The *meso*-(±)- and *erythro*-*threo*-Dichloro-alkane Equilibria

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Summary Equilibration of the 2,3-dichlorobutane or 2,3-dichloropentane diastereomers at 80° leads to equilibrium mixtures in which the (±)- and *threo*-diastereomers are more stable in relation to their *meso*- and *erythro*-forms than was previously thought.

ONLY a few references report experimental information on the relative stabilities of diastereomers. The *meso*-form is usually thought to be more thermodynamically stable than (±)-pairs, and *erythro*-isomers are likely to be more stable than *threo*-isomers for substituted ethane derivatives except in those cases where strong intramolecular bonding is possible.[1] In these instances, *i.e.*, diols and diacids the (±)- and *threo*-diastereomers usually predominate.

Thus, the *meso*-stilbene dichlorides[2] and dibromides[3] have been shown to be more stable than their racemic isomers, although no accurate analysis is available for the dichloride. Linstead and Whalley[4] reported that *meso*-αα′-dimethylsuccinic acid is more stable than the (±)- form. However, Eberson[5] later found that the (±)-isomers of a series of αα′-dialkylsuccinic acids were more stable than the *meso*-diastereomers. Racemic tartaric acid is also more stable than the *meso*-diastereomer.[6] These results are presumably due to hydrogen bonding. Similarly, (±)-butane-2,3-diol has been reported to be more stable than the *meso*-isomer.[7] Surprisingly, the *meso*–(±) equilibrium[8] for the 2,3-dimethyl-2,3-diphenylsuccinonitriles has very recently been shown to favour the (±)- form. This unexpected result was explained by postulating an attractive interaction between nitrile groups.

We report further examples of *meso*–(±)- and *erythro*–*threo*-equilibria in which the (±)- and *threo*-forms are at least as stable as their *meso*- and *erythro*-isomers. When *meso*- or (±)-2,3-dichlorobutane is heated at 80° in a solution of Me_2SO saturated with LiCl a steady-state mixture is obtained which consists of 51% (±)- and 49% *meso*-2,3-dichlorobutane. Similarly, *erythro*- and *threo*-2,3-dichloropentane give 52·5% *threo*- and 47·5% *erythro*-2,3-dichloropentane.

The reasons for these observations may be explained by an attractive interaction between chlorines such as Peterson suggested for nitrile groups.[8] Analogy exists for such speculation with *cis*-dichloroethylene which is considerably more stable than its *trans*-isomer. It has been suggested that a possible explanation for this phenomenon might be attractive London forces between the polarizable chlorines.[9] *trans*-1,2-Dibromocyclohexane exists predominately in the diaxial conformation whereas the dichloride is predominately diequatorial.[10] Any attractive interaction should appear in the diequatorial conformation. Consideration of dipolar repulsion and steric factors may vitiate these arguments considerably. Accurate predictions of diastereomer stability require, therefore, a more detailed understanding of interacting groups than was previously thought.[1]

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