Nonequivalence of Methylene Protons in Asymmetric Ethyl Ethers

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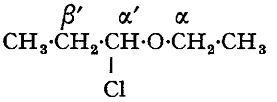
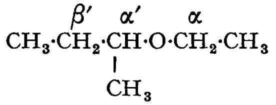
THIS Communication reports an analysis of the proton resonance spectra of α-chloropropyl ethyl ether (I) and ethyl s-butyl ether (II).

Nonequivalence of methylene protons in magnetically or stereochemically asymmetric environments has been reported frequently (for a recent Review see Martin and Martin, *Bull. Soc. chim. France*, 1966, 2117). The origin of the nonequivalence probably lies in the intrinsic asymmetry of the system and hindrance to free rotation, either in the form of statistical conformational preference (*e.g.*, ref. 1) or complete inhibition of rotation. Gutowsky[2] has interpreted these effects mathematically.



$$\overset{\beta'}{CH_3\cdot CH_2}\cdot\overset{\alpha'}{\underset{\substack{|\\Cl}}{CH}}\cdot O\cdot\overset{\alpha}{CH_2}\cdot CH_3$$

(I)



$$\overset{\beta'}{CH_3\cdot CH_2}\cdot\overset{\alpha'}{\underset{\substack{|\\CH_3}}{CH}}\cdot O\cdot\overset{\alpha}{CH_2}\cdot CH_3$$

(II)

The compounds studied here have two methylene groups (designated C-α, C-β′) near to an asymmetric centre (α′). Analysis of the *O*-ethyl proton spectrum (60 Mc./sec.) of (I) as an ABX_3 system with $J_{AX} = J_{BX}$ and J_{AB} negative in sign,[3] gives δ_{AB} 24·8 c./sec. with $J_{AB} = -9{\cdot}56$ c./sec. Analysis of the remaining absorptions by a perturbation method[4] suggests that the C-β′ protons are virtually equivalent with $\delta_{AB} < 3$ c./sec. and $J_{AB} \sim 0$. Thus the methylene nearer to the asymmetric centre shows by far the smaller geminal chemical shift and coupling constant.

Similarly, analysis of the spectrum of compound (II) gives δ_{AB} (for C-α) 8·4 c./sec. and $J_{AB} = -8{\cdot}79$ c./sec., with the C-β′ protons equivalent, $\delta_{AB} < 1$ c./sec. Again the more distant methylene is far more sensitive to the effect of the asymmetric centre. (Values of the coupling constants for the C-β′ protons in both spectra are necessarily subject to considerable error and are thus not quoted).

We suggest that the cause of this effect is an amplification of asymmetry by the oxygen lone-pair electrons. In compound (I), the C-α protons "see" ethyl, hydrogen, and chlorine as the substituents on the asymmetric centre. The C-β′ protons, on the other hand, "see" hydrogen, ethoxyl, and chlorine as substituents. Anisotropy effects due to chlorine and oxygen in organic molecules are known to be very similar[5] and thus the stereochemically asymmetric centre is probably less magnetically asymmetric from the point of view of C-β′ than from C-α. The significance of the difference is hard to assess from this single spectrum, however, since the C-α protons are one bond further removed from the asymmetric centre than those at C-β′, and any effect of the oxygen atom has been ignored.

In compound (II) the C-β′ protons "see" hydrogen, methyl, and ethoxyl as the asymmetric substituents, whilst protons at C-α "see" methyl, ethyl, and hydrogen. In this example despite the similarity of two of the substituents, from the viewpoint of C-α, the C-α protons still show far greater nonequivalence than those at C-β′. Since anisotropy effects decrease according to an r^3 rule[6] the oxygen atom must in some way cause a major amplification of the asymmetric magnetic effects.

Freymann[7] has suggested that modified selective chelation of the methylene protons occurs in this type of ether. Randell *et al.*[8] suggested that anisotropy effects due to relatively "mobile" electrons might well be observed in certain molecules. We believe that the reported spectra are consistent with Randell's suggestion. In detail, the mechanism may be that the asymmetric centre induces an asymmetry in the orbitals of the lone-pair electrons of the oxygen, which would be expected to be far more sensitive to the electrical and magnetic environment than, for example, the bonding electrons in the C–H bonds of C-β'. By "through space" effects, the induced asymmetry of the oxygen atom causes an enhanced magnetic anisotropy in the region of the C-α protons, thus leading to marked nonequivalence. Hindered rotation may play a part in these effects also, but the arguments of Gutowsky[2] apply to the system $R\cdot O\cdot CH_2\cdot R'$ as well as to ethane derivatives, if the oxygen has been rendered "pseudo-asymmetric" by the group R.

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