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Construction of Polycyclic π -Conjugated Systems Incorporating an Azulene Unit Following the Oxidation of
1,8-Diphenyl-9,10-bis(phenylethynyl)phenanthrene
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Polycyclic Aromatic Hydrocarbon with Embedded Azulene Unit

Category

Synthesis of
Materials and
Unnatural Products

Key words

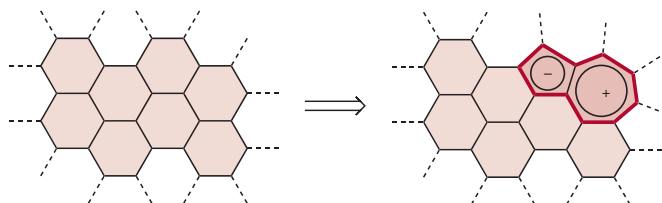
azulenes

non-alternate
hydrocarbons

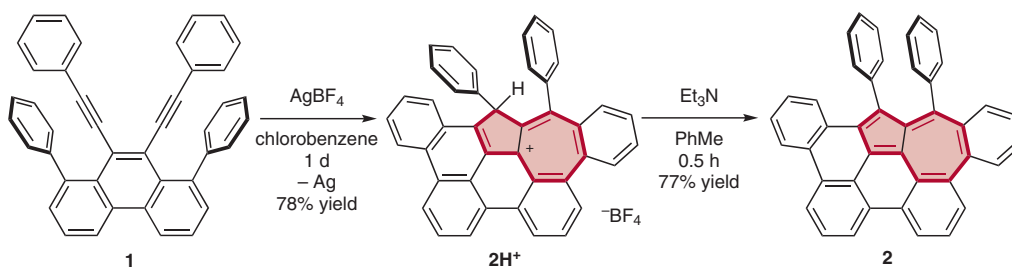
polycyclic aromatic
hydrocarbons

Synfact
of the month

Embedding of azulene structure and electronics into a PAH:



Synthesis of azulenium- and azulene-embedded PAH:



Significance: Incorporation of heptagons and pentagons into a polycyclic aromatic hydrocarbon (PAH) core leads to changes in the molecular geometry and electronic properties of the original PAH. This report demonstrates the use of silver(I) cations to achieve an efficient synthesis of an azulene-embedded PAH **2**, which is a challenging issue that is plagued by limited methodologies.

Comment: Two-electron oxidation of the silver(I) ion promoted a three-fold transannulation reaction between the aromatic and acetylene units of **1** resulting in the selectively embedded azulenium cation **2H⁺**, which could be subsequently deprotonated by trimethylamine to afford the neutral azulene-embedded PAH **2**. Compound **2** exhibited a low-energy absorption band featuring characteristics of the non-alternant moiety, along with reversible one-electron redox events for the oxidation or reduction of **2**, resulting in tropylium cation or cyclopentadienyl anion scaffolds, respectively.

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