



Studies on the synthesis of (poly)arylacetylenes using cardanol and glycerol as raw materials

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INTRODUCTION

Arylacetylenes are precursors for the construction of conjugated polyarylacetylenes, which have been widely used in the preparation of helical artificial polymers for applications in a variety of fields. The design, synthesis and application of helical polymers with helix direction control, have become a field of great interest in recent years.¹ Physical, chemical and electric stimuli interfere dramatically in structure, form and morphology of these polymers, resulting in great importance to achieve smart materials. In achiral (poly)arylacetylenes, the macromolecular helicity with a preferential direction of the helix can be induced by the presence of a chiral component, incorporated into the main chain or into the mesogenic units, making the polymer to serve as a chiral sensor. Rod-shaped helical polymers with an excess of one of the propellers, frequently show chiral liquid-crystalline phase.² Given the importance of these polymers, herein we present a study of synthetic conditions for preparing arylacetylenes from national industry byproducts, cardanol (**1**) (as pendant and mesogenic unit) and glycerol (chirality-inducer) aiming to obtain innovative helical chiral polymers with liquid crystalline features.

RESULTS AND DISCUSSION

The chlorohydrin (**3**) and epoxide (**4**) were obtained from the reaction of cardanol (**1**) and epichlorohydrin (**2**) (derived from glycerol) and used as electrophiles in a S_N2 reaction with ethynylaniline (**5**) to give the arylacetylene (**6**) (Fig. 1).

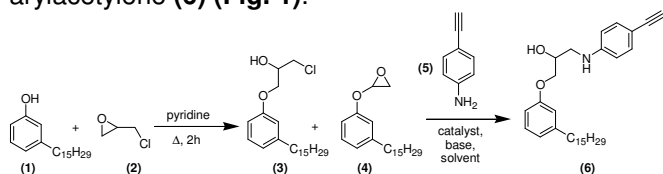


Figure 1. Schematic representation for the synthesis of (**6**) from (**1**) and (**2**).

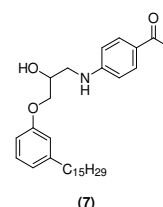
The S_N2 reaction above has proved be tough and some reaction conditions were performed for the coupling between the mixture of (**3**) and (**4**) with (**5**), as shown in **Table 1**. Structures of the products were elucidated by NMR analyses.

Table 1. Reactional conditions for the synthesis of (**6**)

	Solvent	Catalyst	Base	Time (h)	T (°C)	Product /yield
1	CH ₂ Cl ₂	Nal	pyridine	4	*	-
2	THF ³	alumin	-	6	reflux	-
3	ACN ⁴	CoCl ₂ **	-	3	reflux	7/ 50%
4	DMSO	-	pyridine	3	reflux	-
5	CH ₂ Cl ₂ ⁵	Amberlist 15	-	3	reflux	-
6	ACN	-	pyridine	24	reflux	6/ 40%

*Sealed tube.** N₂ atmosphere.

The entry 3, using CoCl₂ as catalyst, was most effective to couple the reagents, however, led to hydrolysis of the alkyne to methyl ketone **7**, in 50% yield.



CONCLUSION

The desired arylacetylene (**6**) could be successfully synthesized using a classical S_N2 approach, and will be used in our continuous research to produce helical chiral polymers with liquid crystalline features.

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REFERENCES

- ¹ Louzao, I.; Seco, J. M.; Quiñoa, E. e Riguera, R. *Angew. Chem. Int. Ed.* **2010**, *49*, 1.
- ² Maeda, K.; Kamiya, N. e Yashima, E. *Chem. Eur. J.* **2004**, *10*, 4000.
- ³ Harrak, Y. e Pujol M. D. *Tetrahedron Lett.* **2002**, *43*, 819.
- ⁴ Iqbal, J. e Pandey, A. *Tetrahedron Lett.* **1990**, *31*, 575.
- ⁵ Vijender, M.; Kishore, P.; Narender, P. e Satyanarayana, B. *J. Mol. Catal. A: Chem.* **2007**, *266*, 290.