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## Optically Active Acylsilanes. Synthesis of Selected 2,3-O-Isopropylidene-1-(Trialkyl/arylsilyl)glyceraldehyde Derivatives

Piotr Raubo and Jerzy Wicha\*

Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44, 01-224 Warsaw, Poland

Abstract: Syntheses of 1-trimethylsilyl-, 1-tert-butyldimethylsilyl, 1-dimethylphenylsilyl- and 1-triphenylsilyl-2,3-O-isopropylideneglyceraldehyde derivatives, 6a, 6b, 6c, and 6d, respectively, is described.

Until recently only a few chiral acylsilanes<sup>1</sup> have been prepared and examined with respect to their application in stereocontrolled synthesis. Even with such a narrow group of examples it has been clearly shown that acylsilanes with a stereogenic centre  $\alpha$  to the carbonyl group in reactions with nucleophiles afford the corresponding products with high diastereoselectivity, both in non-chelation-<sup>2</sup> and chelation - controlled<sup>3</sup> processes. Encouraging diastereoselectivities have also been observed in reactions of the acylsilanes bearing a stereogenic silicon atom<sup>4</sup>. Recently<sup>5</sup>, we have reported an efficient approach to the optically active acylsilane derivatives with an alkoxy group in the  $\alpha$ -position, including 1-(trimethylsilyl)-2,3-isopropylideneglyceraldehyde 6a (Scheme 2); this approach is based upon Korblum-type oxidation of  $\alpha$ , $\beta$ -epoxysilanes. Almost simultaneously with our publication, Cirillo and Panek<sup>6,7</sup> have described an alternative method for the enantioselective synthesis of acylsilanes. These authors have also demonstrated that the stereochemistry of acylsilane reactions depends a great deal upon the nature of substituents on the silicon atom. The products of nucleophilic addition to acylsilanes may be utilized in many ways<sup>1,8</sup>. On the other hand, it has been shown that some acylsilanes may be conveniently transformed into aldehydes<sup>6</sup>, and consequently one may expect that  $\alpha$ -alkoxyacylsilanes may serve as surrogates of the corresponding  $\alpha$ -alkoxyaldehydes, which may be less stable or difficult to obtain by another route.

In continuation of our studies on the synthesis of acylsilanes we prepared 2,3-Oisopropropylideneglyceraldehyde derivatives bearing different silyl groups at the position 1. Herewith we present the details of preparation of compound 6a and describe the synthesis of its derivatives substituted with a *tert*butyldimethylsilyl, dimethylphenylsilyl, and triphenylsilyl group, 6b, 6c, and 6d, respectively. Allylic alcohols 3a - 3d were prepared following the standard procedures. The reagents used and the results obtained are presented in Scheme 1.

Scheme 1

a, b HCH <sub>2</sub> OR	$\rightarrow$ R <sup>1</sup> R <sup>2</sup> <sub>2</sub> Si — CH <sub>2</sub> OH —	$\Rightarrow$ R <sup>1</sup> R <sup>2</sup> <sub>2</sub> Si $\longrightarrow$ OH
1a, R=H 1b, R=CH(OEt)Me 1c, R=CMe <sub>2</sub> (OMe)	2a, R <sup>1</sup> =R <sup>2</sup> =Me 2b, R <sup>1</sup> = <sup>t</sup> Bu, R <sup>2</sup> =Me 2c, R <sup>1</sup> =Ph. R <sup>2</sup> =Me 2d, R <sup>1</sup> =R <sup>2</sup> =Ph	3a, R <sup>1</sup> =R <sup>2</sup> =Me 3b, R <sup>1</sup> = <sup>t</sup> Bu, R <sup>2</sup> =Me 3c, R <sup>1</sup> =Ph. R <sup>2</sup> =Me 3d, R <sup>1</sup> =R <sup>2</sup> =Ph

Reagents: a, BuLi/THF-hexane; b. R<sup>1</sup>R<sup>2</sup><sub>2</sub>SiCl; c. [(CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>AH<sub>2</sub>]Na/toluene-ether

Starting material	R <sup>1</sup> R <sup>2</sup> 2SiCl	<b>Intermediate</b> , yield (%)	Product, yield (%)	
1a	Me <sub>3</sub> SiCl	2a	3a,	65 <sup>a</sup> (from <b>1a</b> )
1b	<sup>t</sup> BuMe <sub>2</sub> SiCl	<b>2b</b> , 76	3b,	89
1b	PhMe <sub>2</sub> SiCl	<b>2c</b> , 87	3c,	78
1c	Ph <sub>3</sub> SiCl	2d <sup>b,C</sup>	3d,	89 (from <b>1c</b> )

<sup>a</sup> Ref. 9c; <sup>b</sup>intermediate was not purified, <sup>c</sup>LiAlH<sub>4</sub> was used for reduction

Catalytic asymmetric epoxidation<sup>9</sup> of alcohols **3a** - **3d** using D-(-)-diisopropyl tartrate (DIPT) or L-(+)-DIPT afforded products **4a** - **4d**. Their yields and enantiomeric purities determined by Moshers method<sup>10</sup> are given in Scheme 2.

Glycidol 4a dissolved in methylene chloride was treated with dimethylsulfoxide (DMSO), allyltrimethylsilane and trimethylsilyl triflate at O to 15 °C. After an appropriate period of time (see Experimental) the mixture was cooled to -78 °C and hexamethyldisilazane was added; after 30 min acylsilane 5a was isolated. This product, without purification, was reacted with 2,2-dimethoxypropane and a catalytic amount of TsOH  $H_2O$ to give 6a which was purified by distillation (72% yield). Similar oxidation of glycidols 4b - 4d, with subsequent transformation of the bis(trimethylsilyl) derivatives into acetonides, afforded acylsilanes 6b - 6d, respectively. Yields and specific rotations of the products are given in Scheme 2. It is noteworthy that the use of hexamethyldisilazane as the base in the oxidation procedure was advantageous, since in parallel experiments where hexamethyldisilazane was replaced by triethylamine markedly lower yields of the acylsilanes were obtained (see Experimental).

To determine the enantiomeric excess of acylsilane 6a, its <sup>1</sup>H NMR spectrum was measured in the presence of tris-[3-heptafluoropropylhydroxymethylene)-d-camphorato]europium(III) [Eu(hfc)<sub>3</sub>] and compared with the respective spectrum of racemic 6a. No signals corresponding to the other enantiomer could be seen. This suggests that during the transformation of trimethylsilylglicidol 4a into acylsilane 6a there is an only small, if any, loss



a,  $R^{1}=R^{2}=Me$ b,  $R^{1}=tBu$ ,  $R^{2}=Me$ c,  $R^{1}=Ph$ ,  $R^{2}=Me$ d,  $R^{1}=R^{2}=Ph$ 

**Reagents**: a. D-(-)-DIPT or L-(+)-DIPT,  $Ti(O^{i}Pr)_{4}$ , <sup>t</sup>BuO<sub>2</sub>H; b. (CH<sub>2</sub>=CHCH<sub>2</sub>)Me<sub>3</sub>Si, DMSO, Me<sub>3</sub>SiOTf, hexamethyldisilazane or Et<sub>3</sub>N; c. 2,2-dimethoxypropane, TsOH

Starting material	DIPT	<b>Epoxide</b> , configuration yield (%), ee (%) specific rotation	Acylsilane, configuration yield (%), specific rotation
3a	L-(+)-	<b>4a</b> (2S,3S) 84 94 $[\alpha]_D^{14}$ -26.5	<b>6a</b> (2S) 72 $[\alpha]_{D}^{22}$ -94.7
3b	L-(+)-	<b>4b</b> (2 <i>S</i> ,3 <i>S</i> ) 94 94 [α] <sub>D</sub> <sup>28</sup> -26	<b>6b</b> (2 <i>S</i> ) 75 [α] <sub>D</sub> <sup>25</sup> -77.1
3c	L-(+)-	<b>4</b> c (2S,3S) 87 97 $[\alpha]_D^{25}$ -12.2	<b>6c</b> (2 <i>S</i> ) 77 [α] <sub>D</sub> <sup>25</sup> -40.6
3d	D-(-)-	<b>4d</b> (2 <i>R</i> ,3 <i>R</i> ) 85 >97 [α] <sub>D</sub> <sup>25</sup> +22.5	<b>6d</b> (2 <i>R</i> ) 50 [α] <sub>D</sub> <sup>22</sup> +47.3

of the enantiomeric purity. It should be noted that we failed to prepare a Mosher ester of the diol corresponding to di-O-trimethylsilyl ether 5a or of the other  $\alpha$ -hydroxy silanes<sup>11</sup>.

In conclusion, optically active acylsilanes 6a - 6d were prepared from propargyl alcohol using as the key steps asymmetric epoxidation of 3-(trialkyl/arylsilyl)allylic alcohols 3a - 3d and Kornblum-type oxidation of glycidols 4a - 4d.

## **Experimental Section**

Melting points were determined on a hot - stage apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker AM 500 (500 and 125 MHz) or Varian GEM (200 and 50 MHz) spectrometers, for CDCl<sub>3</sub> solutions with  $Me_4Si$  as internal standard. MS were obtained with an AMD 604 unit at 70 eV ionizing potential. All reactions involving organometallic reagents were carried out under argon with stirring. Organic solutions were dried over anhyd.  $Na_2SO_4$  and solvents were evaporated on a rotary evaporator. Column chromatography was performed on Merck silica gel 60, 230-400 mesh, and TLC - on Merck silica gel G. Optical rotations were measured using a 8 mL capacity cell (10 cm path length), in CHCl<sub>3</sub>, unless otherwise stated. 3-(Trimethylsilyl)allylalcohol 3a was prepared from 1a according to the published procedure<sup>12</sup>.

3-(*tert*-Butyldimethylsilyl)prop-2-yne-1-ol (2b). To a stirred solution of 1b (5 g, 39 mmol) in THF (60 mL) BuLi (1.3 M in hexane, 30 mL, 39 mmol) was added at -78 °C. The mixture was allowed to warm up to -20 °C, was stirred at this temperature for 0.5 h and then was cooled to -78 °C. A solution of *tert*-butyldimethylsilyl chloride (6 g, 39 mmol) in THF (30 mL) was added dropwise during 15 min. The mixture was set aside for 20 h whereupon it was poured into saturated aqueous NH<sub>4</sub>Cl. The aqueous layer was separated and extracted with ether (3x30 mL). The combined organic layers were dried, filtered and concentrated. The residue was dissolved in MeOH (20 mL) containing a trace of HClO<sub>4</sub> (MeOH : 70% HClO<sub>4</sub> = 100:0.1) and after 0.5 h it was diluted with ether (200 mL), and washed with saturated aqueous NaHCO<sub>3</sub> and brine. The solvent was removed and the residue was distilled under reduced pressure to give 2b as a colourless oil (5.06 g, 76%); bp 80-82 °C/3 mm Hg; IR (KBr) 3332 (OH), 2175 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.11 (s, 6, SiCH<sub>3</sub>), 1.58 (br s, 1, OH), 0.93 (s, 9, SiCCH<sub>3</sub>), 4.27 (s, 2, C<sub>1</sub> H); <sup>13</sup>C NMR  $\delta$  -4.7 (SiCH<sub>3</sub>), 16.4 (SiCCH<sub>3</sub>), 27.0 (SiCCH<sub>3</sub>), 51.5 (C<sub>1</sub>), 88.7 (C<sub>3</sub>), 105.5 (C<sub>2</sub>); Anal. Calcd for C<sub>9</sub>H<sub>18</sub>OSi (170.32): C, 63.46; H, 10.65. Found: C, 63.25; H, 10.92.

**3-(Dimethylphenylsilyl)prop-2-yne-1-ol (2c)** was prepared in an analogous way. The reagents were used as follows: **1b** (4.8 g, 37.5 mmol), THF (50 mL), BuLi (2.1 M in hexane, 17 mL), and then dimethylphenylsilyl chloride (5.13 g, 30 mmol) in THF (10 mL). Product **2c** was obtained (5 g, 87% yield), bp 116-120 °C/3 mm Hg; IR (KBr) 3344 (OH), 2177 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.43 (s, 6, SiCH<sub>3</sub>), 1.62 (t, 1, *J* = 6.2 Hz, OH), 4.31 (d, 2, *J* = 6.2 Hz, C<sub>1</sub> H), 7.35-7.43 (m, 3H), 7.55-7.65 (m, 2H); <sup>13</sup>C NMR  $\delta$  -1.1 (SiCH<sub>3</sub>), 51.6 (C<sub>1</sub>), 88.7 (C<sub>3</sub>), 105.5 (C<sub>2</sub>), 127.9 (C<sub>m</sub>), 129.5 (C<sub>p</sub>), 133.6 (C<sub>0</sub>), 136.5 (C<sub>ipso</sub>); EIMS m/z (rel intensity, %) 175 (M<sup>+</sup>-CH<sub>3</sub>, 35), 75 (100); HRMS calcd for C<sub>10</sub>H<sub>11</sub>OSi (M<sup>+</sup>-CH<sub>3</sub>) 175.0579218, found 175.05772.

3-(Triphenylsilyl)prop-2-yne-1-ol (2d). To a stirred solution of 1c (11.1 g, 86.7 mmol) in THF (60 mL), BuLi (2.25 M in bexane, 38 mL) and triphenylsilyl chloride (23 g, 78 mmol) in THF (60 mL) were added successively, with the temperature maintained below O  $^{\circ}$ C. After 2 h the mixture was warmed up to rt and poured into water. The aqueous layer was separated and extracted with ether (2X50 mL). Combined organic extracts were evaporated. The residue was filtered through silica gel (30 g, hexane-acetone), whereupon it was treated with

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methanol (20 mL) containing a trace of HClO<sub>4</sub>. After 30 min the mixture was diluted with ether (200 mL), washed with aqueous NaHCO<sub>3</sub> and then with brine, and the solvent was removed. So obtained crude 2d was used for the next step without purification. A sample purified by chromatography showed mp 128.5-129.5 °C; IR (KBr) 3210 (OH), 2150 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.78 (t, 1, J = 6.3 Hz, OH), 4.39 (d, 2, J = 6.3 Hz, C<sub>1</sub> H), 7.3-7.5 (m, 9), 7.55-7.70 (m, 6); <sup>13</sup>C NMR  $\delta$  51.9 (C<sub>1</sub>), 85.9 (C<sub>3</sub>), 108.4 (C<sub>2</sub>), 128.0 (C<sub>m</sub>), 130.0 (C<sub>p</sub>), 133.0 (C<sub>ipso</sub>), 135.5 (C<sub>o</sub>); EIMS m/z (rel intensity, %) 314 (M<sup>+</sup>, 0.6), 199 (100), 77 (15). Described<sup>13</sup>: mp 125-126 °C

(*E*)-3-(*tert*-Butyldimethylsilyl)-2-propene-1-ol (3b). To a stirred mixture of Red-Al (3.4 M in toluene, 16 mL, 54.4 mmol) and ether (20 mL) a solution of acetylene 2b (5 g, 29.4 mmol) in ether (25 mL) was added at 0-5  $^{\circ}$ C. The mixture was stirred at rt for 1.5 h whereupon it was cooled to 0  $^{\circ}$ C and the reaction was quenched with 2 M H<sub>2</sub>SO<sub>4</sub>. The aqueous layer was separated and extracted with ether (3x30 mL). The combined organic layers were dried, filtered and concentrated. The residue was distilled to give 3b as a colourless oil (4.46 g, 89%); bp. 70-74  $^{\circ}$ C/2 mm Hg; IR (film) 3317 (OH), 1620 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.03 (s, 6, SiCH<sub>3</sub>), 0.87 (s, 9, SiCCH<sub>3</sub>), 1.44 (t, 1, *J* = 6.0 Hz, OH), 4.20 (ddd, 2, *J* = 1.6, 4.4, 6.0 Hz, C<sub>1</sub> H), 5.90 (dt, 1, *J* = 1.6, 18.8 C<sub>3</sub> H), 6.20 (dt, 1, *J* = 4.3, 18.8 C<sub>3</sub> H); <sup>13</sup>C NMR  $\delta$  -6.2 (SiCH<sub>3</sub>), 16.4 (SiCCH<sub>3</sub>), 26.4 (SiCCH<sub>3</sub>), 65.6 (C<sub>1</sub>), 126.6 (C<sub>3</sub>), 146.2 (C<sub>2</sub>); EIMS m/z (rel intensity) 172 (M<sup>+</sup>, 2), 115 (100), 75 (47); HRMS calcd for C<sub>9</sub>H<sub>20</sub>OSi 172.128344, found 172.12829. (*E*/*Z* = 96:4 by GC)

(*E*)-3-(Dimethylphenylsilyl)-2-propene-1-ol (3c) was prepared from 2c in an analogous way. The reagents were used as follows: 2c (5 g, 26.3 mmol) in ether (25 mL), Red-Al (18 mL) in ether (20 mL). Product 3c was obtained (3.7 g, 73%); bp 116-120 °C/3 mm Hg; IR (KBr) 3318 (OH), 1622 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.36 (s, 6, SiCH<sub>3</sub>), 1.49 (br t, 1, J = 5.4 Hz, OH), 4.21 (m, 2, C<sub>1</sub> H), 6.05 (dt, 1, J = 1.5, 18.7 Hz, C<sub>2</sub> H), 6.26 (dt, 1, J = 4.0, 18.7 Hz, C<sub>3</sub> H), 7.3-7.4 (m, 3) and 7.48-7.56 (m, 2, aromatic H); <sup>13</sup>C NMR  $\delta$  -2.7 (SiCH<sub>3</sub>), 65.4 (C<sub>1</sub>), 127.15 (C<sub>3</sub>), 127.8 (C<sub>m</sub>), 129.0 (C<sub>p</sub>), 133.7 (C<sub>o</sub>), 138.4 (C<sub>ipso</sub>), 146.6 (C<sub>2</sub>). EIMS m/z (rel intensity, %) 193 (M<sup>+</sup>+H, 2) 177 (M<sup>+</sup>-CH<sub>3</sub>, 24), 137 (59), 75 (100); HRMS calcd for C<sub>10</sub>H<sub>13</sub>OSi (M<sup>+</sup>-CH<sub>3</sub>) 177.073569, found 177.07358.

(*E*)-3-(Triphenylsilyl)-2-propene-1-ol (3d). To a mixture of LiAlH<sub>4</sub> (5 g) and THF (160 mL) stirred at 0-5  $^{\circ}$ C a solution of crude compound 2d (25 g) in THF (100 mL) was added dropwise. The mixture was stirred for 1 h whereupon it was cooled to 0  $^{\circ}$ C and the excess of the reagent was decomposed by careful addition of diluted H<sub>2</sub>SO<sub>4</sub> (16 mL conc. H<sub>2</sub>SO<sub>4</sub> in 200 ml of water). The water layer was separated and extracted with ether (3x50 mL). Combined organic extracts were evaporated and the residue was crystallized from a mixture of ether and hexane. Product 3d (22 g, 89% yield from 1c) was obtained; mp 149-150  $^{\circ}$ C; IR (KBr) 3290 (OH), 1625 (C=C)

cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.51 (t, 1, J = 6.2 Hz, OH), 4.29 (ddd, 2, J = 1.6, 3.7, 6.0 Hz, C<sub>1</sub> H), 6.29 (dt, 1, J = 3.7, 18.7 Hz, C<sub>2</sub> H), 6.50 (dt, 1, J = 1.6, 18.7 Hz, C<sub>3</sub> H), 7.3-7.45 (m, 9) and 7.50-7.60 (m, 6, aromatic H); <sup>13</sup>C NMR  $\delta$  65.3 (C<sub>1</sub>), 122.9 (C<sub>3</sub>), 127.9 (C<sub>m</sub>), 129.6 (C<sub>p</sub>), 134.4 (C<sub>ipso</sub>), 135.9 (C<sub>o</sub>), 150.7 (C<sub>2</sub>).

Glycidol 4a was obtained from 3a essentially as described earlier<sup>10c</sup>, yield 84%, 94% ee.

(25,35)-3-(*tert*-butyldimethylsilyl)-2,3-epoxypropane-1-ol (4b). To a suspension of powdered and freshly activated molecular sieves 4A (3 g) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (40 mL), stirred under argon at -20 °C, addition was made of: L-(+)-DIPT (0.4 mL, 1.92 mmol), (E)-3-(*tert*-butyldimethylsilyl)prop-2-ene-1-ol 3b (4.35, 25.2 mmol), Ti(O<sup>i</sup>Pr)<sub>4</sub> (0.48 mL, 1.64 mmol) and (after 15 min) TBHP (3.5 M in toluene, 14.5 mL, 50.8 mmol). Stirring at -20 °C was continued for 5 h and then the mixture was set aside in a freezer (-22 °C) for 16 h. The reaction mixture was transferred to an ice-cooled mixture of FeSO<sub>4</sub>·7H<sub>2</sub>O (8.25 g), tartaric acid (1 g), water (60 mL) and ether (60 mL), and was stirred at 0 °C for 1 h. Solid material was removed by filtration through Celite. The filtrate was washed with brine (200 mL). The aqueous layer was separated and extracted with ether. The combined organic layers were dried (MgSO<sub>4</sub>), filtered and concentrated. The residue was chromatographed on silica gel (50 g, hexane-acetone) to afford the epoxide 4b (4.46 g, 94%); 94% ee,  $[\alpha]_D^{28} - 26.0$  (c 1.4); IR (film) 3417 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  -0.05 and 0.01 (s, 3, SiCH<sub>3</sub>), 0.95 (s, 9, SiCCH<sub>3</sub>), 1.97 (m, 1H, OH), 2.32 (d, 1, *J* = 3.7 Hz, C<sub>3</sub> H), 3.01 (ddd, 1, *J* = 2.4, 3.7, 4.6 Hz, C<sub>2</sub> H), 3.57 (ddd, 1, *J* = 4.6, 7.0, 12.5 Hz, C<sub>1</sub> Ha), 3.98 (ddd, 1, *J* = 2.3, 6.0, 12.5 Hz, C<sub>1</sub> Hb); <sup>13</sup>C NMR  $\delta$  -8.45 and -8.32 (SiCH<sub>3</sub>), 16.6 (SiCCH<sub>3</sub> 26.5 (SiCCH<sub>3</sub>), 46.3 (C<sub>3</sub>), 55.5 (C<sub>2</sub>), 63.4 (C<sub>1</sub>); Anal. Calcd for C<sub>9</sub>H<sub>20</sub>O<sub>2</sub>Si (188.34): C, 57.39; H, 10.70. Found: C, 57.24; H, 10.90.

The Moshers ester of 4b, prepared from (*R*)-(+) acid: <sup>1</sup>H NMR  $\delta$  -0.07 and -0.01 (s, 3, SiCH<sub>3</sub>), 0.94 (s, 9, SiCCH<sub>3</sub>), 2.17 (d, 1, *J* = 3.5 Hz, C<sub>3</sub> H), 3.07 (ddd, 1, *J* = 3.3, 6.3, 6.8 Hz, C<sub>2</sub> H), 3.58 (q, 3, *J* = 1.2, OMe), 4.24 (dd, 1, *J* = 6.3, 12. Hz, C<sub>1</sub> Ha), 4.56 (dd, 1, *J* = 3.2, 12.0 Hz, C<sub>1</sub> Hb), 7.40-7.45 (m, 3), 7.5-7.6 (m, 2); <sup>13</sup>C NMR  $\delta$  -8.5 and -8.4 (Si<u>C</u>H<sub>3</sub>), 16.6 (Si<u>C</u>CH<sub>3</sub> 26.4 (SiC<u>C</u>H<sub>3</sub>), 47.1 (C<sub>3</sub>), 51.8 (OMe), 55.5 (C<sub>2</sub>), 68.2 (C<sub>1</sub>), 120.3 (CF<sub>3</sub>), 127.3 (C<sub>p</sub>), 128.4 (C<sub>m</sub>), 129.6 (C<sub>0</sub>), 132.1 (C<sub>ipso</sub>), 166.3 (C=O).

Moshers esters prepared from racemic material showed additionally diagnostic signals at 2.17 (d, 1, J = 3.6 Hz) and 2.20 (d, 1, J = 3.5 Hz).

(2S,3S)-3-(Phenyldimethylsilyl)-2,3-epoxypropane-1-ol (4c) was prepared in an analogous way. The reagents were used as follows: molecular sieves (3 g), CH<sub>2</sub>Cl<sub>2</sub> (35 mL), L-(+)-DIPT (0.29 mL), Ti(O<sup>i</sup>Pr)<sub>4</sub> (0.35 mL), allylic alcohol 3c (3.44 g, 17.9 mmol), TBHP (10.5 mL, 3.5 M in toluene, 36.75 mmol). The crude product was chromatographed on silica gel (30 g, hexane:acetone). Product 4c was obtained (3.24 g, 87%, 97% ee);  $[\alpha]_D^{25}$ -12.2 (c 1.11); IR (film) 3415 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.33 and 0.37 (2s, 3, SiCH<sub>3</sub>), 1.71 (br t, 1, J = 7 Hz, OH), 2.46 (d, 1, J = 3.6 Hz, C<sub>3</sub> H), 3.02 (ddd, 1, J = 2.4, 3.6, 4.4 Hz, C<sub>2</sub> H), 3.59 (ddd, 1, J = 4.4, 7.0, 12.4 Hz, C<sub>1</sub> Ha), 3.97 (ddd, 1, J = 2.4, 5.7, 12.4 Hz, C<sub>1</sub> Hb), 7.35-7.43 (m, 3), 7.5-7.6 (m, 2); <sup>13</sup>C NMR  $\delta$  -5.4 and -5.1

(SiCH<sub>3</sub>), 47.6 (C<sub>3</sub>), 56.1 (C<sub>2</sub>), 63.2 (C<sub>1</sub>), 127.9 (C<sub>m</sub>), 129.6 (C<sub>p</sub>), 133.8 (C<sub>o</sub>), 135.6 (C<sub>ipso</sub>); Anal. Calcd for  $C_{11}H_{16}O_2Si$  (208.33): C, 63.42; H, 7.74. Found: C, 63.17; H, 8.00.

Moshers ester of 4c, prepared from (R)-(+)-acid: <sup>1</sup>H NMR  $\delta$  0.31 and 0.35 (2s, 3, SiCH<sub>3</sub>), 2.29 (d, 1, J = 3.4 Hz, C<sub>3</sub> H), 3.07 (ddd, 1, J = 3.3, 3.4, 6.7 Hz, C<sub>2</sub> H), 3.54 (q, 3, J = 1.2 Hz, OCH<sub>3</sub>), 4.22 (dd, 1, J = 6.3, -12.0 Hz, C<sub>1</sub> Ha), 4.55 (dd, 1, J = 3.3, 12.0 Hz, C<sub>1</sub> Hb), 7.35-7.45 (m, 6), 7.48-7.55 (m, 4);

Moshers esters prepared from racemic material showed additionally diagnostic signals at 2.29 (d, 1, J = 3.4 Hz) and 2.31 (d, 1, J = 3.4 Hz).

(2*R*,3*R*)-3-(Triphenylsilyl)-2,3-epoxypropane-1-ol (4d) was prepared in an analogous way. The reagents were used as follows: molecular sieves (8 g), CH<sub>2</sub>Cl<sub>2</sub> (100 mL), D-(-)-DIPT (1.2 mL), Ti(O<sup>i</sup>Pr)<sub>4</sub> (1.4 mL), allylic alcohol 3d (22 g, 69.6 mmol), TBHP (40 mL, 3.5 M in toluene, 140 mmol). The crude product was crystallized from a mixture of ether and hexane. Product 4d was obtained (21.5 g, 92% yield, 95% ee). After one recrystallization from the same solvent 19.5 g of the product were obtained (85% yield, >97% ee);  $[\alpha]_D^{25}$  +22.5 (c 1.78); mp 129.5-130.5 °C; IR (KBr) 3420 (OH) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  3.0 (m, 2, C<sub>2</sub> H, C<sub>3</sub> H), 3.60-3.75 (m, 1, C<sub>1</sub> Ha), 3.90-4.05 (m, 1, C<sub>1</sub> Hb), 7.3-7.7 (m, 15, aromat. H); <sup>13</sup>C NMR  $\delta$  46.2 (C<sub>3</sub>), 56.2 (C<sub>2</sub>), 62.8 (C<sub>1</sub>), 128.2 (C<sub>m</sub>), 130.2 (C<sub>p</sub>), 132.1 (C<sub>ipso</sub>), 136.0 (C<sub>o</sub>); EIMS m/z (rel intensity, %) 331 (M<sup>+</sup>-H, 0.8), 276 (33), 259 (100), 199 (47), 181 (35), 77 (8); Anal. Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>Si (332.46): C, 75.86; H, 6.06. Found: C, 75.78; H, 5.98.

Moshers ester of 4d, prepared from (R)-(+)-acid: <sup>1</sup>H NMR  $\delta$  2.86 (d, 1, J = 3.4 Hz, C<sub>3</sub> H), 3.05 (dt, 1, J = 3.8, 5.2 Hz, C<sub>2</sub> H), 3.50 (q, 3, J = 1.2 Hz, OMe), 4.38 (dd, 1, J = 5.2, 12.0 Hz, C<sub>1</sub> Ha), 4.61 (dd, 1, J = 3.8, 12.0 Hz, C<sub>1</sub> Hb), 7.3-7.6 (m, 20H, aromat. H).

Moshers esters prepared from racemic material showed additionally diagnostic signals at  $\delta$  2.84 (d, J = 3.3 Hz, C<sub>3</sub> H) and 3.52 (q, J = 1.2 Hz, OCH<sub>3</sub>).

(S)-2,3-O-Isopropylidene-1-oxo-1-(trimethylsilyl)propan-2,3-diol (6a). To a stirred mixture of trimethylsilylglycidol 4a (2.03 g, 13.9 mmol), (allyl)trimethylsilane (2.23 mL, 14 mmol), DMSO (6 mL), and  $CH_2Cl_2$  (25 mL),  $Me_3SiOTf$  (3.16 mL, 17.4 mmol) was added at O °C. The mixture was stirred at 15 °C for 5 h and then it was cooled to -78 °C whereupon triethylamine (5.85 mL, 42 mmol) was added dropwise. The mixture was allowed to warm up to rt within 30 min and then it was diluted with  $CH_2Cl_2$  (70 mL) and washed successively with saturated aqueous NaHCO<sub>3</sub>, water (3 times) and brine. The organic solution was dried ( $Na_2SO_4$ ) and the solvent was evaporated to give crude acylsilane 5a.

This product was dissolved in  $CH_2Cl_2$  (20 mL) and treated with 2,2-methoxypropane (2.6 mL, 21 mmol) and TsOH monohydrate (125 mg, 0.66 mmol). The mixture was stirred at rt for 3 h and then anhydrous  $K_2CO_3$  (300 mg) was added, followed after a few min by ether (50 mL). The mixture was washed successively with saturated

aqueous NaHCO<sub>3</sub>, water and brine. The organic solution was dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was evaporated. The residue was distilled under reduced pressure. The fraction distilling at 80-84 °C/15 mm Hg was collected to give acylsilane 6a (2.01 g, 72% yield) as a pale yellow liquid:  $[\alpha]_D^{22}$ -94.7 (c 1.01) (a sample was immediately before this measurement redistilled at 60-61 °C/4 mm Hg); v (film) 1649 (Me<sub>3</sub>SiC=O) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 0.24 (s, 9H, SiMe<sub>3</sub>), 1.36 (br s, 3H, CH<sub>3</sub>C), 1.47 (br s, 3H, CH<sub>3</sub>C), 3.87 (dd, 1H,  $J_{3a-3b}$ = 6.4,  $J_{3a-2}$ = 8.4 Hz, C<sub>3</sub> Ha), 4.07 (t, 1H,  $J_{2.3}$ = 8.3 Hz, C<sub>2</sub> H), 4.36 (dd, 1H,  $J_{3b-3a}$ = 6.4,  $J_{3b-2}$ = 7.9 Hz, C<sub>3</sub> Hb); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) -2.6 (SiMe<sub>3</sub>), 24.06, 26.0, 65.0 (C<sub>3</sub>), 85.1 (C<sub>2</sub>), 110.3 (Me<sub>2</sub>C), 246.1 (Me<sub>3</sub>SiC=O). Anal. Calcd for C<sub>9</sub>H<sub>18</sub>O<sub>3</sub>Si (202.32) C, 53.43; H, 8.97. Found: C, 53.55; H, 9.20.

To determine the optical purity of compound 6a, its <sup>1</sup>H NMR spectrum was measured in the presence of  $[Eu(hfc)_3]$ . Protons of the acetonide methyl groups appeared as two singlets. In the spectrum of racemic 6a, in the presence of  $[Eu(hfc)_3]$ , under similar conditions two well-resolved pairs of singlets (four signals) of the equal integration occurred.

(*S*)-2,3-O-Isopropylidene-1-oxo-1-(*tert*-butyldimethylsilyl)propan-2,3-diol (6b). a. To a mixture of epoxysilane 4b (436 mg, 2.3 mmol), allyl(trimethyl)silane (0.37 mL, 2.33 mmol), DMSO (1 mL) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL), stirred at rt, Me<sub>3</sub>SiOTf (0.49 mL, 2.7 mmol) was added. After 16 h hexamethyldisilazane (1 mL) was added and stirring was continued for 1 h. The mixture was diluted with hexane (40 mL) and washed successively with aqueous NaHCO<sub>3</sub> and twice with water. The solvent was removed to give crude acylsilane 5b (759 mg, 86%). The latter was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then was treated with 2,2-dimethoxypropane (1.2 mL), TsOH (20 mg) and methanol (0.07 mL). After stirring for 1.5 h the mixture was diluted with hexane (40 mL) and washed with aqueous NaHCO<sub>3</sub>, water and brine, and the solvent was removed. The residue was chromatographed on silica gel (3 g, hexane:acetone) to give acylsilane 6b (420 mg, 75%, 91% ee); bp 82-83 °C/3 mm Hg;  $[\alpha]_D^{25}$  - 77.1 (c 1.58); IR (film) 1643 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.21 and 0.26 (s, 3, SiCH<sub>3</sub>), 0.94 (s, 9, SiCCH<sub>3</sub>), 1.37 (br q, 3, *J* = 0.6 Hz, Me<sub>2</sub>C), 3.89 (dd, 1, *J* = 6.5, 8.3 Hz, C<sub>3</sub> Ha), 4.07 (dd, 1, *J* = 7.8, 8.4 Hz, C<sub>3</sub> Hb), 4.38 (dd, 1, *J* = 6.5, 7.8 Hz, C<sub>2</sub> H); <sup>13</sup>C NMR  $\delta$  -6.4 and -6.1 (SiCH<sub>3</sub>), 16.7 (SiCCH<sub>3</sub>), 24.6 and 25.8 (CCH<sub>3</sub>), 26.5 (SiCCH<sub>3</sub>), 64.6 (C<sub>3</sub>), 85.3 (C<sub>2</sub>), 110.2 (CCH<sub>3</sub>), 244.5 (C=O); EIMS m/z (rel intensity, %) 244 (M<sup>+</sup>, 0.3), 229 (M<sup>+</sup>-CH<sub>3</sub>, 2), 115 (65), 101 (40), 75 (100); HRMS calcd for C<sub>11</sub>H<sub>21</sub>O<sub>3</sub>Si (M<sup>+</sup>-CH<sub>3</sub>) 229.125998, found 229.12598.

b. To a stirred mixture of epoxysilane 4b (219 mg, 1.16 mmol), allyl(trimethyl)silane (0.19 mL, 1.19 mmol), DMSO (0.6 mL) and  $CH_2Cl_2$  (3 mL),  $Me_3SiOTf$  (0.49 mL, 2.7 mmol) was added. After 16 h triethylamine (0.8 mL) was added and stirring was continued for additional 40 min. The mixture was diluted with  $CH_2Cl_2$  (40 mL) and washed successively with aqueous NaHCO<sub>3</sub> and water. The solvent was removed to give acylsilane 5b which was dissolved in  $CH_2Cl_2$  (3 mL) and then was treated with 2,2-dimethoxypropane (0.28 mL) and TsOH (13 mg).

After stirring for 1 h the mixture was diluted with hexane (30 mL) and washed with aqueous NaHCO<sub>3</sub>, water and brine, and the solvent was removed. The residue was chromatographed on silica gel (2 g, hexane:acetone) to give acylsilane 6b (170 mg, 60%, 91% ee) identical in all respects with the product described above.

(S)-2,3-O-Isopropylidene-1-oxo-1-(dimethylphenylsilyl)propan-2,3-diol (6c). To a stirred mixture of epoxysilane 4c (259 mg, 1.24 mmol), allyl(trimethyl)silane (0.2 mL, 1.26 mmol), DMSO (0.5 mL) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL), Me<sub>3</sub>SiOTf (0.27 mL, 1.49 mmol) was added. After 16 h hexamethyldisilazane (0.9 mL) was added and stirring was continued for 1 h. The mixture was diluted with hexane (40 mL), washed with aqueous NaHCO<sub>3</sub> and twice with water. The solvent was removed to give acylsilane 5c (446 mg, 98%). The latter was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), 2,2-dimethoxypropane (0.4 mL), TsOH (10 mg) and methanol (0.05 mL) were added and the mixture was stirred for 1 h. The mixture was diluted with hexane (40 mL) and washed successively with aqueous NaHCO<sub>3</sub>, water and brine. The solvent was removed and the residue was chromatographed on SiO<sub>2</sub> (1 g, hexane:acetone) to give acylsilane 6c (252 mg, 77%)  $[\alpha]_D^{25}$  - 40.6 (c 2.01, benzene); IR (film) 1649 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  0.53 and 0.58 (s, 3, SiCH<sub>3</sub>), 1.25 (br q, 3, J = 0.6 Hz, Me<sub>2</sub>C), 1.32 (b q, 3, J = 0.6 Hz, Me<sub>2</sub>C), 3.81 (dd, 1, J = 6.4, 8.4 Hz, C<sub>3</sub> Ha), 3.97 (dd, 1, J = 7.7, 8.4 Hz, C<sub>3</sub> Hb), 4.38 (dd, 1, J = 6.4, 7.7 Hz, C<sub>2</sub> H); 7.3-7.45 (m, 3), 7.5-7.6 (m, 2); <sup>13</sup>C NMR  $\delta$  -4.4 and -3.8 (Si<u>C</u>H<sub>3</sub>), 24.8 and 25.6 ([<u>C</u>H<sub>3</sub>]<sub>2</sub>C), 64.9 (C<sub>3</sub>), 85.1 (C<sub>2</sub>), 110.3 ([CH<sub>3</sub>]<sub>2</sub><u>C</u>), 128.0 (C<sub>m</sub>), 129.8 (C<sub>p</sub>), 134.2 (C<sub>o</sub>), 243.6 (C=O); EIMS m/z (rel intensity, %) 249 (M<sup>+</sup>-CH<sub>3</sub>, 0.7), 135 (100); HRMS calcd for C<sub>13</sub>H<sub>17</sub>O<sub>3</sub>Si (M<sup>+</sup>-CH<sub>3</sub>) 249.094698, found 249.09453.

b) In an analogous experiment with the use of triethylamine instead of hexamethyldisilazane acylsilane 6c was obtained in 61% yield.

(*R*)-2,3-O-Isopropylidene-1-oxo-1-(triphenylsilyl)propan-2,3-diol (6d). To a stirred mixture of epoxysilane 4d (215 mg, 0.65 mmol), allyl(trimethyl)silane (0.11 mL, 0.69 mmol), DMSO (0.5 mL) and CH<sub>2</sub>Cl<sub>2</sub> (3 mL), Me<sub>3</sub>SiOTf (0.3 mL, 1.65 mmol) was added. After 44 h hexamethyldisilazane (0.7 mL) was added and stirring was continued for 30 min. The mixture was diluted with hexane (40 mL) and washed with aqueous NaHCO<sub>3</sub> and water. The solvent was evaporated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and 2,2-dimethoxypropane (0.55 mL) and TsOH (20 mg) were added. After 1 h the mixture was diluted with hexane (30 mL) and washed successively with aqueous NaHCO<sub>3</sub>, water and brine. The solvent was removed and the residue was chromatographed on SiO<sub>2</sub> (2 g, hexane:acetone) to give acylsilane 6d (125 mg, 50%);  $[\alpha]_{D}^{22}$  +47.3 (c 2.35); IR (film) 1650 (C=O) cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  1.10 (2, 3, Me<sub>2</sub>C), 1.29 (s, 3, Me<sub>2</sub>C), 3.81-3.95 (m, 2, C<sub>3</sub> H), 4.69 (dd, 1, *J* = 6.3, 7.7 Hz, C<sub>2</sub> H); 7.3-7.7 (m, 15, aromat. H); <sup>13</sup>C NMR  $\delta$  25.0 and 25.2 ([CH<sub>3</sub>]<sub>2</sub>C), 64.8 (C<sub>3</sub>), 85.3 (C<sub>2</sub>), 110.7 ([CH<sub>3</sub>]<sub>2</sub>C), 128.1 (C<sub>m</sub>), 130.3 (C<sub>p</sub>), 130.8 (C<sub>ipso</sub>), 136.3 (C<sub>o</sub>), 239.3 (C=O); Anal. Calcd for C<sub>24</sub>H<sub>24</sub>O<sub>3</sub>Si (388.52): C, 74.20; H, 6.23. Found: C, 74.29; H, 6.19.

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