A Novel Route to Optically Active Organosilicon Compounds

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Summary Monofunctional chiral organosilanes are obtained, with high stereospecificity, by coupling an asymmetric bifunctional organosilicon compound with organometallic reagents.

THE stereochemistry of nucleophilic substitutions at asymmetric silicon has proved of great significance in the study of the mechanism of these reactions. However, until recently very few asymmetric organosilicon compounds were available.[1]

We have previously used optically active bifunctional silicon compounds to obtain the corresponding monofunctional organosilanes, by stereospecific substitution of one leaving-group with organometallic reagents. Our first method, using a chiral dialkoxysilane, has afforded good results, but its applicability was limited by steric effects.[2,3]

However, we have described[4] the synthesis of a bifunctionally substituted organosilicon compound (−),(−)-menthoxy-α-naphthylphenylsilane (I), $[\alpha]^{25}_{D}$ − 66·3° in pentane. It is obtained by asymmetric induction on menthanolysis of ClαNpPhSiH. Reaction of (I) with methylmagnesium bromide in diethyl ether is highly stereospecific.

TABLE

Nucleophilic substitutions at menthyloxy αNpPhSi*H

Reagent			Product RαNpPhSiH		
RMgX	RLi	Solvent	$[\alpha]_D$ in pentane		Stereochemistry
Me		Et_2O	−32·9		R.N.
	Me	Et_2O		−29·0	R.N.
Et		Et_2O	−24·0		R.N.
	Et	Et_2O		−23·9	R.N.
Pr^n		Et_2O	−9·1		R.N.
Bu^n		THF	−14·1		R.N.
	Bu^n	Et_2O		−14·0	R.N.
Pr^i		THF	−13·2		R.N.
Bu^i		THF	−18·1		R.N.
	neopent	Pentane	−15·4		R.N.
	Bu^t	Pentane	−41·5		R.N.
vinyl		THF	−15·6		R.N.
crotyl		Et_2O	−14·4		R.N.
allyl		Et_2O	+9·2		I.N.
benzyl		Et_2O	−5·9		I.N.

We now report the preparation of a series of chiral organosilanes RαNpPhSiH, using (I) as substrate (Table).

Substitutions were carried out with good yields, under mild conditions. To our knowledge, this method affords the best route to optically active organosilicon compounds. In particular, we have obtained the new silanes (−)-RαNpPhSiH, with R = t-butyl or neopentyl.

By analogy with previously reported results,[5] aliphatic Grignard reagents and alkyl-lithium compounds react with retention of configuration. On catalytic hydrogenation, the (−)-crotyl-α-naphthylphenylsilane afforded the (−)-n-butyl-α-naphthylphenylsilane; hence, the reaction of (I) with crotylmagnesium bromide proceeds with retention of configuration. In a previous paper,[6] we reported that the (+)-allyl-α-naphthylphenylsilane and the (−)-n-propyl-α-naphthylphenylsilane had the opposite configuration; hence, the allylmagnesium bromide in diethyl ether substitutes the alkoxy-group with inversion of configuration. Confirmation of these conclusions was obtained by studying the o.r.d. curves of silanes in the range 589—365 nm. Indeed, the compounds (−)-RαNpPhSiH with R = crotyl, n-butyl, and n-propyl, exhibit o.r.d. curves with opposite sign to that of the (+)-allyl-α-naphthylphenylsilane in the same solvent. The (−)-benzyl-α-naphthylphenylsilane has a positive o.r.d. curve, analogous to that of the (+)-allylic compound. We can reasonably conclude that the benzylmagnesium chloride reacts with inversion of configuration in diethyl ether. These results are in accord with previous work.[2,5]

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[1] L. H. Sommer "Stereochemistry, Mechanism and Silicon", New York, McGraw-Hill 1965; see also: L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271; L. H. Sommer, K. W. Michael, and W. D. Korte, *ibid.*, 1967, **89**, 868; L. H. Sommer and K. T. Rosborough, *ibid.*, 1969, **91**, 7067 and refs. therein; R. Corriu and J. Masse, *Chem. Comm.*, 1968, 1373; R. Corriu and G. Royo, *J. Organometallic Chem.*, 1968, **14**, 291.

[2] R. Corriu and G. Lanneau, *Compt. rend.*, 1968, **267**, *C*, 782.

[3] R. Corriu and G. Lanneau, *Tetrahedron Letters*, 1970, 162.

[4] R. J. P. Corriu and G. F. Lanneau, *Tetrahedron Letters*, 1971, 2771.

[5] R. Corriu and J. Masse, *J. Organometallic Chem.*, in the press; R. Corriu and G. Royo, *Tetrahedron*, 1971, **27**, 4289.

[6] R. Corriu, G. Lanneau, and G. Royo, *J. Organometallic Chem.*, in the press.