

Preliminary communication

**STEREOCHEMISTRY OF ACID CLEAVAGE OF THE COMPOUNDS
 (*cis*- AND *trans*-4-METHYLCYCLOHEXYL)Fe(CO)₂(η⁵-C₅H₅)**

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Summary

Cleavage of the title compounds with DCl and CF₃CO₂D in CH₂Cl₂ proceeds with retention of configuration at the α-carbon atom. The mechanism probably involved protonation of the iron, followed by reductive elimination of alkane.

Mechanisms of electrophilic cleavage reactions of σ-bonded alkyl-transition metal compounds have been a subject of considerable debate in recent years. As shown in a recent review [1], numerous kinetic and stereochemical data are now available for reactions of a variety of metal systems with electrophilic reagents such as the proton, mercury(II) salts and the halogens.

A major datum not available at present, however, is knowledge of the stereochemistry at carbon of proton cleavage reactions, which generally proceed [1] as in eq. 1.



(R = alkyl, aryl; X = anion; L = other ligands)

We have undertaken to obtain such information, and report herein the results of cleavage reactions of (*cis*- and *trans*-4-methylcyclohexyl)Fe(CO)₂(η⁵-C₅H₅) (Ia, Ib, respectively) with anhydrous hydrogen chloride-*d*₁ and trifluoroacetic acid-*d*₁.

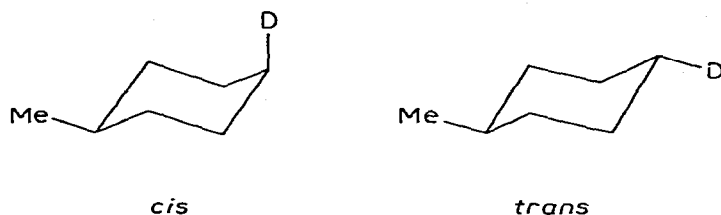
Compounds Ia and Ib were prepared in about 40% yields by treating the corresponding tosylates with Na[η⁵-C₅H₅Fe(CO)₂]; their NMR spectral data agreed with the literature values [2]. Both compounds were cleaved smoothly, Ib faster than Ia, with stoichiometry as in eq. 2.



(X = Cl, CF₃CO₂)

The hydrocarbon products were isolated and identified unambiguously as methyl cyclohexanes using chromatographic techniques. Differentiation of the

cis- and *trans*-isomers was accomplished by infrared spectroscopy in the C—D stretching region*. The strong preference of the methyl group of methyl cyclohexane for the equatorial position (the ratio of the equatorial methyl to the axial methyl conformer is 164/1 at 172 K, [4]) results in the deuterium atoms in *cis*- and *trans*-4-methyldeuterocyclohexane existing almost exclusively in axial and equatorial positions, respectively, i.e.,



As shown by Corey et al. [5] originally, and subsequently by others [6, 7], equatorial C—D stretching frequencies occur 10–20 cm^{-1} higher than do axial C—D stretching frequencies.

The products of reactions of Ia and Ib with the deuterated acids exhibited C—D stretching bands at 2163 ± 1 and 2173 ± 1 cm^{-1} (CH_2Cl_2), respectively (see Fig. 1), assignable to *cis*- and *trans*-4-methyldeuterocyclohexane, respectively [3]. The bands were quite symmetric in each case, suggesting that cleavage reactions of both acids proceeded with a high degree (at least 85% based on the ex-

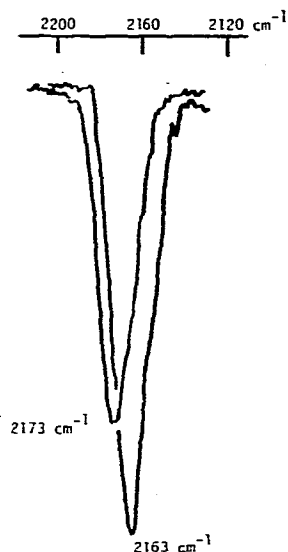
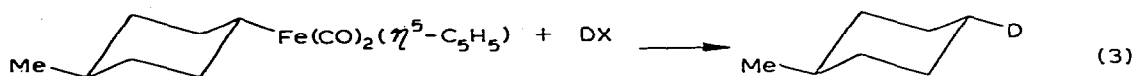


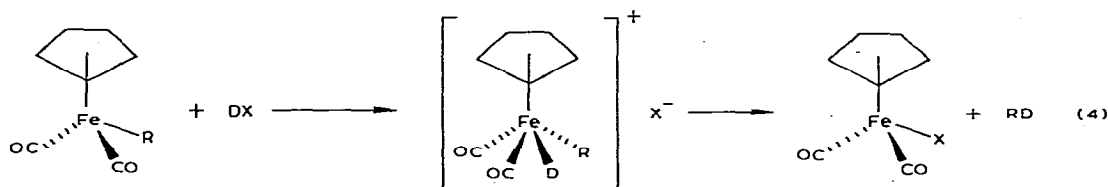
Fig. 1. Infrared spectra of *cis*- and *trans*-4-methyldeuterocyclohexane in the C—D stretching region.

*Jensen [3] has found values of 2163 and 2175 cm^{-1} for *cis*- and *trans*-4-methyldeuterocyclohexane, respectively, solvent not specified.

tent to which shoulders would be observable) of retention of configuration, i.e. for Ib,



A similar result has been obtained for (*cis*- and *trans*-4-methylcyclohexyl)-mercury(II) compounds [8]. Whereas acid cleavage of alkylmercury compounds probably proceeds via attack at the mercury-carbon bond [9], however, the reactions discussed here almost certainly involve protonation of the iron (eq. 4), followed by reductive elimination of alkane. The latter step would be expected to proceed with retention of configuration at carbon.

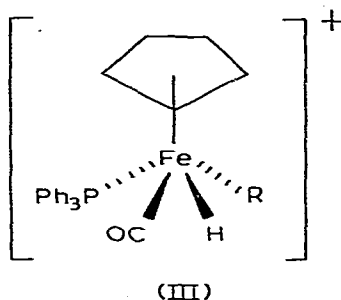


(R = *cis*, *trans*-4-methylcyclohexyl)

The first step is a type of reaction well known in preparative metal hydride chemistry [10]. The highest occupied molecular orbital (HOMO) of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Me}$, of essentially *d* character, lies some 1.4 eV above the metal-carbon σ bonding orbital [11], an energy difference probably typical of this class of iron compounds. Thus attack by an electrophilic reagent would be expected to occur at the iron rather than at the iron-carbon bond. In contrast, the HOMO of dialkylmercury(II) compounds has substantial mercury carbon bonding character, and lies some 6 eV above the 5*d* levels [12].

The iron compounds should, moreover, exhibit basic properties. In spite of the formal oxidation state of the iron (+II), the HOMO of the methyl compound has an ionization potential of only about 7.8 eV [11], comparable with those of trimethyl-amine and -phosphine [13].

The mechanism suggested in eq. 4 is consistent with kinetic studies of the cleavage of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Me}$ with $\text{CF}_3\text{CO}_2\text{H}$ in methylene chloride under essentially the same conditions ($\sim 0.1 M$ solutions in CH_2Cl_2) as maintained here [14]; the rates were found to be first order in both acid and iron compound. The postulated intermediate, II, is also similar to that suggested recently for the acid cleavage of resolved complexes of the type $\eta^5\text{-C}_5\text{H}_5\text{FeCO}(\text{PPh}_3)\text{alkyl}$, which are chiral at iron [15,16]. Although, in the latter cases, all details of the mechanism have not yet been elucidated, cleavage reactions of the phosphine-substituted derivatives proceed with predominant retention of configuration at iron, consistent with reductive elimination of RH from a species such as III.



The relative rates of cleavage of Ia and Ib ($I_b > I_a$) are probably an indication of the relative effects of steric hindrance to protonation, although it is not obvious from molecular models that Ia is more sterically hindered. However, separate studies have shown that hydrogen chloride treatment of mixtures of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ ($\text{R} = n\text{-Pr}, i\text{-Pr}$) in methylene chloride results in selective cleavage of the *n*-propyl derivative [17], an observation readily rationalized on the basis of steric effects.

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