



Synthesis of Chalcogenoacetylenes from Diorgano Diselenides and Terminal Acetylenes employing Bi (III)

Matheus L. Souza (IC), Tiago L. Silva (PG), Daniel S. Rampon (PG), Raoni S. Rambo (PG), Cátia S. Radatz (PG), Ricardo S. Schwab (PQ), Paulo H. Schneider* (PQ)

Instituto de Química, Departamento de Química Orgânica, Universidade Federal do Rio Grande do Sul, UFRGS, 91501-970, Porto Alegre-RS, Brazil.

*e-mail corresponding author paulos@iq.ufrgs.br

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INTRODUCTION

Chalcogenoacetylenes belongs to an important class of compounds on organic synthesis.¹ The literature shows different methodologies to synthesize these compounds using different metals such as copper, indium or magnesium.^{1,2} On the other hand, there are wide lacks of information around bismuth chemistry, especially applied to coupling reaction to afford chalcogenoacetylenes, even its salts presenting low toxicity and low cost when compared with others metals.³ Join together the advantages from bismuth and its salts with *one pot* or multicomponent reactions we fulfill important topics at green chemistry such as atom economy, low toxicity, low cost and short pathways synthesis. Thus, in this work we developed an *one pot* methodology using bismuth and its salts to synthesize chalcogenoacetylenes compounds.

RESULTS AND DISCUSSION

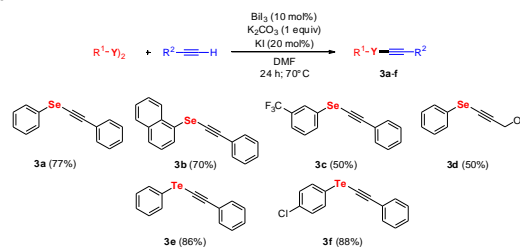
The suitable reaction conditions were established according recent studies of our group on the synthesis of chalcogenoacetylenes using In (III) salts.⁴ In this sense, commercially available diphenyl diselenide **1a** (0.5 mmol), phenylacetylene **2a** (1.0 mmol), bismuth catalysts (10 mol%), KI (20 mol%) and base (1.0 equiv) were allowed to react in DMF (2 mL). The reaction times and temperatures were evaluated, and good conversions to product **3a** were reached under 70°C for 24h for all reaction conditions. The reaction was also effective with several bismuth sources (table 1). In fact, we found out that the combination of less hygroscopic BiI₃ and K₂CO₃ afforded good conversion of product **3a** (entry 8). A variety of solvents were evaluated (toluene, DMF, DMSO, MeCN, EtOH, and water), with best results employing polar aprotic solvents. We also could observe that use of iodide (KI) additive afforded better conversions of **3a**, probably from *in situ* synthesis of more soluble K[BiI₄] catalyst.⁵ The reaction scope is currently under investigation (scheme 1).

Table 1. Optimization of reaction conditions.

Entry ^a	Catalyst	Base	Conversion (%) ^b
1	Bi	K ₂ CO ₃	76
2	BiCl ₃	K ₂ CO ₃	71
3	BiI ₃	K ₂ CO ₃	81
4	BiBr ₃	K ₂ CO ₃	66
5	Bi(NO ₃) ₃ ·5H ₂ O	K ₂ CO ₃	71
6	BiI ₃	(<i>i</i> -Pr) ₂ NH	60
7	BiI ₃	Imidazole	65
8	BiI ₃	K ₂ CO ₃	81
9	BiI ₃	Pyridine	67

^a 0.5 mmol of **1** / 1.0 mmol of **2**. ^b All reactions were performed for 24h and 70°C. ^c GC conversions.

Up to now, we could observe better yields for teluroacetylenes (**3e** and **3f**), suggesting an efficient bismuth catalyzed cleavage of Te-Te bond in the catalytic cycle. We are also working on the study of a probable mechanism.



Scheme 1. Preliminary scope of the bismuth catalyzed synthesis of chalcogenoacetylenes.

CONCLUSION

Currently, our research group developed a multicomponent reaction using bismuth and its salts to promote the coupling reaction between alkynes and dichalcogenides with good yields.

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