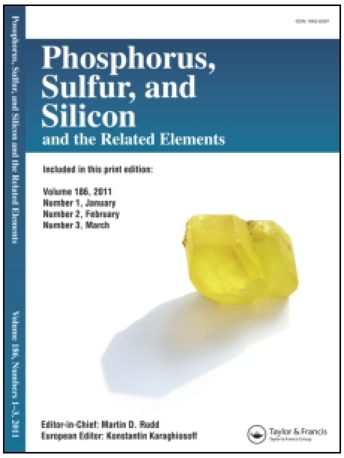

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SYNTHESIS OF OPTICALLY ACTIVE PENTACOORDINATE SILICATES AND CORRESPONDING ASYMMETRIC ALLYLATION OF ALDEHYDES

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SYNTHESIS OF OPTICALLY ACTIVE PENTACOORDINATE SILICATES AND CORRESPONDING ASYMMETRIC ALLYLATION OF ALDEHYDES

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The optically active silicates **3a-c** and disilicates **5a-b** were synthesized. The asymmetric allylation reactions of aldehydes with optically active pentacoordinate allylsilicates were carried out to give optically active homoallylic alcohols **7a-b** with 7–25% ee.

Keywords: chiral pentacoordinate silicate; asymmetric allylation; aldehyde; homoallylic alcohol

Recently, the synthesis, structure and reactivity of pentacoordinate silicates have attracted considerable attention because of their special characteristics and significant Lewis acidity[1]. On the other hand, the allylation of carbonyl compounds with allylsilanes under Lewis acids conditions has been extensively used in organic synthesis for the formation of C-C bonds (Scheme 1).[2] The possibility of using this reaction for asymmetric synthesis of optically active homoallylic alcohols, which can be converted to many important building blocks for optically active natural product synthesis, has been a focus in organic synthesis.[3] Based on their inherent Lewis acidity, pentacoordinate allylsilicates have been applied to the allylation of carbonyl compounds in the absence of a catalyst.[4] However, so far optically active pentacoordinate silicates have not been synthesized, except for a single zwitterionic optically active pentacoordinate disilicate containing two pentacoordinate silicon atoms.[5] Although some examples of asymmetric allylations of aldehydes *via* chiral pentacoordinate interme-

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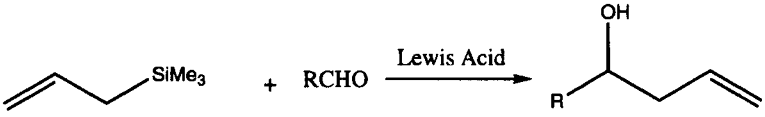
diates generated in situ by a Lewis base were reported,[6] the use of isolated chiral pentacoordinate allylsilicates in asymmetric allylation without catalyst has not been investigated. Herein, we wish to report the synthesis of optically active pentacoordinate silicates and their use in the asymmetric allylation of aldehydes in the absence of catalysts.

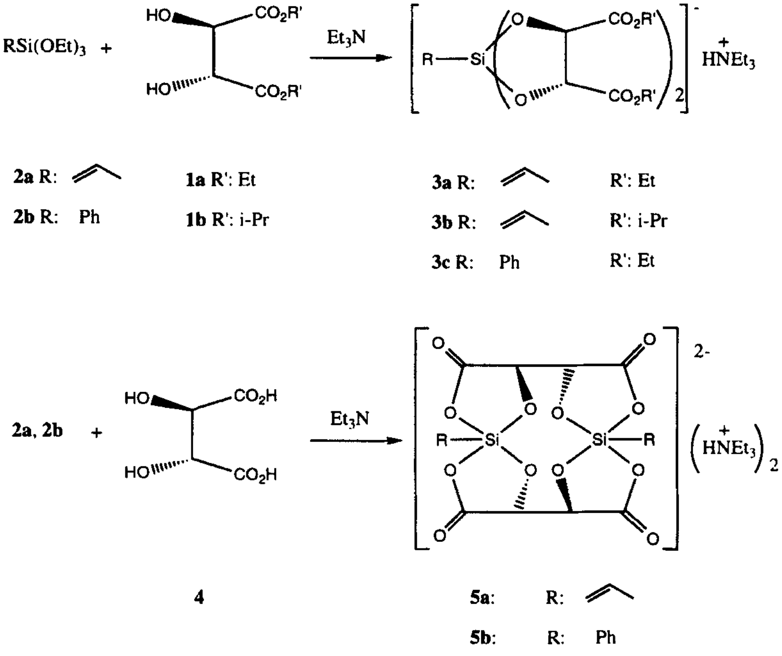


SCHEME 1

According to a known approach,[7] starting from (+)-tartrates **(1a-b)**, allyltriethoxysilane **(2a)** or phenyltriethoxysilane **(2b)**, in triethylamine as the solvent, the optically active pentacoordinate silicates, (+)-triethylammonium bis[(R,R)-tartratato(2-)]silicates **[(+)-3a-c]**, were prepared in yields of 55–68% (Scheme 2). The preparation of **3b** needed stronger reaction conditions (refluxing for 12 h), while only 1 h for **3a** and **3c.** The ^{29}Si NMR signals at –89.80, –89.22 and –96.24 ppm are attributed to the formation of pentacoordinate silicate **3a-c,** respectively. The ^{1}H NMR spectrum of **3a** in $CDCl_3$ shows an overlap of two methyl groups (1.0–1.4 ppm) and a broad peak for the methylene groups (3.2 ppm) due to the triethylammonium cation. However, the ^{1}H NMR signals of **3a** are changed noticeably by the addition of D_2O to the $CDCl_3$ solution of the sample. There is a triplet for the methyl group at 1.02 ppm and a quartet of the methylene group at 2.53 ppm due to free triethylamine which comes from the dissociation of pentacoordinate silicate in aqueous media. The negative-ion FAB-MS of **3a-c** displayed peaks at 477, 533 and 569, respectively, which were assigned to pentacoordinate silicate anion species $(M\text{-}HNEt_3)^-$.

However, by starting from equimolar amounts of (+)-tartaric acid **(4), 2a** or **2b** and triethylamine, the optically active diionic disilicates with two pentacoordinate silicon atoms, **[(+)-5a** or **5b]** were synthesized in yields of 92 and 94%,[8] respectively (Scheme 2). This result contrasts that from a 2:1 mixture of **4** and **2a** in triethylamine stirred at 100 °C which gives a mono-pentacoordinate silicate intermediate **(6)** formed in situ as suggested by Hosomi.[7] The ^{29}Si NMR signals of **5a** and **5b** are at –90.6 and –100.7 ppm, respectively, which support the formation of pentacoordinate silicate.

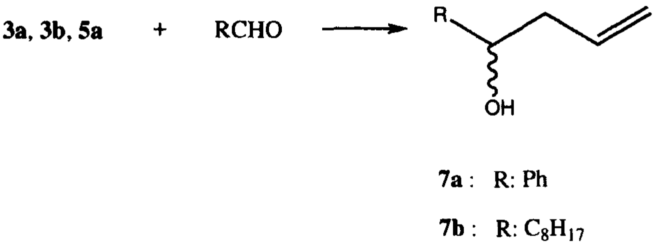
The negative-ion FAB-MS of **5a** and **5b** each shows two peaks 532 and 431 for **5a** and 604 and 503 for **5b.** This can be understood from the dianionic nature of anion. Thus the first peak corresponds to $(M\text{-}HNEt_3)^-$ and the second corresponds to $[(M\text{-}HNEt_3)\text{-}Et_3N]$. The structures of **5a** and **5b** shown on Scheme 2 are also identified by ^1H and ^{13}C NMR spectra. The X-ray analysis of a single crystal of **5b** has been reported in detail.[9] The structure of **5b** is composed of two connected triethylammonium bis[(R,R)-tartrato]diphenylsilicates. In the crystal structure of **5b,** the two Si atoms are pentacoordinate, and the geometry of each Si atom is distorted from a trigonal bipyramid towards a square pyramid along the Berry pesudorotational coordinate by ca 9.8 and 8.9%.



SCHEME 2

By using optically active pentacoordinate silicates **3a-b** and **5a,** the asymmetric allylation reactions of either aromatic or aliphatic aldehydes were carried out without any catalyst to give optically active homoallylic alcohols **7a, b** with 7–25% ee (Scheme 3, Table 1).[10] It is shown in Table

I that the enantioselectivities of the allylation reactions depend on the solvents used. A non-polar solvent, such as hexane, is better for stereocontrol (14–22% ee) than more polar chloroform (7–14% ee). The allylation reactions without solvent exhibit better enantioselectivities (17–25% ee). The ethyl ester moiety of **3a** provides better stereocontrol than the isopropyl ester of **3b** (entry 4 *vs* 5). Whereas, the bis(pentacoordinate allylsilicate) **5a** shows considerably low reactivity, it reacts with benzaldehyde at high temperature (over 100 °C) to afford the homoallylic alcohol with low yield (9%) (entry 9), which is assumed to be from the steric influence of the disilicate upon attack of the aldehyde carbonyl group by an allyl group.[13]

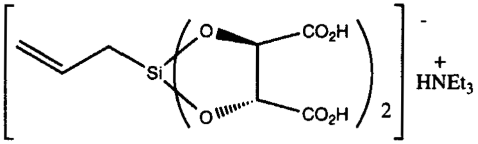


SCHEME 3

TABLE I Asymmetric allylation of RCHO with chiral **3a-b** and **5a**

Entry	*Silicate*	*Aldehyde (R)*	*Solvent*[a]	*Reaction Condition*	*Product*	*Yiled*[b] *%*	*[α]$_D$*	*Ee, % (Config.)*[c]
1	**3a**	C_6H_5	A	reflux, 48 h	**7a**	trace		
2	**3a**	C_6H_5	B	reflux, 48 h	**7a**	36	-4.8	10 (S)
3	**3a**	C_6H_5	C	60°C, 48 h	**7a**	43	-6.5	14 (S)
4	**3a**	C_6H_5	D	60°C, 48 h	**7a**	40	-11.9	25 (S)
5	**3b**	C_6H_5	D	60°C, 48 h	**7a**	41	-8.0	17 (S)
6	**3a**	C_8H_{17}	B	60°C, 60 h	**7b**	53	+0.7	7.0 (R)
7	**3a**	C_8H_{17}	C	60°C, 60 h	**7b**	54	+2.3	22 (R)
8	**3a**	C_8H_{17}	D	60°C, 60 h	**7b**	55	+2.0	18 (R)
9	**5a**	C_6H_5	E	reflux, 12 h h	**7a**	9.0	-8.8	19 (S)

[a] solvent: A, CH_2Cl_2; B, $CHCl_3$; C, Hexane; D, without solvent; E, Toluene; [b] isolated yield; [c] assigned by comparison with references, **7a** with ref. 11 and **7b** with 12.



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Acknowledgements

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[8] Typical procedure for **5:** A solution of **2b** (0.96 g, 4.0 mmol), (+)-(R. R)-**4** (0.60 g, 4.0 mmol), triethylamine (0.40 g, 4.0 mmol) in absolute ethanol (30 mL) was stirred at 60 °C for 18 h. The formed precipitate was filtered and washed with ether, then dried at room temperature in vacuum to give **5b** (1.32 g, yield 94%). mp 212~213 °C; $[\alpha]_D = +37.2$ (c 1.4, $CHCl_3$); IR (KBr) 3420, 1715, 1675 cm^{-1}; NMR ($CDCl_3$) ppm δ_H: 1.45 (t, 18 H, J =7.30 Hz. CH_3), 3.21 (dq, 12 H, J =2.09, 7.30 Hz, NCH_2), 4.66 (s, 4 H, CH), 7.20–7.50 (m, 10 H, PhH-), 8.20 (bs, 2 H, NH); δ_C: 8.38, 45.40, 75.90, 127.12, 128.63, 134.89, 139.10, 175.29; δ_{Si}: −100.72; Anal. Calcd. for $C_{32}H_{46}O_{12}N_2Si_2$: C, 54.37; H, 6.56; N, 3.96. Found: C, 54.36, H, 6.47, N, 4.03. The same procedure for the preparation of **5a:** yield 92%, mp 95~97 °C; $[\alpha]_D$= +34. 1 (c 1.4, $CHCl_3$); IR (KBr) 3450, 3040, 1690, 1620 cm^{-1}; NMR ($CDCl_3$) ppm δ_H: 1.33 (t, 18 H, J =7.30 Hz, CH_3), 1.60–1.80 (m, 4 H, CH_2Si), 3.23 (dq, 12 H, J =2.09, 7.30 Hz, CH_2N), 4.45 (s, 4 H, CH), 4.65–4.90 (m, 4 H, CH_2=), 5.65–5.90 (m, 2 H, CH=), 8.50 (bs, 2 H, NH); δ_C: 8.48, 25.06, 46.36, 75.68, 112.38, 136.0, 175.6; δ_{Si}: −90.63; Anal. Calcd. for $C_{26}H_{46}O_{12}N_2Si_2$: C, 49.19; H, 7.30; N, 4.41. Found: C, 48.91; H, 7.33; N, 4.50.

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[10] Typical procedure for allylation reactions: A mixture of chiral pentacoordinate allylsilicate (1.7 mmol) and aldehyde (1.5 mmol) in solvent was stirred at the given temperature and for the given reaction time. Then ethyl ether and hydrochloric acid were added to quench the reaction. The mixture was stirred for 1 h. The aqueous layer was extracted with ether. The combined ether layer was washed with water, aqueous KOH, water and brine successively, and then dried over $MgSO_4$. The solvent was removed by rotary evaporator, and the crude product was purified by flash chromatography (ethyl acetate-petroleum ether) to give the optically active homoallylic alcohol.

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