

New Efficient Diastereoselective Synthesis of *dl*-Hydrobenzoin_s by Reductive Dimerization of Aldehydes with the System Fe(CO)₅–HMPA

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Hydrobenzoin_s (1,2-diphenylethane-1,2-diols) are widely used as chiral auxiliaries, ligands, and synthetic intermediates [1, 2]. The most straightforward method for stereoselective synthesis of hydrobenzoin_s is reductive dimerization of aldehydes and ketones. Systems on the basis of lowest-valence metal complexes are generally used as reducing agents, e.g., CpV(CO)₄–Zn–Me₃SiCl [3], Cp₂TiCl₂–Mn–Me₃Py·HCl [4], Ti(salen)–Zn–Me₃SiCl [2], NiCl₂(Cat)–Mg–Me₃SiCl [5], etc. The reactions are carried out under heterogeneous conditions, and in some cases, the catalyst must be prepared preliminarily. We were the first to use as reducing agent the system Fe(CO)₅–HMPA, which allowed us to develop a new, simple, and effective procedure for diastereoselective synthesis of *dl*-hydrobenzoin_s. The reaction is homogeneous, and there is no need of using anhydrous solvents and inert atmosphere. In the reduction of pentafluorobenzaldehyde and *p*-chlorobenzaldehyde, only one *dl*-diastereoisomer is formed.

From benzaldehyde and *p*-methoxybenzaldehyde we obtained the corresponding 1,2-diols as mixtures of diastereoisomers at a *dl*/*meso* ratio of ~8:2; the *dl*-isomers were isolated as individual substances. Their purity and configuration were confirmed by GLC, X-ray analysis, and comparison of the melting points with published data (the 4-methoxy derivative was identified as racemate by analogy). Presumably, the mechanism of reductive dimerization includes

successive electron transfer from pentacarbonyliron to aldehyde via coordination of two aldehyde molecules to the metal; the presence of two bulky aryl groups favors predominant formation of the corresponding *dl*-diol.

General procedure for reductive dimerization of aldehydes with the Fe(CO)₅–HMPA system. A solution of 1 mmol of aldehyde, 2 mmol of Fe(CO)₅, and 4 mmol of HMPA in 1 ml of benzene was heated for 4 h at 80°C. The mixture was diluted with benzene, washed with dilute hydrochloric acid and water, and dried. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent.

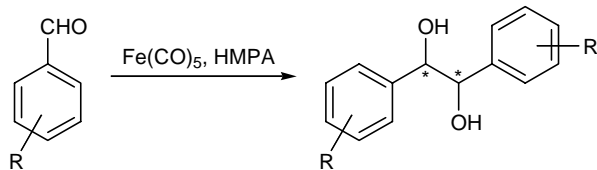
***rac*-1,2-Diphenylethane-1,2-diol.** Yield 50%, mp 120°C [6]. ¹H NMR spectrum, δ, ppm: 4.80 s (2H, CH), 2.86 s (2H, OH).

***rac*-1,2-Bis(pentafluorophenyl)ethane-1,2-diol.** Yield ~90%, mp 185°C [7]. ¹H NMR spectrum, δ, ppm: 5.38 d and 5.40 d (1H each, CH, *J* = 6 Hz), 2.50 d and 2.52 d (2H, OH, *J* = 6 Hz). Found, %: C 42.94; H 1.20; F 46.81; OH 9.75. C₁₄H₄F₁₀O₂. Calculated %: C 42.6; H 1.0; F 48.2; OH 8.6.

***rac*-1,2-Bis(*p*-chlorophenyl)ethane-1,2-diol.** Yield ~90%, mp 147–148°C [8]. ¹H NMR spectrum, δ, ppm: 4.69 s (2H, CH), 2.90 s (2H, OH).

***rac*-1,2-Bis(*p*-methoxyphenyl)ethane-1,2-diol.** Yield ~75% (on the reacted aldehyde), mp 112–114°C [2]. ¹H NMR spectrum, δ, ppm: 4.70 s (2H, CH), 2.70 s (2H, OH).

GLC analysis was performed on an LKhM-80 chromatograph equipped with a thermal conductivity detector and a steel column (1300×3 mm) packed with 15% of SKTFT-50Kh on Chromaton-N-AW; carrier gas helium, flow rate 60 ml/min. The ¹H NMR spectra were recorded on a Bruker WP-200 spectrometer at



R = H, F₅, *p*-Cl, *p*-MeO.

200 MHz from solutions in CDCl₃; the chemical shifts were measured relative to tetramethylsilane. X-Ray analysis was performed on a Bruker SMART-1000 diffractometer at 120°C.

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