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Synthesis of Non-Estrogenic Polymer Precursors by Isomerizing Metathesis

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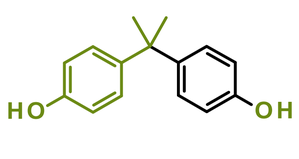
Abstract

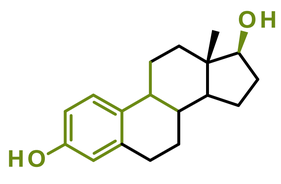
The increasing concern about the side-effects of Bisphenol A (BPA), one of the most common polymer precursors, is raising the interest in finding safer, non-toxic alternatives. Isomerizing metathesis was applied to renewable resources such as eugenol or cashew nut shell liquid (CNSL) in order to obtain stilbene derivatives as potential replacements for BPA. We measured the estrogenic activity of these monomers and studied their reactivity in polymer synthesis in comparison to BPA.

Introduction

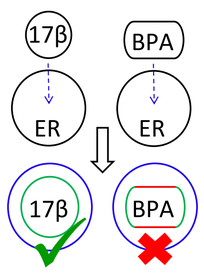
Bisphenol A is the main precursor of polycarbonates and epoxy resins[1] used in the fabrication of many materials and commodity chemicals. However, BPA mimics the activity of estradiol (17β)[2] and upon leaching from food packages, it causes side-effects such as cardiovascular diseases or fertility issues.[3]



Bisphenol A



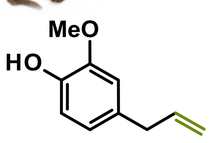
Estradiol



Different interaction with estrogen receptors (ER)

Stilbene derivatives as alternatives to BPA

For a sustainable synthesis of monomers, widely available renewable resources, such as eugenol and cashew nut shell liquid (CNSL) were chosen as starting materials.[4,5]

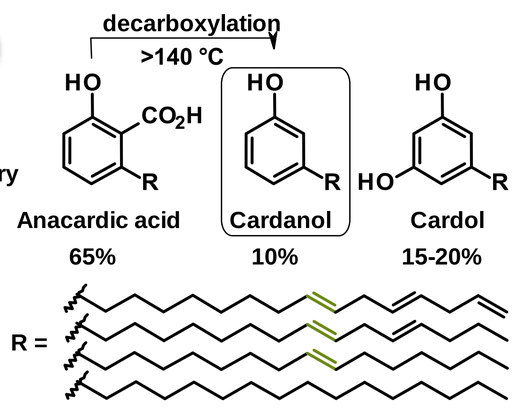


Eugenol

occurs in essential oils (clove, basil)

CNSL

by-product of cashew nut industry

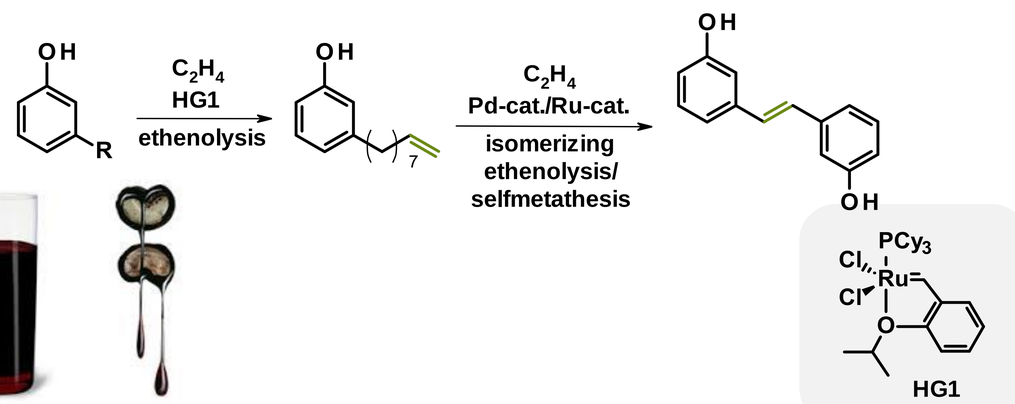


The aliphatic side chain is shortened using isomerizing metathesis as key step.[6] This process is mediated by the uniquely active isomerization catalyst $[Pd(\mu\text{-}Br)(^tBu_3P)]_2$ (**Pd-cat.**)[7] and state-of-the-art ruthenium metathesis catalysts.

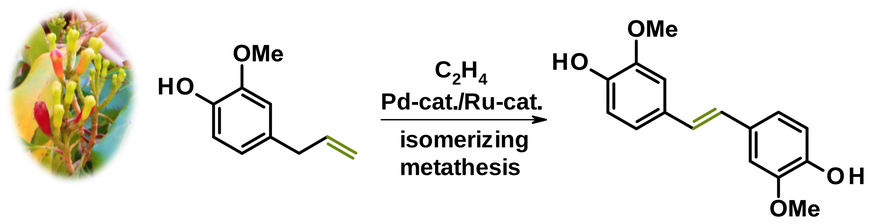
The isomerization catalyst continuously moves a double bond along a carbon chain, while the metathesis catalyst simultaneously shuffles the substituents at the double bond to form the stilbene.

Synthesis of Polymer Precursors

The cardanol mixture was converted into 3-(non-8-enyl)phenol after ethenolysis and distillation. This reaction was followed by a one-pot derivatization consisting of an isomerizing ethenolysis and a subsequent double bond metathesis, which leads to the dihydroxystilbene.

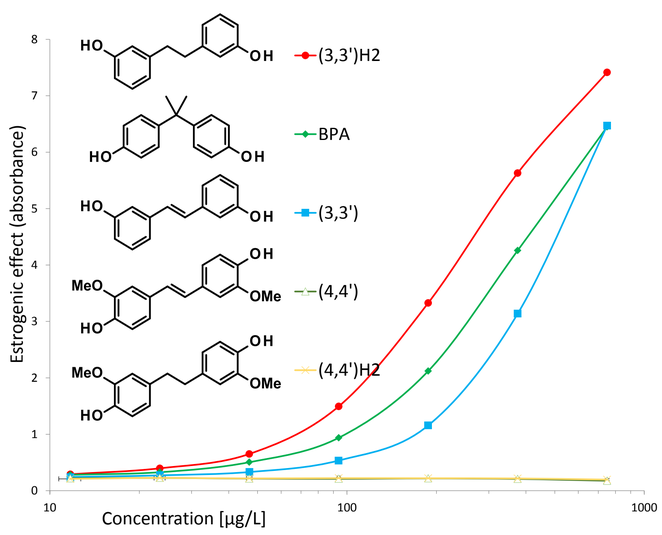


Starting from eugenol, a one-pot reaction afforded the corresponding stilbene.



For diversification of the building blocks, diphenylethane analogues of both stilbenes could be synthesized after a one-pot hydrogenation step.

Estrogenicity assay – Yeast Estrogen Screen (YES)[8]



Polycarbonate synthesis and the sustainable thiol-ene polymerization were chosen as applications to test the reactivity of these substrates towards polymer synthesis.

The polymers present similar properties to the ones derived from BPA, showing the potential of these monomers as alternatives structures.

References:

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