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Preliminary communication

THE STEREOCHEMISTRY OF THE HYDROBORATION OF FERROCENYLALKENES

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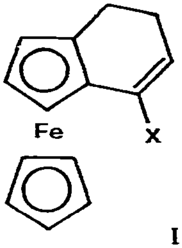
Summary

The hydroboration of π-cyclopentadienyl(6,7-dihydro-π-indenyl)iron affords (after oxidation) a considerable amount (34%) of π-cyclopentadienyl(*endo*-4,5,6,7-tetrahydro-4-hydroxy-π-indenyl)iron. This stereochemical result is a proof of the preliminary complexation of the borane with iron. The regioselectivity of the hydroboration of cyclic and open ferrocenylalkenes appears to be controlled by both steric and electronic factors.

In connection with our studies on the hydroboration-oxidation of ferrocenylalkenes in order to find a convenient route to the preparation of 2-ferrocenylalkanols [1], we investigated the stereochemistry of the hydroboration of π-cyclopentadienyl(6,7-dihydro-π-indenyl)iron (I) and of its 4-methyl derivative II. The hydroboration was performed under the usual conditions [2] with $NaBH_4/BF_3$ etherate in THF, and, after the oxidation with H_2O_2, gave a mixture of isomeric alcohols, as shown in Table 1.

Compound I affords a considerable amount of π-cyclopentadienyl(*endo*-4,5,6,7-tetrahydro-4-hydroxy-π-indenyl)iron (III, 34%) and of π-cyclopentadi-



I X=H
II $X=CH_3$

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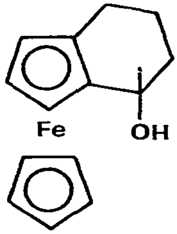
TABLE 1

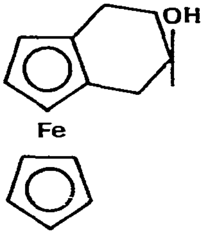
HYDROBORATION-OXIDATION OF SOME FERROCENYL ALKENES[a]

Alkene	Alcohols formed[b,c] (%)		Total yield (%)
	α	β	
I	*endo*, 34 *exo*, 6	*endo*, 2 *exo*, 58	95
II	*endo*, 0 *exo*, 1	*endo*, 1 *exo*, 98	90
Ferrocenylethene	3	97	100
1-Ferrocenylpropene	53	47	95
2-Ferrocenylpropene	1	99	93

[a] At 20—25°C. [b] By GC or HPLC analysis. The standard alcohols were prepared by literature methods. [c] The α and β positions are referred to the carbons of the double bond: the α-carbon is adjacent to the ferrocenyl group.



III



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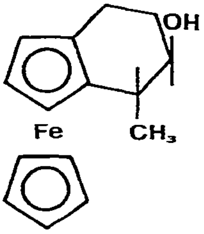
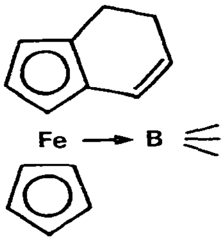


V

enyl(*exo*-4,5,6,7-tetrahydro-5-hydroxy-π-indenyl)iron (IV, 58%). Compound II gives V quantitatively.

The results show that borane may attack the double bond from both *exo* and *endo* directions. The *endo* attack was unexpected, since hydroboration proceeds preferentially from the less hindered site in cyclic alkenes with rigid structure [3] and the preferred attack of nucleophiles and electrophiles (such as H^+) on the ferrocenyl system occurs from the *exo* direction [4,5,6]. It may reasonably be accounted for by a preliminary Lewis acid/base interaction between iron and borane (structure VI) which orients the electrophile in the proper position for the *endo* attack. The *exo* attack appears to follow the general mechanism suggested for the common alkenes [3,4,7].



VI

The results of the hydroboration of I, II and of the open ferrocenylalkenes further indicate that the regioselectivity of the hydroboration from the *exo* and *endo* directions is controlled by steric and electronic factors (see Table 1).

The hydroboration of ferrocenylethene is essentially centred on the β-carbon, where the steric effects are negligible and the partial positive charge developing on the α-carbon is strongly stabilized by the ferrocenyl group. For 1-ferrocenylpropene (as for I) the attack at the α-carbon is more favoured than for ferrocenylethene owing to the steric hindrance of the carbon chain linked to the β-carbon. When the α-carbon becomes crowded by the introduction of a methyl group, as in 2-ferrocenylpropene and II, the attachment of the boron occurs at the β-carbon exclusively.

The stereochemical results for the hydroboration of I and II are an unequivocal demonstration of the disputed role played by iron as primary site of the electrophilic attack, the supporting evidence being only indirect and qualitative [8—11]. They also suggest that the hydroboration may be useful for the stereospecific synthesis of ferrocenyl derivatives.

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