Tetrahedron Letters, Vol. 34, No. 3, pp. 393-394, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

ALKYNYL SULFIDES AND SELENIDES FROM ALKYNYL BROMIDES AND DIORGANOYL CHALCOGENIDES PROMOTED BY COPPER(I) IODIDE

Antonio L. Braga[a], Aurélia Reckziegel[a], Paulo H. Menezes[a], Hélio A. Stefani[b]*

[a]Departamento de Química, Universidade Federal de Santa Maria, 97119-900 - Santa Maria - RS - Brazil
[b]Instituto de Química, Universidade de São Paulo - P.O.Box 20780 - São Paulo - SP - Brazil

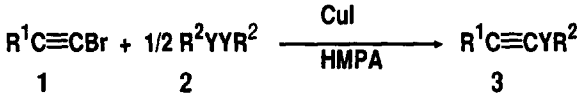
Key Words: Alkynyl Sulfides, Alkynyl Selenides, Alkynyl Bromides and Diorganoyl Chalcogenides

Abstract: Alkynyl sulfides and selenides were obtained in good yields by reacting alkynyl bromides with diorganoyl disulfides and diselenides in hexamethylphosphoric triamide (HMPA) in the presence of copper (I) iodide.

Alkynyl sulfides and selenides are synthetic intermediates of great potentiality.[1,2,3] In previous reports we demonstrated that they can be easily transformed into mono- and disubstituted alkynes by reaction with n-butyllithium, and electrophiles.[4,5] Moreover, selenium free acetylenes are obtained in high yields[6] by oxidation of alkynyl selenides with MCPBA and subsequent treatment with aqueous sodium hydroxide. However, selenium free dimeric acetylenes are obtained when the base treatment is omitted.[7] Z or E vinylic selenides can be prepared by stereoselective reduction of alkynyl selenides.[8]

Some methods to prepare alkynyl selenides were developed by us[4,5,9] and by others;[1,3] all such methods suffer disadvantages in terms of yields, generality or unattractive reaction conditions.

In this communication we describe a new and efficient method of synthesizing alkynyl selenides starting from diorganoyl diselenides, alkynyl bromides and copper(I) iodide, under neutral conditions, according to the following general scheme.



$$\underset{\mathbf{1}}{R^1C{\equiv}CBr} + 1/2\,\underset{\mathbf{2}}{R^2YYR^2} \xrightarrow[\text{HMPA}]{\text{CuI}} \underset{\mathbf{3}}{R^1C{\equiv}CYR^2}$$

Y = S, Se

In this method, no basic conditions or complex metal hydrides for generating the organoselenolate anions are used. The products are formed in good yields by mixing and stirring the reagents in stoichiometric amounts in HMPA at room temperature.[10] The same procedure was used for the synthesis of thioacetylenes. However, in this case, the yields were lower than for the selenium analogs (see entries 9,10, Table 1).

The study of the reaction of 1-bromo-2-phenylethyne (**1**) with diphenyl diselenide (**2**) was undertaken in several solvents; in dimethylformamide (DMF) and dimethylsulfoxide (DMSO), besides compound (**3**) appreciable amounts of dimeric acetylenes (**4**) were formed. In THF no selenides were produced (Table 2).

We also examined the behaviour of other copper salts under the same experimental conditions (CuBr, CuCl, CuCN). Copper (I) iodide was the only one to promove the chalcogenylation efficiently (Table 2).

The results described in this communication constitute an improvement of the method recently described by us[9] for the synthesis of alkynyl selenides. Several synthetic applications for alkynyl chalcogenides are presently under investigation and will be disclosed in future publications.

Table 1. Alkynyl Chalcogenides 3 Prepared According to Scheme

R^1	R^2	Y	Yield^{a,b} (%)	R^1	R^2	Y	Yield^{a,b} (%)
1. Ph	Ph	Se	75	6. C_5H_{11}	n-Bu	Se	60
2. Ph	4-ClC_6H_4	Se	85	7. Ph	t-Bu	Se	70
3. Ph	n-Bu	Se	70	8. C_6H_{13}	t-Bu	Se	60
4. C_5H_{11}	4-ClC_6H_4	Se	83	9. Ph	Ph	S	55
5. C_5H_{11}	Ph	Se	70	10. C_6H_{13}	Ph	S	50

[a] - Isolated yield after column chromatography.

[b] - All alkynyl chalcogenides products exhibit spectral properties (^1H NMR, IR and GC/MS) according with the assigned structures.

Table 2. Selenide Formation in Various Solvents and Copper (I) Salts$^{(a)}$

$$\underset{1}{PhC{\equiv}CBr} + \underset{2}{PhSeSePh} \longrightarrow \underset{3}{PhC{\equiv}CSePh} + \underset{4}{(PhC{\equiv}C)_2}$$

Solvent	Copper (I) Salts	Yield (%) 3	4
HMPA	CuI	75	10
DMF	CuI	60	30
DMSO	CuI	45	50
THF	CuI	-	50
HMPA	CuBr	30	60
HMPA	CuCl	(60)^b	-
HMPA	CuCN	-	65

[a] - 1-bromo-2-phenylacetylene, 1 mmol; diphenyl diselenide, 0.5 mmol; copper (I) salts, 1 mmol; solvent, 2 ml; 2 h, r.t.

[b] - The reaction was performed at 160 °C.

Acknowledgments: The authors are indebted to Prof. J.V.Comasseto and Profª Liliana Marzorati for discussions of manuscript and to FAPERGS, CNPq and GTZ for financial support.

References and Notes

1. Radchenko, S.I.; Petrov, A.A.; *Russ. Chem. Rev.*, **1989**, *58*, 948 and references cited therein.
2. Magriotis, P.A.; Brown, J.T.; Scott, M.E.; *Tetrahedron Lett.*, **1991**, *32*, 5047.
3. Lang, H.; Keller, H.; Imhof, W.; Martin, S.; *Chem. Ber.*, **1990**, *123*, 417.
4. Braga, A.L., Comasseto, J.V.; Petragnani, N.; *Tetrahedron Lett.*, **1984**, *25*, 1111.
5. Braga, A.L., Comasseto, J.V.; Petragnani, N.; *Synthesis*, **1984**, 240.
6. Comasseto, J.V.; Silveira, C.C.; Ferreira, J.T.B.; Catani, V.; *Synth. Commun.*, **1986**, *16*, 283.
7. Comasseto, J.V.; Catani, V.; Ferreira, J.T.B.; Braga, A.L.; *J. Chem. Soc., Chem. Commun.*, **1986**, 1067.
8. Comasseto, J.V.; *J. Organomet. Chem.*, **1983**, *253*, 131.
9. Dabdoub, M.; Comasseto, J.V.; Braga, A.L.; *Synth. Commun.*, **1988**, *18*, 1979.
10. *A Typical Experimental Procedure is as follows:* A mixture of anhydrous CuI (381 mg, 2 mmol), diorganoyl dichalcogenide (1 mmol) and the appropriate alkynyl bromide (2 mmol) in HMPA (4 ml) was stirred for 2 h at r.t., under N_2 atmosphere. The resulting mixture was washed with sat. $CuSO_4$ solution (4 x 5 ml) and dried ($MgSO_4$). After concentration of the solution, the residue was chromatographed on silica gel (eluted with hexane).

(Received in USA 14 August 1992; accepted 14 October 1992)