LETTERS TO THE EDITOR

ASYMMETRIC REDUCTION OF ACETOPHENONE BY HYDROSILANES CATALYZED BY CHIRAL HYDRIDORHODACARBORANES

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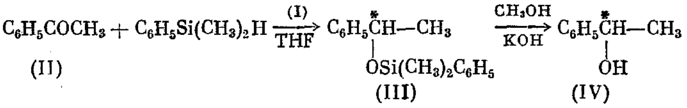
We have found that chiral hydridorhodacarboranes, (+)- and (−)-1-Ph-3,3-$(Ph_3P)_2$-3H-3,1,2-$RhC_2B_9H_{10}$ (I) [1], which contain a chiral carborane ligand, catalyze the asymmetric reduction of acetophenone (II) by phenyldimethylsilane



$$\underset{\text{(II)}}{C_6H_5COCH_3} + C_6H_5Si(CH_3)_2H \xrightarrow[\text{THF}]{\text{(I)}} \underset{\text{(III)}}{C_6H_5\overset{*}{C}H(OSi(CH_3)_2C_6H_5)-CH_3} \xrightarrow[\text{KOH}]{CH_3OH} \underset{\text{(IV)}}{C_6H_5\overset{*}{C}H(OH)-CH_3}$$

A solution of acetophenone (4 g), phenyldimethylsilane (5 g), and (I) (0.2 g) in THF (15 ml) was refluxed in an atmosphere of argon for 15 h. The reaction product was twice distilled under vacuum and analyzed by GLC for (III) [2]; $[\alpha]_D$ was determined without solvent. Together with (III) the reaction formed the vinylsilyl ether, which gave acetophenone on hydrolysis. Compound (IV) was isolated by treating (III) with KOH in aqueous methanol by the procedure of [2]. We obtained optically active phenylmethylcarbinol, which was twice distilled under vacuum; $[\alpha]_D$ was determined without solvent. Ketone (II) in the presence of (−)-(I) [1] gave (III), $[\alpha]_D$ +23°, from which we derived (IV), $[\alpha]_D$ +18.5°, optical yield 42% [2], overall yield 48%. In the presence of (+)-(I) [1], (II) gave (III), $[\alpha]_D$ −10.8°, from which we derived (IV), $[\alpha]_D$ −5.3°, optical yield 14%, overall yield 41%.

LITERATURE CITED

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2. I. Ojima, T. Kogure, M. Kumagai, S. Horiuchi, and T. Sato, J. Organomet. Chem., 122, 83 (1976).

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