Category

Synthesis of Materials and Unnatural Products

Key words

annulenes

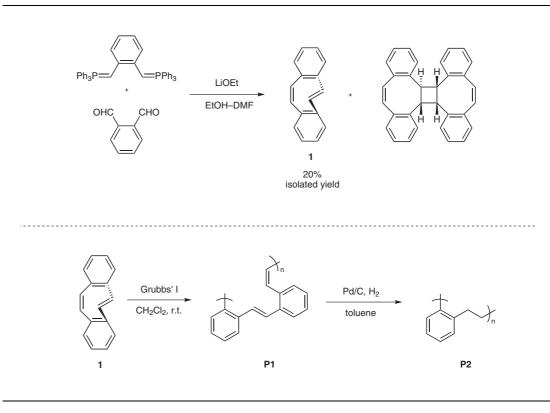
metathesis

cyclooctatetraenes



M. CARNES, D. BUCCELLA, J. DECATUR, M. L. STEIGERWALD, C. NUCKOLLS* (COLUMBIA UNIVERSITY, NEW YORK, USA) Helical (5*Z*,11*E*)-Dibenzo[*a*,*e*]cyclooctatetrene: A Spring-Loaded Monomer *Angew. Chem. Int. Ed.* **2008**, *47*, 2982-2985.

A Spring-Loaded ROMPer



Significance: The [8]annulene 1, with one double bond in the trans configuration was synthesized in 20% yield on a 20 mmol scale. Compound 1 was shown to be kinetically stable but thermodynamically unstable, with the cis, cis isomer being thermodynamically favored. Compound 1 winds into a helical conformation in the solid state and both enantiomers of 1 are present within the unit cell of a crystal. The calculated strain energy for 1 is 18 kcal/mol, which allows it to participate in ringopening metathesis polymerization (ROMP), unlike its *cis,cis* isomer. Compound **1** forms living polymers when mixed with Grubbs' catalyst (1st gen.) and additional tricyclohexylphosphine ligand. In this fashion, regioregular poly(phenylene vinylene) (PPV) with all-ortho linkages was prepared and its hydrogenated derivate characterized by GPC and ¹H and ¹³C NMR spectroscopy.

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Comment: The authors reinvestigated chemistry pursued by Wittig et al. (*Justus Liebigs Ann. Chem.* **1955**, *593*, 127) and correctly identified a monomer that displays unique reactivity and yields interesting polymers. The regioselectivity of the ROMP imparts a well-defined secondary structure to **P1** that can be exploited in sensing or molecular recognition schemes.