



Synthesis of Thiophene Acetylenes via Sonogashira Cross-Coupling Reactions

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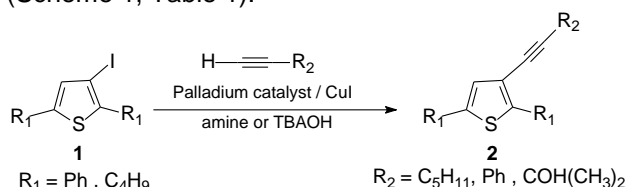
Keywords: Sonogashira cross-coupling reactions; 3-iodothiophenes; thiophene acetylenes, TBAOH.

INTRODUCTION

Organochalcogene compounds (S, Se and Te) have been investigated in recent decades because of their many applications in synthetic organic chemistry, preparation of new materials, and medicinal chemistry. Among them, the thiophene group has emerged in recent years as one of the most-studied compounds by synthetic organic chemists, due to being found in various chemical compounds, with a broad range of applications in the electronics industry to produce electroluminescent diodes (OLED), organic field effect transistors (OFET), photovoltaic cells, sensors, semiconductors, liquid crystals and "displays".¹ Because of the strong interest in the synthesis of new thiophene compounds and its applications, in this communication we show our results in the synthesis of thiophene acetylenes through Sonogashira cross coupling reactions.²

RESULTS AND DISCUSSION

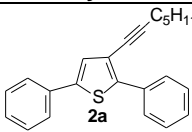
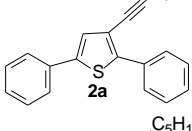
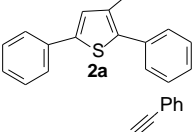
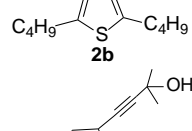
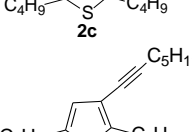
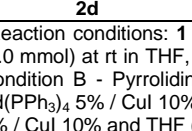
For the synthesis of the thiophene acetylenes type **2**, Sonogashira cross-coupling reactions were performed using 3-iodothiophene **1** (1mmol) and heptyne (2mmol) in THF (3ml), PdCl₂(PPh₃)₂ 5% and Cul 10% as catalytic system and 2 equiv. of Et₃N. In this case, thiophene acetylene **2a** was obtained in 62% yield after 48 h of reaction at room temperature (Scheme 1, Table 1).



Considering of the elevated time reaction we made a systematic study, changing palladium catalysts, amines, and use of TBAOH 40% in water as phase transfer catalyst (PTC).²

In Table 1 we show the results in different reactions conditions. The use of TBAOH in substitution to the Et₃N or pyrrolidine, showed the best results (Scheme 1, Table 1).

Table 1: Thiophene acetylenes synthesized^a

Thiophene acetylenes	Reaction conditions	Time (Yield %) ^b
	A	48h (62%)
	B	24h (81%)
	C	2h (95%)
	C	3.5h (83%)
	C	2h (94%)
	C	2h (91%)

^aReaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), Condition A - Et₃N (2.0 mmol) at rt in THF, catalytic system: PdCl₂(PPh₃)₂ 5% / Cul 10%, Condition B - Pyrrolidine (2.0 mmol) at rt in THF, catalytic system: Pd(PPh₃)₄ 5% / Cul 10%, Condition C -TBAOH (2.0 mmol), Pd(PPh₃)₄ 5% / Cul 10% and THF (3.0 ml) / MeOH (3ml) at rt. ^bisolated products.

CONCLUSION

The results obtained in the synthesis of thiophene acetylenes using Pd(PPh₃)₄ / Cul and TBAOH as PTC in substitution of amines were very satisfactory.

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