Nuclear Magnetic Resonance Experiments on Ketals:[1] Chair–Chair Inversion in *cis*-2,2,7,7-Tetramethoxydecalin

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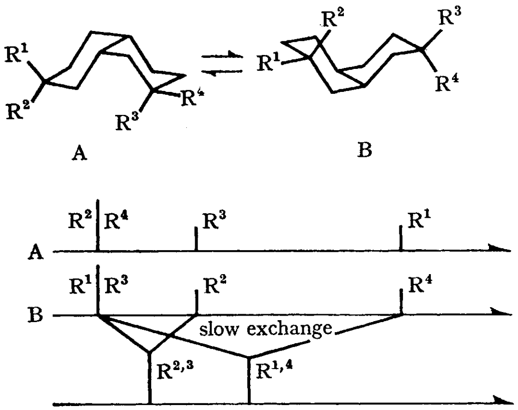
THE chair–chair inversion process in *cis*-decalin systems has recently aroused considerable interest.[2] With substituents at appropriate positions in both rings, it is possible to study inversion between two equi-energetical conformers. This is a report of such a derivative, i.e. *cis*-2,2,7,7-tetramethoxydecalin. The ^{1}H n.m.r. spectrum was recorded in carbon disulphide from room temperature to 210°K with a Varian HA 100 MHz. apparatus.

The fast-exchange spectrum shows two signals for the methoxy-protons, separated by about 2 Hz. The slow-exchange spectrum consists of three lines, with intensity ratio 2 : 1 : 1, and separated by respectively 2 Hz. (*2* : *1* : 1) and 6 Hz. (*2* : 1 : *1*). (The tentative shift contributions implicit in the Figure are based on comparison compounds).[3] At first sight, an alternative explanation could be offered. One line of the fast-exchange spectrum might split upon cooling, but not the other one. Such an interpretation, however, is definitely excluded both by the line shape at intermediate rates and by the shift differences.



FIGURE

The overlap of signals at intermediate exchange rates made it impossible to obtain reaction rates at different temperatures. However, a coalescence temperature for both collapses, *e.g.*, $R^{1,4} \rightarrow R^1\text{–}R^4$ and $R^{2,3} \rightarrow R^2\text{–}R^3$ could be obtained. They yielded the same free energy of activation $\Delta F^{\ddagger} = 12{\cdot}4$ kcal./mole at 236° and 226°K.

The ground state of *cis*-2,2,7,7-tetramethoxydecalin is strained by a 1,3-diaxial oxygen–methylene interaction, amounting to about 2 kcal./mole.[4] Yet the free energy of activation is essentially the same as for unsubstituted *cis*-decalin $\Delta F^{\ddagger}_{255} = 12{\cdot}8$ kcal./mole (Jensen and Beck[2]). This parallels results from the cyclohexane series.[5] The transition state in *cis*-decalin will be studied further, using the isomeric *cis*-2,7-dimethoxydecalins.

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[4] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformation Analysis", Interscience, New York, 1965, p. 249.

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