

REDUCTION OF CARBONYL GROUP TO METHYLENE GROUP IN FERROCENE AND RUTHENOCENE  
DERIVATIVES BY SODIUM BOROHYDRIDE IN THE PRESENCE OF PROTONIC AND LEWIS ACIDS

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UDC 541.1'13+546.722

We have already shown [1] that carbonyl derivatives of ferrocenophanes are reduced to ferrocenophanes by  $\text{NaBH}_4$  in the presence of  $\text{BF}_3$  or  $\text{AlCl}_3$  in dimethoxyethane medium. In the present work, we show the generality of the discovered reaction, and its applicability for a very convenient and rapid preparation of any alkyl derivatives of ferrocene and ruthenocene from the corresponding acyl compounds.

The reduction reaction is carried out by carefully adding, with stirring, small portions of an acid (concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{BF}_3$ ,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ,  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ) to a mixture acylmetallocene and sodium borohydride in dioxane, dimethoxyethane, or tetrahydrofuran. After 5-20 min, the solution becomes yellow, an excess of water is added to it, and the products are extracted with chloroform. The chloroform layer is washed with water and dried, and after the evaporation of the solvent, the residue is recrystallized from alcohol or chromatographed. By this method, the following compounds in particular were obtained: from acetylferrocene - ethylferrocene, by reduction with a  $\text{NaBH}_4$ - $\text{BF}_3 \cdot \text{Et}_2\text{O}$  mixture in dioxane (yield 89%); from benzoylferrocene - benzylferrocene (reducing agent -  $\text{NaBH}_4$ - $\text{AlCl}_3$  in dimethoxyethane, yield 84%); from 1,1'-dipropionylferrocene - 1,1'-dibutylferrocene ( $\text{NaBH}_4$ - $\text{BF}_3$  in dioxane, yield 75%); from 1,1'-diacetylferrocene - a mixture of 1,1'-diethylferrocene and 1-ethyl-1'-acetylferrocene ( $\text{NaBH}_4$ - $\text{H}_2\text{SO}_4$  in dioxane, yields 27 and 32%, respectively); and from 1,1'-diacetyl ruthenocene - 1,1'-diethylruthenocene ( $\text{NaBH}_4$ - $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in dimethoxyethane, yield 95%). The synthesized compounds were identified by melting points,  $R_f$  values, and PMR spectra.

LITERATURE CITED

1. A. N. Nesmeyanov, G. B. Shul'pin, M. V. Tolstaya, and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, 232, 1319 (1977).