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THE CONFORMATIONAL EQUILIBRIUM CONSTANT OF DIVALENT SULFUR

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IN the previous letter,[1] a conformational free energy difference[2] of 0.8 kcal/mole was reported for the $-SC_6H_5$ group. The small magnitude of this difference agrees with the finding of Chiurdoglu and coworkers[3] for -SH based on infrared study and is also in line with findings for other single atoms, such as F, Cl, Br or I[4] and two-atom groups, such as -OX[1] and HgBr.[5] The reason for these low values has been discussed elsewhere.[6]

However, whereas our finding for $-SC_6H_5$ suggests that the group is more stable in the equatorial position, Chiurdoglu and coworkers assign infrared bands such that they suggest a preference of the -SH group for the axial position, contrary to earlier findings.[7] In the present communication we report a completely independent determination of the -SR value which corroborates the preference of the -SR group for the equatorial position.

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[1] E.L. Eliel and M. Gianni, preceding letter, Tetrahedron Letters No. 3, 97 (1962).

[2] cf. E.L. Eliel, J. Chem. Educ. **37**, 126 (1960).

[3] G. Chiurdoglu, J. Reisse and M. Vander Stichelen Rogier, Chem. & Ind. 1874 (1961).

[4] A.J. Berlin and F.R. Jensen, Chem. & Ind. 998 (1960).

[5] F.R. Jensen and L.H. Gale, J. Amer. Chem. Soc. **81**, 6337 (1959).

[6] E.L. Eliel and R.G. Haber, J. Amer. Chem. Soc. **81**, 1249 (1959).

[7] O. Bastiansen and O. Hassel, Tidsskr. Kjemi Bergv. Met. **6**, 96 (1946); some of the older electron diffraction measurements have recently been revised using more modern techniques, e.g. V.A. Atkinson, Acta Chem. Scand. **15**, 599 (1961).

Treatment of 4-t-butylcyclohexanone with mercaptoethanol in the presence of acid[8] gave a mixture of diastereoisomeric hemithioketals in 94% yield. Column chromatography on alumina (73% total recovery) yielded, besides recovered ketone (4%) a liquid (36%) and a solid (60%) hemithioketal, eluted in that order by hexane. The liquid isomer, upon distillation (b.p. 96-98°/0.2 mm) and low-temperature crystallization from ethanol melted at 1-2°. (Found: C, 67.41; H, 10.33. $C_{12}H_{22}OS$ requires C, 67.23; H, 10.35). The solid isomer, upon recrystallization from acetone-methanol, melted at 74-75°. (Found: C, 67.62; H, 10.48). Tentative assignment of configuration was made on the basis of n.m.r. spectra. The liquid isomer had $\delta = -177$ c.p.s. (assigned to $C\underline{H}_2S$) and -243 c.p.s. (assigned to $C\underline{H}_2O$). The solid isomer had $\delta = -175$ c.p.s. and -245 c.p.s. for the corresponding protons. (Chemical shifts are reported at 60 mc with respect to tetramethylsilane as standard). The assignments are based on analogies in the literature and the reality of the difference was confirmed by recording the

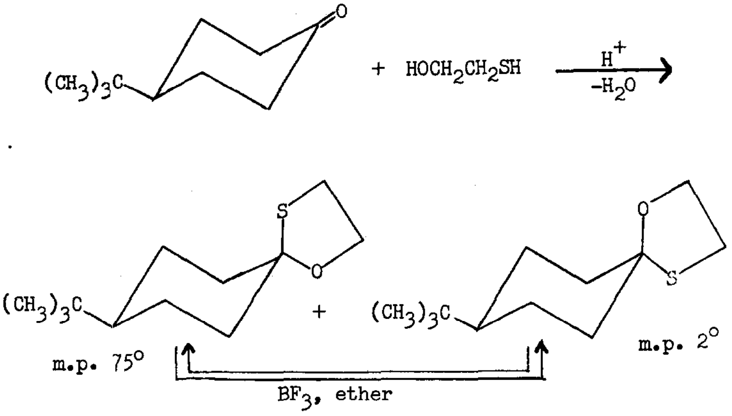

FIG. 1

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[8] C. Djerassi and M. Gorman, J. Amer. Chem. Soc. 75, 3704 (1953).

spectrum of a mixture of the two ketals in which both the CH_2S and CH_2O triplets showed doubling. A tentative assignment of configuration can be made on the basis of the spectra of the 4-t-butylcyclohexyl methyl ethers, the axial methoxyl absorbing at -193 c.p.s. and the equatorial at -195 c.p.s. Thus the protons at lower field appear to correspond to the equatorial groups and it may be inferred that the liquid isomer has equatorial sulfur and axial oxygen whereas the solid isomer has axial sulfur and equatorial oxygen.

The two isomers (Fig. 1) were readily equilibrated to an approximately 50:50 mixture by boiling for 24 hr with an excess of boron trifluoride in ether. The position of equilibrium was established by infrared spectroscopy. and (more accurately) column chromatography of the isomerized mixture. As it was feared that the size of the oxygen atom in the ketals might have been exaggerated through complex formation with boron trifluoride,[9] equilibration was repeated with a catalytic amount of BF_3. Under these conditions it took six months until the solid and liquid isomers (sealed in ampoules) arrived at identical composition, equilibrium corresponding approximately to 58% solid isomer and 42% liquid isomer ($K = 1.38$). If the slight distortion involved in forming the hemithioketal ring is disregarded, it may be inferred that oxygen has a greater tendency to be equatorial than sulfur by about 0.2 kcal/mole. Taking the conformational free energy difference for -OR as 0.6 kcal/mole[1] this gives a corresponding value for -SR of 0.4 kcal/mole in fair agreement with the NMR value[1] of 0.8 kcal/mole for -SPh. Our values agree with those of Chiurdoglu and coworkers[3] for -SH in magnitude but not in sign. If the band assignment of the Belgian investigators is indeed correct, this would suggest that an alkyl substituent on sulfur in place of hydrogen changes the preference of that atom from

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[9] Cf. E.L. Eliel and M. Rerick, J. Amer. Chem. Soc. **82**, 1367 (1960).

axial to equatorial.

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