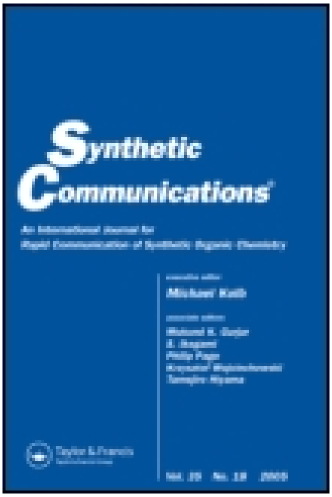


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Stereoselective Synthesis of (Z)-1,2-Diarylthio-1-alkene via the Reaction of Diaryl Disulfides with Terminal Alkynes Catalyzed by Cesium Hydroxide

Kang Bing Zou [a] , Xian Hong Yin [b] , Wen Qi Liu [b] , Ren Hua Qiu [a] , Ruo Xin Li [a] , Ling Ling Shao [a] , Yin Hui Li [a] , Xin Hua Xu [a] & Rong Hua Yang [a]
[a] College of Chemistry and Chemical Engineering , Hunan University , Changsha, China
[b] Department of Chemistry , Xiangnan University , Chenzhou, China

To cite this article: Kang Bing Zou , Xian Hong Yin , Wen Qi Liu , Ren Hua Qiu , Ruo Xin Li , Ling Ling Shao , Yin Hui Li , Xin Hua Xu & Rong Hua Yang (2009) Stereoselective Synthesis of (Z)-1,2-Diarylthio-1-alkene via the Reaction of Diaryl Disulfides with Terminal Alkynes Catalyzed by Cesium Hydroxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:14, 2464-2471, DOI: 10.1080/00397910802654831

To link to this article: http://dx.doi.org/10.1080/00397910802654831

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Downloaded by [University of Glasgow] at 10:33 20 December 2014

Synthetic Communications®, 39: 2464–2471, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802654831

Stereoselective Synthesis of (Z)-1,2-Diarylthio-1-alkene via the Reaction of Diaryl Disulfides with Terminal Alkynes Catalyzed by Cesium Hydroxide

Kang Bing Zou,[1] Xian Hong Yin,[2] Wen Qi Liu,[2]
Ren Hua Qiu,[1] Ruo Xin Li,[1] Ling Ling Shao,[1] Yin Hui Li,[1]
Xin Hua Xu,[1] and Rong Hua Yang[1]
[1]College of Chemistry and Chemical Engineering, Hunan University, Changsha, China
[2]Department of Chemistry, Xiangnan University, Chenzhou, China

Abstract: In the presence of a catalytic amount of cesium hydroxide under a nitrogen atmosphere, terminal alkynes reacted with diaryl disulfides at room temperature in dimethylformamide to give almost exclusively (Z)-1,2-diarylthio-1-alkene in good yields, but under an air atmosphere, the reaction gave a mixture of alkynyl sulfide and (Z)-1,2-diarylthio-1-alkene.

Keywords: Cesium hydroxide, diaryl disulfide, (Z)-1,2-diarylthio-1-alkene, terminal alkyne

Many different classes of organochalcogen compounds have been prepared and studied to date. For their syntheses, vinyl sufides have been used extensively because vinyl sulfides can be conveniently converted to functional alkenes[1,2] stereoselectively. Among the common vinyl sulfides, 1,2-dithio-1-alkenes are of much importance because of their use as bidentante ligands in coordination chemistry, precursors of new optical materials for microelectronics,[1] and important intermediates for

Received September 15, 2008.

Address correspondence to Xin Hua Xu and Rong Hua Yang, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. E-mail: xhx1581@yahoo.com.cn; yangrh@pku.edu.cn

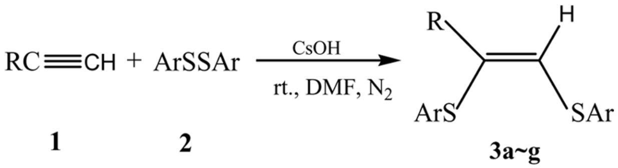
organic synthesis. Traditionally there are two kinds of paths for the preparation of 1,2-dithio-1-alkenes: one involves the addition of disulfides to terminal alkynes[3–11] and the other is the addition of thiol to alkynyl sulfides.[12–17] In most cases, both methods need transition-metal catalysis. In this article, we report a stereoselective synthesis of (Z)-1,2-diarylthio-1-alkenes via cesium hydroxide–catalyzed reaction of disulfides with terminal alkynes.

Cesium base has received increasing interest in the past few years. It has been shown recently that cesium hydroxide could catalyze the reaction of terminal alkynes with aldehydes and ketones to give propargyl alcohols, with nitriles to give unsaturated adduct,[18] and with phenylselenyl bromide to give alkynyl selenides.[19] Our group also reported that cesium hydroxide–catalyzed addition of diaryldiselenides to terminal alkynes under N_2 gave (Z)-1,2-bis(arylseleno)-1-alkenes[20] selectively and the reaction of diarylditelluride with terminal alkynes under an air atmosphere gave alkynyl tellurides.[21] Lothar et al. have also reported that in the presence of K_2CO_3 and a catalytic amount of copper(I), diphenyl disulfide and ditelluride reacted with terminal alkynes to give alkynyl sulfides and tellurides.[22] These results prompted us to investigate the reaction of diaryl disulfides with terminal alkynes in the presence of a catalytic amount of cesium hydroxide.

We first tested the reactions of 3-methyoxy propyne with diphenyl disulfide. The experiment showed that under an air atmosphere, 3-methyoxy propyne (2.2 mmol) reacted with diphenyl disulfide (1.0 mmol) in the presence of cesium hydroxide (0.2 mmol) at room temperature in dimethylformamide (DMF) to give a 6:4 mixture of 3-methyoxy propynyl phenylsulfide and Z-1,2-diphenylthio-3-methyoxy propene in 81% yield. Though the yield is satisfactory, the selectivity is not. However, much to our delight, it gave almost exclusively (Z)-1,2-diphenylthio-3-methyoxy propene in 80% yield when the reaction

Table 1. Reaction of terminal alkynes with diaryl disulfides to synthesize (Z)-1,2-diarylthio-1-alkenes

Entry	R	Ar	Yields (%)
3a	$HO(CH_3)_2C$	Ph	61
3b	$HOCH_2$	p-$CH_3C_6H_4$	69
3c	CH_3OCH_2	Ph	82
3d	CH_3OCH_2	p-$CH_3C_6H_4$	77
3e	$PhOCH_2$	Ph	75
3f	$PhOCH_2$	p-$CH_3C_6H_4$	73
3g	Ph	Ph	71

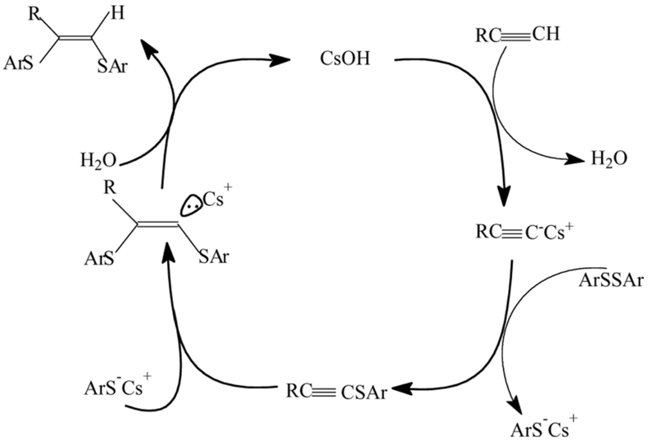


Scheme 1. The synthesis of (Z)-1,2-diarylthio-1-alkenes.

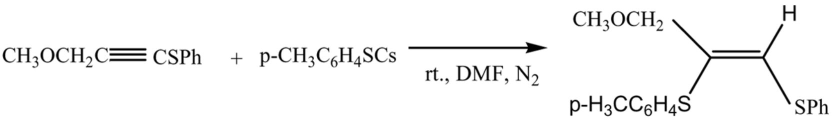
was run under N_2. We reasoned that if the reaction was performed under an air atmosphere, some sulfide ions would be transformed into the starting disulfides because of air oxidation, and the reaction would give a mixture of alkynyl sulfide and (Z)-1,2-diarylthio-1-alkene. Therefore it is important to run the reaction in the absence of air. With the fine-tuned method in hand, we set out to investigate the scope of the reaction. A variety of (Z)-1,2-diarylthio-1-alkenes were synthesized by reacting different alkynes with diphenyldisulfide or di(*p*-methylphenyl)disulfide (Scheme 1), and the results are summarized in Table 1.

A possible reaction mechanism for the reaction of terminal alkynes with diaryl disulfides is depicted in Scheme 2. First, terminal alkynes reacted with cesium hydroxide to give cesium alkynides and H_2O. Second, the alkynides reacted with diaryl disulfides to form alkynyl sulfides and cesium arylsulfides. Finally, the cesium arylsulfides underwent nucleophilic addition to the alkynyl sulfides to give the desired (Z)-1,2-diarylthio-1-alkenes.

To shed some light on the reaction mechanism, the reaction of *p*-$CH_3C_6H_4SCs$ with 3-methoxy propanyl phenylsulfide in DMF at room



Scheme 2. The mechanism for the reaction of terminal alkynes with diaryl disulfides.



Scheme 3. The addition of *p*-$CH_3C_6H_4SCs$ to 3-methoxy propynyl phenylsulfide.

temperature was performed. The fact that 1-phenylthio-2-(p-methylphenyl)thio-3-methoxy propene was isolated in almost 100% yield proved that (Z)-1,2-diarylthio-1-alkene was indeed produced through the alkynylsulfide intermediate (Scheme 3).

The analysis of ^1H NMR and ^{13}C NMR spectra showed that all vinyl sulfides prepared presented data in full agreement with their assigned structures. The stereochemistry of trisubstituted alkenes were determined by nuclear Overhauser effect (NOE) experiments. For example, when compound **3c** was irradiated at the peak of vinylic proton (6.99 ppm), 6% enhancement of CH_2 (3.94 ppm) was observed, showing a *cis* relation between them.

In conclusion, a mild, efficient, and selective method for the stereoselective synthesis of (Z)-1,2-diarylthio-1-akenes was developed. Compared with the known methods, our methods use only a catalytic amount of cesium hydroxide and require neither the preparation of alkynyl sulfides nor the use of expensive transition metals. It could provide a new and expedient way for the preparation of (Z)-1,2-diarylthiol-1-alkenes.

EXPERIMENTAL

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard, chemical shifts are quoted and *J* values are given in hertz, and elemental analyses were performed on a Yanaco MT-3CHN elemental analyser. Mass spectra were determined on an HP5989A spectrometer. Reactions were monitored by thin-layer chromatography (TLC) using silica-gel F_{254} aluminum sheets.

General Procedure for the Reaction of Terminal Alkyne with Diaryl Disulfide to Synthesize (Z)-1,2-Diarylthio-1-alkene

Diaryl disulfides (1.0 mmol) and cesium hydroxide (0.2 mmol) were added to a solution of alkyne (2.2 mmol) in DMF (5.0 mL). The reaction mixture was stirred at room temperature under a nitrogen atmosphere for

30 h. Then 20 mL of water was added to the residue and extracted with petroleum ether (3 × 10 ml). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel, giving **3a–3g**.

Data

Compound **3a**

(*Z*)-1,2-Bis(phenylthio)-3-hydroxy-3-methyl-1-butene: ^1H NMR 1.46 (s, 6H), 2.28 (s, 1H), 7.12–7.42 (m, 11H); ^{13}C NMR 29.3, 75.1, 125.4, 127.0, 127.5, 128.8, 129.0, 130.2, 134.8, 134.9, 135.1, 137.7; Ms (m/z): 302 (M^+). Anal. calcd. for $C_{17}H_{18}OS_2$: C, 67.5; H, 6.00; found: C, 67.3; H, 6.01.

Compound **3b**

(*Z*)-1,2-Bis(*p*-methylphenylthio)-3-hydroxy-1-propene: ^1H NMR 2.18 (s, 1H), 2.33 (s, 3H), 2.34 (s, 3H), 4.10 (s, 2H), 6.98 (t, $J = 1.02$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H);^{13}C NMR 21.1, 67.4, 124.6, 126.5, 130.1, 130.2, 132.2, 132.9, 133.4, 137.7, 137.9; Ms (m/z): 302 (M^+). Anal. calcd. for $C_{17}H_{18}OS_2$: C, 67.5; H, 6.00; found: C, 67.3; H, 6.02.

Compound **3c**

(*Z*)-1,2-Bis(phenylthio)-3-methoxy-1-propene: ^1H NMR 3.30 (s, 3H), 3.94 (s, 2H), 6.99 (s, 1H), 7.21–7.36 (m, 6H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR 58.0, 74.4, 126.8, 127.1, 127.3, 129.0, 129.1, 130.0, 130.3, 133.3, 134.6, 134.9; Ms (m/z): 288 (M^+). Anal. calcd. for $C_{16}H_{16}OS_2$: C, 66.6; H, 5.59; found: C, 66.7; H, 5.58.

Compound **3d**

(*Z*)-1,2-Bis(*p*-methylphenylthio)-3-methoxy-1-propene: ^1H NMR: 2.33 (s, 3H), 2.35 (s, 3H), 3.26 (s, 3H), 3.91 (s, 2H), 6.95 (t, $J = 1.02$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR 21.1, 57.8, 76.5, 124.9, 126.8, 129.0, 130.0, 130.1, 132.9, 133.1, 133.3, 137.6, 137.8; Ms (m/z): 316 (M^+). Anal. calcd. for $C_{18}H_{20}OS_2$: C, 68.3; H, 6.37; found: C, 68.5; H, 6.38.

Compound **3e**

(*Z*)-1,2-Bis(phenylthio)-3-phenoxy-1-propene: ^{1}H NMR 4.57 (s, 2H), 6.79 (d, $J = 8.0$ Hz, 2H), 6.93 (t, $J = 7.2$ Hz, 1H), 7.23 (t, $J = 8.0$ Hz, 2H), 7.28–7.29 (m, 6H), 7.47 (s, 1H), 7.49–7.51 (m, 2H), 7.57–7.60 (m, 2H); ^{13}C NMR 72.0, 114.8, 121.1, 127.1, 127.5, 128.5, 129.2, 129.3, 129.3, 130.4, 132.6, 132.7, 134.0, 157.9; Ms (m/z): 350 (M^+). Anal. calcd. for $C_{21}H_{18}OS_2$: C, 72.0; H, 5.18; found: C, 71.9; H, 5.19.

Compound **3f**

(*Z*)-1,2-Bis(*p*-methylphenylthio)-3-phenoxy-1-propene: ^{1}H NMR 2.33 (s, 6H), 4.53 (s, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.92 (t, $J = 6.8$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 4H), 7.20–7.25 (m, 2H), 7.38 (m, 3H), 7.48 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR 21.4, 72.3, 115.2, 121.3, 124.9, 127.1, 127.4, 129.6, 130.4, 130.4, 133.3, 133.5, 133.8, 138.0, 138.1, 158.3; Ms (m/z): 378 (M^+). Anal. calcd. for $C_{23}H_{22}OS_2$: C, 72.9; H, 5.86; found: C, 72.8; H, 5.87.

Compound **3g**

(*Z*)-1,2-Bis(phenylthio)styrene: ^{1}H NMR 7.07 (s, 1H), 7.21–7.34 (m, 9H), 7.42–7.50 (m, 6H); ^{13}C NMR 126.0, 126.5, 127.4, 127.6, 128.2, 128.6, 128.8, 129.2, 129.3, 130.5, 134.5, 135.2, 136.4, 138.7; Ms (m/z): 320 (M^+). Anal. calcd. for $C_{20}H_{16}S_2$: C, 74.9; H, 5.03; found: C, 75.1; H, 5.27.

ACKNOWLEDGMENTS

Projects 20372020 and 02JJY4053 were supported by the National Nature Science Foundations of China and Hunan, respectively.

REFERENCES

1. Beletskaya, I.; Moberg, C. Element–element addition to alkynes catalyzed by the group 10 metals. *Chem. Rev.* **1999**, *99*, 3435–3462.
2. Kondo, T.; Mitsudo, T. Metal-catalyzed carbon–sulfur bond formation. *Chem. Rev.* **2000**, *100*, 3205–3220.
3. Heiba, E. I.; Dessau, R. M. Free-radical addition of organic disulfides to acetylenes. *J. Org. Chem.* **1967**, *32*, 3837–3840.
4. Kuniyasu, H.; Ogawa, A.; Miyazaki, S. I.; Ryu, I.; Kambe, N.; Sonoda, N. Palladium-catalyzed addition and carbonylative addition of diaryl disulfides

and diselenides to terminal acetylenes. *J. Am. Chem. Soc.* **1991**, *113*, 9796–9803.

5. Moro, A. V.; Nogueira, C. W.; Barbosa, N. B. V.; Mendes, P. H.; Rocha, J. B. T.; Zeni, G. Highly stereoselective one-pot procedure to prepare unsymmetrical bis- and tris-chalcogenide alkenes via addition of disulfides and diselenides to terminal alkynes. *J. Org. Chem.* **2005**, *70*, 5257–5268.
6. Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P. Mechanistic study of palladium-catalyzed S-S and Se-Se bonds addition to alkynes. *J. Organomet. Chem.* **2003**, *687*, 451–461.
7. Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P. The first example of polymer-supported palladium-catalyst for stereosective S-S bond addition to terminal alkynes. *Synlett* **2005**, *6*, 1015–1017.
8. Ananikov, V. P.; Beletskaya, I. P. Palladium-catalyzed addition of disulfides and diselenides to alkynes under solvent free conditions. *Org. Biomol. Chem.* **2004**, *2*, 284–287.
9. Ananikov, V. P.; Kabeshov, M. A.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y. New catalytic system for S-S and Se-Se bond addition to alkynes based on phosphite ligands. *Organometallics* **2005**, *24*, 1275–1283.
10. Usugi, S. I.; Yorimitsu, H.; Shinokubo, H.; Oshima, K. Disulfidation of alkynes and alkenes with gallium trichloride. *Org. Lett.* **2004**, *6*, 601–603.
11. Benati, L.; Montevecchi, P. C.; Spagnolo, P. Free-radical reactions of benzenethiol and diphenyl disulphide with alkynes: Chemical reactivity of intermediate 2-(phenylthio)vinyl radicals. *J. Chem. Soc., Perkin Trans. 1* **1991**, *9*, 2103–2110.
12. Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. Highly regio- and stereocontrolled synthesis of vinyl sulfides via transition-metal-catalyzed hydrothiolation of alkynes with thiols. *J. Am. Chem. Soc.* **1999**, *121*, 5108–5114.
13. Kondoh, A.; Yorimitsu, H.; Oshima, K. Palladium-catalyzed anti-hydrothiolation of 1-alkynylphosphines. *Org. Lett.* **2007**, *9*, 1383–1385.
14. Manarin, F.; Roehrs, J. A.; Prigol, M.; Alves, D.; Nogueria, C. W.; Zeni, G. Regio- and stereoselective synthesis of vinyl sulfides via PhSeBr-catalyzed hydrothiolation of alkynes. *Tetrahedron Lett.* **2007**, *48*, 4805–4808.
15. Dabdoub, M. J.; Guerrero, P. J. Jr. Hydroalumination of phenylthioacetylenes: Synthesis and reactions of (Z)- and (E)-1-butyltelluro-1-phenylthio-1-alkenes. *Tetrahedron Lett.* **2001**, *42*, 7167–7172.
16. Watanabe, S. I.; Mori, E.; Nagai, H.; Iwamura, T.; Iwama, T.; Kataoka, T. A novel stereoselective preparation of various vinyl sulfide derivatives using β-alkylthioalkenylselenonium salts. *J. Org. Chem.* **2000**, *65*, 8893–8898.
17. Huang, X.; Xu, X. H.; Zheng, W. X. Stereoselective synthesis of (E)-vinylsulfides via the reaction of vinylzirconium compounds with disulfides. *Synth. Commun.* **1999**, *29*, 2399–2404.
18. Tzalis, D.; Knochel, P. Cesium hydroxide: A superior base for the catalytic alkynylation of aldehydes and ketones and catalytic alkenylation of nitriles. *Angew. Chem. Int. Ed.* **1999**, *38*, 1463–1465.

19. Cohen, R. J.; Fox, D. L.; Salvatore, R. N. A novel and highly efficient synthetic route to unsymmetrical organoselenides using cesium bases. *J. Org. Chem.* **2004**, *69*, 4265–4268.
20. Zeng, J. C.; Lu, R. L.; Xu, X. H. Highly selective synthesis of (Z)-1,2-bis(arylseleno)-1alkenes via addition of diaryldiselenides to terminal acetylenes catalyzed by cesium hydroxide. *Chin. J. Org. Chem.* **2004**, *24*, 1482–1484.
21. Zou, K. B.; Qiu, R. H.; Fang, D. W.; Liu, X. Y.; Xu, X. H. Cesium hydroxide-catalyzed reaction of terminal alkynes with diarylditellurides to synthesize alkynyl tellurides. *Synth. Commun.* **2008**, *38* (13), 2237–2242.
22. Bieber, L. W.; Silva, M. F.; Menezes, P. H. Short and efficient preparation of alkynyl selenides, sufides, and tellurides from terminal alkynes. *Tetrahedron Lett.* **2004**, *45*, 2735–2737.