Tetrahedron 74 (2018) 1454-1460

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

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

Nobukazu Taniguchi¹

Department of Chemistry, Fukushima Medical University, Fukushima 960-1295, Japan

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.

© 2018 Elsevier Ltd. All rights reserved.

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

¹ Tel./fax: +81245471369.

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-Nal^{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 cobaltcatalyzed sulfonylation of alkynes in the presence of KI was completed. In this article, it will be described about the developed methodology.





E-mail address: taniguti@fmu.ac.jp.

(a) A catalytic reaction using sulfonyl chloride with metal catalysts

$$R \longrightarrow + ArSO_2CI \longrightarrow R \xrightarrow{CI} (eq. 1)$$

(b) A stoichiometric reaction using sodium sulfinate with oxidants

$$R \longrightarrow + ArSO_2Na \xrightarrow{NXS (X = Cl or Br)}_{CAN or I_2} \xrightarrow{X}_{SO_2R^3} (eq. 2)$$

(c) A reaction using sodium sulfinate with copper catalyst

$$R \longrightarrow + ArSO_2Na \xrightarrow{KX, cat.Cul} R \xrightarrow{X} (eq. 3)$$
$$X = I, Br, Cl$$

Fig. 1. Sulfonylation of alkynes.

$$R \longrightarrow \text{or } R \xrightarrow{\qquad ArSO_2Na} \xrightarrow{\qquad X} \\ \hline cat.Co, air or O_2 \xrightarrow{\qquad R} SO_2R^3 \\ X = O \text{ or } OH \\ Lower yield \\ \hline delta = 0 \\ Catrice Content \\ Content Content \\ Content Content \\ Content \\$$

Scheme 1. Cobalt-catalyzed sulfonylation of alkynes or alkenes.

2. Results and discussion

To determine suitable conditions, numerous combinations of cobalt catalyst with ligands were initially surveyed (Table 1). Consideration of Table 1 Entries 1–2, shows that the reaction did not proceed in the absence of a cobalt catalyst or KI. However, when $CoBr_2$ (5 mol%) was added, the corresponding β -iodoalkenyl sulfone **3a** was obtained with 57% yield as a single isomer (Entry 3). Fortunately, the addition of bpy as a ligand increased the yield to 87% without the formation of diiodoalkene and other isomers (Entry 4).¹⁴ The stereochemistry of **3a** was (E)-isomer. Although other amine ligands (Phen or Phen · H₂O) also produced excellent results, no reaction using phosphine ligands proceeded (Entries 5-6, 9-10). The reaction afforded best result at 100 °C (Entries 7-8). Other solvents (DMF, DMSO or PhMe) could not promote the reaction (Entries 11-13). Thus, the procedure proceeds smoothly under acidic condition. Furthermore, other cobalt compounds, such as $CoCl_2$ or $Co(OAc)_2$ were ineffective in promoting the reaction (Entries 14-15). Unfortunately, it was not possible to introduce the bromide or chloride ion into the procedure via KBr or KCl (Entries 16 - 17).

On the basis of developed procedure, the iodosulfonylation of various alkynes was evaluated (Table 2). When the reaction of terminal alkynes **1** (0.3 mmol) with sodium sulfinates **2** (0.33 mmol) was performed, the expected β -iodoalkenyl sulfones **3** were obtained in excellent yields (Entries 1–15). Furthermore, this reaction is not only successful for terminal alkynes but also for internal alkynes (Entries 16–18). The stereochemistry of these compounds was determined by comparison with ¹H NMR of authentic samples and previous reported literatures (Schemes 2 and 3).^{6,15} These results suggested the addition was *anti*-selective. Unfortunately, the procedure using diphenyl acetylene or terminal aliphatic alkynes hardly proceeded with a recovery of alkynes (Entries 19–20).

The iodosulfonylation of alkynes was achieved through the use

Table 1

Investigation of suitable conditions.^a

Ph─ <u>─</u> ──────── + 1a	4-MeC ₆ H₄SO₂Na 2b	KX, [Co]-L (1:1, 5 mol%) AcOH, air, 100 °C 18 h	$R^{1} \xrightarrow{R^{2}} SO_{2}C_{6}H_{4}Me-4$ 3a
Entry	[Co]-L	KX	3a (%) ^g
1	None	Nor	ie O
2	None	KI	0
3	CoBr ₂	KI	57
4	CoBr ₂ -bpy	KI	87
5	CoBr ₂ - Phen	KI	85
6	CoBr ₂ - Phen · H	H ₂ O KI	87
7 ^b		KI	80
8 ^c		KI	12
9	CoBr ₂ -PPh ₃	KI	0
10	CoBr ₂ -dppb	KI	trace
11 ^d	CoBr ₂ - Phen · H	H ₂ O KI	trace
12 ^e	$CoBr_2$ - Phen H_2O		trace
13 ^f	CoBr ₂ - Phen · H	H ₂ O KI	0
14	CoCl ₂ - Phen · H	H ₂ O KI	61
15	Co(OAc)2- Phe	en∙H₂O KI	68
16	CoBr ₂ - Phen I	H ₂ O KBr	0
17	CoBr ₂ -Phen · H	I ₂ O KCl	0

^a Reaction condition: The mixture of **1a** (0.3 mmol), **2b** (0.33 mmol), KI (0.33 mmol) and CoX₂-L (1:1, 5 mol%) was treated in AcOH (0.3 mmol) at 100 °C. ^b At 80 °C.

^c At 60 °C.

^d DMF (0.3 mmol) was used as a solvent.

^e DMSO (0.3 mmol) was used as a solvent.

^f PhMe (0.3 mmol) was used as a solvent.

^g Isolated yield.

Table 2

Preparation of β-iodoalkenyl sulfones.^a

$R^1 - = -R^2 +$		KI, CoBr ₂ -Phen•H ₂ O (1:1, 5 mol%)	$A = B^2$
R ¹	R SO ₂ Na	AcOH, air, 100 °C	R^{1} O_2R^3
	2	18 h	3

Entry	R ¹	R ²	R ³	3	3 (%) ^b
1	4-MeC ₆ H ₄	Н	Ph	3ba	82
2	4-MeC ₆ H ₄	Н	4-MeC ₆ H ₄	3bb	86
3	4-MeC ₆ H ₄	Н	4-MeOC ₆ H ₄	3bc	74
4	4-MeC ₆ H ₄	Н	4-ClC ₆ H ₄	3bd	72
5	4-MeC ₆ H ₄	Н	$4-FC_6H_4$	3be	76
6	4-MeC ₆ H ₄	Н	1-Naph	3bf	77
7	4-MeC ₆ H ₄	Н	Me	3bg	80
8	Ph	Н	4-MeC ₆ H ₄	3ab	87
9	Ph	Н	4-AcHNC ₆ H ₄	3ai	38
10	Ph	Н	4-FC ₆ H ₄	3ae	83
11	4-MeOC ₆ H ₄	Н	4-MeC ₆ H ₄	3cb	71
12	4-PhC ₆ H ₄	Н	4-MeC ₆ H ₄	3db	73
13	4-FC ₆ H ₄	Н	4-MeC ₆ H ₄	3eb	79
14	2-MeC ₆ H ₄	Н	4-MeC ₆ H ₄	3fb	80
15	1-Cyclohexenyl	Н	4-MeC ₆ H ₄	3gb	59
16	Ph	Me	4-MeC ₆ H ₄	3hb	71
17	Ph	Et	4-MeC ₆ H ₄	3ib	80
18	Ph	CH ₂ OAc	4-MeC ₆ H ₄	3jb	60
19	Ph	Ph	4-MeC ₆ H ₄	3kb	trace
20	n-Hex	Н	4-MeC ₆ H ₄	3lb	trace

 $^a\,$ Reaction condition: The mixture of 1 (0.3 mmol), 2 (0.33 mmol), KI (0.33 mmol) and CoBr_2-Phen $\cdot H_2O$ (1:1, 5 mol%) was treated in AcOH (0.3 mmol) at 100 $^\circ$ C. $^b\,$ Isolated yield.

Download English Version:

https://daneshyari.com/en/article/7827464

Download Persian Version:

https://daneshyari.com/article/7827464

Daneshyari.com