The Rearrangement of 11,13-Dibromo-9,10-dimethoxy-9,10-propanoanthracen-12-ones to the Corresponding Favorskii Products

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Summary. Submitting cis- and trans-11,13-dibromo-9,10-dimethoxy-9,10-propanoanthracen-12-one (4a,b) to Favorskii conditions (MeOH/KOH, 60 °C) afforded the Favorskii ester 5a and the α-keto acetal 5b in 46% overall yield. Almost all reactions resulted in the formation of a single isomer which could be shown to be the most favored one by molecular mechanics calculations (MM2).

Keywords. Allylic rearrangement; Tetrabromoacetone; 9,10-Dimethoxy-9,10-propanoanthracen-12-ones; Ring contraction; Molecular mechanics calculations (MM2).

Introduction

The rearrangement of α-halo- and α, α'-dihaloketones under the influence of base was first described by Favorskii in 1892 [1, 2]. This rearrangement is usually stereoselective, though subsequent cis to trans isomerization under the influence of base often obscures this feature. Although the Favorskii reaction is pretty well known, studies concerning its mechanism are still in progress.

The mechanism of the Favorskii rearrangement has been studied in detail, and the general mechanism proposed by Bordwell is in agreement with the reactivity of derivatives in which the bromine atoms can adopt axial positions [3]. However, the use of strong bases generally favours the rearrangement processes [4–10]. Therefore, a detailed investigation of this issue seemed to be of interest.
Results and Discussion

9,10-Dimethoxyanthracene (2) was prepared and allowed to add to tetra-bromoacetone (3) using the Zn-Cu coupling procedure to give the isomeric cycloadducts 4a,b in 40.5% yield (trans-axial-equatorial (a, e, 4a, 85%) and cis-axial-axial (e, e, 4b, 15%)). The cis isomer 4b is flipped into the isomer 4c (Schemes 1 and 2). It is interesting that the $^1$H NMR spectrum of the cycloadduct 4b displays a long-range coupling between H-11 and H-13, in contrast to the usual behaviour of planar configured H-C-C-C-H chains.

The MM2 calculations of the conformation 4b (two possibilities: H-11 and H-13 are cis-diequatorial (e, e) or H-11 and H-13 are cis-diaxial (a, a)) favour the formation of 4c, where H-11 and H-13 again are cis-diequatorial (e, e). The $^1$H NMR spectrum (200 MHz, CDCl$_3$) revealed a $^4$J coupling of 1.5 Hz for H-11 and H-13. This cannot occur if H-11 and H-13 are not cis-diequatorial. MM2 calculations of the isomers 4a-c agreed with the $^1$H NMR spectroscopic data. The Favorskii rearrangement of the $\alpha$, $\alpha'$-dibromocycloadducts 4a, b lead to the ring contracted cycloadduct 5a and the $\alpha$-keto acetal 5b. Upon reaction of the $\alpha$, $\alpha'$-dibromocycloadducts 4a, b with MeOH/KOH at 60 °C for 3 hours, 5a and 5b could be obtained in 46% overall yield (Scheme 3).