzed synthesis of vinyl sulfones is an important methodology that is widely used in organic chemistry.¹ This is because these compounds are useful as convenient synthetic intermediates.² To synthesize vinyl sulfones, numerous procedures have been developed,³ including the Horner-Emmons reaction,⁴ aldol condensation,⁵ and oxidation of alkenyl sulfides.⁶

By comparison, reactions employing sodium sulfinate are restricted to the Michael reaction,⁷ or a transition-catalyzed cross-coupling with alkenyl halides.⁸ Furthermore, reports of catalytic sulfonylation of nonactivated alkynes using sodium sulfinate are limited.⁹ The exploration of a simple catalytic procedure is therefore necessary.

To prepare β -halovinyl sulfones, several procedures are employed (Fig. 1). For example, reactions of sulfonyl chlorides with alkynes have been widely reported for use in the preparation of alkenyl sulfones (eq. (1)).¹⁰ Furthermore, these reactions can be performed in the presence of a copper or an iron catalyst. Sulfonyl radicals or cations generated from sulfonyl chlorides can work as promoting reagents. Although these reactions are typically used because they are convenient, the halogen that is introduced is

generally limited to chlorine. On the other hand, stoichiometric reactions using sodium sulfinates have been also investigated.¹¹ This method usually requires addition of NXS (X = Cl or Br),^{10a} CAN-NaI^{10b} or iodine^{10c} (eq. (2)) wherein these reagents result in the oxidation of the sulfonyl anion. In a similar manner, copper-catalyzed sulfonylation of alkynes has also been recently reported,⁹ and the procedure proceeds via the copper-catalyzed oxidation of the sulfonyl anion (eq. (3)). Therefore, the generation of the sulfonyl radical or cation is the most important step to perform the sulfonylation of alkynes.

Transition metal catalysts are known to be oxidants of sulfonyl anions.^{3b-c,3g,9,12} In particular, the reactivity of copper and nickel catalysts has been extensively investigated. The cobalt-catalyzed oxidation of the sulfonyl anion has not been the subject of research; however, the oxidation of sulfides has been performed.¹³ Via our previous studies, it has been shown that the cobalt catalyst itself could not promote sulfonylation of alkenes or alkynes satisfactorily (Scheme 1). To address this issue, the addition of the iodide ion as an oxidant precursor was attempted. As a general, iodine radical is able to produce by the oxidation of KI. This can work as oxidants of sulfonyl anions whereas the generation of diiodoalkenes is also worried. However in this investigation, a cobalt-catalyzed sulfonylation of alkynes in the presence of KI was completed. In this article, it will be described about the developed methodology.

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