

C₂-SYMMETRIC DIBENZOSUBERANES AS OPTICALLY SWITCHABLE MEMORY DEVICE

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We have recently developed a new type of chiral templates, dibenzosuberanes (DBS). These C₂, symmetric diaryl modifiers have been successfully applied to the synthesis of chiral triarylcarbenium ions. They can serve as catalysts in the asymmetric Mukaiyama aldol reactions with moderate enantioselectivities of up to 50% [1]. We have subsequently identified one major side reaction between the catalyst and the substrate-silyl ketene acetal with release of extra silyl-X species which is responsible for the erosion of asymmetric induction. The DBS scaffold was found essential to prevent this type of side reaction. For the selection of carbenium counter ions, we have resorted to the chloride in order to suppress the undesired silyl catalysis [2].

We have successfully installed the dibenzosuberane skeletons into functional helicenes which may serve as optical switches in liquid crystalline materials. A concise synthesis of various model and C₂-symmetric dibenzosuberane-5-thiones was achieved by thiation of the corresponding ketones with P₄S₁₀ or Lawesson's reagent. When coupled with diazo compounds of varying steric and conjugation demands, derived from dihydrophenanthrenones and α -tetralone derivatives, the respective thiones can be converted into episulfides in moderate to good yields (41-97%). Stereospecific desulfurization of the episulfides by Cu powder in refluxing xylene or HMPT at ambient temperature led to respective dissymmetric helicenes in good yields (> 90%). In most instances, the structural identities of both episulfides and helicenes were conformed by X-ray crystallographic analyses. The X-ray analysis of the 10*R*,11*R*-diethyl derived episulfide **1** unravels the preferred conformation of the dibenzosuberane skeleton to be diequatorially oriented 10,11-ethyl groups. The absolute configuration of the sulfide moiety in **1** was determined to be *S*, which can lead to a *P* helical turn after desulfurization of the corresponding episulfide **1**. On the basis of the observed Cotton effects in the Circular Dichroism spectroscopy of **1**, we were able to successfully predict the absolute configurations and preferred conformations of the other two chiral episulfides and helicenes as well as those of the model compounds by CD spectroscopic correlations. We have established an unprecedentedly powerful tool for the chirality assignments of all helicenes by utilizing our