cis–trans-Isomerism about the Carbon–Oxygen Bond in the Diethyl Ketone–Boron Trifluoride Adduct: Nuclear Magnetic Resonance Study

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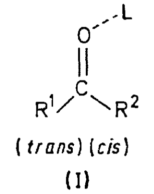
Summary N.m.r. spectra of the $Et_2CO–BF_3$ 1 : 1 complex in $CHCl_2F$ solution at temperatures below −120° show separate signals from the two ethyl groups, attributed to *cis–trans*-isomerism about the carbon–oxygen bond.

IT has been shown by n.m.r. techniques that the reorientation around the carbon–oxygen bond in protonated dialkyl ketones is slow on the n.m.r. time scale at temperatures below *ca.* 0°, and that this slow reorientation results in a *cis–trans*-isomerism about the carbon–oxygen bond in the protonated species.[1,2] No *cis–trans*-isomerism appears to have been observed in the closely analogous adducts (I) of dialkyl ketones and Lewis acids (L). In the solid state the $C{=}O \cdots L$ bond angle has been found to deviate from 180° in some adducts.[3–5] If this type of asymmetric binding persists in liquid solutions, one would expect to observe non-equivalence of the alkyl groups in the n.m.r. spectra of adducts of symmetric ketones (I; $R^1 = R^2$), provided the rate of isomerisation around the C=O bond is sufficiently slow.



(I)

In the acetone–boron trifluoride adduct only one signal from the methyl protons has been observed.[6,7] Lappert,[6] who made his observations at −70°, attributes this to the rapid *inter*molecular exchange of boron trifluoride among the donor molecules. Gillespie and Hartman[7] have found that the methyl signal is broadened at −90°, and they suggest that this arises from a small unresolved coupling of the methyl protons to boron or to fluorine and a long range coupling between the protons in the two non-equivalent methyl groups *cis* and *trans* to boron trifluoride.

We have examined the 100 MHz ^{1}H n.m.r. spectrum of the diethyl ketone–boron trifluoride adduct in $CHCl_2F$ solutions at various temperatures down to *ca.* −125°. The Figure shows the methyl signal from the Et_2CO–BF_3 adduct at 100 MHz, at four temperatures. At −123° the methyl signal consists of two triplets shifted 0·23 p.p.m. from each other and with the coupling constants *ca.* 5·8 Hz (high-field triplet) and *ca.* 6·8 Hz (low-field triplet) to the neighbouring methylene groups. The peaks are broad at this low temperature due to the high viscosity of the solvent, but the splitting is clearly seen. At about −111° the two triplets coalesce into one broad peak, and at higher temperature the methyl signal consists of one sharp triplet. Two methylene signals are also observed in the adduct at −123°. These signals overlap partly and are considerably broader than the methyl signals, presumably due to unresolved four-bond spin couplings across the trigonal carbon atom. The n.m.r. spectra thus clearly show the ethyl groups in the diethyl ketone–boron trifluoride adduct to be non-equivalent at low temperatures. We ascribe this non-equivalence to *cis–trans*-isomerism about the carbon–oxygen bond.

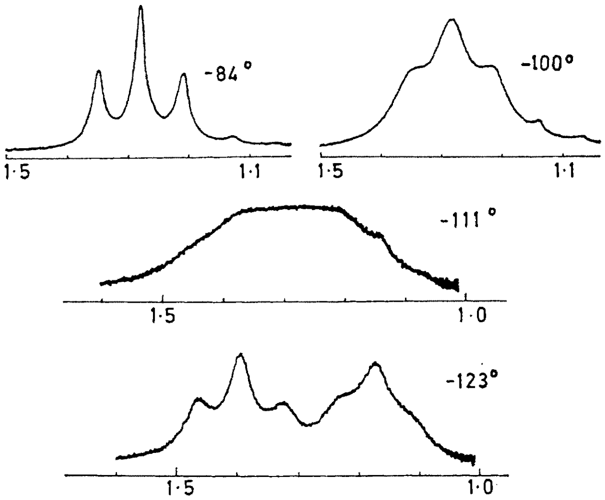


FIGURE. *The* 100 *MHz n.m.r. spectrum of the methyl protons of* $Et_2CO{\cdot}BF_3$ *in* $CHCl_2F$ *solution. Chemical shifts are given in p.p.m. from* Me_4Si. *Small peaks from impurities are seen at* 1·06 *and* 1·13 *p.p.m.*

Gillespie and Hartman[7] have found that the *inter*molecular exchange of boron trifluoride is slow for the pinacolone–boron trifluoride adduct at −90° even when boron trifluoride is present in excess. It therefore seems reasonable to attribute the broadening and coalescence of the two methyl triplets in the Et_2CO–BF_3 adduct observed when the temperature is raised, to an increase of the rate of *intra*molecular reorientation around the carbon–oxygen partial double bond. This reorientation may occur either as an internal rotation around the carbon–oxygen bond or as an inversion at the oxygen atom.

We have estimated the free energy of activation for this *intra*molecular reorientation in the Et_2CO–BF_3 adduct to be *ca.* 8 kcal mol^{-1} from the line-shapes at −100° and −111°. This value may be compared with the minimum value at 17 kcal mol^{-1} for the free energy of activation for the intramolecular reorientation in protonated ethyl methyl ketone, as determined by Brouwer.[2]

(*Received, July 20th,* 1970; *Com.* 1172.)

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