The Stereospecific Rearrangement of 1,3,5-Cycloheptatriene-7-carboxaldehyde Dimethyl Acetal to *cis*-β-Methoxystyrene

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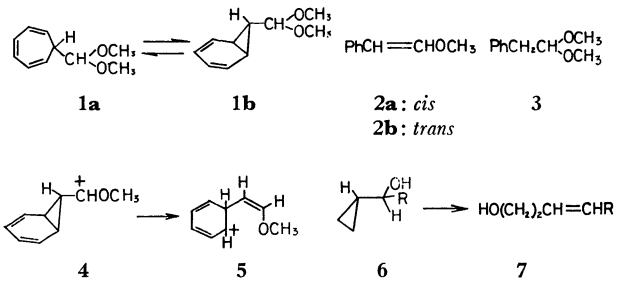
During our continuing studies of the intramolecular addition of a carbene located at a side chain to the cycloheptatriene ring,[1] 1,3,5-cycloheptatriene-7-carboxaldehyde dimethylacetal (**1**)[2] has emerged as a promising potential precursor to generate 1,3,5-cycloheptatriene-7-methylene, because the 2,4-dinitrophenylhydrazone of the aldehyde was successfully synthesized from **1** in a high yield without any isolation of the aldehyde.[2,3] Thus, we tried to prepare the corresponding tosylhydrazone or hydrazone, which is a precursor of the carbene, from Compound **1** by the application of a similar manner; however, this attempt was unsuccessful. Instead, we found a curious rearrangement of **1** during the hydrolysis of **1** and wish to report the outlines of the result obtained.

Dimethylacetals of 1,3,5-cycloheptatriene-3-carboxaldehyde[4] and 1-formylbicyclo[3.2.0]hepta-3,6-diene,[5] upon treatment with methanolic hydrochloric acid, provided the corresponding aldehydes, whereas the dimethylacetal (**1**) on treatment with dilute hydrochloric acid, afforded only a rearranged product, phenylacetaldehyde.[2,3] On the other hand, when **1** was warmed in anhydrous acetic acid, a clean reaction took place and *cis*-β-methoxystyrene (**2a**) was mainly formed (the ratio of *cis* to *trans* was 5). The structure of **2a** was established on the basis of the NMR (J= 7.0 Hz, *cis* –CH=CH–) and by a comparison of the retention time in vpc with that of an authentic sample. The rearrangement was a first-order reaction $k=1.46\times10^{-5}$ sec^{-1} at 40°C),[6] and the *cis*: *trans* ratio (about 5) was almost constant from 40 to 60°C. In addition, the prolonged heating of **1** under the same conditions (20 hr at 40°C) resulted in the slow formation of phenylacetaldehyde dimethylacetal (**3**).[3] The possibility of interconversion between *cis*- (**2a**) and *trans*-β-methoxystyrene (**2b**) and of the formation of **2a** or **2b** by the elimination of methanol from **3** could be excluded by the following control experiments. When the *cis*-isomer (**2a**) was subjected to the solvolysis at 60°C for 4 hr in the presence of one equivalent of methanol-d_4, deuterium incorporation took place only in **3**, and the formation of *trans*-isomer (**2b**) was not observed, indicating that **3** is a secondary product. Under the same conditions, the product (**3**) was stable, in addition, the *trans*-isomer (**2b**) was not converted into the *cis*-isomer (**2a**). These facts established that *cis*-β-methoxystyrene (**2a**) was directly formed from 1,3,5-cycloheptatriene-7-carboxaldehyde dimethylacetal (**1**) by stereospecific rearrangement.

In the solvolysis of 1,3,5-cycloheptatrien-7-ylmethylcarbinol 3,5-dinitrobenzoate, Sargent *et al.* observed a novel type of rate enhancement promoted by the participation of the cyclopropane ring which exists in its valence isomer, the norcaradiene form.[7]



1a **1b** **2a**: *cis* **2b**: *trans* **3** **4** **5** **6** **7**

Similarly, the enhancement in the rate of the solvolysis of **1** can be attributed to the assistance of the cyclopropane ring of the corresponding norcaradiene form (**1b**). The styrene derivative (**2**) should be produced from the norcaradienylcarbinyl cation (**4**) by the cleavage of the cyclopropane ring to the homoallyl cation (**5**), followed by aromatization leading to β-methoxystyrene (**2**).[3,7,8] Thus, this rearrangement can be seen as an example of the general cyclopropylcarbinol-homoallyl carbinol rearrangement, as is shown from **6** to **7**. The geometry of the homoallyl carbinols obtained by this rearrangement has been widely studied.[9] For example, 1-cyclopropyl-1-methoxyethane[10] and (bicyclo[4.1.0]heptan-7-yl)benzyl alcohol,[11] upon solvolysis, rearranged to the corresponding *trans*-allyl derivatives, but not to *cis*-isomers. The preferable formation of *cis*-β-methoxystyrene (**2a**) from **1** is in sharp contrast to these examples. Therefore, the present results raise interesting questions concerning the conformation of the intermediate in the norcaradienylcarbinyl-styryl rearrangement (**4**→**5**), especially as to the location of the methoxy group in the transition state.

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