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Diastereoselective allylboration of carbonyl derivatives of [2.2]paracyclophane

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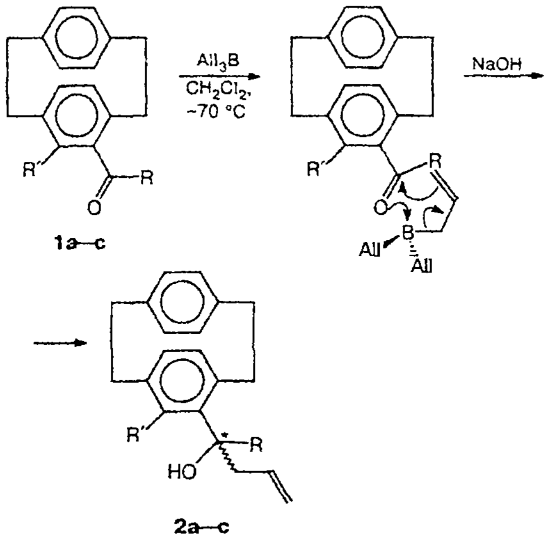
In this work, we performed for the first time the diastereoselective nucleophilic addition at the C=O bond in monosubstituted carbonyl derivatives of [2.2]paracyclophane ([2.2]PC).

Monosubstituted [2.2]PC possess planar chirality, and the thermal and conformational stability of compounds of this class make them promising as auxiliary reagents and ligands for the development of catalysts for asymmetrical synthesis.[1]

Organomagnesium and -lithium reagents react with monosubstituted carbonyl derivatives of [2.2]PC to give the corresponding alcohols; however, these reactions are not stereoselective.[2,3] It is also known[4] that β,γ-unsaturated (allylic) boron derivatives react with carbonyl compounds similarly to classical organometallic reagents, *i.e.*, *via* 1,2-addition to the C=O bond. Allylboration occurs with the 1,3-rearrangement through a chair-like six-centered transition state (2π+2π+2σ-process),[5] which allows enantio- and diastereoselective allylboration to be performed with the corresponding reagents.[6] Based on these data, we have studied for the first time the allylboration of planar chiral derivatives of [2.2]PC.

Carbonyl derivatives of [2.2]PC (4-formyl[2.2]PC (**1a**), 4-acetyl[2.2]PC (**1b**), and 4-hydroxy-5-formyl[2.2]PC (**1c**)) react with triallylborane in CH_2Cl_2 at −70 to +40 °C to give, after treatment with an aqueous solution of alkali, the corresponding homoallylic alcohols (**2a—c**) in 80—99% yields (Scheme 1). The existence of one or two signals of protons of diastereotopic groups (—C*H*(OH), —CH(O*H*), —C*H*$_2$—CH=, —C*H*=CH$_2$) in the ^{1}H NMR spectra of the reaction mixture made it possible to study the diastereoselectivity of allylboration for racemic carbonyl compounds of [2.2]PC.

Scheme 1



1a—c

2a—c

1a, **2a**: R = R′ = H
1b, **2b**: R = Me, R′ = H
1c, **2c**: R = H, R′ = OH

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The reaction of aldehyde **1a** with an equimolar amount of All_3B, *i.e.*, in fact with a threefold excess of the allylboron groups with respect to the carbonyl group, proceeded nonselectively, resulting in the formation of racemic alcohols **2a** (*de* = 0%). The subsequent change in the **1a**/All_3B ratio to 2/1 and 3/1, *i.e.*, a decrease in the excess of the allylboron groups with respect to the carbonyl group to the equivalent ratio, resulted in a change in the ratio of the diastereomeric pairs to 1.5/1 (*de* = 20%) and 2.2/1 (*de* = 38%), respectively. This dependence is most likely related to the fact that esters of mono- and diallylboric acid, All_2BOR^1 and $AllB(OR^1)_2$, containing the bulky paracyclophanylic fragment (R^1) are the allylborating agents along with triallylborane All_3B. When this reaction was carried out with fourfold dilution, a greater increase in the diastereoselectivity was observed, and the ratio of the diastereomers reached 3.5/1 (*de* = 56%).

The reaction of 4-acetyl[2.2]PC (**1b**) with triallylborane occurred stereoselectively to give only one pair of diastereomers (*de* > 99%) regardless of the ratio of the reagents (**1b**/All_3B = 1/1 or 2/1). Up to the present time, the reactions of **1b** with various nucleophiles (MeMgI, PhLi, MeLi) afforded only the corresponding racemic alcohols.[2,3]

The reaction of *ortho*-disubstituted derivative **1c** with an equimolar amount of All_3B resulted in the formation of only one pair of diastereomers (*de* > 99%), which is most likely due to the formation of chelates of the oxygen atoms of the phenol and formyl groups with the boron atom. These results agree with the previously obtained data on the addition of the organomagnesium and -lithium reagents at the carbonyl group of this compound.[7]

Thus, the experiments show that the reactions of 4-hydroxy-5-formyl[2.2]PC and 4-acetyl[2.2]PC with triallylborane occur diastereoselectively (*de* > 99%). This suggests the possibility of using intermediate allylboric esters $All_2B{-}OR^1$ and $AllB{-}(OR^1)_2$, the corresponding optically active derivatives of [2.2]PC, as reagents for asymmetrical allylboration.

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