Tetrahedron Letters No. 36, pp 3185 - 3186, 1974. Pergamon Press. Printed in Great Britain.

ON THE CONFORMATIONAL EQUILIBRIA IN THE 3,3,5,5-TETRAMETHYLCYCLOHEXANONE-BF_3 ADDUCT

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(Received in UK 22 July 1974; accepted for publication 31 July 1974)

In a previous communication in this journal [1], low-temperature ^{1}H-NMR spectral changes of the title compound were interpreted in terms of a decreased chair-chair inversion rate (Fig. 1).

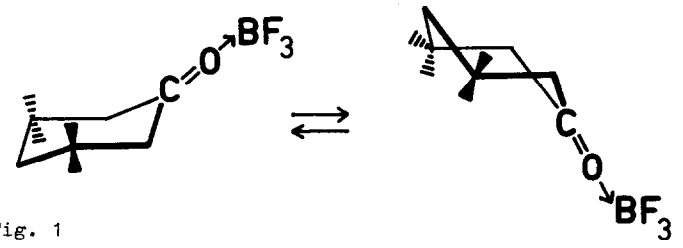


Fig. 1

We have confirmed these bandshape changes (the slightly broadened singlet from the 2-methylene protons separates into two singlets below ≈ -80°C <u>via</u> an intermediate broadened signal). However, we find the original interpretation questionable, since in a fixed chair form a significant geminal spin-spin coupling of the order of 10-15 Hz [2] between the 2-methylene protons should be observed. We would suggest, as an alternative interpretation, a slowed-down exchange between two preferred binding directions at the carbonyl oxygen (Fig. 2), while the chair-chair inversion rate remains fast.

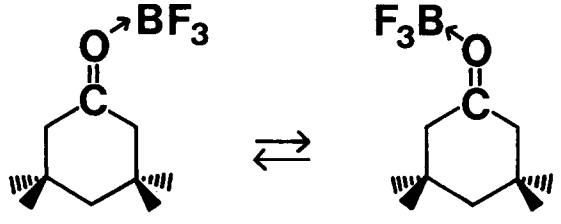
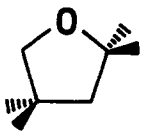


Fig. 2

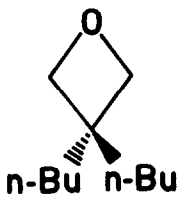
This type of exchange seems to be consistent with the observed spectra and has previously been reported to be of intermediate rate on the NMR time scale near this temperature range in the diethyl ketone- BF_3 adduct [3].

It is of interest to note that although an analogous type of conformational preference is expected in ethers, we have been unable to observe any clear indications of this in 60 MHz ^{1}H-NMR spectra of the BF_3 adducts of compounds I-III even at -135°C [4].



I

II



III

REFERENCES.

[1]. J.P. Rosset, G. Torri, A. Pagliardini and M. Azarro Tetrahedron Letters, 1971, 1319

[2]. Geminal spin-spin couplings in this type of system are not known, and might be small, but an exploratory study of the $SbCl_5$-epicamphor adduct at -20°C suggests a value of 12 Hz, which is slightly larger than in uncomplexed epicamphor. Epicamphor has an unstrained 6-ring system similar to 3,3,5,5-tetramethylcyclohexanone.

[3]. U. Henriksson and S. Forsén, J. Chem. Soc. (D), 1970, 1229

[4]. Approximately 0.2 M solutions of the adducts in $CHFCl_2$ were used. Compound I is commercially available (Frinton Laboratories), II was a generous gift from Professor L. Eberson, Organic Chemistry 1, Lund University and compound III was a generous gift from Dr. K. Nyberg of the same department.