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OPTICALLY ACTIVE DIALLYLBIS(2-PHENYLBUTYL)TIN. SYNTHESIS AND APPLICATION TO ASYMMETRIC SYNTHESIS OF HOMOALLYL ALCOHOLS

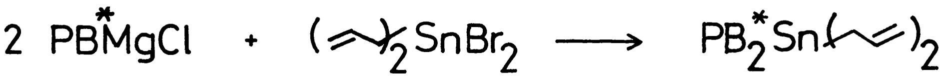
Junzo OTERA,* Yuzuru KAWASAKI, Hirofumi MIZUNO, and Yasumi SHIMIZU
Okayama University of Science, Ridai-cho, Okayama 700

Optically active diallylbis(2-phenylbutyl)tin (1) was successfully obtained by the Grignard method. Enantioselective reaction of 1 with various aldehydes afforded homoallyl alcohols in 20 - 80% optical yields, which are not affected by solvent effect, but are highly dependent on aldehydes.

Although a considerable number of optically active organotin compounds have been prepared,¹⁾ their synthetic application is rather limited.²⁾ This is quite surprising judging from rapidly expanding synthetic utilization of oragnotin compounds.

Enantioselective synthesis of homoallyl alcohols from aldehydes and optically active allylmetal compounds such as boron,³⁾ silicon,⁴⁾ and chromium⁵⁾ has received much attention recently. Since allylation of carbonyl compounds by allyltin compounds has been well established,⁶⁾ exploitation of optically active allyltin compounds would provide a new method for an asymmetric synthesis of homoallyl alcohols. Herein we wish to report synthesis of optically active diallylbis(2-phenylbutyl)tin (1) and its enantioselective reaction with aldehydes.

Compound 1 was synthesized as follows. To a THF solution (20 cm^3) of 2-phenylbutylmagnesium chloride (PB*MgCl) prepared from (+)-1-chloro-2-phenylbutane⁷⁾ (18.0 g, 107 mmol, 97% optically pure) was added diallyltin dibromide (12.8 g, 36 mmol) at



(1)

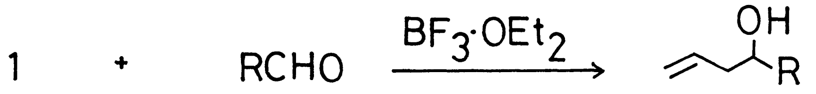
1

$[\alpha]_D^{23}$ -38.1°

(c 0.97, benzene)

room temperature. The reaction mixture was stirred at this temperature for 1 h and further heated under reflux for 30 min. Hexane (100 cm^3) was added to the mixture, which was, then, filtered. The filtrate was evaporated to leave an oil, distillation of which yielded 1[8)] (15.1 g, 90%, bp 210 °C/0.15 mm, Kugelrohr bath temperature).

Next, synthetic application of 1 to optically active homoallyl alcohols was investigated. It was found that reaction of 1 with aldehydes proceeds in the presence of $BF_3 \cdot OEt_2$[9)] at -78 °C (Eq. 2). The results are summarized in Table 1. The values of ee and absolute configurations were determined by comparison of $[\alpha]_D^{23}$ with the reported data. The notable features of this study are as follows. (1) n-Alkyl aldehydes give rise to higher ee than branched-alkyl aldehydes. (2) Little significant solvent effect was observed. (3) Employment of 2 equiv. of aldehydes except nonanal, in general, resulted in a slight decrease in ee. In these reactions little second equiv. of aldehydes was consumed, while more than one equiv. of nonanal was consumed. It has been disclosed that the reaction of allyltin compounds with aldehydes proceeds via a homoallyloxytin intermediate.[10)] Therefore, it is apparent that enantioselectvivty of the reaction of the monoalkoxide 3 with the second aldehydes is much decreased. (4) The absolute configuration of homoallyl alcohols obtained is accounted for by the addition of the allyl group on the re face of aldehydes. (5) Recovery of 1 from the reaction mixture is successfully achieved according to the following procedure in 60 - 70% overall yields.



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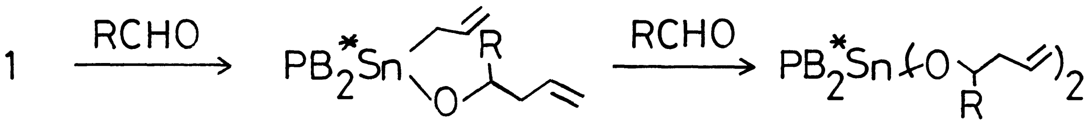
(2)



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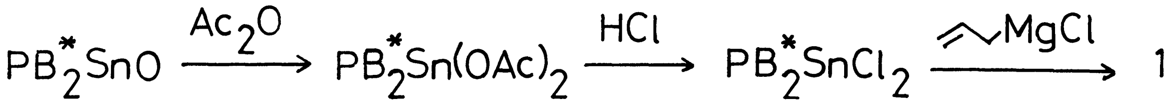

$$PB^*_2SnO \xrightarrow{Ac_2O} PB^*_2Sn(OAc)_2 \xrightarrow{HCl} PB^*_2SnCl_2 \xrightarrow{CH_2{=}CHCH_2MgCl} 1$$

Table 1. Enantioselective Reaction of 1 with Aldehydes (RCHO).

				Homoallyl alcohol			
R	Molar ratio of RCHO/Sn	Solvent	Reaction time/h	Yield[a] (%)	$[\alpha]_D^{23}$ (c)[b] (deg)	% ee	Config
C_2H_5	1.5	ether	6.5	63	-2.97(10.76)	49[c,d]	S
n-C_3H_7	1.0	ether	4.0	50	-6.16(10.22)	43[c,d]	S
	2.0	ether	11	54	-5.15(10.22)	36	S
i-C_3H_7	1.0	ether	4.0	46	+0.75(11.82)	20[c,d]	R
	2.0	ether	11	48	+0.60(11.82)	16	R
t-C_4H_9	1.0	ether	4.0	45	+2.39(10.88)	21[c,d]	R
n-C_8H_{17}	1.0	ether	6.0	79[f]	-8.45(2.50)[g]	79[e]	S
	1.0	CH_2Cl_2	3.0	84[f]	-8.79(2.50)[g]	82	S
	1.0	hexane	3.0	91[f]	-8.00(2.50)[g]	75	S
	2.0	ether	11	73[f]	-4.68(2.50)[g]	44	S
$C_6H_5CH=CH_2$	1.0	ether	4.0	96[f]	-8.35(10.08)[h]	56[c]	R
	1.0	CH_2Cl_2	4.0	94[f]	-7.76(10.08)[h]	52	R
C_6H_5	1.0	ether	3.0	91[f]	+8.10(7.38)	17[c,d]	R
	1.0	CH_2Cl_2	3.0	73[f]	+11.9(7.38)	22	R
	2.0	ether	11	60[f]	+11.0(7.38)	23	R

[a] Based on aldehydes employed. Isolated by distillation unless otherwise noted.

[b] In benzene unless otherwise noted.

[c] Ref. 3a.

[d] Ref. 3c.

[e] Ref. 11.

[f] Isolated by column chromatography.

[g] In CCl_4.

[h] In ether.

Following procedure is representative. To an ether solution (20 cm^3) of 1 (5.05 g, 10.8 mmol) and 1.06 cm^3 of 47% ether solution of $BF_3 \cdot OEt_2$ (5.4 mmol) was added propanal (0.94 g, 16.2 mmol) at -78 °C. The reaction mixture was stirred at this temperature for 6.5 h, and shaken with 0.5 M NaOH solution (30 cm^3). The organic layer was separated, washed with 1 M HCl solution and water, and dried ($MgSO_4$). After distillation of ether, the residue was carefully distilled to give 5-hexen-3-ol (1.02 g, 63%). The residue of distillation (4.5 g) was dissolved in acetic anhydride (10 cm^3). The mixture was heated under reflux for 1 h followed by evaporation of acetic anhydride. The resulting oil was stirred in 1:2 methanol-3 M HCl for overnight. Extraction of this mixture with CH_2Cl_2, and evaporation of the organic layer yielded $PB_2^*SnCl_2$. The chloride thus obtained was treated with the allyl Grignard reagent (2 equiv.) in ether at -10 °C followed by heating under reflux for 1 h. Workup as already described and distillation afforded 1 (3.28 g, 65%).

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