Formation of Quaternary Stereogenic Centers by Wagner-Meerwein Rearrangement – Synthesis of Optically Active Cyclopentadienyl Complexes from Borneol and Fenchol

Christian Färber\textsuperscript{a}, Gotthelf Wolmershäuser\textsuperscript{b}, and Helmut Sitzmann\textsuperscript{b}

\textsuperscript{a} FB 18 der Universität, Mönchebergstraße 19, D-34109 Kassel, Germany
\textsuperscript{b} FB Chemie der TU, Erwin-Schrödinger-Straße 54, D-67663 Kaiserslautern, Germany

Reprint requests to Prof. Dr. Helmut Sitzmann. Fax: +49-631-205-4676. E-mail: sitzmann@chemie.uni-kl.de

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The development of optically active cyclopentadienyl complexes as enantioselective catalysts calls for simple synthetic procedures for cyclopentadienes with optically active alkyl substituents. While \textit{exo}-bornyl chloride and \textit{exo}-fenchyl bromide do not react or exclusively eliminate hydrogen halide with cyclopentadienylmetal compounds in ether solvents or ammonia, they undergo Wagner-Meerwein rearrangement and substitution with cyclopentadienylmagnesium chloride in toluene. The bornyl cation yields racemic \textit{exo}-bornylcyclopentadiene and partially racemized isocamphyl-cyclopentadiene, but for the fenchyl cation no racemization pathway is available, and the main diastereomer among the lithium salts of the ensuing substituted cyclopentadienes can be isolated in 95\% diastereomeric purity by solvent extraction. This material with the IUPAC name lithium (2\textit{R})-2,5,5-trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienide carries an alkyl substituent having no trivial name so far. \textit{Exo}-norbornylcyclopentadiene could be synthesized in high yield with a similar procedure. The same protocol works with 1-bromoadamantane. The novel alkylcyclopentadienes have been converted to ferrocenes and molybdenum complexes of the type [\textit{Cp}\textsuperscript{\textit{R}}\textit{Mo(CO)}\textsubscript{3}\textit{CH}_3]. (2\textit{R})-2,5,5-Trimethylbicyclo[2.2.1]hept-2-ylcyclopentadienide with an optical purity of 78\% \textit{ee} (the optical purity of the starting material fenchol) was converted into an optically active titanocene dichloride and tested in the catalytic hydrogenation of 2-phenyl-1-butene. The hydrogenation product was obtained with 31\% \textit{ee}, which compares favorably with results obtained with other group 4 metalloocene dichlorides with one optically active alkyl substituent on each ring ligand. Facile procedures for the synthesis of the starting compounds \textit{exo}-bornyl chloride and \textit{exo}-fenchyl bromide based on the tosylate method have been developed with a tosylate melt or with toluene serving as solvents.

\textit{Key words:} Bornyl Chloride, Fenchyl Bromide, Optical Activity, Enantioselective Hydrogenation, Titanocene Dichloride