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Simple Preparation of the Optically Active γ-Hydroxy Vinylstannanes Using Lipase-Catalyzed Hydrolysis

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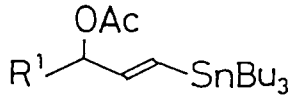
An efficient optical resolution of γ-hydroxy vinylstannanes was achieved by the lipase-catalyzed enantioselective hydrolysis of the corresponding racemic acetates using lipase PS(Pseudomonas sp.).

Among organotin compounds, optically active γ-hydroxy vinylstannanes have received significant attention as precursors to chiral biologically active compounds by organic chemists.[1] For example, the vinylstannane 2a(R^1=n-C_5H_{11}) has been used for the precursor of the ω-side chain to prostaglandin synthesis.[2] Therefore, a simple method for the preparation of optically active γ-hydroxy vinylstannanes would be very desirable.[3]

This report describes the first use of a lipase to affect the simple preparation of optically active γ-hydroxy vinylstannanes. The enantioselective hydrolysis of racemic acetate 1 with lipase PS (Pseudomonas sp.)[4] was accomplished in a buffered aqueous medium at pH 7.2 with acetone as the cosolvent. When the hydrolysis of 1a(R^1=n-C_5H_{11})[2] was allowed to proceed, the alcohol, 2a, was obtained in the optically pure state. The enantiomeric excess(%ee) of the stannane, 2, was determined by 188 MHz ^{19}F NMR analysis of the corresponding (S)-(+)-α-methoxy-α-(trifluoromethyl) phenylacetate (MTPA ester).[5] The results are summarized in Table 1, from which it is understandable that the hydrolysis so for studied resulted in satisfactory resolution. The ee of the remaining ester, 3, was also determined by hydrolysis to the corresponding alcohols with a 0.5 M KOH (in MeOH) solution and esterification with (S)-(+)-MTPA chloride. We could not obtain the hydrolyzed product from the cis isomer of 1a. It was also discovered that long-term reaction should be avoided, because both decomposition and racemiza-



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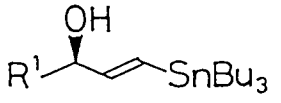

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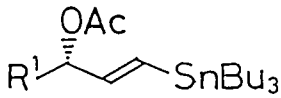

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a: R^1 = n-C_5H_{11}, b: R^1 = n-C_8H_{17}, c: R^1 = $PhCH_2CH_2$

Table 1. Kinetic resolution of esters 1 by the lipase hydrolysis

1	Time/h (Conv./%)	2 Y/%	2 %ee[a]	2 $[\alpha]^{23}_D$/°[b]	3 Y/%	3 %ee[a]	3 $[\alpha]^{23}_D$/°[b]	(E)[6]
a	24(50)	50	>98(R)	-3.1(c 0.62)	41	>98(S)	-22.5(c 1.12)	>460
b	69(50)	40	>98(R)	-1.1(c 1.40)	47	>98(S)	-37.3(c 1.10)	>460
c	48(10)	8.5	98(R)[c]	-9.2(c 0.35)	62	11(S)	-2.8(c 1.34)	>110

a) Determined by 188 MHz ^{19}F NMR analysis. b) In $CHCl_3$. c) The reaction stopped about this ratio even when using large amount of the lipase (200 w% based on the substrate) with 92 h stirring.

tion of the product were observed during the reaction. The absolute configuration of 2a was established by converting it into vinyl iodide.[7] According to the specific rotation of the resulting iodide, 1-iodo-3-hydroxy-1-octene($[\alpha]^{21}_D$ -8.2° (c 0.785, MeOH), lit.,[7] +9.9° (S)), the absolute configuration of 2a was determined as R. The absolute configuration assignment of 2b and 2c was presumed by the diastereomeric difference in the ^{19}F NMR analysis of the corresponding (+)-MTPA ester.

A typical procedure for the preparation of optically active γ-hydroxy vinylstannyl compounds is as follows. A solution of 1a(292 mg, 0.65 mmol) in 0.1 M phosphate buffer(pH 7.2, 3.2 mL) and acetone(0.3 mL) was incubated with lipase PS(146 mg) at RT. After 24 h, the mixture was extracted with Et_2O. Optically active 2a(130 mg, 0.32 mmol, 50%, >98%ee) and 3a(119 mg, 0.26 mmol, 41%, $[\alpha]^{25}_D$ -22.5° (c 1.12, $CHCl_3$), >98%ee) were obtained by the purification using SiO_2 flash column chromatography (hexane/ethyl acetate=50/1).

It should be emphasized here that we are now able to obtain chiral γ-hydroxy vinylstannanes very easily using cheap and commercially available lipase "reagent". Further experiments examining the scope and limitation of this reaction are in progress.

References

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