A simple Palladium catalyst system for the efficient cyclotrimerization of acetylenes

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Abstract

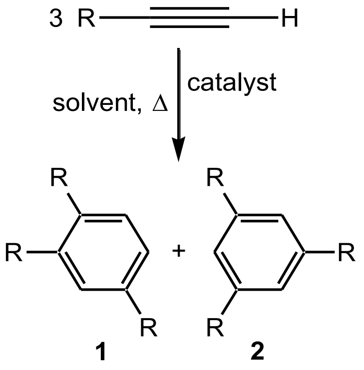
A cyclotrimerization of 4-R-phenylacetylenes variously substituted is performed using Pd(OAc)$_2$ and Ph$_3$P as catalytic system. The substituted 1,3,5-triphenylbenzenes and 1,2,4-triphenylbenzenes isolated were characterized by NMR spectroscopy and a reaction mechanism is also proposed.

INTRODUCTION

The importance of the C-C triple bond chemistry has been well recognized since this function was shown to be one of the main building blocks of organic and material chemistry.[1]

Recently, alkyne scaffolds have been used as starting compounds for the synthesis of nanotubes.[2]

It has been found also that a large number of arylethynes and alkylethynes can undergo cyclooligomerization reaction (named the Rappe cyclotrimerization[3]) in the presence of a catalytic amount of Rhodium or Ruthenium porphirins,[4] of Cobalt containing disulfide[5] or diamine[6] ligands, and of zwitterionic complexes M^+-CH_2-$AlCl_3^-$.[7] Scheme 1.



Scheme 1

MATERIALS AND METHODS

A similar reaction has been found in our laboratory using Pd(0) as catalyst. The 4-R-phenylacetylene (1.0 mmol), the Pd(OAc)$_2$ (0.02 mmol), and the Ph$_3$P (0.08 mmol) were solubilized in tetrahydrofuran (10 ml) and heated at reflux temperature under N$_2$, (R = Ph, 4-OCH$_3$-Ph, 4-NC-Ph). The reaction was monitored by GC and GC-MS; after 15 h the 4-R-phenylacetylene disappeared. The crude product was purified by column chromatography on silica gel (eluent: diethyl ether:petroleum ether = 1:9) affording **1** and **2** as inseparable mixture. ^{1}H-NMR an ^{13}C-NMR spectroscopic data were in agreement with the assigned structures.

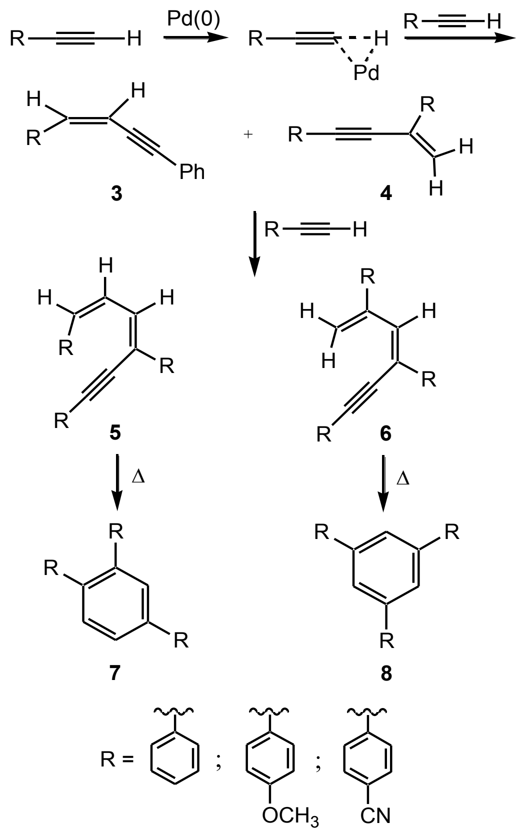
RESULTS AND DISCUSSION

Variously substituted 1,3,5-triphenylbenzenes and 1,2,4-triphenylbenzenes were prepared by cyclotrimerization reaction using Pd(0) as catalyst.

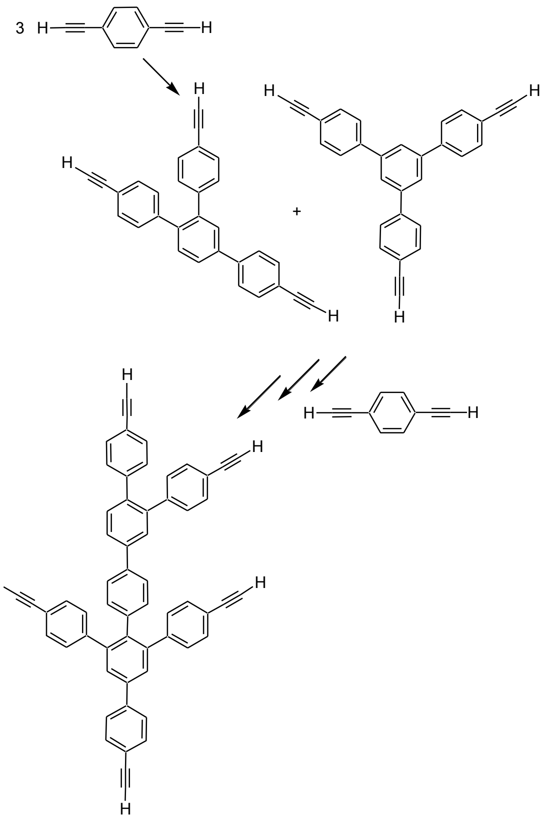
For this reaction we have also suggested a different mechanism compared with that reported in literature, Scheme 2.

The isolated compounds show a good π-conjugation extended to the whole molecule surface. This property make them suitable substrates for various applications in the field of material sciences such as self-assembly of π-stacked systems, or starting materials for OLEDs.

Encouraged by the obtained results and in order to synthesize scaffolds even more conjugated, we have reacted, in the same experimental conditions above reported, the 1,4-diethynylbenzene having two unsaturated moieties. This substrate, allowing the trimerization with both ethynic groups, has afforded different planar polymers showing similar structure



Scheme 2



Scheme 3

but different molecular weight, Scheme 3.

The number of polymers having different molecular weight is dependent on the reaction time at reflux. The reaction could be monitored by TLC and HPLC. The Figure 1 shows the TLC result of the reaction mixture after 10 min. at reflux compared to 15h at reflux, (eluents: ethyl acetate/petroleum ether = 5/95). After 10 min. (A) several spots can be seen due to the formation of several oligomers, while the only spot observed after 15h (B) is due to the formation of a unique big polymer.

The next challenging step will be the study of the applications of these oligomers in the material science field.

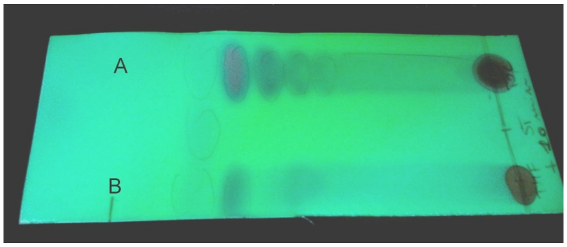


Figure 1

ACKNOWLEDGEMENTS

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