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CONVENIENT PREPARATION OF ALKYNYL SELENIDES, SULFIDES AND TELLURIDES FROM TERMINAL ALKYNES AND PHENYLCHALCOGENYL HALIDES IN THE PRESENCE OF COPPER(I) IODIDE

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Abstract : Alkynyl selenides, sulfides and tellurides were obtained under very mild conditions by reacting terminal alkynes with phenylchalcogenyl halides in the presence of copper iodide(I).

Alkynyl selenides, sulfides and tellurides are compounds that have been not widely investigated, but are synthetic intermediates of great potentiality.[1-6] We have obtained di-and trisubstituted vinylic selenides through vicinal difunctionalization of alkynyl selenides by reaction with lithium butylcyano cuprate followed by capture of the intermediate vinyl cuprate with several electrophiles.[7]

Some methods of preparing alkynyl selenides were developed by us[6,8-10] and by others.[1,3] Most of these methods suffer from disadvantages in terms of yields, generality or unattractive reaction conditions. In this communication we report a new, general and efficient method to prepare this class of organoselenium compounds.

Previously we found that copper(I) iodide assisted reaction of diorganoyl dichalcogenides with alkynyl bromides in HMPA provided alkynyl chalcogenides in good yields.[8] This method is sometimes disadvantageous since alkynyl bromides are difficult to obtain. In this work we observed that when a mixture of terminal alkynes and phenyl selenenyl bromide is treated with excess of copper(I) iodide at room temperature, alkynyl selenides are obtained in good yields according to the following general scheme :

$$RC{\equiv}CH \quad + \quad C_6H_5YX \quad \xrightarrow[DMF]{CuI} \quad RC{\equiv}CYC_6H_5$$

Y = Se, S, Te
X = Cl, Br

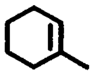
By this method, no basic conditions for generating the alkynides are used and the preparation of the starting alkynyl bromides is avoided. The same procedure could be extended for the synthesis of the corresponding thioacetylenes and telluroacetylenes. However, in this case, the yields were lower than for the selenium analogs (see entries 11-14, Table 1).

It was established that treatment of a DMF solution of the appropriate alkyne with 2 equiv. of CuI(I) and 1 equiv. of phenylselenenyl bromide at room temperature for 2 hours affords the 1-phenylseleno alkyne in good yield (Table 1). It should be noted that under the same conditions; phenyl selenenyl chloride gives the alkynyl selenide in lower yield (entry 2, Table1).[11]

These very mild reaction conditions do not affect alcohols, amines, double bonds and other functional groups (entry 3-7, Table1).

The present procedure nicely complements the method recently described by us,[8,10] offering several advantages such as the easier availability of the starting material, compatibility with various functional groups, and avoidance of the use of the very toxic HMPA.

Table 1 : Alkynyl Chalcogenides Prepared According to Scheme

R	Y	X	Yield [a,b](%)
1. C_5H_{11}	Se	Br	82
2. C_5H_{11}	Se	Cl	76
3. $ClCH_2$	Se	Br	78
4. $HOCH_2$	Se	Br	52
5. 	Se	Br	67
6. 	Se	Br	52
7. $CH_3CO_2CH_2$	Se	Br	70
8. C_6H_5	Se	Br	68
9. $4\text{-}BrC_6H_4$	Se	Br	74
10. C_6H_5Se	Se	Br	58
11. C_6H_5	Te	Br	42
12. C_5H_{11}	Te	Br	28
13. C_5H_{11}	S	Cl	46
14. C_6H_5	S	Cl	38

[a] - Isolated yield after column chromatography

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

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References e Notes

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11. *A Typical Experimental Procedure is as follows :* A mixture of anhydrous CuI (0,381 g, 2 mmol), phenylchalcogenyl halides (1 mmol)and the appropriate alkynes (1 mmol) in DMF (2 mL) was stirred for 2h at r.t., under N_2 atmosphere. The resulting mixture was washed with an aqueous NH_4OH solution (4 x 5 mL) and dried ($MgSO_4$). After concentration of the solution, the residue was chromatographed on silica gel (eluted with hexane).

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