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STEREOCHEMICAL COURSE OF HYDROGENATION OF BICYCLO[2.1.0]PENTANES (1)

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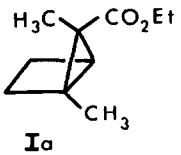
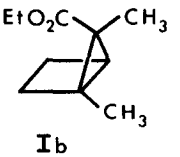
The stereochemistry of the formation of the strained internal bond in bicyclo[2.1.0]pentane (2,3) and that of its reactivity in addition reactions (4,5,6,7) has been the subject of recent attention. Whether reaction occurs by the approach of the reagent from the exo or endo side of the molecule has been established only for cycloadditions (6,7). Thus, addition of 4-phenyl-1,2,4-triazolin-3,5-dione to 2,3-dideuteriobicyclo[2.1.0]pentane-5-spirocyclopropane (6) and of maleic anhydride to 2,3-dideuteriobicyclo[2.1.0]pentane (7) occur exclusively from the more hindered endo side. The electronic basis for this stereochemistry is puzzling.

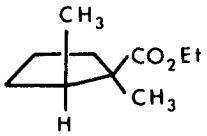
It was of interest to examine whether this stereochemistry might be general of addition reactions to the internal bond. A study of the stereochemistry of the hydrogenation of the two isomeric bicyclo[2.1.0]pentanes Ia and Ib (8) was undertaken for this reason. Reduction of Ib with platinum in ethanol proceeded slowly to give only two products, A and B, in the ratio of 90:10. Hydrogenation of Ia led to a mixture of A and B in a ratio of 30:70. The structures of A and B were established as the ethyl 1,2-dimethylcyclopentanecarboxylates IIa and IIb, respectively, by their independent synthesis via hydrogenation of ethyl 1,2-dimethyl-2-cyclopentene-1-carboxylate, which was prepared according to a literature route (9). The assignment of geometry to A and B was made on the basis of the very large difference in their saponification rates; under conditions which led to complete hydrolysis of B, isomer A could be recovered unchanged. It is apparent on steric grounds that isomer A corresponds to the more hindered ester



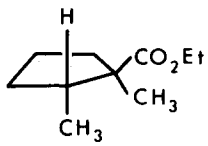
Ia



Ib



IIa



IIb

IIa (10).

Correlation of the stereochemistry of the starting material with that of the hydrogenation product leads to the conclusion that the addition of hydrogen takes place preferentially from the exo side of the molecule. The stereospecificity is high for Ib; in the case of Ia addition takes place less selectively. Whether the lower specificity noted for Ia is due to the incursion of an endo stereochemical pathway or is due to trans addition of hydrogen cannot be decided upon without more subtle experiments on suitable derivatives. It is noteworthy that in contrast to the more highly strained bicyclo[2.1.0]pentanes, recently reported by Kristinsson and Hammond (11), no skeletal rearrangements result during the hydrogenation of I.

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8. M. J. Jorgenson, J. Am. Chem. Soc., 88, 3463 (1966). The stereochemistries of Ia and Ib were assigned such that they are in accord with steric considerations derived from the related stereoisomeric ethyl 5-methyl[2.1.0]-pentane-5-carboxylates. In this derivative, that isomer containing the more highly shielded methyl group is the endo 5-methyl isomer and is the less abundant isomer at thermal equilibrium (ΔF at 150° 1.2 kcal/mole). Thus, an endo 5-methyl is sterically much more demanding than an endo 5-carboethoxy group in bicyclo[2.1.0]pentane. Since steric interactions operative on the 5-endo methyl in Ia are clearly larger than those exerted on the 5-exo methyl in Ib, the latter is favored, by a factor of 2.5, in a thermal equilibrium at 150°. A more detailed stereochemical analysis will be provided in a forthcoming publication on the thermal chemistry of I.

9. R. Granger and H. Techer, Compt. Rend., 250, 1282 (1960).

10. The chemistry and stereochemistry of II and related derivatives will be treated in detail in a separate publication.

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