

SYNTHESIS OF TRIPODAL CYCLOTRIVERATRYLENE (CTV) DERIVATIVES AS SCAFFOLDS FOR BINDING SUGARS

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INTRODUCTION

In recent years, significant progress has been made in the area of synthetic or artificial receptors containing two binding arms, which have been often designated as tweezers-like synthetic receptors.[1,2]

To increase diversity, possibly affinity, selectivity, and other properties, we are interested in the development of artificial receptors containing three binding arms, that is, tripodal molecules containing ultimately three different sites of interaction. Still, the number of suitable molecules to serve as suitable scaffolds for attachment of three binding sites is very limited. Noteworthy examples in the literature include steroids,[3] diverse macrocycles,[4] Kemp's triacid,[5] amidopyridine,[6] and hexasubstituted benzenes.[7]

We have been particularly interested in the cyclotrimeratrylene (CTV) scaffold. Here, we describe the obtaining of deprotected CTV for the construction of versatile CTV-scaffold derivatives as tripodal artificial synthetic receptor.

RESULTS

A completely and partially deprotected tripodal cyclotrimeratrylene (CTV)-based scaffolds intermediate (*compound 04*, **Figure 2**) have been prepared.

The CTV(O-Allyl)₃, (*compound 03*, **Figure 1**) (as intermediate compound in obtaining CTV-scaffold derivatives), was synthesized in two steps on a multigram scale starting from vanillyl alcohol.[8]

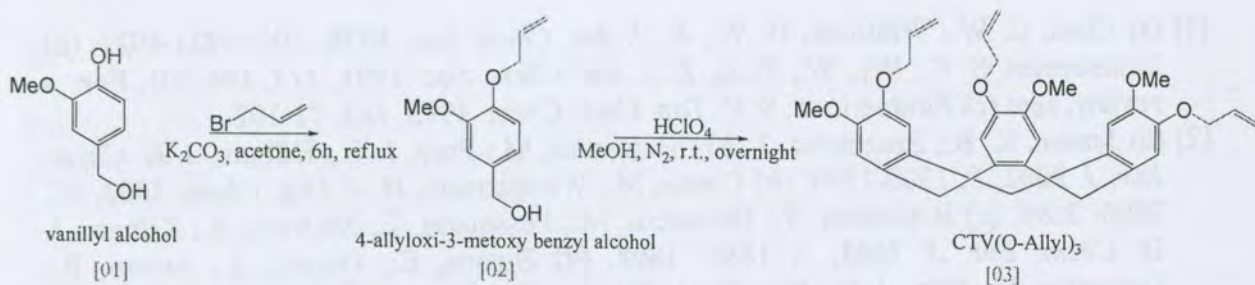


Figure 1. CTV(O-Allyl)₃ synthesis

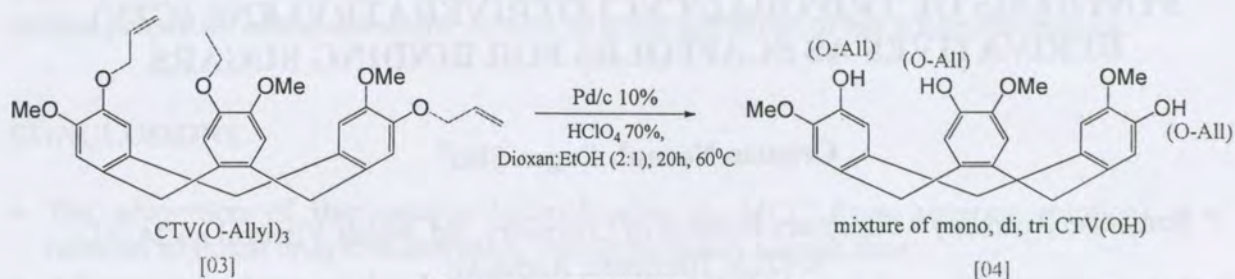


Figure 2. CTV(OH)₃ synthesis

EQUIPMENT AND METHODS

All reagents were purchased from commercial sources and used without further purification. When was needed, anhydrous solvents were used.

NMR spectra were recorded on a Varian 300 MHz spectrometer against the line of the solvent (CDCl₃). Chemical shifts are given in ppm.

The TLC (thin layer chromatography) analysis was performed on Kieselgel Merck plates with fluorescence indicator.

Column chromatography was carried out using 220-400 mesh silica (Aldrich). Visualization of the chromatograms was accomplished with a UV lamp.

CONCLUSIONS

- The CTV(O-Allyl)₃ deprotection reaction has been tried by few methods, those with Pd/c 10%, HClO₄ (70%) giving the best results.
- The CTV deprotection allow attaching later a number of natural amino compounds like (aminoacids, peptides, proteins) and non-natural amino compounds like (dyes, synthetic porphyrins or polyamides).
- Obtaining quantitative results in the deprotection reaction is still a not solved problem and is now under study.

LIST OF REFERENCES

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- [2] (a) Jensen, K. B.; Braxmeier, T. M.; Demarcus, M.; Frey, J. G.; Kilburn, J. K. *Chem. Eur. J.* **2002**, *8*, 1300-1309. (b) Conza, M.; Wennermers, H. *J. Org. Chem.* **2002**, *67*, 2696- 2698. (c) Braxmeier, T.; Demarcus, M.; Fessmann, T.; McAteer, S.; Kilburn, J. D. *Chem. Eur. J.* **2001**, *7*, 1889- 1898. (d) Botana, E.; Ongerì, S.; Ariezo, R.; Demarcus, M.; Frey, J. G.; Piarulli, U.; Potenza, D.; Gennari, C.; Kilburn, J. D. *Chem. Commun.* **2001**, 1358-1359.

