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AN NMR STUDY OF CONFORMATIONAL EXCHANGE IN SOME KETONE-BF_3 AND ETHER-BF_3 ADDUCTS

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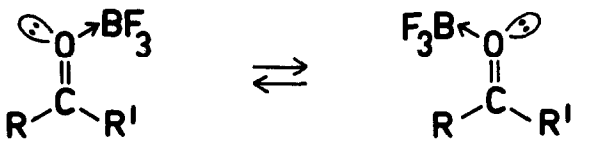
In numerous studies following the initial work by Diehl,[1] ^1H nmr adduct formation shifts of donor molecules have been found to occur to low field, attenuating rapidly as the number of bonds from the donor site increases. Recently ^{13}C nmr studies of adducts of Lewis acids with various donor molecules have appeared.[2] It appears that, although adduct formation induces large electron-withdrawal effects on the donor molecule, several types of shielding changes occur, so that the ^{13}C resonances move either upfield or downfield. The average shielding changes are, however, much larger than in ^1H nmr, and this facilitates nmr studies of the adducts.

We have now investigated the syn-anti exchange (eq. 1) between the two



(1)

possible BF_3 bonding sites at the carbonyl group in ketone-BF_3 adducts[3] by ^{13}C nmr. Although ^1H nmr indicated that there are significant rate differences between different ketone-BF_3 adducts,[3] complex spectra and small shift differences prevented detailed ^1H nmr studies.

Figure 1 summarizes ^{13}C chemical shifts of the BF_3 adducts I-X. The adduct formation shift differences in the series I, II and III indicate that the C=O-BF_3 conformation has a significant effect (>3 ppm) on the α-carbon shifts. In II the BF_3 is probably mainly syn to the α-methyl due to decreased steric hindrance, as apparently is the case in protonated methyl ethyl ketone.[4] On complexation the α-methyl ^{13}C signal shifts 2.0 ppm to high field, while the α-methylene, probably anti to BF_3, shifts 2.2 ppm to low field. In I and III the α-carbon adduct

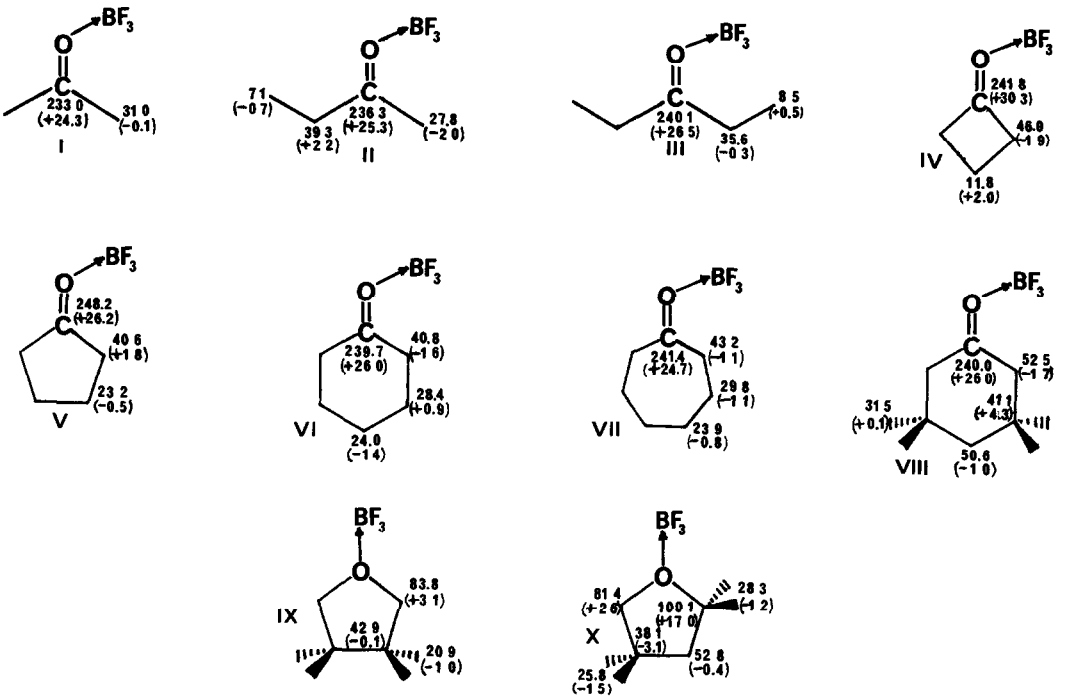


Fig. 1 Observed ^{13}C δ shifts in 5-20% solutions of I-X in 1:4 $CDCl_3$-$CHFCl_2$ at -30°. The adduct formation shifts are given within parenthesis. Downfield shift changes are positive. The position of BF_3 in the drawings is schematic only, and the shifts refer to an average value between all conformers.

formation shifts are very small, apparently due to cancellation of the opposing syn and anti-BF_3 effects.

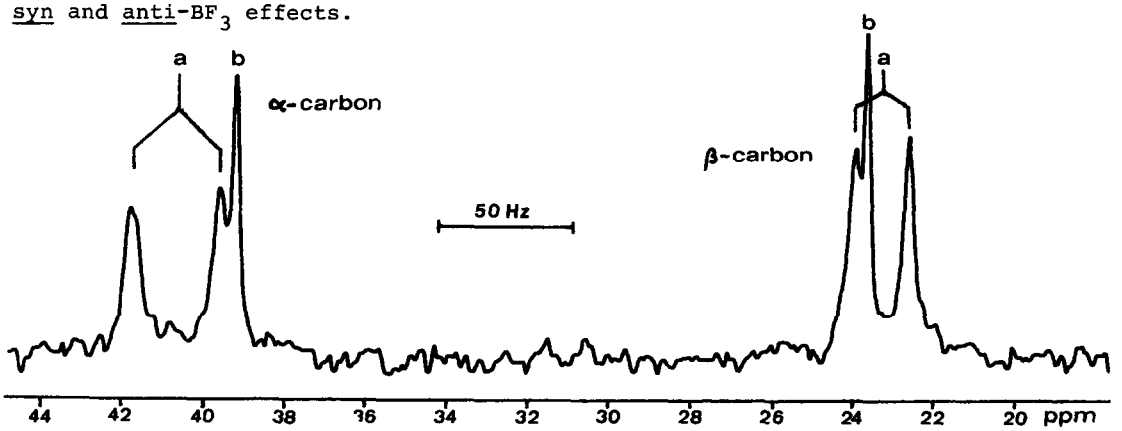


Fig. 2 15.1 MHz ^{13}C spectrum of cyclopentanone-BF_3 (molar ratio 1.7:1) at -100°C. Signals from adduct (a) and excess donor (b) are shown.

^{13}C spectra of III, V, VI, VII and VIII below -70° to -110° were consistent with slow syn-anti exchange. An example is shown in Fig. 2. Equal-intensity doublets were observed in place of the -30° singlets for the α- and β-carbons and also the γ-carbons of VII (Table 1). The only resonances which split into doublets were those predicted to do so if syn-anti exchange were slow, i.e. no carbonyl carbon or γ-carbon resonance (in the cyclohexanones) was affected in the symmetrical donors. The observed low-temperature spectra of VIII cannot be explained by a slow chair-chair inversion process, as proposed in a previous ^{1}H nmr study.[5]

Table 1. 15.087 MHz ^{13}C nmr evidence for slow syn-anti exchange at low temperatures.

Peak separations (Hz) with coalescence temperatures within parentheses.

	α-carbon	β-carbon	γ-carbon	methyl carbon	$\Delta G^{\neq}(T_c)$ [a]
III[b]	30 (168 K)	48 (172 K)	---	---	8.3 (172 K)
V	32 (209 K)[c]	20 (206 K)[c]	---	---	10.3 (209 K)[c]
VI[b]	40 (197 K)	(1-2[d])	---	---	9.6 (197 K)
VII[b]	48 (198 K)	8 (183 K)	5 (183 K)	---	9.6 (198 K)
VIII[b]	52 (200 K)	8 (184 K)	---	(≃3[d])	9.7 (200 K)

a. In kcal/mol. b. Analogous signal separations have been reported in the proton spectra for compounds III,[3] VI,[5] VII[5] and VIII[6] and confirmed in this work. Exchange rates calculated from ^{1}H and ^{13}C data agree well. ^{1}H signals do not separate in the other adducts. c. With excess donor present (see text). d. Estimated from excess broadening, compared to the γ-carbon signal, at low temperatures.

BF_3-adduct I was too insoluble in the solvent used to allow a ^{13}C nmr study at low temperatures. ^{13}C spectra of II, IV, IX and X show no sign of exchange broadening at -110°. Probably one conformation of II predominates. Unless syn and anti α-carbon shifts of VI are similar, IV does undergo syn-anti exchange too rapidly to be detected at -110°. The possible exchange process in the methyl-substituted tetrahydrofurans IX and X, i.e. interconversion between oxygen lone-pairs on opposite sides of the ring, is apparently rapid at -110°.[7] The lack of exchange broadening for II, IV, IX and X cannot be due to rapid donor-acceptor bond breaking, since ^{1}H, ^{13}C and/or ^{19}F nmr and approximate lineshape calculations show that intermolecular exchange is a slow process on the ^{13}C nmr time scale at the studied temperatures.

In the case of V presence of excess donor, as compared to presence of excess BF_3, increases the coalescence temperature for the doublets in the ^{13}C spectrum by 30°, at which temperature they also coalesce with the signal from excess cyclopentanone. In all other systems, where doublets in the nmr spectra of the adduct occured, the coalescence temperature of these did not change between

excess-BF_3 and excess-donor conditions. The donor-donor exchange under excess-donor conditions was also significantly slower than the syn-anti exchange.

The apparent anomaly in the cyclopentanone-BF_3 case may be due to interaction of the adduct with excess BF_3, possibly due to the lower sterical hindrance in the carbonyl-BF_3 region for the five-membered ketone as compared to non-cyclic and the six- or seven-membered ketones.

We can conclude that the barrier to intramolecular syn-anti exchange increases in the order IV < III < VI ≃ VII ≃ VIII < V. IV can fairly reliably be included in this series since neither ^1H nor ^{13}C spectra showed any effects of slow exchange, and it seems unlikely that syn and anti signals would coincide in both cases.

During the preparation of this manuscript a report of observed slow syn-anti exchange in ^{13}C spectra of BF_3 adducts of some ketosteroids and cyclohexenone has appeared (Ref. 2g).

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In some of these publications (b-e) the metal halide is referred to as a shift reagent. However,we feel that this new nomenclature is unnecessary and may cause confusion, since it is well established that donor-acceptor adduct formation between metal halides and organic donor molecules induces chemical shift changes in nmr spectra of the donor molecule, previously referred to as adduct formation shifts.
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7. Both the proton and carbon resonances of the 2-methyl group of X were significantly broadened when compared to the 4-methyl resonance. This might be due to a small (.5-1 Hz) through-space coupling to fluorine. A further indication of an abnormal effect, perhaps prenounced crowding, in this adduct, is provided by the abnormally large complexation shift of the 2-carbon.