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CHAIR-CHAIR INTERCONVERSION EQUILIBRIUM IN 3,3,5,5-TETRAMETHYLCYCLOHEXANONE COMPLEX WITH BORON TRIFLUORIDE

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Our recent nuclear magnetic resonance studies (1) have shown that cyclanones 1:1 adducts with boron trifluoride in methylene chloride undergo a rapid reversible reaction, namely breaking and reforming of the donor-acceptor bond between carbonyl bond and boron trifluoride. Most of the crystalline donor-acceptor adducts of cyclanones BF_3 have been reported to be more stable at room temperature than aliphatic BF_3 adducts (2,3).

EXPERIMENTAL RESULTS AND DISCUSSION

Therefore we have studied various mixtures of the 3,3,5,5-tetramethylcyclohexanone adduct with boron trifluoride in different ratios and recorded at low temperature spectra showing kinetics and conformational phenomena occuring in such molecules. As we saw for cyclopentanone and cyclohexanone complexes room temperature proton spectra of methylene chloride solution of 3,3,5,5-tetramethylcyclohexanone with BF_3, in various molar ratios, contain a single set of resonances corresponding to the spectrum of the ketone. The chemical shifts of the peaks vary linearly with the ratio BF_3/ketone as the relative proportion of ketone is increased up to the ratio 1:1. Separate resonances were not observed for free and complexed forms and no modification on shifts frequencies was observed.

At -40°C, only a single set of ketone resonances could be observed in any of the sample studies. At -60°C, however each sample containing more moles of ketone than of BF_3 yielded a spectrum containing one set of peaks with chemical shifts corresponding to those of the free ketones and a second set with chemical shifts corresponding to those of the 1:1 complex. Coalescence temperature was about -50°C. At temperature below -70°C, the peak due to the resonance of the α-methylene protons in complexed form began to broaden and was separated into two peaks of equal areas the chemical shift difference being of δ = 12,2 Hz.

Such a phenomenon was not observed with a solution of 3,3,5,5-tetramethylcyclohexanone in methylene chloride at low temperature even in the slow exchange limit.

We postulated that this phenomenon might arise from the chair-chair interconversion equilibria, between axial and equatorial conformation of α-methylene protons as previously described (4) , the chemical shift difference between the two forms being due to the anisotropy of the O-B bond in the complexed molecule.

The coalescence temperature was about -80°C. The changes in signal shape with temperature were used in a kinetic study of the conformational equilibrium in a solution of 3,3,5,5-tetramethylcyclohexanone and BF_3 in 1:1 ratio in methylene chloride with tetramethyl silane as internal standard.

A least squares calculation of the activation enthalpy $\Delta H^{\neq}$ gave a value of 11,5 Kcal/mole and the error in this value may be ± 0,5 Kcal/mole, the Arrhenius plot giving a good straight line and a good correlation.

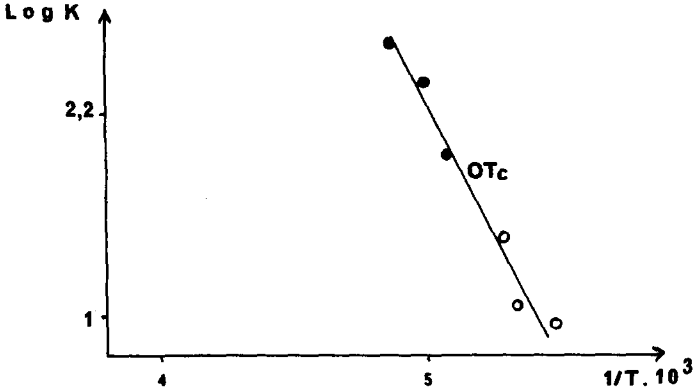

Fig. 1 : Arrhenius plot for chain-chain interconversion of complexed 3,3,5,5-tetramethylcyclohexanone in the ratio 1:1

● above coalescence temperature from the width at half height difference between TMS and the coalescence signals.

○ below coalescence temperature from experimental chemical shifts difference between signals in the slow exchange limit.

EXPERIMENTAL SECTION : N.M.R. Spectra were obtained on a Varian A 60 A N.M.R. spectrometer operating at 60 MHz. A Varian V-6040 variable temperature N.M.R. probe was used to adjust the spinning sample tube to the required temperature.

CALCULATIONS : An IBM 1130 computer was used for a least square calculation of the activation enthalpy. Exchange rates were calculated with the formulae employed by FORSEN et al. (5).

MATERIALS : The 1:1 adduct was obtained in a vacuum line by passing through a methylene chloride solution of ketone (5%) and TMS (1%), the necessary amount of anhydrous boron trifluoride as previously described by L. ELEGANT et al. (6).

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