

REDUCTION OF α -OXO AND α -HYDROXY DERIVATIVES
OF FERROCENOPHANES BY SODIUM BOROHYDRIDE
IN THE PRESENCE OF A LEWIS ACID
(ALUMINUM CHLORIDE OR BORON TRIFLUORIDE)

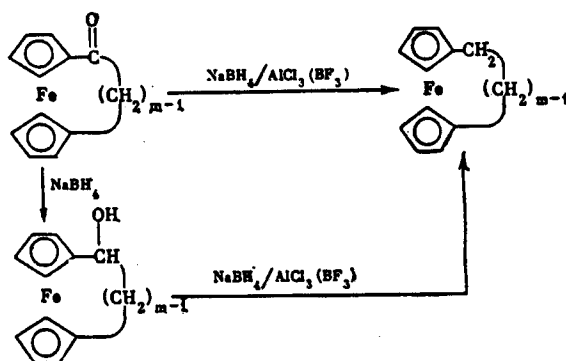
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Several methods are known for the reduction of ketones of the ferrocene series, particularly of the oxo derivatives of the ferrocenophanes [1-5]. In the present report we shall propose a new method for obtaining ferrocenophanes involving the reduction of their α -oxo and α -hydroxy derivatives.

The reaction of sodium borohydride in ethanol with acylferrocenes, as in the case of aryl and alkyl ketones, results in the formation of the α -hydroxyalkyl derivatives [6]. It is also known that the addition of aluminum chloride to sodium borohydride in the case of the reduction of aryl ketones does not cause a qualitative change in the reaction products, i.e., α -hydroxyalkylaryl derivatives [7].

We found that the reduction of the α -oxo derivatives of ferrocenophanes by sodium borohydride in the presence of Lewis acids (aluminum chloride or boron trifluoride) produces ferrocenophanes with pure carbon bridges. Similarly, ferrocenophanes form from the α -hydroxyalkyl derivatives, i.e.,



The more thorough reduction of the ferrocenophane derivatives is apparently due to the far greater stability of the α -ferrocenyl carbocation [8] in comparison to the respective aryl cation.

The proposed method for obtaining ferrocenophanes is simple and convenient. Anhydrous aluminum chloride, gaseous boron trifluoride, or boron trifluoride etherate can serve as the Lewis acid, and tetrahydrofuran or diglyme can serve as the solvent, but dimethoxyethane provides the best results. The order of the addition of the reagents is not crucial, but it is better to add the sodium borohydride and then the Lewis acid (aluminum chloride is added in portions, boron trifluoride etherate is added dropwise, or gaseous boron tri-

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TABLE 1. Reduction of Ferrocenophane Derivatives

No.	Compound reduced	Solvent*	Lewis acid	Compound re-duced; NaBH ₄ ratio	Reaction product	Yield, %
1		THF	AlCl ₃	1 : 6		95
2		DME	AlCl ₃	1 : 18		100
3		Diglyme	AlCl ₃	1 : 6		100
4		DME	AlCl ₃	1 : 6		98
5		DME	AlCl ₃	1 : 3		85
6†		DME‡	BF ₃	1 : 4		87
7		DME‡	BF ₃ ·(C ₂ H ₅) ₂ O	1 : 8		85
8		DME	AlCl ₃	1 : 6		90

* Here DME is dimethoxyethane, and THF is tetrahydrofuran.

† The compound obtained was characterized according to the data from the PMR and mass spectra.

‡ The solvent used was DME containing 3-5% water.

fluoride is bubbled through the solution) to a solution of the compound to be reduced in the organic solvent. If BF₃ or its etherate is used up to 15% water may be present in the solvent.

The reaction proceeds within several minutes at room temperature and permits the reduction of both mono- and di- α -oxo and di- α -hydroxy ferrocenophane derivatives.

The reduction method indicated can also be used in the ruthenocene series, as we have demonstrated in the case of 3-phenyl[5]ruthenocenophane [9]. The proposed method involving reduction by sodium borohydride in the presence of a Lewis acid is protected by patents [10-12].

The following is an example of a reduction reaction employing sodium borohydride in the presence of a Lewis acid. The results of the experiments have been summarized in Table 1. The compounds were identified according to their melting points, by thin-layer chromatography on Silufol, and from their PMR-spectroscopic data.

Reduction of 3-Phenyl[5]ferrocenophane-1,5-diol. A 1.4-g portion of sodium borohydride is added to a suspension of 0.7 g of 3-phenyl[5]ferrocenophane-1,5-diol in 40 ml of dimethoxyethane, and then 1.6 g of aluminum chloride is added in small portions with stirring. After 10 min, 50 ml of water and 50 ml of dilute hydrochloric acid are added to the solution. The 3-phenyl[5]ferrocenophane precipitate is filtered off and dried. The product consists of 0.64 g of the compound (~100% of the theoretical value).

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