



C₂-Symmetric 1,2-di(flourenylidene)cyclobutanes: syntheses, structures, rearrangements and reactivity



Sandra Milosevic, Helge Müller-Bunz, Yannick Ortin, Dominique Schreiber, Andrew D. Phillips*, Michael J. McGlinchey*

School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

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ABSTRACT

Attempted deprotonation of 1,2-di(flourenylidene)cyclobutane, **8**, using *n*-butyl or *tert*-butyl-lithium led instead to 1,4-addition across the 1,3-butadiene unit to yield the 1-(9*H*-flourenyl)-2-(9-butyl-9*H*-flourenyl)cyclobutene **10** or **11**, respectively; analogously, *n*-butyl-lithium and *trans*-3,4-bis(trimethylsilyl)-1,2-di(flourenylidene)cyclobutane, **12**, furnished the corresponding 1,4-adduct **13**. Bromination of **8** with *N*-bromosuccinimide led to mono-, di- and tri-bromo derivatives whereby, in the *trans*-di-bromo systems, the helical character of the *trans* bromines could either match (in **16**) or oppose (in **17**) the helicity of the flourenylidenes. In accordance with DFT calculations, the diastereomer **17** is the favoured product, and a pure sample of **16** in solution underwent equilibration via cleavage of the C(3)–C(4) linkage such that **17** became the major isomer. Attempted addition of bromine to 3,4-di(flourenylidene)-1,2-diphenylcyclobutene, **24**, unexpectedly yielded the diketone 2,3-di(9*H*-flouren-9-ylidene)-1,4-diphenylbutane-1,4-dione, **25**. The structures of **10**, **11**, **13**, **16**, **17** and **25** were determined by X-ray crystallography.

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1. Introduction

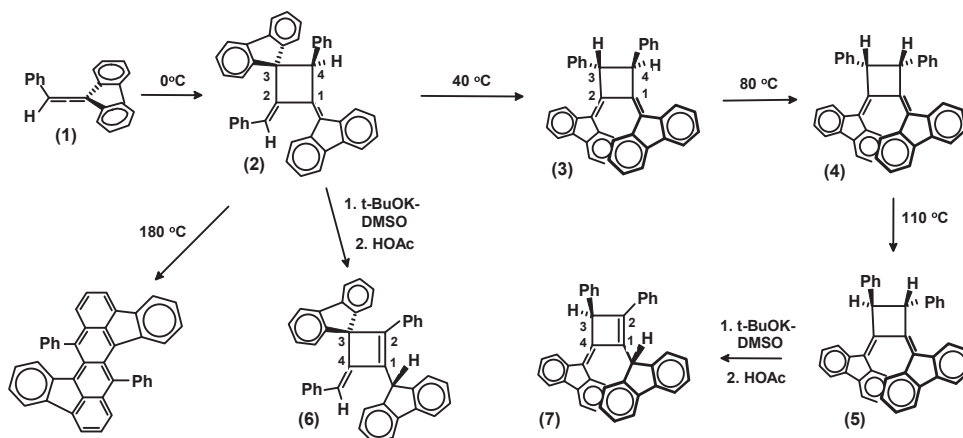
In the course of our recent studies on the chemistry of flourenylidene-allenes,^{1–6} in particular their dimers that undergo thermal rearrangement to form ultimately electroluminescent diindenotetracenes, we prepared a series of racemic C₂-symmetric 1,2-di(flourenylidene)cyclobutanes.^{7–12} The two-fold axial symmetry of these systems arises as a consequence of the overlap of the flourenylidene substituents with their large (ca. 8.8 Å) wingspans.^{8,9} As a result of this structural rigidity, one can envisage the existence of three isomers bearing identical substituents at the C(3) and C(4) positions. Indeed, as shown in Scheme 1, dimerization of 3,3-(biphenyl-2,2'-diyl)-1-phenylallene, **1**, yields initially the head-to-tail product, **2** and then sequentially the *trans*, *cis* and *trans* tail-to-tail isomers **3**, **4** and **5**, respectively.⁸

In **3**, the *trans*-3,4-diphenyl groups adopt the same helicity as the overlapping flourenylidenes;⁸ in contrast, in **5** the helical senses of the two *trans* phenyls and the two flourenylidenes are opposed,

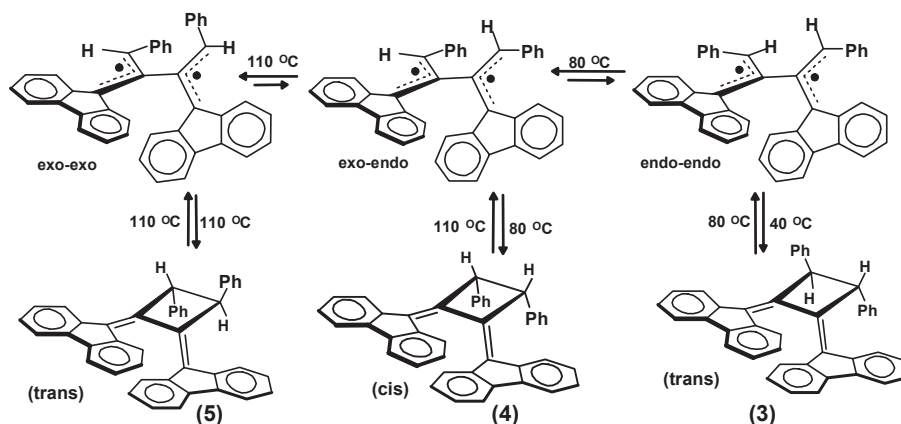
thus minimizing the steric interactions between the large substituents. A common structural feature in these molecules is the unusually long C(3)–C(4) linkage, which ranges from 1.587 to 1.605 Å,^{8–10} and implies that cleavage of this bond to form the appropriate diradicals has a relatively low barrier. Indeed, the mechanism of sequential formation of these isomers has been rationalized in terms of homolysis of the C(3)–C(4) bond in **2** to generate a tetramethylene-ethane diradical, which can exist in three isomeric forms: *endo,endo*, *endo,exo* and *exo,exo*, where *endo* and *exo* refer to the orientations of the phenyl substituents relative to the two allyl fragments, as depicted in Scheme 2.⁸ Now, following the allene dimerization mechanism proposed by Christl,¹³ conrotatory ring closure of the *endo,endo* form leads to the *trans* isomer **3**, while at successively higher temperatures *exo,endo* and *exo,exo* diradicals lead to the *cis* and *trans* products **4** and **5**, respectively.

The ready availability of these palindromic¹⁴ two-fold axially symmetrical systems, whose structures are controlled by the overlapping flourenylidenes, is reminiscent of *binap* and related molecules that exhibit severely restricted rotation of naphthyl substituents and are very widely used in asymmetric catalysis.¹⁵ To this end, we chose to probe the reactivity of the 1,2-di(flourenylidene)cyclobutane framework with the longer term goal of incorporating two phosphino groups or other potentially chelating substituents, as in Scheme 3 below.

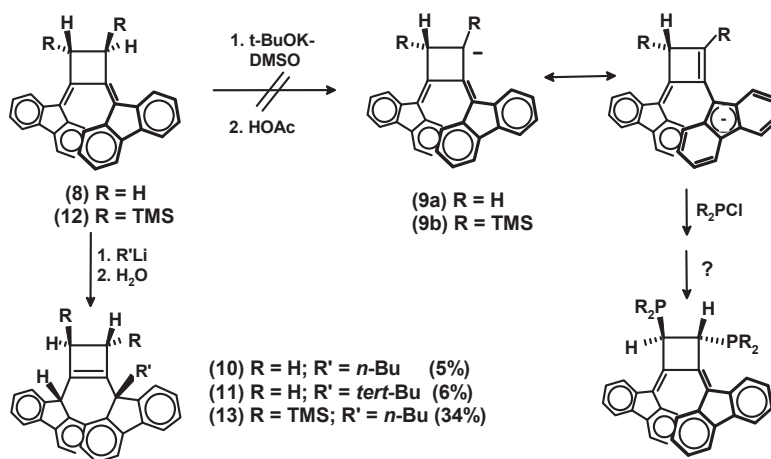
* Corresponding authors. Tel.: +353 1 716 2075; fax: +353 1 716 1178; e-mail addresses: andrew.phillips@ucd.ie (A.D. Phillips), michael.mcglinchey@ucd.ie (M.J. McGlinchey).



Scheme 1. Dimerization of a fluorenylidene-allene to form di(fluorenylidene)cyclobutanes.



Scheme 2. Interconversion and conrotatory ring closure of diallyl radicals.



Scheme 3. Reactions of di(fluorenylidene)cyclobutanes with alkyl-lithium reagents.

2. Results and discussion

2.1. Reactions of 1,2-di(fluorenylidene)cyclobutane with alkyllithium reagents

It has already been shown that the head-to-tail and tail-to-tail dimers, **2** and **5**, respectively, of 3,3-(biphenyl-2,2'-diyl)-1-

phenylallene can be deprotonated by potassium *tert*-butoxide in DMSO to form intensely coloured anions; in each case, reprotonation with acetic acid yields the corresponding 1,3-hydrogen migration product, **6** and **7**, respectively, in very good yield (Scheme 1). All products **1** through **7**, and also the resulting tetracenes, were characterized X-ray crystallographically.⁸ Attempts to deprotonate the 'parent' molecule, **8**, with potassium *tert*-butoxide

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