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THE STEREOCHEMICAL COURSE OF THE HYDROGENOLYSIS OF CYCLOPROPANE RINGS

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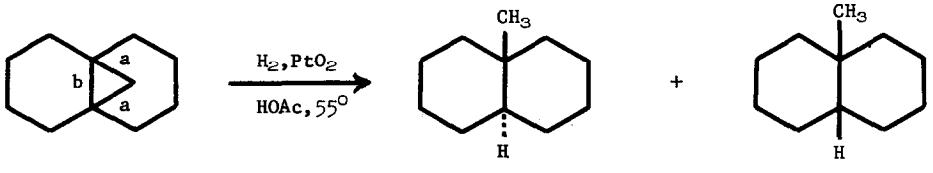
The stereochemical course of the hydrogenolysis of the particularly strained cyclopropane rings in the two isomeric ethyl 1,5-dimethylbicyclo[2.1.0]pentane 5-carboxylates was studied recently in order to ascertain the direction of attack, endo or exo (1). Unfortunately, both starting isomers gave mixtures of the ring-opened products, cis and trans ethyl 1,2-dimethylcyclopentane carboxylates. While the products corresponding to exo attack by hydrogen predominated in both cases, substantial amounts (10 and 30%) of the "endo" isomers were produced. There are two possible reasons for the formation of these minor products: 1) the cyclopropane ring hydrogenolysis is stereospecific, but both endo and exo attack take place; or 2) the hydrogenolysis of cyclopropane rings is not a stereospecific reaction.

We have studied this problem with a substrate, tricyclo[4.4.1.0]undecane (I) (2), which is free from the complications of endo vs. exo attack. As expected (3), the equivalent bonds a in I are ruptured in preference to the more highly substituted bond b, and 9-methyldecalin (II) is produced rather than bicyclo[4.4.1]undecane. The fact that nearly equimolar amounts of cis-II and trans-II are formed demonstrates that the opening of cyclopropane rings by catalytic hydrogenation can be stereochemically quite unspecific.



I trans-II cis-II

I was prepared by reduction of 11,11-dibromotricyclo[4.4.1.0]undecane (4) with tri-n-butyltin hydride, followed by glc purification. A 0.25 M solution of I in acetic acid was subjected at 55° to the action of hydrogen at a pressure of 3.8 atm in the presence of a platinum catalyst prepared from PtO_2. Reactions were carried out for 6, 25, and 75 hours in order to monitor the process. The products, cis-II and trans-II, were easy to identify and to analyze quantitatively because of known features of their nmr spectra (5). The methyl proton resonances of both isomers appear at positions intermediate between the main absorptions of I and II (δ = 65-110 Hz), and the cyclopropane CH_2 resonance (δ = 18.$_4$ Hz) of unreacted starting material, I. Cis-9-methyldecalin (cis-II) was found to have a sharp methyl peak at δ = 58.$_2$ Hz (half-height width broadening, relative to the TMS peak, was 0.1$_4$ Hz), while trans-II gave a methyl resonance at δ = 50.$_3$ Hz (relative half-height broadening = 0.70 Hz) (5).

Isomerization of the products on the catalyst was ruled out by the observation that the 1:1 product ratio did not change as a function of reaction time, despite the known (6) greater stability of trans-II than cis-II. After 6 hours, 59% reduction had been attained, and the product ratio consisted of 48.5 ± 2% cis-II and 51.5 ± 2% trans-II. At 25 and 75 hours, reduction was more nearly complete, but the product ratio was unchanged, within the error limits given.

Attention has been called recently to the synthetic utility of cyclopropane ring hydrogenolyses, especially for the construction of quaternary carbon atoms (3). The present result shows that angular methyl groups can also be introduced by this method, albeit not stereospecifically. This difficulty can probably be overcome by the use of the cis or trans isomers of tricyclo[5.4.0.$0^{1,3}$]undecane -- instead of I -- as starting material.

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