

HYDROGEN BONDING IN FERROCENYL ALCOHOLS

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## ABSTRACT

Spectral evidence has been found which indicates that  $\alpha$ -hydroxy ferrocenyl alcohols may form hydrogen bonds directly with the iron atom. Investigations are now in progress of the isomerization of the exo and of the endo forms of  $\alpha$ -hydroxy-1,2-tetramethylene ferrocene toward the equilibrium mixture, using aluminum isopropoxide in isopropanol plus a trace of acetone as the isomerizing agent. Preliminary results indicate the equilibrium ratio of endo isomer to exo to be roughly 3:1 (75% endo; 25% exo).

## DISCUSSION

It has been shown by Hill and Richards<sup>1,2</sup> that  $\alpha$ -metallocenyl carbonium ions are stabilized by direct interaction with the metal atom.<sup>1,2</sup> This conclusion was reached after close examination of the solvolysis mechanisms of variously substituted  $\alpha$ -metallocenyl alcohols and acetates. Trifan and Backsai have concluded that hydrogen bonding with the metal atom occurs in ferrocenyl carbinols by analyzing the differences between the infrared spectra of several such compounds, particularly the exo and endo isomers of  $\alpha$ -hydroxy-1,2-tetramethylene ferrocene.<sup>3</sup> The observation, from NMR spectra, that protons bonded to metallocene nuclei in strongly acidic media occupy positions of equivalent symmetry with respect to all of the ring hydrogens further demonstrates that bonding interaction with the metal atom is a reality.<sup>4</sup>

The exo and endo isomers of  $\alpha$ -hydroxy-1,2-tetramethylene ferrocene should present a good system for observing hydroxy-iron hydrogen bonding. In one case (exo) the hydroxyl group is restrained from approaching close enough to the metal atom to hydrogen bond with it, and in the other (endo) it is held in a position very favorable to such bonding. Thus the endo isomer should be fully hydrogen bonded, whereas the exo isomer should not be able to hydrogen bond in this manner at all.

It is of interest to know what the strength of such a bond is. If the only difference between the exo and endo isomers is the presence of the hydrogen bond, the bond strength is equal to the difference in enthalpy between them. Such a bond strength value may be calculated in the usual way by use of the van't Hoff equation, if the equilibrium constant is known at two or more different temperatures. The isomer ratio at equilibrium is

of course equal to the equilibrium constant in this system. It can best be determined by measuring isomeric composition versus time under isomerizing conditions (aluminum isopropoxide in refluxing isopropanol plus a trace of acetone<sup>5,6,7</sup>) and determining the value of the equilibrium asymptote by extrapolation. Approaching equilibrium from both the exo and the endo sides should allow one to find a reasonably accurate value for the equilibrium isomer ratio, and concomitantly of the equilibrium constant.

During a trial isomerization, enough exo peak had appeared in the infrared spectrum of the sample after almost 80 hours of reaction to show conclusively that the conditions used do facilitate isomerization. These preliminary results indicate the equilibrium ratio of exo isomer to endo to be 1:3 (25% exo; 75% endo). The rate of isomerization is much slower than had been anticipated, so the apparatus has been slightly improved to permit reaction for periods as long as a week or so without excessive loss of solvent.

The quantitative isomerizations from which the equilibrium ratios will be determined are now in progress.

#### EXPERIMENTAL

$\alpha$ -Hydroxy-1,2-tetramethylene ferrocene.  $\alpha$ -Keto-1,2-tetramethylene ferrocene (502 mg., 2.2 millimoles), which had been recrystallized from hexane, m. p. 85.5-85.7, was dissolved in about 3 ml. of anhydrous ethyl ether. Lithium aluminum hydride (318 mg., 8.4 millimoles) was weighed into a clean, dried 50 ml. Erlenmeyer flask, and thoroughly powdered with a glass rod. Anhydrous ethyl ether was added, the flask was set on a magnetic stirrer,

and the mixture was agitated rapidly. The solution of ketone was quickly added with a dropper, but not so quickly as to produce too much bubbling. Reaction was allowed to proceed for 15 minutes. At the end of this time, the reaction was quenched by addition of about 25 drops of water (until bubbling subsided somewhat). The ethereal solution was removed with an eyedropper and transferred to a small separatory funnel; rinsings brought the total volume to around 30 ml. After washing four times with water, the solution was placed in a large round-bottomed flask for final drying by evaporation. (Drying agents such as magnesium sulfate cannot be used as they cause decomposition.) Benzene was added and the resulting solution was evaporated in vacuo with a rotary evaporator in a water bath not above 50 C. After several such treatments, water droplets no longer formed in the neck of the flask. The final solution volume was about 20 ml.

The reaction product was chromatographed on neutral alumina which had been partially deactivated by  $4\frac{1}{2}$  hours exposure to the air. The column was prepared in 30% ethyl ether, 70% benzene, and during the course of the chromatographic development the percentage of ether was increased to 70%. To elute the last band, it was necessary to add 1% methanol to the solvent. Two bands were found: the faster moving was deep golden yellow in color, and passed through the column not much more slowly than the solvent. The other band was smaller and lighter in color, and was eluted as mentioned above. On evaporation of solvent, the fractions containing the first band yielded a thick orange liquid, and those containing the second band a crystalline orange solid. Infrared spectra were taken in spectral grade carbon tetrachloride of both samples, with the following results: hydroxyl stretch of the first band -  $3561\text{ cm.}^{-1}$ ; of the second band -  $3610\text{ cm.}^{-1}$ . These results indicate

the first band to be the endo isomer and the second to be the exo, in agreement with Hill's results.<sup>8</sup> The samples were stored under nitrogen in the refrigerator without further purification.

Isomerization. A trial isomerization was carried out to examine the feasibility of the method described above. A simple apparatus, consisting of a 50 ml. Erlenmeyer flask fitted with micro-condenser, nitrogen flushing, magnetic stirrer, and hypodermic needle (for removing samples without interruption of the reaction), was assembled. Endo-~~α~~-hydroxy-1,2-tetramethylene ferrocene (50 mg., 1.3 millimoles) was dissolved in 20 ml. of isopropanol and 0.2 ml. of acetone, this solution placed in the isomerization apparatus, and about 10 mg. of unpurified aluminum isopropoxide added. This system was stirred and refluxed on an oil bath at 89-92° C. Samples were removed at intervals and checked for isomeric composition. The solvent was removed from each sample in vacuo, about 2 ml. of distilled water containing a little isopropanol was added and slurried, and this solvent was also removed. About 2 ml. of benzene was then added and evaporated (to remove water); this was done three times. The final residue was dissolved in spectral grade carbon tetrachloride and examined in the hydroxyl stretching region of the infrared.

A certain amount of evaporation of solvent took place through the condenser, so the volume in the reaction flask was maintained by occasional addition of small aliquots of isopropanol. Also, as this was intended only as a qualitative investigation of the isomerization procedure, and as the rate of isomerization was initially very slow, more aluminum isopropoxide was added over the first 30 hours or so, bringing the total amount present to roughly 50 mg.

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