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Asymmetric Synthesis of Silicon Compounds Using Chiral 5,6-Dimethoxy-1,3,2-dioxasilacycloheptane Derivatives

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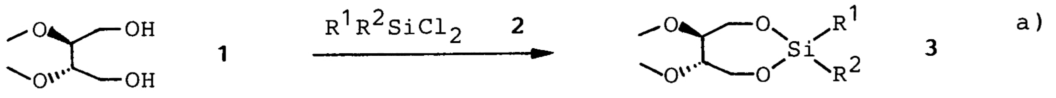
Asymmetric synthesis of silicon compounds was achieved in high optical yield by the substitution reaction of some chiral 5,6-dimethoxy-1,3,2-dioxasilacycloheptane derivatives with organometallic reagents followed by lithium aluminium hydride reduction. These starting dioxasilacycloheptanes were obtained by the coupling reaction of (S,S)-2,3-dimethoxybutanediol and corresponding prochiral dialkyldichlorosilanes.

The asymmetric synthesis using the compounds of C_2 symmetry have been widely studied in carbon chemistry,$^{1)}$ however little effort has been devoted to such an asymmetric synthesis in silicon chemistry. In this regard, we have recently reported that several optically active silicon compounds had been obtained by the stepwise substitution reaction of chiral (S,S)-N,N,N',N'-tetramethyl-4,5-bis(dimethylamino)-2-methyl-2-phenyl-1,3,2-dioxasilolane constituting the structure of C_2 symmetry in a portion of the five-membered ring.$^{2)}$ But such silolane derivatives are known to be unstable and dimerize easily.$^{3)}$ So we tried to synthesize the optically active silicon compound from chiral 5,6-dimethoxy-1,3,2-dioxasilacycloheptane derivatives **3** (Table 1), since it has been pointed out recently that the monomer and dimer of 1,3,2-dioxasilacycloheptane derivatives have no tendency to equilibrate on standing.$^{4)}$

3 was prepared in 25-67% yield by the coupling reaction of (S,S)-2,3-dimethoxybutanediol **1** ($[\alpha]_D$ 5.05° (c 22.8, EtOH)) which was derived from L-tartaric acid according to the literature methods$^{5)}$ and prochiral dialkyldichlorosilane **2** in diethyl ether with blowing enough anhydrous ammonia at room temperature for 3 h. All of **3** had S,S-configuration and gave satisfactory ^{1}H-NMR and IR spectra summarized in Table 1. A typical experimental procedure is described for the asymmetric synthesis of ethylmethylphenylsilane by the stepwise substitution reactions of **3A** with ethylmagnesium bromide (EtMgBr) and lithium aluminium hydride ($LiAlH_4$) (Table 2). To a solution of **3A** (10 mmol) in dry ether (80 ml) was added dropwise an ether solution of EtMgBr (about 12 mmol) at 0 °C with stirring. After 30 min, $LiAlH_4$ (about 0.5 g) was added to the reaction solution, followed by stirring at room temperature for 1 h. The resulting mixture was poured into dil aqueous HCl containing crushed ice and the product was extracted several times with diethyl ether. The combined ether layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The distillation of the residue gave a 75% yield of (R)-**4** with

Table 1. Synthesis of (S,S)-5,6-Dimethoxy-1,3,2-dioxasilacycloheptane Derivatives



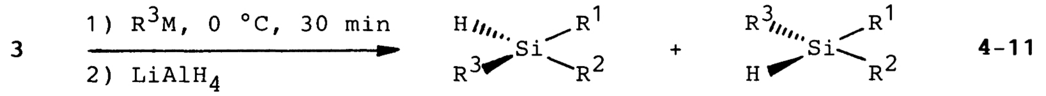
	2		3				
	R^1	R^2	Yield/%b)	Bp/°C(Torr)	$[\alpha]_D$/deg.c)	^{1}H NMR(δ ppm)($CDCl_3$)d)	IR(ν/cm^{-1})e)
A	Me	Ph	67	133 (0.6)	46.1 (c 11.63)	0.40(s,3H)(SiMe)	2830(OMe)
						3.48(s,3H)(OMe)	1430(Ph)
						3.49(s,3H)(OMe)	1260(SiMe)
						7.35-7.71(m,5H)(Ph)	
B	Me	1-Np	57	154 (0.4)	38.2 (c 9.35)	0.56(s,3H)(SiMe)	2830(OMe)
						3.49(s,3H)(OMe)	1260(SiMe)
						3.54(s,3H)(OMe)	780(Np)
						7.49-8.39(m,7H)(Np)	
C	Me	Allyl	27	100 (6)	61.8 (c 11.45)	0.13(s,3H)(SiMe)	2830(OMe)
						1.61(d,J=1.2,2H)($-CH_2-$)	1630(Allyl)
						3.44(s,6H)(OMe)	1260(SiMe)
						4.84-5.02(m,2H)($=CH_2$)	
						5.60-7.25(m,H)(-CH=)	
D	Et	Ph	25	128 (0.2)	48.3 (c 12.05)	0.87-1.07(Et)	2830(OMe)
						3.49(s,6H)(OMe)	1460(Et)
						7.36-7.68(m,5H)(Ph)	1430(Ph)
E	Ph	1-Np	53	220 (0.2)	79.5 (c 12.51)	3.51(s,3H)(OMe)	2830(OMe)
						3.57(s,3H)(OMe)	1430(Ph)
						7.32-8.35(m,12H)(Ph,Np)	780(Np)

a) Molar Ratio **1** : **2** = 1 : 1.2 b) Based on **1**, Isolated yield. c) Solvent, PhH. d) Selected signals. e) Selected absorptions. Measured as neat liquid.

a specific optical rotation of -6.01° (c 6.05, CCl_4) (Entry 1). Some other results are listed in Table 2. Clearly, the Grignard reagents as nucleophile were superior to the alkyllithium reagents (Entries 1,3, and 6-9). The alkylzinc or the alkylaluminium reagents could not react even at elevated temperature (30 °C) (Entries 4 and 5). The optical yield appeared to increase by lowering the reaction temperature (0 to -78 °C) (Entries 1 and 2). In this connection, the values of the specific optical rotation of **4** obtained were extremely higher than the reported data (2.53°).6)

The stereochemical results are summarized as follows and briefly shown in Scheme 1. If the bulkinesses of the substituents R^1, R^2 are assumed to be R^1 < R^2, all the absolute configuration of the products **4**, **5**, and **11**,6-8) can be depicted as **[A]**. The smaller R^1 preferentially occupies an axial position in the silacycloheptane ring of **3**. In the asymmetric alkylation reaction on such a silicon, the absolute configuration of the products depends on the faceselectivity of the nucleophile, regardless of its stereospecificity (inversion or retention). Furthermore considering the fact that the $LiAlH_4$ reduction of the Si-O bonds nearly proceeds with retention,[9] the enantiomer excess of the products exactly reflects the faceselectivity of the nucleophilic attack, and which is taking place from the more accessible face of the anion, that is *a* face. Although the precise reasons for the *a*-faceselectivity of the nucleophile in these reactions can not be delineated at the moment, a simple interpretation is obtained if one imagines the quasi five-membered ring intermediate **3'** illustrated in the center of Scheme 1. The formation of the chiral intermediate **3'** seems to be easy, as the difference of the bulkinesses of R^1, R^2 is large. Thus, the reaction of PhMgBr with **3B** (R^1= Me, R^2= 1-Np) gives the product **5** with high optical purity, 70.3% ee (Entry 13), but

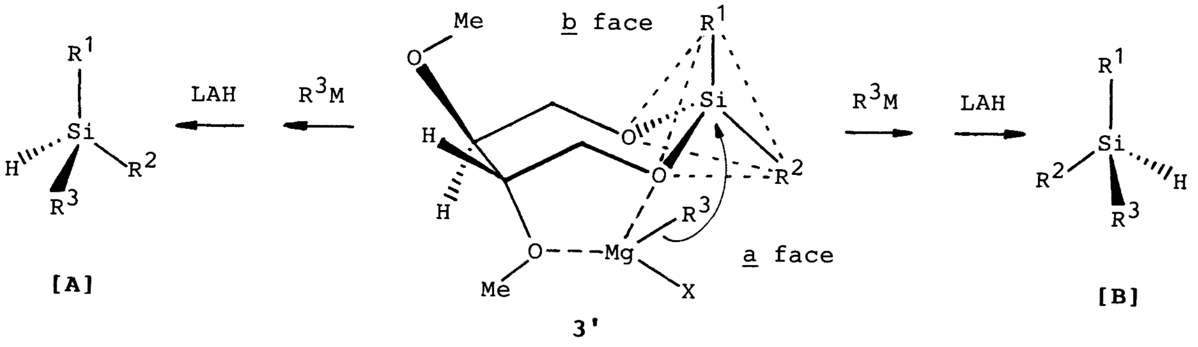
Table 2. Asymmetric Synthesis of Silicon Compounds by the Stepwise Substitution of **3** with R^3M and $LiAlH_4$



a)

Entry	3	R^3M $^{b)}$		Product			
			Yield/%$^{c)}$	$[\alpha]_D$/deg.	ee(%)	Abs.Config.	
1	**A**	EtMgBr	75	-6.01 (c 6.05, CCl_4)	-$^{f)}$	R	**4**
2	"	" (-78 °C)	72$^{d)}$	-6.97 (c 5.65, ")	-$^{f)}$	R	**4**
3	"	EtLi	90$^{d)}$	-0.52 (c 5.69, ")	-$^{f)}$	R	**4**
4	"	Et_2Zn(0-30 °C)	-$^{e)}$	-	-	-	
5	"	Et_3Al(0-30 °C)	-$^{e)}$	-	-	-	
6	"	1-NpMgBr	34$^{d)}$	-2.05 (c 8.07, c-hexane)	6.0$^{g)}$	S	**5**
7	"	1-NpLi	10	-0.95 (c 5.03, ")	2.8$^{g)}$	S	**5**
8	"	BuMgBr	84$^{d)}$	-5.55 (c10.02, CCl_4)	-$^{h)}$	-	**6**
9	"	BuLi	87$^{d)}$	-0.58 (c 9.99, ")	-$^{h)}$	-	**6**
10	"	PrMgBr	87$^{d)}$	-5.47 (c10.57, ")	-$^{h)}$	-	**7**
11	"	AllyMgCl	55$^{d)}$	-6.58 (c10.27, pentane)	-$^{h)}$	-	**8**
12	"	$PhCH_2MgCl$	70$^{d)}$	+9.55 (c 6.97, CCl_4)	-$^{h)}$	-	**9**
13	**B**	PhMgBr	65	+24.11 (c10.01, c-hexane)	70.3$^{g)}$	R	**5**
14	"	EtMgBr	83	+1.49 (c10.05, PhH)	-$^{h)}$	-	**10**
15	**C**	PhMgBr	86	-0.45 (c 3.98, pentane)	-$^{h)}$	-	**8**
16	**D**	MeMgI	50	+2.74 (c11.80, CCl_4)	-$^{f)}$	S	**4**
17	**E**	"	45	-6.71 (c14.59, c-hexane)	19.6$^{g)}$	S	**5**
18	"	EtMgBr	12	-1.86 (c 3.17, ")	7.6$^{i)}$	S	**11**

a) Molar Ratio **3** : R^3M = 1 : 1.5-2.5 in Et_2O. b) Unless otherwise noted, all the reactions were carried out at 0 °C to rt. c) Based on **3**, Isolated yield. d) Based on **3**, GC yield. e) Not reacted. f) Reported (S)-**4**, $[\alpha]_D$ +2.53° (c 10.1,CCl_4).[6] g) Based on (R)-MePh(1-Np)SiH, (R)-**5**, $[\alpha]_D$ +34.3° (c 10.9, c-hexane).[7] h) Not reported. i) Based on (R)-EtPh(1-Np)SiH, (R)-**11**, $[\alpha]_D$ +24.6° (CCl_4).[8]



Scheme 1.

the reaction of MeMgI with **3E** (R^1= Ph, R^2= 1-Np) gives one with not so high optical purity, 19.6% ee (Entry 17). Furthermore the reaction of 1-NpMgBr with **3A** (R^1= Me, R^2= Ph) gives the product **5** with lower optical purity than that of MeMgI with **3E** does, even though the difference of the bulkinesses of R^1, R^2 in **3A** is larger than that in **3E** (Entries 6 and 17). This result suggests that a bulkier nucleophile is hard to form such the quasi ring intermediate as **3'**.

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