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Helical Atropisomers of Strained Phenanthrenes by Photochemistry of Aromatic Pauson–Khand Cycloadducts

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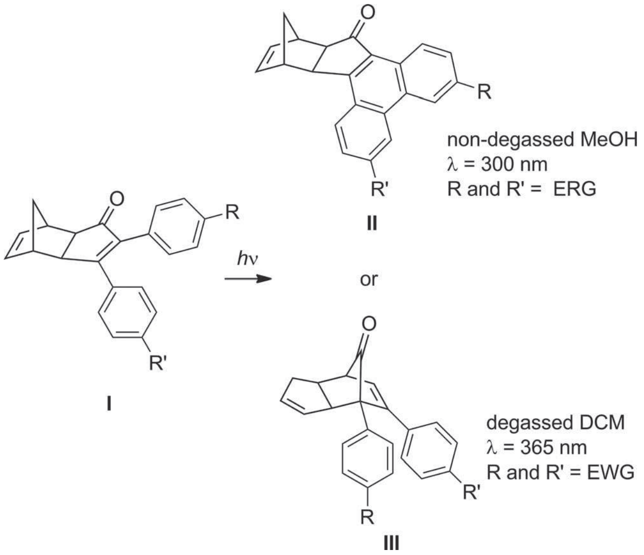
Norbornene and norbornadiene Pauson–Khand adducts of bis(3,5-dimethylphenyl)acetylene and bis(3,4,5-trimethylphenyl)acetylene were prepared. These compounds were subjected to a photochemical 6π-electrocyclic oxidative aromatization reaction to give the corresponding phenanthrene compounds in satisfactory yield in the case of norbornene derivatives. The helical twist imposed by the methyl groups at the 3- and 5-positions on the aromatic rings led to two atropisomers as a result of the non-planar helical phenanthrene structure. The molecular structures and conformational stabilities of these atropisomers were examined by X-ray crystallography and variable temperature NMR studies.

Introduction

Photochemical reactions are among the most convenient tools for the synthesis of strained compounds. During the last decade, we have uncovered several photochemical reactions involving cyclopentenones obtained from Pauson–Khand reactions (PKRs).[1,2] We have recently studied[2] the photochemistry of aromatic cycloadducts **I**, which, by choosing suitable reaction conditions, can selectively provide either electrocyclized (**II**) or photorearranged (**III**) products (Scheme 1). The starting cyclopentenones are easily obtained either in racemic or enantioenriched form[3] by Pauson–Khand cycloaddition of bis-aromatic acetylenes with norbornadiene.

The straightforward access to phenanthrene compounds **II** from diaryl acetylenes led us to study the synthetic applications of compounds **II** further. We envisioned that a suitable substitution pattern in the 3- and 5-positions or the 3-, 4-, and 5-positions of the aryl groups would result in conformationally restricted phenanthrene compounds. A relatively bulky alkyl group (R) would cause severe van der Waals repulsion between the two closely arranged substituents in the 3- and 5-positions, and distortion of the aromatic plane would be expected in order to relieve such steric congestion. If this occurred, the molecule would adopt a helical structure, leading to two possible isomers ($\mathbf{V_M}$ and $\mathbf{V_P}$; Scheme 2). Thus, if the interconversion barrier between the two conformers, which in turn is dependent on the steric volume of the alkyl groups, is high enough, the stereoisomers could be separated, thus leading to compounds with helical chirality.



Scheme 1. Electrocyclization or photorearranged products arising from aromatic cycloadducts **I**.

Helicenes[4,5] have attracted increasing attention because of their extraordinary optical[6] and electronic properties,[4c,4d,7] which are closely associated with their helically chiral structure. Therefore, we addressed whether the chirality of the bicyclic cyclopentenone skeleton could be transmitted to the putative helicenic chirality of the phenanthrene, thus allowing atropisomeric compounds $\mathbf{V_M}$ and $\mathbf{V_P}$ to be formed in a stereoselective way (Scheme 2).[8] In other words, we aimed to determine whether the electrocyclic

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