Journal of Organometallic Chemistry, 54 (1973) C45–C47

Preliminary communication

Asymmetric hydrosilylation of ketones catalyzed by a chiral cationic rhodium complex

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(Received April 3rd, 1973)

SUMMARY

A cationic rhodium complex with an optically active phosphine as ligand can function as a catalyst for the asymmetric hydrosilylation of alkyl phenyl ketones.

In a previous paper[1] we have reported that the asymmetric hydrosilylation of simple ketones is catalyzed by platinum(II) complexes with chiral phosphine as ligands.

Schrock and Osborn[2] have reported that the cationic species, $[\mathrm{Rh(PPhMe_2)_2H_2S_2}]^+$ (S = solvent), catalyzes the reduction of ketones under mild conditions, and a catalytic asymmetric reduction of simple ketones has also been achieved[3]. These facts are significant in suggesting that the ketones may easily coordinate to the cationic rhodium complex and as a result undergo the addition of hydrosilanes more effectively.

We now find that an analogous complex with an optically active phosphine as ligand catalyzes the asymmetric addition of hydrosilanes to alkyl phenyl ketones in high reaction yield. The chiral cationic complex, $[\mathrm{Rh\{(\mathit{R})\text{-}(PhCH_2)MePhP\}_2H_2S_2}]^+\mathrm{ClO_4}^-$ (S = solvent), was prepared *in situ* from $[\mathrm{Rh(NBD)\{(\mathit{R})\text{-}(PhCH_2)MePhP\}_2}]^+\mathrm{ClO_4}^-$ (NBD = 1,5-norbornadiene) according to the reported procedure[4], the latter being of little use as catalyst for asymmetric hydrosilylation.

$$\mathrm{RCOPh + R'Me_2SiH \xrightarrow{[RhL_2H_2S_2]^+} RPh\overset{*}{C}HOSiMe_2R'}$$

R = Me, Et, and t-Bu; R′ = Me and Ph;
L = (*R*)-(+)-(PhCH$_2$)MePhP (70% optical purity)

Addition of phenyldimethylsilane (40 mmoles) to acetophenone (40 mmoles) in the presence of the cationic rhodium complex ($2 \cdot 10^{-2}$ mmole) dissolved in $\mathrm{CH_2Cl_2/C_6H_6}$

(1/2) gave α-phenethyl phenyldimethylsilyl ether (I), b.p. 118°/3 mm, $[\alpha]_D^{20}$ −19.21° (neat), in 97% yield. Methylation of (I) with excess of methyllithium followed by acid hydrolysis gave the known (*S*)-α-phenylethanol, with a rotation which indicated a 22.1% optical purity for (I).

Hydrosilylation of acetophenone with trimethylsilane produced, after methylation, the same alcohol of lower optical purity (3.6%). The results for other alkyl phenyl ketones examined are summarized in Table 1..

TABLE 1

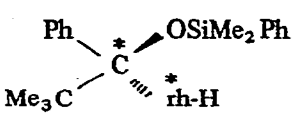
ASYMMETRIC HYDROSILYLATION OF ALKYL PHENYL KETONES WITH R_3SiH CATALYZED BY $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+$ (S = solvent) AT 50°, FOR 40 HOURS

Alkyl group in alkyl phenyl ketone	*Silyl ether*[a] *$[\alpha]_D^{20}$ (neat)*	*Yield (%)*	*Carbinol*[b] *$[\alpha]_D^{20}$*	*Configuration*	*Optical yield*[c] *(%)*
$R_3SiH = PhMe_2SiH$					
Methyl	−19.21	97	− 9.61	*S*	31.6
Ethyl	−24.54	94	− 8.47	*S*	43.1
t-Butyl	−24.92	84	−11.20[d]	*S*	61.8
$R_3SiH = Me_3SiH$					
Methyl	− 2.25	100	− 1.55	*S*	5.1
Ethyl	− 3.23	92	− 1.26	*S*	6.4
t-Butyl	+10.50	81	+ 5.10[d]	*R*	28.1

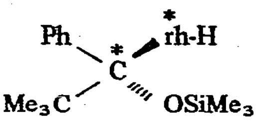
[a] Satisfactory elemental analyses, IR and NMR spectra were obtained for these silyl ethers. [b] Specific rotation was measured neat unless otherwise noted. [c] Optical yield was calculated from the specific rotation of the pure enantiomers which were reported in the literature (*cf.* ref. 1), and calibrated for the optical purity of chiral phosphine used (70%). [d] Specific rotation in benzene.

Generally, the asymmetric hydrosilylation of ketones gave (*S*)-carbinols predominantly, except in case of addition of trimethylsilane to t-butyl phenyl ketone. This is in good agreement with our previous work[1] where the platinum(II) complex containing the same chiral phosphine as one used here was also found to catalyze the addition of methyldichlorosilane to a series of alkyl phenyl ketones to give rise to optically active silyl ethers of alkylphenylcarbinols with consistent (*S*)-configuration. It is noteworthy, however, that the rhodium complex is not active for methyldichlorosilane but for a trialkylsilane and a dialkylsilane, while the latter two can not be used in conjunction with platinum(II) catalysts.

Considerable variation in optical yield with silane structure should be noted. Phenyldimethylsilane gave the silyl ethers with an optical yield about six times as high as that from trimethylsilane in cases of acetophenone and ethyl phenyl ketone. On the other hand, the addition of phenyldimethylsilane to t-butyl phenyl ketone gave the silyl ether of (*S*)-t-butylphenylcarbinol, while trimethylsilane led to the (*R*)-enantiomer. Obviously, the steric need for a match of catalyst (chiral phosphine) and reactants is different in the diastereomeric key intermediates (II) and (III). Steric effects similar to



(II)



(III)

those mentioned above are found in the stereoselective hydrosilylation of terpene ketones[5]. Furthermore, chlorotris(triphenylphosphine)rhodium(I) has recently been found to be an effective catalyst for hydrosilylation of carbonyl compounds[6], whereas its utility for hydrogenation is generally limited to the reduction of unsaturated carbon—carbon bonds[7].

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