

REGIOSELECTIVE SYNTHESIS OF TRIAZOLE-OLIGOMERS VIA 1,3-DIPOLAR Cu(I)-CATALYZED CYCLOADDITION

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ABSTRACT: Polyoxyethylene bis(4-substituted 1,2,3-triazole) ethers were prepared from copper(I) catalyzed [3+2] dipolar cycloaddition of azide to bis(propargyl) polyoxyethylene ethers.

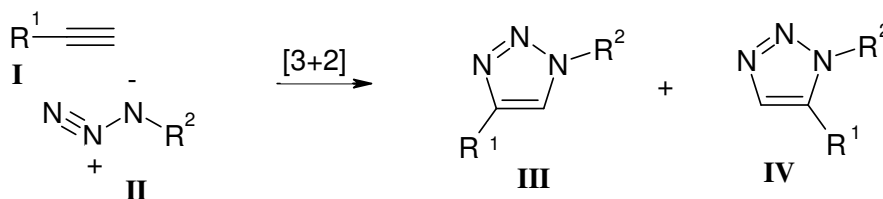
RESUME: Les bis(1,2,3-triazole 4-substitué) éthers de polyoxyéthylène sont préparés par la réaction de cycloaddition [3+2] dipolaire, catalysée par Cu(I) des azides avec les bis(propargyl) éthers de polyoxyéthylène.

Keywords: 1,2,3-Triazole, bis(triazole), perfluoroalkylethyl azide, 1,3-dipolar cycloaddition, Bis(propargyl) polyoxyethylene ethers.

INTRODUCTION

1,2,3-Triazoles constitute an important variety of heterocyclic compounds. They are used in several industrial fields [1], such as agrochemicals [2], corrosion inhibitors [3] dyes [4], optical brighteners [5], biologically active agents [6], cytostatic [7] virostatic [8], antiproliferative agents [9] and GABA-antagonists [10,11] and as synthetic intermediates of antibiotics [12-14] and antihistaminic agents [15]. On the other hand, polyoxyethylene chains are also an interesting variety of molecules, employed in several fields such as the synthesis of surfactants [16] and polymers [17], rather known in the medical [18], pharmaceutical [19], and biological fields [20]. In particular, the triazole-oligomer derivatives obtained from cross-coupling of triazoles and polyoxyethylene chains were described as binder-linkages for high-energy systems [21]. The length of the chain linking the two triazole moieties has a remarkable impact on mechanical properties of matrices produced by the triazole-cured polymers [22].

The most used approach for the synthesis of 1,2,3-triazoles is the thermal 1,3-dipolar cycloaddition of alkyne to azide compounds described by Huisgen (Scheme 1) [23]. This reaction is by far, the most well-known example of the "Click Chemistry". It was adopted thereafter to synthesize several types of molecules [24].



Scheme 1

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The uncatalyzed reaction requires heating at high temperatures which can lead to the decomposition in some cases and results in poor regioselectivity, giving a mixture of 1,4- and 1,5-disubstituted isomers with low yields of the desired 1,2,3-triazole (Scheme 1) [25].

At moderate temperatures, only the activated alkyne compounds were shown to react with azides [26]. This reaction has known an important development with the use of a Cu(I)-containing catalyst which leads to the predominant formation of 1,4-disubstituted triazoles **III** (Scheme 1) [27].

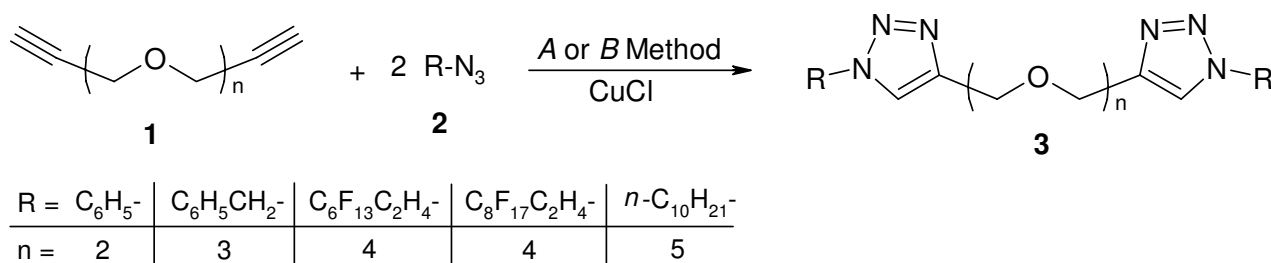
Alkyl and aryl azides are communally used in cycloaddition reactions [28, 29], whereas the perfluoroalkylethyl azides are less known [30]. They were used as intermediates to prepare perfluoroalkylated amines [31], imines [32] and recently employed in cycloaddition reactions [33, 34], resulting in products that have interesting surface properties [34].

We have shown that the radical addition of perfluoroalkyl iodides or perfluoroalkylethane thiols to bis(propargyl) polyoxyethylene ethers **1** [35] gave perfluoroalkyl polyadducts [36]. On the other hand, we have also shown that the same ethers **1** produced the corresponding tetraketones which, in the presence of aqueous hydrazine, were transformed into polyoxyethylene bis(pyrazoles) [37].

Here, we report the synthesis of a series of 1,4-disubstituted polyoxyethylene bis(1,2,3-triazoles) **3**, via reaction of alkyl, aryl and perfluoroalkylethyl azides **2** with polyoxyethylene bis(propargyl) ethers **1**, showing that the latter products (**1**) can undergo two simultaneous cycloaddition reactions on the two terminal triple bonds.

RESULTS AND DISCUSSION

Bis(propargyl) ethers **1** react regioselectively with azides **2** to give a series of polyoxyethylene bis(1,2,3-triazole) ethers **3**. As in the case of simple triazole compounds [17-20], the corresponding 1,4-disubstituted triazoles **3** were formed by thermal 1,3-dipolar cycloaddition (Scheme 2).



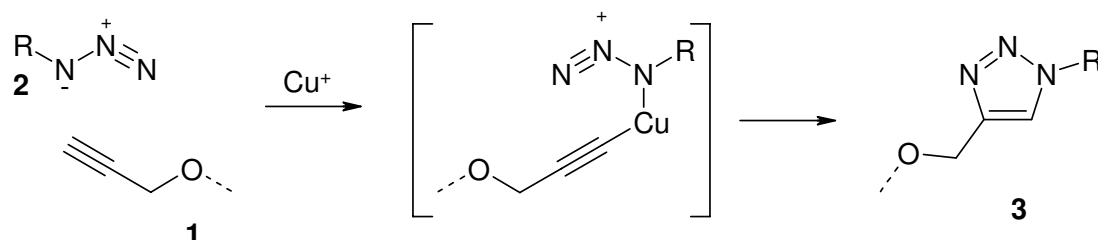
Scheme 2

Using the thermal Cu(I) catalyzed 1,3-dipolar cycloaddition (Method A) [1, 27], or the moderately catalyzed cycloaddition, at room temperature in aqueous medium (Method B) [30c], the reaction affords selectively the 1,4-disubstituted isomer **3**. The yields obtained according to method A were slightly higher than those using method B.

Table I: Polyoxyethylene bis(triazole) **3**

R	n	Bis(triazole) 3	Y (%) A	Y (%) B
C ₆ H ₅ -	2	3a	95	85
C ₆ H ₅ -CH ₂ -	3	3b	96	87
C ₆ F ₁₃ C ₂ H ₄ -	4	3c	90	79
C ₈ F ₁₇ C ₂ H ₄ -	4	3d	94	81
n-C ₁₀ H ₂₁ -	5	3e	95	85

The mechanism of the copper(I)-catalyzed reaction, proposed by Palacios *et al.* [38] and reinvestigated in detail by Himo *et al.* [39], involves the addition of a Cu(I)-acetylide to an azide in a stepwise sequence and gives the five-membered propargyl cuprate as an intermediate which leads to the 1,4-disubstituted triazole product (Scheme 3). Similarly, the formation of products **3** (Scheme 2) is believed to undergo the same mechanism.



Scheme 3

CONCLUSION

New bis(triazol) compounds were synthesized by two different Cu(I) catalyzed methods, a thermal method and a mild condition reaction method. In these compounds, the 1,2,3-triazolic heterocycles are bridged by a hydrophilic tunable polyoxyethylene chain [40] and linked to a hydrophobic fluorinated, hydrocarbon or aryl side group. Such a composition may give to these compounds interesting surface [41], complexing [42] and biological [6-15] properties.

EXPERIMENTAL

1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AC 300 spectrometer at 300, 75 and 282 MHz respectively, using TMS as standard reference for 1H and ^{13}C spectra and $CFCl_3$ for the ^{19}F ones. HRMS spectra in chemical ionization mode, were carried out on a MAT 95 SBE spectrometer. The silica gel used is of Merck 7734 type.

Preparation of polyoxyethylene bis(propargyl) ethers **1**:

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). The volatiles were evaporated and the crude product was distilled under vacuum to give compounds **1**.

Preparation of perfluoroalkyl, benzyl, and *n*-decane azides **2**:

A mixture of 8 mmol of (perfluoroalkyl tosylate, benzyl bromide or *n*-decane bromide), 2 g of sodium azide, 0.5 g of ammonium chloride in 5 mL of water and 20 mL of methanol was stirred for 24 h at 80 °C. The methanol was evaporated, the crude product extracted with diethyl ether (3 x 80 mL), washed with water, dried with $MgSO_4$ and purified on silica gel chromatography column using diethyl ether as eluant to obtain compounds **2**.

Preparation of phenyl azide **2**:

Aniline 3.72 g (40.00 mmol) was added to H_2O (20 mL) and $HCl_{conc.}$ (20 mL). The mixture cooled at 0 °C and $NaNO_2$ (2.95 g, 42.70 mmol) dissolved in H_2O (5 mL) was added dropwise, stirred for 10 min, then NaN_3 (2.61 g, 40.15 mmol) dissolved in H_2O (5 mL) was added slowly, keeping the temperature under 2 °C. The resultant suspension was stirred for 20 more min, and then the phases were separated. The aqueous phase was extracted with diethyl ether (3 x 50 mL). The combined organic phases were dried under Na_2SO_4 and the solvents evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2), giving the product as a yellow oil. Yield: 3.75 g (75 %).

Typical procedure for synthesis of polyoxyethylene bis(triazole) ethers 3:

Method A: A mixture of dipropargylic ether **1** (5 mmol), alkyl, aryl or perfluoroalkyl azide **2** (11 mmol) and 10 mg of CuCl in 15 mL of dry toluene was heated at 100 °C for 16 h. The toluene was evaporated, the crude product, purified on silica gel chromatography column, using a mixture of ethyle acetate/acetone (80/20) as eluant to obtain compounds **3** as viscous oils.

Method B: A mixture of (5 mmol), dipropargylic ether **1**, alkyl, aryl or perfluoroalkyl azide **2** (11 mmol), CuCl (10 mg), triethylamine (5 mmol), acetonitrile (6 mL) and water (10 mL) was stirred at room temperature for 36 h. Then 10 mL water was added, the mixture was extracted with ether (3 x 10 mL), the combined organic layer was washed with saturated brine and dried with sodium sulfate. After removal of solvent, the crude product was purified on silica gel chromatography column, using a mixture of ethyle acetate/acetone (80/20) as eluant to obtain pure compounds **3**.

Spectral Data for Compounds 3a-e

1,6-bis(1-Phenyl-1H-1,2,3-triazol-4-yl)-2,5-dioxahexane (3a): ^1H NMR (CDCl_3): δ 3.79 (s, 4H, $2\text{CH}_2\text{-O}$), 4.80 (s, 4H, $2\text{O-CH}_2\text{-C=}$), 7.35-7.85 (m, 10H, Ph), 8.09 (s, 2H, $=\text{CH}$, triazol); ^{13}C NMR (CDCl_3): δ 64.59 (s, 2C, $\text{O-CH}_2\text{-C=}$), 69.83 (s, 2C, $\text{CH}_2\text{-O}$), 119.83 (s, 4C, $=\text{CH}$, Ph), 120.76 (s, 2C, $=\text{CH}$, triazol), 125.95 (s, 2C, $=\text{CH}$, Ph), 129.91 (s, 4C, $=\text{CH}$, Ph), 136.93 (s, 2C, N-C=C) ppm; HRMS calcd.: 376.16477, found: 376.16447, $\Delta(\text{umm}) = -0.3$.

1,9-bis(1-Benzyl-1H-1,2,3-triazolo-4-yl)-2,5,8-trioxanone (3b): ^1H NMR (CDCl_3): δ 3.58-3.65 (m, 8H, $4\text{CH}_2\text{-O}$), 4.63 (s, 4H, $2\text{CH}_2\text{-C=}$), 5.48 (s, 4H, $\text{CH}_2\text{-N}$), 7.23- 7.34 (m, 10H, Ph), 7.54 (s, 2H, CH=); ^{13}C NMR (CDCl_3): δ 54.05 (s, 2C, $\text{CH}_2\text{-N}$), 64.56 (s, 2C, $\text{CH}_2\text{-C=}$), 69.59 (s, 2C, $\text{CH}_2\text{-O}$), 70.39 (s, 2C, $\text{CH}_2\text{-O}$), 122.73 (s, 2C, CH=C), 128.07, 128.65, 128.86 (10C, CH , Ph), 134.65 (s, 2C, C= , Ph), 145.39 (s, 2C, N-C=) ppm; HRMS calcd.: 448.22244, found: 448.22206, $\Delta(\text{umm}) = -0.4$.

1,12-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-1H-1,2,3-triazol-4-yl)-2,5,8,11-tetraoxadodecane (3c): ^1H NMR (CDCl_3): δ 2.83 (m, 4H, $\text{CH}_2\text{-CF}_2$, $^3J_{\text{HF}} = 14.21$ Hz), 3.64 (m, 12H, $\text{CH}_2\text{-O}$), 4.72 (m, 8H, $2\text{CH}_2\text{-C=}$, $2\text{CH}_2\text{-N}$), 7.68 (s, 2H, $2=\text{CH}$); ^{13}C NMR (CDCl_3): δ 31.71 (t, 2C, $\text{CH}_2\text{-CF}_2$, $^2J_{\text{CF}} = 21.22$ Hz), 42.22 (s, 2C, $\text{CH}_2\text{-N}$), 64.37 (s, 2C, $\text{CH}_2\text{-C=}$), 69.52 (2C, $\text{CH}_2\text{-O}$), 70.52 (s, 2C, $\text{CH}_2\text{-O}$), 123.33 (s, 2CH=C), 146.19 (s, 2C=); ^{19}F NMR (CDCl_3): δ -127.39 (m, 4F, $2\text{CF}_{2\omega}$), -124.68 (m, 4F, $2\text{CF}_{2\gamma}$), -123.07 (m, 4F, $2\text{CF}_{2\delta}$), -123.01 (m, 4F, $2\text{CF}_{2\beta}$), -115.34 (m, 4F, $2\text{CF}_{2\alpha}$, $^3J_{\text{HF}} = 14.21$ Hz), -82.02 (t.t., 6F, 2CF_3 , $^3J_{\text{FF}} = 9.65$ Hz) ppm; HRMS calcd.: 1004.16003, found: 1004.16053, $\Delta(\text{umm}) = 0.5$.

1,12-bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl-1H-1,2,3-triazol-4-yl)-2,5,8,11-tetraoxadodecane (3d): ^1H NMR (CDCl_3): δ 2.85 (m, 4H, $\text{CH}_2\text{-CF}_2$, $^3J_{\text{HF}} = 14.75$ Hz), 3.65 (m, 12H, $\text{CH}_2\text{-O}$), 4.70 (m, 8H, $2\text{CH}_2\text{-C=}$, $2\text{CH}_2\text{-N}$), 7.70 (s, 2H, CH=); ^{13}C NMR (CDCl_3): δ 31.85 (t, 2C, $\text{CH}_2\text{-CF}_2$, $^2J_{\text{CF}} = 21.70$ Hz), 42.36 (s, 2C, $\text{CH}_2\text{-N}$), 64.65 (s, 2C, $\text{CH}_2\text{-C=}$), 69.78 (2C, $\text{CH}_2\text{-O}$), 70.65 (s, 2C, $\text{CH}_2\text{-O}$), 123.46 (s, 2CH=C), 146.50 (s, 2C=); ^{19}F NMR (CDCl_3): δ -127.24 (m, 4F, $2\text{CF}_{2\omega}$), -124.51 (m, 4F, $2\text{CF}_{2\gamma}$), -123.82 (m, 4F, $2\text{CF}_{2\delta}$), -122.99 (m, 8F, $4\text{CF}_{2\epsilon}$), -122.73 (m, 4F, $2\text{CF}_{2\beta}$), -115.24 (m, 4F, $2\text{CF}_{2\alpha}$, $^3J_{\text{HF}} = 14.75$ Hz), -81.94 (t.t., 6F, 2CF_3 , $^3J_{\text{FF}} = 9.74$ Hz) ppm; HRMS calcd.: 1204.14742, found: 1204.14801, $\Delta(\text{umm}) = 0.6$.

1,15-bis(1-decyl-1H-1,2,3-triazol-4-yl)-2,5,8,11,14-pentaoxapentadecane (3e): ^1H NMR (CDCl_3): δ 0.90 (t, 6H, 2CH_3), 1.30 (m, 28 H, 14CH_2), 1.90 (m, 4H, 2CH_2), 3.65 (m, 16H, $8\text{CH}_2\text{-O}$), 4.35 (m, 4H, $2\text{CH}_2\text{-N}$), 4.65 (d, 4H, $2\text{CH}_2\text{-C=}$), 7.58 (d, 2H, CH=C); ^{13}C NMR (CDCl_3): δ 14.10 (s, 2C, CH_3) 22.64 (s, 2C, $\text{CH}_2\text{-CH}_3$), 26.48- 31.85, 48.52 (s, 2C, $\text{CH}_2\text{-N}$), 50.35 (2C, $\text{CH}_2\text{-}$

C=), 61.04- 70.22 (8C, $\underline{\text{CH}_2\text{-O}}$), 122.46 (s, 2C, $\underline{\text{CH}=\text{C}}$), 145 (2C, $\underline{\text{C}=\text{}}$) ppm; HRMS calcd.: 636.49397, found: 636.49466, $\Delta(\text{umm}) = 0.7$.

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