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ASYMMETRIC HYDROSILYLATION OF α,β-UNSATURATED CARBONYL COMPOUNDS

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Catalytic hydrosilylation of ketones[1] and imines[2] may be considered as a synthetically equivalent means to the reduction of these compounds The reaction is of considerable use for enantioselective reduction of C=O[3] or C=N[4] bonds when chiral rhodium complexes are employed as catalysts

As an extension of our studies on the asymmetric hydrosilylation of prochiral olefins[5] and ketones[3a] catalyzed by Group VIII transition metal complexes with chiral phosphine ligands, we report here the asymmetric 1,4-addition of hydrosilanes to α,β-unsaturated ketones using chiral phosphine-rhodium complexes as catalysts.

In 1959, Sadykh-Zade and Petrov reported that chloroplatinic acid-catalyzed hydrosilylation of α,β-unsaturated carbonyl compounds takes place in a 1,4 fashion.[6] Recently, Ojima, Kogure, and Nagai have found that highly selective 1,2- as well as 1,4-addition of hydrosilanes to α,β-unsaturated terpene ketones can be achieved, the selectivity depending markedly on the nature of the hydrosilane employed [7]

We have now found that the chiral cationic complex, $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (S = solvent),[3a] prepared *in situ* catalyzes the asymmetric hydrosilylation of α,β-unsaturated ketones under mild conditions. A catalytic system of rhodium(I) with (-)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(-)-diop][3c] was also used in the present reactions.

Thus, addition of dimethylphenylsilane (30 mmoles) to (*E*)-4-phenylpent-3-en-2-one (1) (30 mmoles) in the presence of the chiral cationic complex (3×10^{-2} mmole) dissolved in benzene at room temperature gave only a 1,4-adduct, 2-dimethylphenylsilyloxy-4-phenylpent-2-ene (3),[8] bp. 121-123°/0.04 mm, α_D^{20} -0.68° (0.1 dm, neat), in 76% yield Hydrolysis of 3 with potassium hydroxide in aqueous methanol gave 4-phenylpentan-2-one (7),[9] $[\alpha]_D^{20}$ -5.31° (neat).

(1)

1, R^1 = Me R^2 = Ph
2, R^1 = Ph or Me

3, R^1 = Me, R^2 = Ph
4, R^1 = Me, R^2 = Me
5, R^1 = Ph, R^2 = Ph
6, R^1 = Ph, R^2 = Me

7, R^1 = Me
8, R^1 = Ph

$[Rh^*] = [Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (abbr. $R_3P^*\text{-}Rh^+$)
$\frac{1}{2}[(C_6H_{10})RhCl]_2$ + (-)-diop (abbr. diop-Rh)

Hydrosilylation of 1 with trimethylsilane produced, after hydrolysis, the same saturated ketone (7) of lower optical activity 7 was further converted into 2-phenylpropanol (9)[10] in order to confirm optical purity (eq. 2).

$$\mathrm{PhMe\overset{*}{C}HCH_2COMe} \xrightarrow[\mathrm{CHCl_3}]{\mathrm{PhCO_3H}} \mathrm{PhMe\overset{*}{C}HCH_2OCOMe} \xrightarrow{\mathrm{KOH/H_2O}} \mathrm{PhMe\overset{*}{C}HCH_2OH} \qquad (2)$$

7, $[\alpha]_D^{25}$ -5.31° 9, $[\alpha]_D^{20}$ -2.14°

Hydrosilylation was also carried out with (*E*)-1,3-diphenylbut-2-en-1-one (2) in the presence of $R_3P^*\text{-}Rh^+$ or diop-Rh to give optically active 1-dimethylphenylsilyloxy-1,3-diphenylbut-1-ene (5)[11] or its trimethylsilyloxy analog (6), respectively. 5 and 6 were converted by hydrolysis into known 1,3-diphenylbutan-1-one (8).[12] 8 ($[\alpha]_D^{25}$ -1.47°) was successively treated with perbenzoic acid and lithium aluminum hydride to obtain 3-phenylbutanol (10)[13] ($[\alpha]_D^{25}$ -3.94°). The results thus obtained are summarized in Table 1.

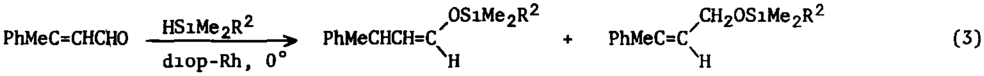
Table 1. Asymmetric Hydrosilylation of α,β-Unsaturated Ketones Catalyzed by Chiral Phosphine-Rhodium Complexes[a] at Room Temperature.

R^1	R^2	Catalyst	Yield (%)	Silyl enol ether α_D^{20} (0.1 dm, neat)	Ketone $[\alpha]_D^{25}$	Configuration	Optical yield (%)
Me	Ph	$R_3P^*\text{-}Rh^+$	76	-0 680	-5 31[b]	*R*	15.6[c]
Me	Ph	diop-Rh	92	-0.356		*R*	6.4
Me	Me	$R_3P^*\text{-}Rh^+$	90	-0 153	-0 47[b]	*R*	1 4[c]
Ph	Ph	$R_3P^*\text{-}Rh^+$	72	-2.62[d]		*R*	10.0[c]
Ph	Ph	diop-Rh	83	-1 09[d]	-0 48[e]	*R*	3.3
Ph	Me	$R_3P^*\text{-}Rh^+$	94	-0 123	-1.09[e]	*R*	9.5[c]
Ph	Me	diop-Rh	87	-0.162	-1.47[e]	*R*	10.1

[a] [Rh*] = 0 1 mole%. [b] Neat. [c] Calibrated for the optical purity of the chiral phosphine used (79%) [d] Specific rotation in benzene (c 10). [e] In CCl_4 (c 5).

It is noted that in all cases R_3P^*-Rh^+ or diop-Rh catalyzes the addition reaction to give (*R*)-ketones preferentially, that is, the addition in a sense of selecting a *si-si* face of carbon-carbon double bonds of α,β-unsaturated ketones in an *E* form whether R^1 is methyl of phenyl group

Attempted asymmetric hydrosilylation of β-methylcinnamaldehyde (11) with trialkylsilane resulted in giving not only 1,4-adduct (12) but 1,2-adduct (13) (eq. 3), the ratio of 12 to 13 was 64/36 with trimethylsilane, and 59/41 with dimethylphenylsilane, respectively However, 12 was obtained in an optically inactive form



$$\mathrm{PhMeC{=}CHCHO} \xrightarrow[\text{diop-Rh, }0^\circ]{\mathrm{HSiMe_2R^2}} \mathrm{PhMeCHCH{=}C}\begin{matrix}\diagup\mathrm{OSiMe_2R^2}\\ \diagdown\mathrm{H}\end{matrix} + \mathrm{PhMeC{=}C}\begin{matrix}\diagup\mathrm{CH_2OSiMe_2R^2}\\ \diagdown\mathrm{H}\end{matrix} \qquad (3)$$

11 12 13

Of particular significance is the preparation of optically active silyl enol ethers, which are well suited for generation of metal enolate species.[14] We are currently investigating the asymmetric hydrosilylation of certain cyclic enones and alkylation of the resulting chiral enolates

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8. This compound consists of (*E*)- and (*Z*)-isomers in a ratio of 20.80 on the basis of NMR analysis of the mixture. NMR ($\mathrm{CCl_4}$/TMS): (*E*)-**3**, δ 0.36 (s, $\mathrm{SiC}H_3$), 1.22 (d, *J* = 7.6 Hz, $\mathrm{CHC}H_3$), 1.81 (broad s, $=\mathrm{CC}H_3$), 3.2-4.0 (m, $\mathrm{C}H\mathrm{CH_3}$), 4.45-4.85 (d, $=\mathrm{C}H$), and 6.9-7.6 ppm (m, $\mathrm{C_6}H_5$). (*Z*)-**3**, δ 0.41 (s, $\mathrm{SiC}H_3$) and 1.69 ppm (s, $=\mathrm{CC}H_3$), and other signals are indistinguishable from those of (*E*)-**3**.

9. Cookson and Kemp [*Chem. Commun.*, 385 (1971)] have reported the specific rotation of optically pure **7** to be $[\alpha]_D$ -74.5° (*c* 1, benzene). The value, however, is inconsistent with that correlated with optical purity of the alcohol **9** (*cf.* ref. 13).

10. S. P. Bakshi and E. E. Turner, *J. Chem. Soc.*, 171 (1961); (*S*)-2-phenylpropanol (**9**) has $[\alpha]_{D\ \max}$ -17.4° (neat).

11. NMR indicates only a (*Z*)-isomer. NMR ($\mathrm{CCl_4}$/TMS) δ 0.32 (s, $\mathrm{SiC}H_3$), 1.23 (d, *J* = 7.2 Hz, $\mathrm{CHC}H_3$), 3.53-4.06 (double q centered at 3.78, $\mathrm{C}H\mathrm{CH_3}$), 5.24 (d, *J* = 9.6 Hz, $=\mathrm{C}H$), and 6.9-7.6 ppm (m, $\mathrm{C_6}H_5$).

12. T. L. Leitereg and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 4011 (1968), Optically pure (*R*)-1,3-diphenylbutan-1-one (**8**) has $[\alpha]_D$ -14.6° (*c* 1.8, $\mathrm{CCl_4}$).

13. This conversion indicates that the optical purity of the ketone (**8**) corresponds exactly with that of the alcohol (**10**), *cf.* H. Rupe and F. van Walraven, *Helv. Chim. Acta*, **13**, 361 (1930); $[\alpha]_{D\ \max}$ -39.56° (neat).

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