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CHIRAL SILICON COMPOUNDS. ASYMMETRIC REDUCTION OF KETONES.

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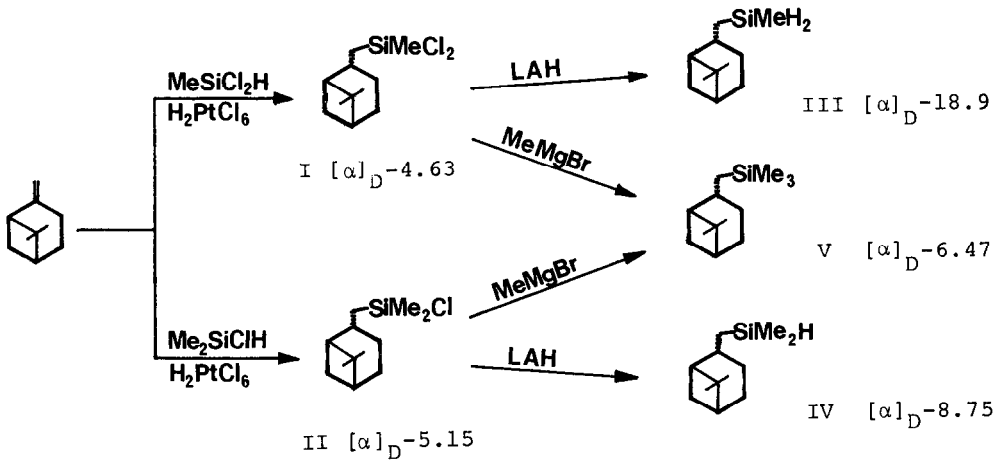
Summary: *A number of optically active organosilicon compounds are prepared by the hydrosilylation of (-)-β-pinene. The reduction of several pro-chiral ketones with the chiral silane III was investigated.*

The increasing importance of organosilicon reagents in organic synthesis suggests that chiral organosilicon compounds may play a useful role in inducing asymmetry in many of the reaction products. While many optically active organosilicon compounds with chirality at silicon are known and have been studied extensively in mechanistic investigations[1], it seemed to us that their use in organic synthesis may be somewhat limited. This is primarily due to the unavoidably tedious optical resolution necessary in securing these compounds. Another consideration is the fact that silicon compounds undergo inversion or retention or racemisation at silicon in many of their reactions[1,2]. Recovery of the valuable optically active organosilicon compounds with its optical purity intact cannot be guaranteed.

We have thus concentrated our attention on using chiral organosilicon compounds with its chirality located at a site remote from silicon. It is hoped that such compounds can be prepared in synthetically useful quantities from readily available optically active natural products to avoid the resolution step This communication describes our work in this area.

Hydrosilylation of (-)-β-pinene with either methyldichlorosilane[3] or dimethylchlorosilane gave the corresponding optically active organosilicon compounds I and II in good yields. Lithium aluminum hydride reduction gave silanes III and IV respectively again in good yield. The two chlorosilanes I and II[4] are shown to be of the same stereochemistry by conversion to the same trimethylsilane V on reaction with methylmagnesium bromide (scheme 1). The stereochemistry of the silanes II, IV and V (and consequently I and II) can be deduced by comparing the ^{1}H nmr spectra with the four pinanes VI to IX[5]

(Table I). From the chemical shifts of the anti- and the syn-methyl protons, it is clear that all three silanes have the silylmethyl moiety trans- to the gem-dimethyl bridge. Since (-)-β-pinene has the 1S, 5S configuration[5], the silanes I to V have the 1S, 2S, 5S configuration.

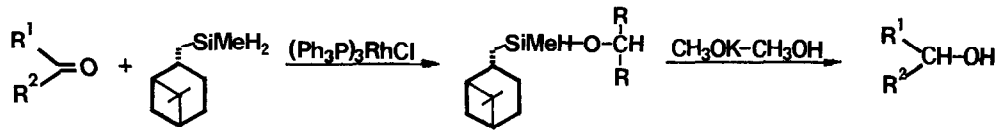


Scheme 1

Table 1: ^{1}H nmr of pinane derivative III to IX; Syn- and Anti-Methyl protons only in δ ppm.

Structure	Syn-Me	Anti-Me	Structure	Syn-Me	Anti-Me
SiMe3 V	0.82	1.19	CH3 VI	1.01	1.20
SiMe2H IV	0.83	1.19	CH3 VII	0.82	1.20
SiMeH2 III	0.82	1.19	CH2OH VIII	0.97	1.18
			CH2OH IX	0.82	1.20

Asymmetric Reduction of Ketones. Prochiral ketones have previously been reduced by silanes to give optically active alcohols by using chiral catalysts[6]. We have examined the reduction of prochiral ketones with silane III using the Wilkinson catalyst $(Ph_3P)_3RhCl$ according to scheme 2. From results in Table II, it is clear that asymmetric induction can be achieved with modest success. The enantiomeric excess of the product alcohols increased somewhat when the reduction was carried out at a lower temperature, but with a sacrifice in yield. An interesting feature is the observation that aryl ketones gave alcohols of opposite chirality from that of alkyl ketones.



Scheme 2

Other application of chiral organosilicon compounds in organic synthesis will be reported in due course.

References

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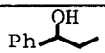
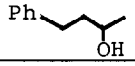
Table 2: Reduction of Prochiral Ketones with III[†]

Ketone	Reaction Condition	Alcohols	% Yield	$[\alpha]_D^{20}$	e.e. %	Configuration
2-octanone	Rt, 4 hrs	2-octanol	96	-2.23	22.5	R
	0°, 5 hrs	"	68	-2.55	25.7	R
2-Hexanone	Rt, 4 hrs	2-Hexanol	94	-2.50	20.8	R
Acetophenone	40°, 3 hrs	α-phenylethanol	83	-5.83°	11.1	S
	0°, 2 hrs		65	-8.50°	16.2	S
	40°, 5 hr		79	-3.98	14.2	S
	40°, 3 hrs		85	-1.71	8.8	R

[†]Typical Experimental Condition

To a mixture of 0.7 g (5.5 mmol) of octanone-2 and 1.1 g (6 mmol) silane III, 15 mg of $(PPh_3)RhCl(3.5x10^{-3}M/M)$ was added. The hydrosilation was completed within 4 hr at room temperature. n-Hexane was added to the mixture, which was filtered and the solvent was evaporated. The residue was hydrolysed in the condition of CH_3OK-CH_3OH to give octanol-2. The product was purified by circular TLC. The pure alcohol was identified by GC, IR and ^1H nmr. The yield of reduction was determined by GC with internal standards.

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