

New One-Pot Method for the Synthesis of Alkynyl Sulfonate Esters Using Ultrasound

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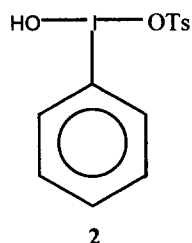
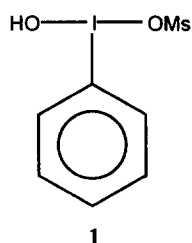
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Abstract: A new one-pot method for the preparation of alkynyl sulfonate esters from terminal alkynes is reported. A metal-assisted, ultrasound-enhanced nucleophilic acetylenic displacement through the alkynyl(phenyl)iodonium salts provides a direct and rapid access to novel alkynyl sulfonates in good yields in a simple one-step procedure.

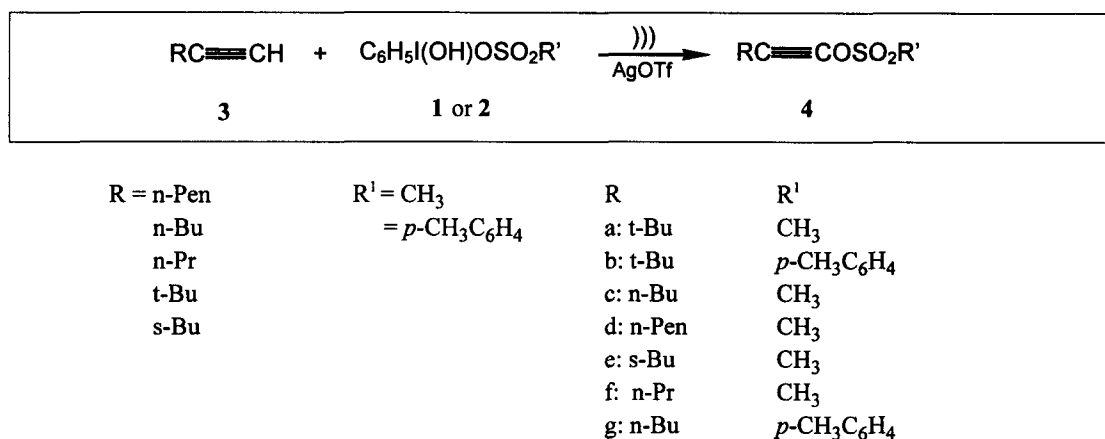
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Presently there is considerable interest in organohypervalent iodine(III) compounds because of their novel properties and reactivities.^{1,2} Recently alkynyl(phenyl)iodonium salts have become valuable reagents in organic chemistry,³ and they have been utilized to prepare the first examples of alkynyl sulfonates.⁴ Starting with terminal alkynes, this methodology provides access for the first time to a variety of alkynyl sulfonates. Unfortunately, this approach involves two steps with very long reaction times (14 – 54 h) and low yields. We report here a simple, quick, one-step, ultrasound-enhanced method for the synthesis of alkynylsulfonates from a variety of terminal alkynes utilizing [hydroxy(mesyloxy)iodo]benzene **1** or [hydroxy(tosyloxy)iodo]benzene **2**.



Ultrasound has been utilized recently to accelerate a number of synthetically useful reactions.^{5,6} Most of the observed effects are due to cavitation:⁵ the formation, growth and collapse of bubbles in an irradiated liquid. Cavitation induces very high local temperatures and pressures inside the bubbles and enhanced mass transfer and turbulent flow in the liquid. We recently reported⁷ an ultrasound-enhanced method for the preparation of alkynyl(phenyl)iodonium salts. We have therefore investigated the direct conversion of terminal alkynes to alkynyl sulfonates using ultrasound- and metal-assisted nucleophilic acetylenic displacement through these salts (Scheme 1). The results are summarized in Table 1.

Scheme I



[Hydroxy(mesyloxy)iodo]benzene and [hydroxy(tosyloxy)iodo]benzene are both largely insoluble in acetonitrile under ambient conditions. Upon application of ultrasound, however, they both disperse and react with terminal alkynes in the presence of AgOTf to afford the novel alkynyl mesylates or alkynyl tosylates in short reaction times with good yields. In a typical experiment,⁸ 0.392g (1mmol) of 1 was added to a solution of 1.5 mL of the alkyne and 5 mL of 0.2 M AgOTf in 5 mL acetonitrile in a reaction vessel immersed in a water bath at 35°C. The vessel was purged with Ar for 10 minutes and subjected to sonication under Ar using a Vibracell Ultrasonic Processor (Sonics and Materials, 20 kHz, 0.5 in. Ti horn at $\approx 50 \text{ W/cm}^2$) for 10-25 minutes with a reaction temperature of 50°C. The reaction solution was concentrated in vacuo, and the residue was dissolved in 10 mL of dichloromethane, washed with water and then dried over MgSO₄. The solvent was distilled off under reduced pressure to yield the crude product, which afforded the alkynyl mesylate after column chromatography.

Table 1. Reaction Conditions and Yields^{a,b,c}

Product	Reaction Temp. (°C)	Reaction Time (min)	% Yield
4a	35	25	77
4b	35	25 ^d	49
4c	25	10	44
4d	35	20	42
4e	45	25 ^d	63
4f	35	20	41
4g	35	25 ^d	43

^aYields are based upon isolated pure products. In parallel, non-sonicated experiments, the alkynes were stirred magnetically with 1 or 2 in acetonitrile in the presence of AgOTf for 25 minutes at the corresponding reaction temperatures: no products were detected in the absence of ultrasound.

^bThe products were purified by column chromatography using silica. The column was eluted first with hexane to remove iodobenzene and then with 10% CH₂Cl₂ in hexane to isolate the product.

^cSatisfactory spectral data (MS, IR, ¹H and ¹³C NMR) were obtained on all the products.

^dIn these experiments, AgOTf was added after 15 min. of sonication and the reaction mixture was sonicated an additional 10 minutes.

Ultrasound promises to be a new and powerful technique in hypervalent iodine chemistry.^{7,9} The methodology reported here provides a simple, one-step access to novel alkynyl sulfonates from terminal alkynes in short reaction times. We presume the increase in reactivity originates from the rapid dispersion of the insoluble [hydroxy(mesyloxy)iodo]benzene or [hydroxy(tosyloxy)iodo]benzene into acetonitrile during ultrasonic irradiation to afford the alkynyl(phenyl)iodonium salts. The rate of the metal assisted nucleophilic acetylenic displacement is also accelerated by ultrasound.¹⁰ We are currently investigating the scope of this technique in other hypervalent iodine reactions.

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REFERENCES AND NOTES

1. Varvoglis, A. *The Organic Chemistry of Polycordinated Iodine*; New York: VCH Publishers, 1992.
2. For recent reviews, see:
 - a) Varvoglis, A. *Synthesis* **1984**, 709.
 - b) Moriarity, R.M.; Vaid, R.K. *Synthesis* **1990**, 431.
 - c) Stang, P.J. *Angew Chem. Int. Ed. Eng.* **1992**, 31, 274.
 - d) Stang, P.J.; Zhdankin, V.V. *Chem. Rev.* **1996**, 96, 1123.
 - e) Kitamura, T.; Fujiwara, Y. *Organic Preparations and Procedures Int.* **1997**, 29, 409.
 - f) Varvoglis, A. *Tetrahedron* **1997**, 53, 1179.
3.
 - a) Stang, P.J.; Kitamura, T.; Arif, A.M.; Karni, M. Apeloig, Y. *J. Am. Chem. Soc.* **1990**, 112, 374.
 - b) Stang, P.J.; Kitamura, T. *J. Am. Chem. Soc.* **1987**, 109, 7561.
 - c) Williamson, B.L.; Stang, P.J.; Arif, A.M. *J. Am. Chem. Soc.* **1993**, 115, 2590.
 - d) Kitamura, T.; Tanaka, T.; Taniguchi, H.; Stang, P.J. *J. Chem. Soc. Perkin Trans. 1* **1991**, 2892.
 - e) Kitamura, T.; Nagata, K.; Taniguchi, H. *Tetrahedron Lett.* **1995**, 36, 1081.
 - f) Lodaya, J.S.; Koser, G.F. *J. Org. Chem.* **1990**, 55, 1510.
 - g) Zhang, J.; Chen, Z. *Synth. Comm.* **1997**, 27, 3757.
 - h) Zhang, J.; Chen, Z. *Synth. Comm.* **1997**, 27, 3881.
4.
 - a) Stang, P.J.; Surber, B.W. *J. Am. Chem. Soc.* **1985**, 107, 1452.
 - b) Stang, P.J.; Surber, B.W.; Chez, Z.; Roberts, K.A.; Anderson, A.G. *J. Am. Chem. Soc.* **1987**, 109, 228.
5.
 - a) Suslick, K.S.; Ed. *Ultrasound: Its Chemical, Physical and Biological Effects*; New York: VCH Publishers, 1988.
 - b) Suslick, K.S. *Science*, **1990** 247, 1439.
 - c) Suslick, K. S. *Kirk-Othmer Encyclopedia of Chemical Technology*; 4th Ed. New York: John Wiley, 1998, vol. 26, 517-541.
6.
 - a) Einhorn, C.; Einhorn, J.; Luche, J.L. *Synthesis* **1989**, 787.
 - b) Mason, T.J. *Chem. Soc. Rev.* **1997**, 26, 443.
 - c) Mason, T.J.; Luche, J.L. *Chemistry Under Extreme or Non-classical Conditions*, Ed. van Eldick, R.; Hubbard, C.D. New York: John Wiley, 1997, 317.
7. Tuncay, A.; Zolodz, M.; Suslick, K.S. *Tetrahedron Lett.* submitted.
8. **1** and **2** was prepared according to the standard literature methods.¹¹
9. Tuncay, A.; Dustman J.A.; Fisher, G.; Tuncay, C.I.; Suslick, K.S. *Tetrahedron Lett.*, **1992** 33, 7647.
10. If desired, the iodonium salts can be isolated, purified, and then reacted with AgOTf in CH₃CN using ultrasound. Alkynyl sulfonates are then obtained in short reaction times.
11. Koser, G.I.; Wettach, R.H. *J. Org. Chem.*, **1977** 42, 1476.