SYNTHESIS OF BIS(PROPARGYL) POLYOXYETHYLENE ETHERS

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RESUME : Les éthers dipropargyliques de polyoxyéthylène sont obtenus, avec de bons rendements, par action du bromure de propargyle sur les éthers de polyoxyéthylène glycols. La réaction est réalisée en milieu basique, en utilisant l'hydrogénosulfate de tétrabutylammonium comme catalyseur de transfert de phase.

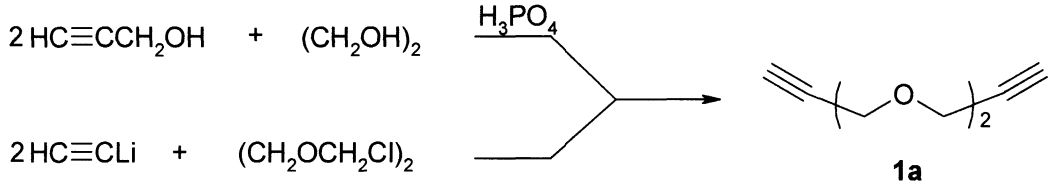
ABSTRACT : Bis(propargyl) polyoxyethylene ethers were obtained, in good yields, by action of propargylbromide on polyoxyethylene glycol ethers. The reaction occured in basic medium, using tetrabutylammonium hydrogenosulfate (TBAHS) as a catalyst.

Key words : *bis(propargyl) polyoxyethylene ether, propargylbromide, polyoxyethylene glycol ethers.*

INTRODUCTION

Few dipropargylic compounds were described and used as precursor in the preparation of crown ethers [1] and in complexation reaction [2].

Very few synthesis of dipropargyl polyoxyethylene ethers were reported. Only the preparation of ethylene glycol dipropargyl ether **1a** by condensation of propynol with ethylene glycol in presence of phosphoric acid, or by action of lithium acetylide on ethylene bis(chloromethyl) ether were described [3] (Scheme 1).

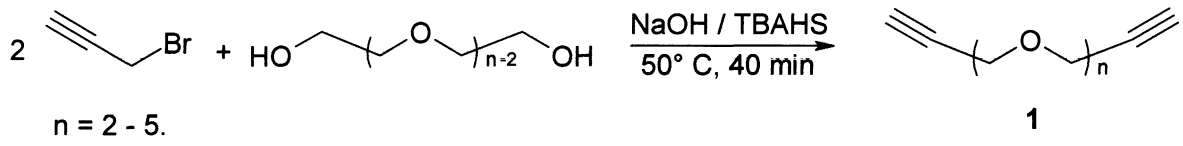


Scheme 1

RESULTS AND DISCUSSION

In the present work, we extend the method used for the preparation of polyoxyethylene diallyl ethers [4, 5] to realize the synthesis of polyoxyethylene dipropargyl ethers **1a-d**.

In this case the condensation occurs, in basic medium, between propargyl bromide and polyoxyethylene glycol (Scheme 2). The yield of the reaction is notably increased when TBAHS is added as a catalyst (Table I)



Scheme 2 : *Condensation of propargyl bromide on polyoxyethylene glycol ethers.*

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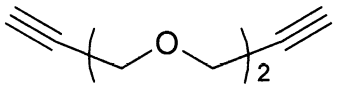
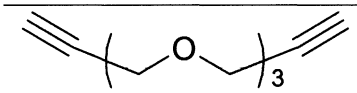
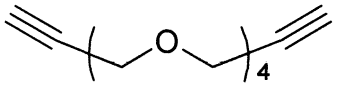
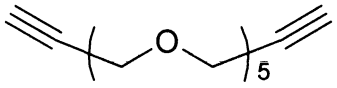
Table I : Synthesized polyoxyethylene dipropargyl ethers.

Dipropargyl ether **1**		Rdt(%)	T_{eb} (°C/mmHg)
	**1a**	66	95/15
	**1b**	70	94/0.1
	**1c**	74	110/0.1
	**1d**	80	127/0.1

As can be shown from table I, a series of symmetrical polyoxyethylene dipropargyl ethers were prepared in good yields.

The known ethylene dipropargylic ether **1a** was described as being an effective inhibitor of the acid corrosion of metals [3]. It may be interesting to study the evolution of this property when the polyoxyethylene chain becomes longer (**1b**, **1c** and **1d**). This analytical work is in progress.

On the other hand, ionic [6], radical additions [7] and polymerisation [8] reactions may prove to be useful in the synthesis of many classes of products using these polyoxyethylene dipropargylic ethers as starting materials [9].

EXPERIMENTAL

The IR spectra were recorded on a Perkin Elmer Paragon 1000 PC. The ^{1}H and ^{13}C NMR spectra were recorded on a Brüker AC 300 at 300 MHz and 75 MHz respectively. TMS was used as standard reference for ^{1}H and ^{13}C NMR spectra. HRMS spectra (IC mode) were recorded on MAT 95 SBE. Propargyl bromide, polyoxyethylene glycols, TBAHS and sodium hydroxide are Fluka commercial products.

General procedure: To a vigorously stirred mixture of sodium hydroxide (6 g, 0.15 mol), water (0.5 mL), TBAHS (0.2 g) and polyoxyethylene glycol (25 mmol) at 45 °C, 0.15 mol of propargylbromide was added. The mixture was filtered, and the salt was washed with methylene chloride (2 x 25 mL). After drying on Na_2SO_4, the solvent was evaporated. The excess of propargyl bromide was removed and the residue was distilled under vacuum to give compounds **1a-d** (Table I).

The spectroscopic NMR ^{1}H, ^{13}C and HRMS data were grouped respectively in tables II, III and IV.

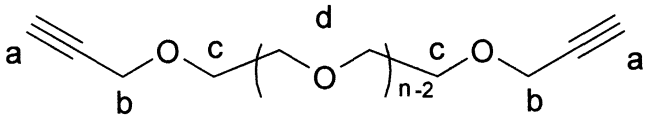


Table II : ^{1}H NMR spectral data ($CDCl_3$).

	δHa	δHb	δHc	δHd
1a	(t) 2.51	(d) 4.19	3.72	-
1b	(t) 2.50	(d) 4.10	(m) 3.65 - 3.71	(m) 3.53 - 3.63
1c	(t) 2.50	(d) 4.13	(m) 3.65 - 3.70	(m) 3.52 - 3.62
1d	(t) 2.49	(d) 4.16	(m) 3.65 - 3.70	(m) 3.52 - 3.62

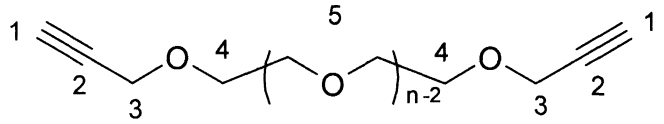


Table III : ^{13}C NMR spectral data.

	δC_1	δC_2	δC_3	δC_4	δC_5
1a	79.68	74.88	58.29	68.75	-
1b	79.69	74.75	58.31	69.03	70.35
1c	79.70	74.79	58.24	69.20	70.37
1d	79.71	74.81	58.27	69.52	70.32

Table IV: HRMS values of compounds **1**

	SM Calculated	SM Found	Δ (umm)
1a	138.068079	138.068700	0.6
2b	182.094294	182.093494	-0.8
2c	226.120509	226.121003	0.5
2d	270.146723	270.146031	-0.7

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