Tetrahedron Letters Vol. 21, pp 1871 - 1874
0040-4039/80/0501-1871$02.00/0

ASYMMETRIC HYDROSILYLATION OF OLEFINS CATALYZED BY A CHIRAL FERROCENYLPHOSPHINE-PALLADIUM COMPLEX. ASYMMETRIC SYNTHESIS OF OPTICALLY ACTIVE ALCOHOLS AND BROMIDES FROM OLEFINS

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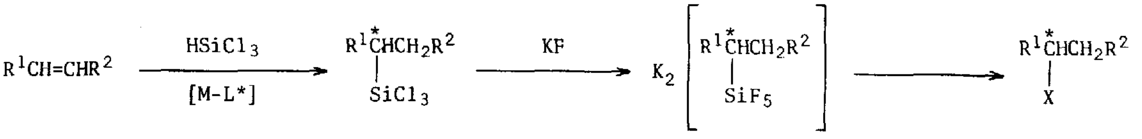
Summary: Optically active norbornyl and 1-phenylethyl alcohols and bromides were obtained, respectively, from norbornyl- and 1-phenylethylpentafluorosilicates which were prepared by asymmetric hydrosilylation of norbornene and styrene with trichlorosilane catalyzed by a chiral ferrocenylphosphine-palladium complex followed by treatment with potassium fluoride.

The most efficient and promising use of chiral reagents for asymmetric syntheses is their use as catalysts. Although several kinds of asymmetric syntheses[1] have been developed for preparing optically active alcohols or halides from prochiral olefins by use of stoichiometric amounts of chiral reagents, e.g., di-3-pinanylborane,[2] no catalytic procedure has been known for such reactions. Here we report a new approach to catalytic asymmetric synthesis of certain alcohols and bromides.

Our method, shown in Scheme I, consists of three steps: (1) Asymmetric hydrosilylation of a prochiral olefin (1) in the presence of a chiral phosphine-transition metal complex;[3] (2) conversion of the resulting alkylsilane (2) to the alkylpentafluorosilicate (3); and (3) stereospecific cleavage of the carbon-silicon bond in 3 to an optically active alcohol (4) or bromide (5).

Scheme I



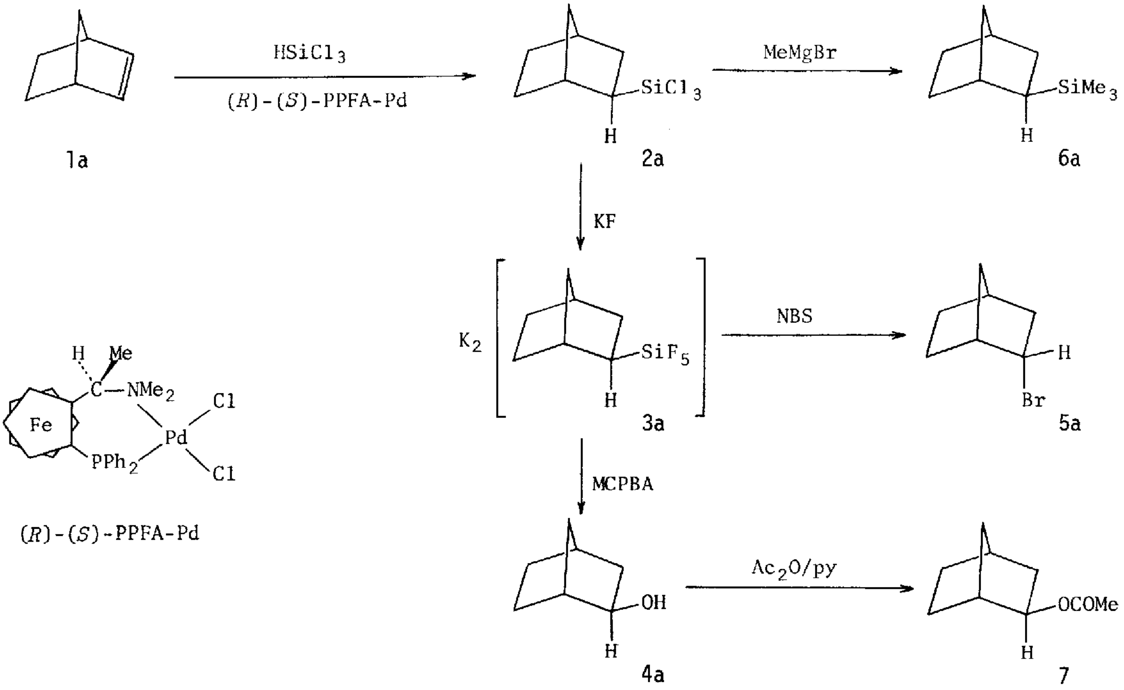
$$R^1CH{=}CHR^2 \xrightarrow[\text{[M-L*]}]{HSiCl_3} \underset{SiCl_3}{R^1\overset{*}{C}HCH_2R^2} \xrightarrow{KF} K_2\left[\underset{SiF_5}{R^1\overset{*}{C}HCH_2R^2}\right] \longrightarrow \underset{X}{R^1\overset{*}{C}HCH_2R^2}$$

1 2 3

4: X = OH
5: X = Br

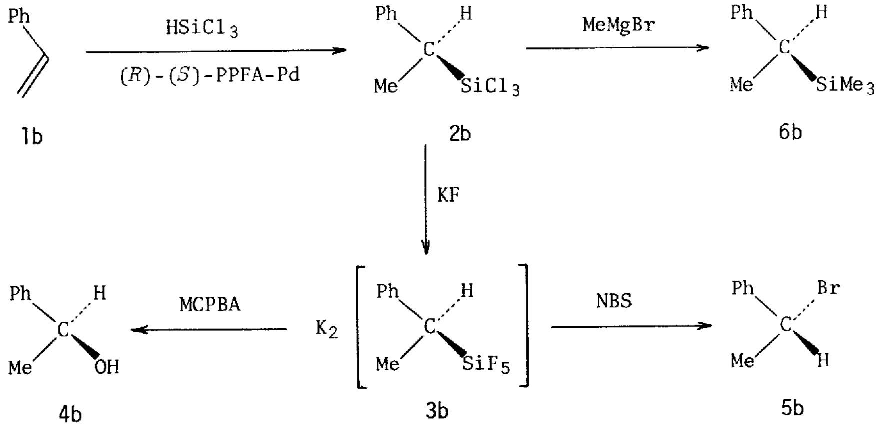
Palladium and platinum complexes of several optically active ferrocenylphosphine ligands[4] were examined with regard to the catalytic activity and enantioselectivity in the reaction of styrene or norbornene with trichlorosilane. Among the complexes, dichloro[(*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine]palladium(II) (abbreviated (*R*)-(*S*)-PPFA-Pd)[5] turned out to be the best catalyst giving rise to about 50% enantioselectivity.

A mixture of norbornene (1a) (120 mmol), trichlorosilane (140 mmol), and (*R*)-(*S*)-PPFA-Pd (0.012 mmol, 0.01 mol%) was heated in a degassed sealed glass tube at 70°C for 40 hr. Distillation of the reaction mixture gave *exo*-norbornyltrichlorosilane (2a) in 53% yield. Methylation of 2a with methylmagnesium bromide in THF gave *exo*-norbornyltrimethylsilane (6a) ($[\alpha]_D^{20}$ -18.3° (neat), d_4^{20} 0.8566). Trichlorosilane 2a was converted into *exo*-norbornylpentafluorosilicate (3a) by treatment with a large excess of potassium fluoride in water. Silicate 3a was allowed to react with NBS (1.1 equiv.) in methanol at 50°C for 4 hr.[6] This substitution reaction proceeded with inversion of configuration to afford *endo*-norbornyl bromide (5a) of >95% epimeric purity in 79% yield.[7] The specific rotation of bromide 5a was $[\alpha]_D^{25}$ -9.1° (*c* 2.64, $CHCl_3$), which corresponds to 53% optical purity of (1*R*, 2*S*, 4*S*) isomer.[8] Oxidative cleavage of the carbon-silicon bond in 3a with *m*-chloroperoxybenzoic acid (MCPBA) (1.2 equiv.)[9] in DMF gave, with retention of configuration at carbon,[10] *exo*-norbornanol (4a) in 47% yield. Due to the small maximum rotation



value of 4a,[11] it was found difficult to determine its correct optical purity by measurement of the optical rotation. Alcohol 4a was converted (acetic anhydride/pyridine) into *exo*-norbornyl acetate (7), $[\alpha]_D^{25}$ -4.4° (c 1.1, $CHCl_3$). The enantiomeric purity of acetate 7 was established by NMR to be 50 ± 3% using a chiral shift reagent $Eu(facam)_3$[12] which achieved separation of the acetate methyl signals.

Asymmetric synthesis starting with styrene (1b) was carried out in a similar manner. Hydrosilylation of 1b in the presence of (*R*)-(*S*)-PPFA-Pd (0.01 mol%) at 70°C gave 1-phenylethyltrichlorosilane (2b) in over 95% yield, which was then converted into its pentafluorosilicate (3b) with potassium fluoride in ethanol. 1-Phenylethyltrimethylsilane (6b), obtained by methylation of 2b, showed $[\alpha]_D^{20}$ -8.05° (neat); $[M]_D^{20}$ -14.3°.[13] Oxidation of pentafluorosilicate 3b with MCPBA (1.5 equiv.) in DMF gave (*S*)-1-phenylethanol (4b) in 65% yield, $[\alpha]_D^{21}$ -22.7° (neat), 52% ee.[14] Since the oxidation step occurs with retention of configuration at carbon, the asymmetric hydrosilylation product 2b must have *S* configuration of at least 52% optical purity. Treatment of silicate 3b with NBS (1.1 equiv.) in benzene led to the formation of (*R*)-1-phenylethyl bromide (5b) with lower optical purity (3-10% ee).[15] The loss of optical purity in the bromination may be accounted for by a partial racemization of 5b under the reaction conditions.



In summary, the present study shows a useful feature of the catalytic asymmetric hydrosilylation in that prochiral olefins can be converted, via pentafluorosilicates, into optically active functionalized compounds.

Acknowledgement We thank the Ministry of Education, Japan, for Grant-in-Aid for Scientific Research (No. 411109, 403521, 475666, 485214), Asahi Glass Foundation for the Contribution to Industrial Technology and Shin-etsu Chemical Co., Ltd. for partial financial support of this work.

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(5) This complex was prepared as follows: To a suspension of 259 mg (1.0 mmol) of dichlorobis(acetonitrile)palladium(II) in 10 ml of benzene was added with stirring a solution of 441 mg (1.0 mmol) of (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine ((*R*)-(*S*)-PPFA) in 10 ml of benzene. After 12 hr at room temperature, the reddish brown precipitate formed was collected by filtration, washed with benzene, and dried *in vacuo*. The precipitate was recrystallized from dichloromethane/hexane to give (*R*)-(*S*)-PPFA-Pd (550 mg, 90% yield) as red needles.

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(Received in Japan 15 February 1980)