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THERMODYNAMICS OF THE INTERCONVERSION OF CERTAIN BRIDGED RING HYDROCARBONS BY RHODIUM CATALYSTS

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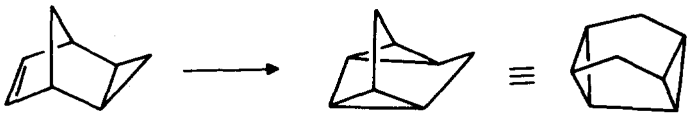
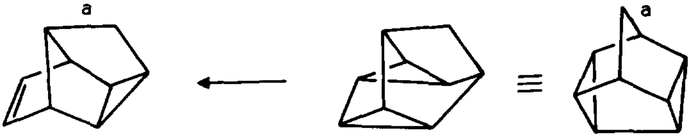
Exo-tricyclo[3.2.1.0^{2,4}]octene (I) was first converted into tetracyclo[3.3.0.0^{2,8}.0^{4,6}]-octane (II) by the action of light (1), but it has recently been found that this interconversion can also be effected by [Rh(CO)$_2$Cl]$_2$ at room temperature (2), by RhCl[(C$_6$H$_5$)$_3$P]$_3$ at 90° (3), and by 5% rhodium on carbon at 130° (3). A compound closely related to I is tetracyclo-[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (III) (4), and the analogous conversion of it to pentacyclo-[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (IV) (4c,5,6) has also been effected with light (4c,5). But, as was found a few years ago, with 5% rhodium on carbon at 185° for 42 hr. III is largely unchanged; it is converted in 5% yield to a dimer, and there is no evidence that IV is formed (4a). We have also found that neither [Rh(CO)$_2$Cl]$_2$ at room temperature for two days nor



I

II

1



III

IV

2

RhCl[(C$_6$H$_5$)$_3$P]$_3$ at 170° for three days converts III to IV.* This seems surprising, since it is difficult to see how the small change at the top of molecule I relating it to III, the introduction of a methylene bridge, could interfere with the mechanism of the rhodium catalyzed reaction, which almost surely involves interaction of catalyst with hydrocarbon at the bottom

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* III is recovered.

of the molecule.

In fact the rhodium catalysts do effect the interconversion of III and IV, but the change is of IV to III. Thus when IV is allowed to stand at room temperature for four days with $[Rh(CO)_2Cl]_2$ (6 mole percent) in chloroform solution, or shaken at 150° with 5% rhodium on carbon (1.6 mole percent contained rhodium) in a sealed tube for one and one half days, IV is completely consumed and III is formed.

It must be that while the equilibrium **1** lies to the right, the analogous equilibrium **2** lies to the left. We believe the reason for this difference can be traced to the following in a Born-Haber cycle including I, II, III, and IV: that the free energy liberated in closing bond a in III is less than that liberated in closing bond a in IV, because, as indicated by the model in fig. **1**, the molecular distortion required to close the latter is greater. The mechanism for the conversion of IV to III is presumably the reverse of that converting I to II; the difference between the two interconversions is thermodynamic.

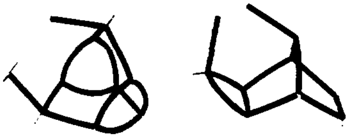

Figure 1. Models of III and IV with bond a open

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