Pergamon

Tetrahedron Letters, Vol. 37, No. 21, pp. 3717-3720, 1996
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0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)00649-1

A New Straightforward Synthesis of Alkynyl Sulfones via the Sonochemical Coupling between Alkynyl Halides and Copper Sulfinates

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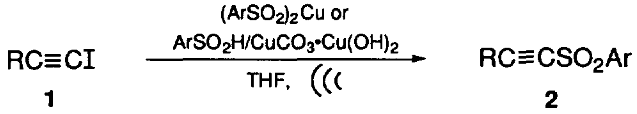
Abstract: Alkynyl aryl sulfones **2** were easily obtained in moderate to good yields by treating alkynyl iodides **1** with copper arenesulfinates in a tetrahydrofuran suspension under ultrasonic irradiation.

The use of alkynyl sulfones as a dienophile,[1] dipolarophile,[2] or nucleophile[3] has been proven to be a powerful strategy in organic synthesis. The sulfonyl group acts therein not only as an activator of triple bond but also as an easily removable protective unit. In spite of their potentials, however, known synthetic routes to alkynyl sulfones are yet limited in convenience and generality. Previous methods involve oxidation of the corresponding sulfides,[4] elimination from α,β-unsaturated sulfones,[5] β-keto sulfones[6] or 5-amino-4-isoxazolyl sulfones,[7] and sulfonylation of alkynyliodonium salts[8] or alkynylsilanes.[9]

Sulfinic acid salts are widely used as the sulfonylating agent for alkyl halides. However, alkynyl halides are inert toward most of nucleophiles and, therefore, no successful cases have to date been reported for the nucleophilic sulfonylation of alkynyl halides. In this paper, we wish to report that alkynyl iodides can be efficiently converted to the corresponding alkynyl sulfones simply by treating them with copper sulfinate in a tetrahydrofuran (THF) suspension under sonication.

We have recently observed that (2-iodoethynyl)benzene **1a** reacted with sodium *p*-toluenesulfinate in DMF to afford phenylethynyl 4-methylphenyl sulfone **2a** in a low yield. In order to improve the yield, the effect of various transition metal salts were scrutinized using **1a** as a common substrate under similar conditions. The results obtained revealed that copper salt was most effective in producing **2a**; however, 1,4-diphenylbutadiyne **3** was the additional major product (for example, 34% of **2a** and 39% of **3** were obtained in the presence of 1.0 equiv CuI). Other metal salts such as iron(III), cobalt(II), nickel(II) and silver(I) salts were all ineffective for the formation of the required sulfone **2a**. After many unfruitful attempts, we have finally found that copper(II) arenesulfinate was efficient for converting alkynyl iodide **1a** to sulfone **2a** in a THF suspension under ultrasonic irradiation. The formation of diyne **3** was mostly suppressed under these heterogeneous conditions. Sonication shortened the reaction time considerably and, after reaction, copper salt could be easily removed by filtration. The use of alkynyl bromides led to the formation of significant amounts of unidentified by-products, lowering the yield of alkynyl sulfones. Various alkynyl aryl sulfones were obtained in moderate to good yields by the present procedure. The representative results are shown in Table.



$$\underset{\mathbf{1}}{RC\equiv CI} \xrightarrow[\text{THF, (((}]{(ArSO_2)_2Cu \text{ or } ArSO_2H/CuCO_3\cdot Cu(OH)_2} \underset{\mathbf{2}}{RC\equiv CSO_2Ar}$$

Typically, a mixture of iodoalkyne **1a** (0.23 g, 1.0 mmol), naphthalene-1-sulfinic acid (0.26 g, 1.34 mmol), commercial basic copper carbonate (purchased from Nacalai Tesque, Inc., approximate composition, $CuCO_3\cdot Cu(OH)_2\cdot H_2O$; 0.08 g, 0.34 mmol), and THF (3 mL) was sonicated[10] for 4 h under an argon atmosphere. The mixture was diluted with THF (10 mL) and filtered through a Celite bed. The filtrate was evaporated under reduced pressure to leave a solid residue, which was chromatographed on silica gel (hexane/AcOEt as eluent) to give 1-naphthyl phenylethynyl sulfone **2c** as a colorless solid, mp 141-143 °C (decomp.) (0.27 g, 94%). ^{1}H NMR ($CDCl_3$) δ 7.2-7.8 (m, 8 H), 8.0 (m, 1 H), 8.1-8.2 (m, 1 H), 8.4-8.5 (m, 1 H), 8.8-8.9 (m, 1 H); IR (KBr) ν_{max} 2180, 1505, 1330, 1165, 1130 cm^{-1}; MS (EI) *m/z* 292 (M^+, 1), 228 (100), 226 (52), 202 (14). Anal. Calcd for $C_{18}H_{12}O_2S$: C, 74.0; H, 4.1. Found: C, 74.3; H, 4.1.

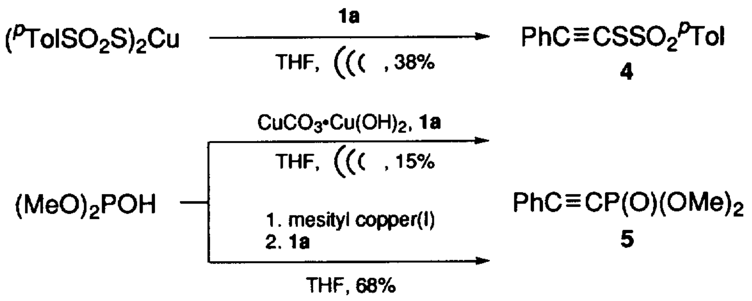
Copper(II) arenesulfinates are conveniently prepared as a pale green powder by stirring an appropriate arenesulfinic acid and commercial basic copper(II) carbonate in dry THF. Alternatively, the copper sulfinate *in situ* generated from sulfinic acid/copper carbonate or from sodium sulfinate/methanesulfonic acid/copper carbonate may be used without appreciable effect on the yield of alkynyl sulfones.

Table. Preparation of Alkynyl Sulfones.[a]

Halide 1[b]		Reagent[c]		Sulfone 2[d]	Yield, %[e]
1a	PhC≡CI	$(^p\text{TolSO}_2)_2\text{Cu}\cdot4\text{H}_2\text{O}$	**2a**	$\text{PhC≡CSO}_2{}^p\text{Tol}$	77
1a		$^p\text{TolSO}_2\text{H}$, Cu carbonate	**2a**		75
1a		PhSO_2H, Cu carbonate	**2b**	$\text{PhC≡CSO}_2\text{Ph}$	73
1a		1-NptSO_2H, Cu carbonate	**2c**	PhC≡CSO_2(1-Npt)[f]	94
1a		$4\text{-MeCONHC}_6\text{H}_4\text{SO}_2\text{H}$, Cu carbonate	**2d**	$\text{PhC≡CSO}_2(4\text{-MeCONHC}_6\text{H}_4)$	66
1a		$4\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{H}$, Cu carbonate	**2e**	$\text{PhC≡CSO}_2(4\text{-O}_2\text{NC}_6\text{H}_4)$	50
1b	^{p}TolC≡CI	$^p\text{TolSO}_2\text{H}$, Cu carbonate	**2f**	$^p\text{TolC≡CSO}_2{}^p\text{Tol}$	49
1c	^{n}HexC≡CI	$(^p\text{TolSO}_2)_2\text{Cu}\cdot4\text{H}_2\text{O}$	**2g**	$^n\text{HexC≡CSO}_2{}^p\text{Tol}$	34
1d	^{n}HexC≡CBr	$(^p\text{TolSO}_2)_2\text{Cu}\cdot4\text{H}_2\text{O}$	**2g**		14

[a] For reaction conditions, see the typical procedure. [b] Alkynyl halides 1 were prepared according to the reported methods.[11] [c] Cu carbonate = $\text{CuCO}_3\cdot\text{Cu(OH)}_2\cdot\text{H}_2\text{O}$. [d] Satisfactory elemental analyses were obtained for all new compounds. [e] Isolated yield. [f] Npt = naphthyl.

As an extension of our methodology, we have investigated the reactions of alkyne **1a** with copper *p*-toluenethiosulfonate and copper dimethyl phosphite under similar conditions, which led to *S*-phenylethynyl *p*-toluenethiosulfonate **4** and dimethyl phenylethynylphosphonate **5**, respectively, in acceptable yields. In the latter case, considerable improvement of yield was observed when mesityl copper(I)[12] was employed for the generation of copper dimethyl phosphite.



In summary, the sonochemical reaction between alkynyl iodides and copper arenesulfinates provides a new direct route to a variety of alkynyl aryl sulfones. Ready accessibility of starting materials coupled with mild conditions and simple manipulation make the present procedure a new attractive addition to the existing methodology for alkynyl sulfone synthesis.

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(*Received in Japan* 4 *March* 1996; *revised* 1 *April* 1996; *accepted* 3 *April* 1996)