Asymmetric Induction at Silicon from Prochiral Silaethylenes

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Summary Prochiral silaethylene intermediates react with chiral alcohols to give unequal amounts of diastereomeric pairs of alkoxysilanes (up to 30% enantiomeric excess); this is the first example of asymmetric induction observed at a silicon centre involving a trigonal silicon species.

IN organic chemistry a trigonal carbon centre is one of the most important of prochiral sites allowing asymmetric induction.[1] For a long time silicon analogues of unsaturated compounds were believed to be nonexistent.[2] However, in the last few years evidence for the transient existence of these π-bonded silicon molecules has been found through kinetic and spectral studies and also by trapping reactions.[3] This communication reports the first examples of asymmetric induction in the addition of chiral alcohols to prochiral silaethylenes.†

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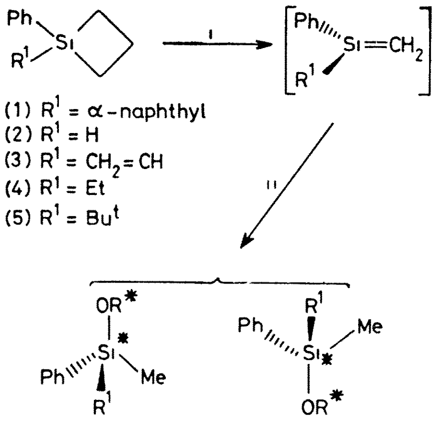
† For other accounts of this work see G. Bertrand, Thesis, Université Paul-Sabatier, Toulouse, France, 1979, no. 890; G. Bertrand, J. Dubac, and P. Mazerolles, Réunion de la Société Chimique de France, Toulouse, June 1979.

TABLE

Silacyclobutane[a]	Alcohol R*OH	Product	δ SiMe (^{1}H)[b]	δ SiMe (^{13}C)[b]	δ SiOC(^{13}C)[b]	r[c]
(**4**)	(−)-Borneol	(**12**)[d]	0.34, Δδ 0.0	−3.37, −3.45	77.87, 77.93	50:50
,,	(−)-Menthol	(**13**)[d]	0.38, Δδ 3.2			50:50
,,	(−)-Isoborneol	(**14**)	0.32, Δδ 1.0[e]	−3.41, −3.51[f]	79.95, 80.05[f]	62:38
(**5**)	(−)-Borneol	(**15**)	0.37, Δδ 0.0	−4.25, −4.75	77.60, 77.78	50:50
,,	(−)-Menthol	(**16**)	0.38, Δδ 4.5[f]			53:47
,,	(−)-Isoborneol	(**17**)	0.35, Δδ 3.0[e]	−5.80, −6.23[f]	79.90, 80.14[e]	65:35

[a] The ratio of the diastereoisomers obtained from silacyclobutanes (**2**) and (**3**) is 50:50 and is independent of the alcohol. [b] δ values (250 MHz) for products in p.p.m. from Me_4Si; solvent C_6D_6 + $CDCl_3$. [c] The ratio of the diastereoisomers of PhR^{1}MeSi*OR*. [d] These compounds have been recently described (W. J. Richter, *J. Organomet. Chem.*, 1979, **169**, 9). [e] The more intense signal is upfield. [f] The more intense signal is downfield.

Short-lived prochiral silaethylenes were generated by photolysis (λ 2537 Å) of silacyclobutanes (**1**—**5**) bearing two different substituents on the heteroatom, in the presence of a stoicheiometric amount of a chiral alcohol (Scheme 1).



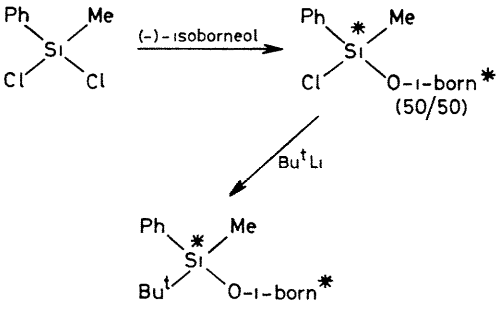
(6)-(17)

SCHEME 1 i, hν (2537 Å), benzene; ii R*OH.

As the absolute configuration and maximum specific rotation of α-naphthylphenylmethyl-(−)-menthoxysilane is known,[4] (**1**) was photolysed in the presence of (−)-menthol. Unfortunately, under the experimental conditions used no reaction occurred, probably owing to the absorption of the α-naphthyl group.

All the other reactions studied gave almost quantitative yields of alkoxysilanes. The relative yields of the two diastereoisomers were determined by ^{1}H and/or ^{13}C n.m.r. spectroscopy and the results obtained for (**4**) and (**5**) are given in the Table.

In order to prove that the ratio of the diastereoisomers (**17**) (65:35) was not the thermodynamic ratio, (**17**) was synthesized in a different way (Scheme 2). The ratio of the diastereoisomers (50:50) remained constant when (**17**) prepared by the method in Scheme 2 was irradiated at 2537 Å.



(17) (50/50)

SCHEME 2

Thus, the results obtained for compounds (**14**), (**16**), and (**17**) are consistent with an asymmetric induction at a trigonal silicon atom. Our results are in good agreement with recent theoretical[5] and spectral[6] data which suggest that silaethylene is planar in its $^1A_1$ singlet ground state.

However, considerable variation in optical yield with the chiral alcohols used and with the nature of the substituents attached to the silicon atom should be noted. Only very sterically hindered alcohols (*e.g.*, isoborneol) give good asymmetric induction. Moreover, it seems that at least one relatively bulky substituent on the silicon atom is necessary. This phenomenon must be due to the high reactivity of silicon π-bonded intermediates.

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