

Short and efficient preparation of alkynyl selenides, sulfides and tellurides from terminal alkynes

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Received 16 January 2004; revised 6 February 2004; accepted 10 February 2004

Abstract—Diphenyl diselenide reacts with terminal alkynes at room temperature in DMSO in the presence of catalytic amounts of copper iodide to give good to excellent yields of alkynyl phenyl selenides. The reaction occurs under neutral conditions and the solvent acts as the oxidant. Diphenyl disulfide and ditelluride undergo the analogous reaction, but require the presence of a weak inorganic base.

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Alkynyl chalcogenides are useful intermediates for the synthesis of several compounds and can be used as versatile building blocks for a variety of chemical purposes.¹

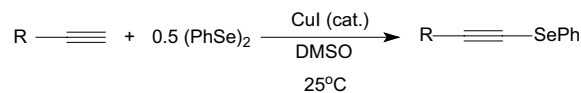
Many methods based on selenium have been developed into standard procedures in organic chemistry. Alkynyl selenides, for example, can be transformed into the corresponding functionalized vinylic selenides by hydroamination,² hydrohalogenation,³ hydrosulfonation,⁴ hydrostannylation,⁵ hydrozirconation⁶ and hydroboration.⁷ Additionally, these compounds can be used in cycloaddition reactions,⁸ addition of nucleophiles such as butyl cyanocuprate⁹ and in the formation of selenonium salts.¹⁰ Likewise, alkynyl sulfides can be used in cycloaddition,¹¹ and cross-coupling reactions,¹² as well as in the preparation of self-assembled monolayers in the production of composite materials.¹³

During the last few years, alkynyl tellurides have been studied little. Although organotellurium compounds have attracted considerable interest as reagents and intermediates in organic synthesis,¹⁴ as monomers for conducting materials,¹⁵ as MOCVD precursors to metal telluride films¹⁶ and in medical applications.¹⁷

Most of the methodologies to synthesize alkynyl chalcogenides are based on the generation of organometallic

species, which has to be performed under strictly anhydrous conditions, limiting thus the scope to base resistant substrates. Although methodologies based on the use of copper were also described,¹⁸ these procedures suffer disadvantages in terms of yields, or unattractive reaction conditions. Indeed, the tedious work up procedure under basic conditions necessary to eliminate large amounts of cuprous and cupric salts affected purity and yield of the isolated products, especially in the case of functionalized alkynes. Similar procedures using diphenyl disulfide and ditelluride gave even less satisfactory results. An alternative preparation has reported comparable yields using iodobenzene diacetate, a rather exotic and expensive oxidant.¹⁹

Although there are no specific mechanistic studies, all such reactions suggest alkynyl radicals as intermediates. Having in mind the known dimerization of copper acetylides on thermolysis or in the presence of oxygen and the well established reactivity of diphenyl diselenide as a radical scavenger, we envisaged the possibility that alkynes might react with diphenyl diselenide in the presence of base and a catalytic amount of copper (I), which should be recycled by oxygen or another oxidant according to Scheme 1.



Scheme 1.

Keywords: Alkynyl selenides; Alkynyl sulfides; Alkynyl tellurides.

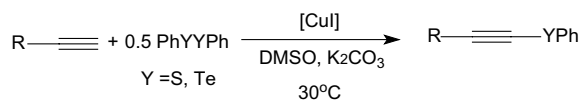
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First attempts using propargyl alcohol carried out in commercial, undried acetonitrile or DMF in an air atmosphere showed no reaction at all in the presence of copper iodide (0.05 equiv) and potassium carbonate (1.0 equiv). However, when DMSO was chosen as the solvent a smooth and clean reaction took place in 4 h at room temperature yielding 56% of the desired selenide (Table 1, entry 1). In the absence of base, the reaction rate was slower, but the yield raised to 69% after 20 h (entry 2). CuI proved to be the best catalyst, as reactions in the presence of CuCl, CuBr, CuCN and CuCl₂ gave only trace amounts of product (entries 3–6). A control experiment in the absence of any copper catalyst showed no reaction at all. On the other hand, the CuI catalyzed reaction worked equally well in carefully degassed solution under Ar atmosphere; this surprising result together with the lack of reactivity in other solvents suggests that DMSO acts not only as the solvent, but also as the oxidant.²⁰

When the optimized procedure of entry 2 was used with other alkynols, aliphatic and aromatic alkynes and ethyl propiolate, complete reaction and nearly quantitative yields of selenides were obtained (Table 2).²¹ In all cases chromatographic purification was unnecessary and pure products were obtained after aqueous workup, extraction and crystallization or short path distillation.

Encouraged by these results we examined analogous reactions with diphenyl disulfide and ditelluride (Scheme 2).

In the absence of base, no reaction at all was observed with both reagents even after several days at room temperature. However, 1 equiv of solid potassium



Scheme 2.

Table 3. Alkynyl sulfides and tellurides prepared according to Scheme 2

Entry	R	Y	Time (h)	Yield (%)
1	CH ₂ OH ^a	S	20	50
2	CH ₂ CH ₂ OH ^a	S	20	80
3	C(CH ₃) ₂ OH	S	20	94
4	C ₆ H ₅	S	20	99
5	<i>n</i> -C ₄ H ₉ ^a	S	72	96
6	CO ₂ C ₂ H ₅	S	20	85
7	TMS ^a	S	20	80
8	CH ₂ OTHP	S	20	90
9	CH ₂ OTBDMS	S	20	82
10	CH ₂ OH ^a	Te	72	30 ^b
11	CH ₂ CH ₂ OH ^a	Te	20	69
12	C(CH ₃) ₂ OH ^c	Te	20	50
13	C ₆ H ₅	Te	72	83
14	<i>n</i> -C ₄ H ₉ ^a	Te	72	92
15	CO ₂ C ₂ H ₅ ^c	Te	20	80
16	TMS ^a	Te	20	30
17	CH ₂ OTHP	Te	20	65
18	CH ₂ OTBDMS	Te	20	65

^a An excess of 0.5 mmol of alkyne was used.

^b Determined by ¹H NMR in the crude extract.

^c KHCO₃ was used as a base.

carbonate was sufficient to produce alkynyl phenyl sulfides in excellent yields (Table 3, entries 1–9).

The only exception was propargyl alcohol, which once more gave the lowest yield (Table 3, entry 2). The same alcohol gave even less satisfactory results with diphenyl ditelluride; large amounts of disproportionation and degradation products were formed under standard conditions (Table 3, entry 10). The protected derivatives, however, gave the desired products in good yields (Table 3, entries 8, 9, 17 and 18). Other alkynols and unfunctionalized alkynes reacted better and even ethyl propiolate gave a clean reaction when the weaker base KHCO₃ was used (Table 3, entries 11–16).

In summary, we reported here a general, mild and efficient synthesis of alkynyl phenyl chalcogenides. Its major advantages in comparison with known methods are: atom economy by the use of both chalcogen atoms of the starting material, catalytic amounts of copper iodide, undried and nontoxic solvent, no inert atmosphere, simple reaction and work up procedures.

Acknowledgements

We gratefully acknowledge the support from CNPq and CNPq/PROFIX (54045/01-4).

Table 1. Influence of catalyst on the formation of selenides

$$\text{HO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{H} + 0.5 (\text{PhSe})_2 \xrightarrow{\text{conditions}} \text{HO}-\text{CH}_2-\text{C}\equiv\text{C}-\text{SePh}$$

Entry	Conditions	Yield (%)
1	DMSO, CuI, K ₂ CO ₃ , 30 °C, 20 h	56
2	DMSO, CuI, 30 °C, 20 h	69
3	DMSO, CuCl, 30 °C, 20 h	2
4	DMSO, CuBr, 30 °C, 20 h	2
5	DMSO, CuCN, 30 °C, 20 h	3
6	DMSO, CuCl ₂ , 30 °C, 20 h	2

Table 2. Alkynyl selenides prepared according to Scheme 1

Entry	R	Time (h)	Yield (%)
1	CH ₂ OH ^a	20	69
2	CH ₂ CH ₂ OH ^a	72	71
3	C(CH ₃) ₂ OH	20	95
4	C ₆ H ₅	20	97
5	<i>n</i> -C ₄ H ₉ ^a	72	90
6	CO ₂ C ₂ H ₅	20	96
7	TMS ^a	20	80
8	CH ₂ OTHP	20	85
9	CH ₂ OTBDMS	20	90

^a An excess of 0.5 mmol of alkyne was used.

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21. General experimental procedure: A mixture of 0.25 mmol of the alkyne, 0.125 mmol of diphenyl dichalcogenide, 0.01 mmol of CuI and 0.5 mmol of base (where indicated) in 1.0 ml of commercial, undried DMSO was stirred at room temperature for the indicated time. After aqueous acidic work up and extraction with ether or dichloromethane, the crude products were purified by crystallization or distillation.