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BASE CATALYZED DEUTERATION OF NORCAMPHOR AND DEHYDRONORCAMPHOR

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In a recent communication (1) the peculiar behavior of isofenchone, camphor and norcamphor in base catalyzed deuteration was described. It was observed that the deuterium exchange occurs preferentially or exclusively at the exo-3 position rather than at the endo-3 position.

In the course of our work on secondary deuterium isotope effects we have also attempted to prepare some deuterated bicycloheptyl derivatives by base catalyzed exchange and consider the results worth reporting.

Norcamphor (I, 4 g.) was added to 60 ml. of a solution prepared from deuterium oxide (120 ml.), methanol-d (28 ml.) and sodium methoxide (29.6 g.). The solution of the ketone was sealed in an ampule and heated to 100° for 12 hours (2). After cooling, the mixture was extracted with ether, the extract washed with deuterium oxide, dried with magnesium sulfate and the solvent evaporated. Sublimation of the residue yielded a norcamphor containing 50 % of 2 atoms deuterium per molecule (n.m.r.). The deuterium content rose to 65 %

after the second exchange. Thus, our results are in agreement with those reported by Thomas and Willhalm (1).

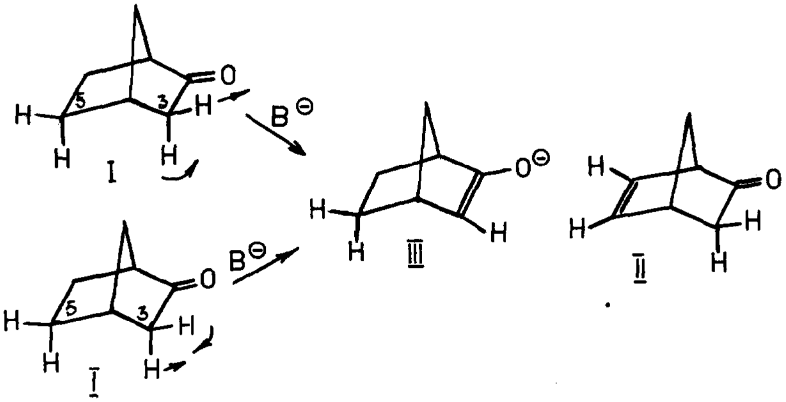
On the other hand, the behavior of dehydronorcamphor (II) was found to be strikingly different from the one described for norcamphor and other bicycloheptanons. Here, a single deuterium exchange, carried out as described above, yielded a product containing 95 % of 2 atoms of deuterium per molecule.

The reported observations can be rationalized in the following manner. In norcamphor (and derivatives), contrary to dehydronorcamphor, there exists a strong transannular repulsion between the endo-hydrogens bound to carbon atoms 3 and 5. Forming the norcamphor enolate ion (III), through which the deuterium exchange proceeds, relieves the strain due to this non-bonded repulsion. The stereospecificity of the deuteration will, therefore, be determined by the relative amount of strain that is relieved in the transition state leading to the enolate ion through abstraction of exo-3 and endo-3 hydrogen respectively. From FIG. I it can be seen that the abstraction of the exo-3 proton leads to the movement of the endo-3 hydrogen up and away from the nearby endo hydrogen at carbon atom 5. As the latter movement is connected with the release of steric strain, enolization through abstraction of the exo-3 proton should be a favorable reaction path.

A similar stabilization of the transition state for the abstraction of the endo-3 hydrogen is difficult to achieve. As seen from FIG. I, any release of steric strain through movement of the endo-3 hydrogen along the axis connecting it with the *endo*-5 hydrogen will be opposed by a simultaneous movement of the *exo*-3 hydrogen *down and against* the proton being abstracted.

By reversal of the enolization step, deuterium will enter preferetially into the *exo*-3 position.

FIG. I



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