Synthesis of (Z)-thiobutenynes using NaOH or TBAOH as activator: a comparative study

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Keywords: Hydrothiolation; 1,3-diacetylenes; organylthiolate anion; (Z)-thiobutenynes; TBAOH.

INTRODUCTION

Organylthioenynes have became useful synthons recently, due their possible applications on the synthesis of enediynes and thiophenes.

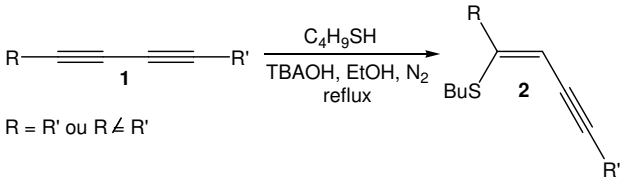
Recently the preparation of (*Z*)-thiobutenynes through hydrothiolation of 1,3-diacetylenes using $NaBH_4$ and $C_4H_9SSC_4H_9$ to generate nucleophilic sulfur species such as BuS^- and PhS^- was reported by us.[1]

This systematic study allowed us to understand the limitations and potential of this methodology in the preparation of (*Z*)-thiobutenynes. However, (*Z*)-thiobutenyne **2**, was obtained in low yield (40%) using this methodology.

RESULTS AND DISCUSSION

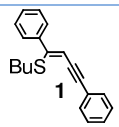
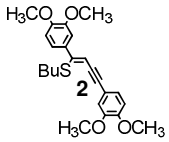
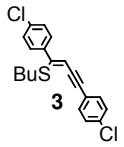
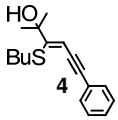
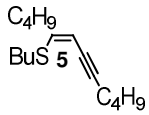
In order to improve the synthesis of (*Z*)-thiobutenynes with high yields we investigated the hydrothiolation reaction to prepare **2** with traditional method using $C_4H_9SH/NaOH$,[2] and other using TBAOH 40% in H_2O (1.4 equiv), as phase transfer catalyst, to generate the anion $C_4H_9S^-$ from the C_4H_9SH (1.4 equiv) (Scheme 1).

Scheme 1. Hydrothiolation reaction



The hydrothiolation reaction in the presence of TBAOH and NaOH have proved to be highly region-, stereo-, and chemoselective. However, the five examples of (*Z*)-thiobutenynes synthesized by new approach were obtained in better yields and shorter reaction time than ones prepared only using NaOH (Table 1).

Table 1. (*Z*)-thiobutenynes synthesized

(*Z*)-thiobutenynes	Time (Yield %)[b] NaOH	Time (Yield %)[b] TBAOH
	8h (71)	30 min. (93)
	24h (56)	15 min. (90)
	8h (52)	15 min. (78)
	1h (71)	5 min. (83)
	24h (65)	9 h (89)

[a] Reactions performed in the presence 1,3-diacetylene, TBAOH (1.4 equiv), BuSH (1.4 equiv) in EtOH under reflux. [b] Product isolated and purified by column chromatography.

CONCLUSION

In conclusion, we developed a new and highly efficient procedure to prepare (*Z*)-thiobutenynes in good to excellent yields on shorter reaction time. Studies are being conducted to demonstrate the generality of this methodology.

ACKNOWLEDGEMENTS

FUNDECT-MS, PROPP-UFMS, CNPq

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