EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Preparation of Functionalized Acylsilanes via Diol Cleavage of Cyclic 1,2-Dihydroxysilanes

Authors: Patrick Zimdars, Kristin Böhlig, and Peter Metz

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201900726

Link to VoR: http://dx.doi.org/10.1002/ejoc.201900726

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

WILEY-VCH

FULL PAPER

Preparation of Functionalized Acylsilanes via Diol Cleavage of Cyclic 1,2-Dihydroxysilanes

Patrick Zimdars, Kristin Böhlig, and Peter Metz*[a]

Abstract: We report a study on diol cleavage of cyclic 1,2-dihydroxysilanes for the preparation of functionalized acylsilanes. Sodium periodate turned out to be an efficient reagent for this transformation, resulting in good to excellent yields. The method is characterized by mild reaction conditions, and sometimes simple aqueous workup of the reaction mixture was sufficient to obtain the acylsilanes in high purity. An acyclic 1,2-dihydroxysilane was readily cleaved as well.

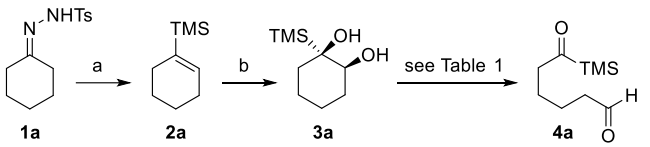
Introduction

Acylsilanes represent an important compound class in organic chemistry with exceptional spectroscopic and chemical properties.[1–7] Classical reactions of acylsilanes involve nucleophilic addition, occasionally followed by rearrangement of the resultant silyl alkoxide intermediate.[1] Several reviews give a detailed and excellent overview on the versatile reactivity of acylsilanes.[1–7] Furthermore, recent applications include photo-redox-catalyzed generation of acyl radicals and subsequent addition to electron-deficient olefins,[8] photoinduced acylsilane-aldehyde coupling,[9] enantioselective 1,2-rearrangement to secondary alcohols,[10] and stereoselective synthesis of allyl ethers from α,β-unsaturated acylsilanes.[11]

Commonly, acylsilanes are synthesized either by umpolung of an aldehyde via the Corey–Seebach methodology, subsequent nucleophilic substitution of a silyl halide and deprotection, or by nucleophilic attack of a silyl anion to a carbonyl compound.[1] Some other, more specialized methods to generate acylsilanes are also described in the reviews mentioned above. In the context of our studies on the synthesis of neoclerodane diterpenes,[12,13] we became interested in the diol cleavage of cyclic 1,2-dihydroxysilanes. In 2013, Strand et al. developed a protocol for the synthesis of formylsilanes by oxidative cleavage of α-silyl glycols.[14] Except for this work of Strand, the synthesis of acylsilanes via glycol cleavage remained unexplored. Herein we present a study on the diol cleavage of cyclic 1,2-dihydroxysilanes.

Results and Discussion

To find optimal reaction conditions for the diol cleavage of 1,2-dihydroxysilanes, we chose the 6-membered cyclic *cis* diol **3a**[15,16] as a model substrate. As depicted in Scheme 1, **3a** was synthesized from the commercially available tosylhydrazone **1a** by formation of vinylsilane **2a** via Shapiro reaction[17] and subsequent *cis* dihydroxylation using catalytic amounts of osmium tetroxide and *N*-methyl-morpholine *N*-oxide (NMO).[16] With **3a** in hand, we tested several conditions for diol cleavage (see Table 1). The use of phenyliodine diacetate (PIDA) as oxidant resulted in the formation of the desired and previously reported[18] acylsilane **4a** in 43% yield (entry 1) determined by ^{1}H NMR integration with $MeNO_2$ as internal standard. While lowering the reaction temperature to 0 °C resulted in a decrease of the yield (entry 2), shortening of the reaction time up to 10 min had only minor effects (entries 3 and 4). Afterwards we screened various oxidants. Use of $Pb(OAc)_4$ led to decomposition of the starting material (entry 5). To our delight, $NaIO_4$ – either pure or supported on silica gel – provided acylsilane **4a** in excellent (96%, entry 6) or good yield (75%, entry 7). Unfortunately, **4a** cannot be purified by column chromatography (which was tried under various conditions using silica gel, NEt_3 as additive, or Alox) due to decomposition. However, simple aqueous workup of the reaction mixture, extraction, washing the organic layer and subsequent evaporation of all solvents gave **4a** showing only minor impurities in the ^{1}H and ^{13}C NMR spectra.



Scheme 1. Synthesis of model substrate **3a** and subsequent diol cleavage. Reagents and conditions: (a) 1. BuLi, pentane/TMEDA (tetramethylethylenediamine), –50 °C to r.t., 4 h; 2. TMSCl, 0 °C to r.t., 20 h, 67%; (b) cat. OsO_4, $NMO{\cdot}H_2O$, acetone/*t*BuOH/H_2O, 45 °C, 26 h, 79%.

[a] M. Sc. Patrick Zimdars, B. Sc. Kristin Böhlig, Prof. Dr. Peter Metz
Fakultät Chemie und Lebensmittelchemie, Organische Chemie I
Technische Universität Dresden
Bergstrasse 66, 01069 Dresden, Germany
E-mail: peter.metz@chemie.tu-dresden.de
Homepage: https://tu-dresden.de/mn/chemie/oc/oc1

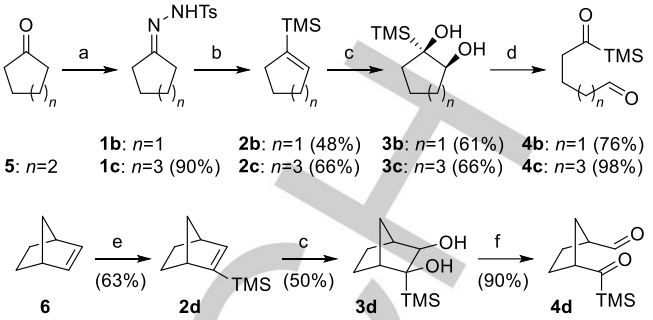
Supporting information for this article is given via a link at the end of the document.

Table 1. Reagents and conditions for oxidative cleavage of diol **3a**.[a]

Entry	Oxidant	Solvent	Time	Yield **4a** [%][b]
1	PIDA (1.2 equiv)	CH_2Cl_2	1.5 h	43
2[c]	PIDA (1.2 equiv)	CH_2Cl_2	1.5 h	15
3	PIDA (1.2 equiv)	CH_2Cl_2	30 min	48
4	PIDA (1.2 equiv)	CH_2Cl_2	10 min	41
5[d]	$Pb(OAc)_4$ (1.3 equiv)	CH_2Cl_2	30 min	decomp.
6	$NaIO_4$ (2.0 equiv)	EtOH/H_2O	23 h	96[e]
7	$NaIO_4$/silica (2.1 equiv)	EtOH/H_2O	44 h	75

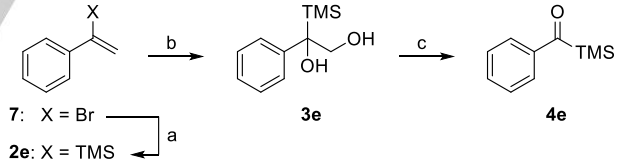
[a] The reaction was carried out at room temperature if not mentioned otherwise. [b] Yield determined by ^{1}H NMR integration using nitromethane as internal standard. [c] Run at 0 °C. [d] Run at –78 °C. [e] Isolated yield.

With optimized conditions in hand, we examined the diol cleavage for other 1,2-dihydroxysilanes, specifically 5- and 7-membered cyclic diols **3b** and **3c** together with bicyclic diol **3d**. The synthesis of these diols and the results of the subsequent oxidative cleavage are depicted in Scheme 2. The tosylhydrazone of cyclohexanone (**1c**) was prepared from ketone **5**, while **1b** was purchased. Hydrazones **1b** and **1c** were transformed into the vinylsilanes **2b** and **2c** analogously to the preparation of **2a** (Scheme 1). Different from that strategy, vinylsilane **2d** was prepared via deprotonation of norbornene (**6**) and subsequent quenching with TMSCl.[19] Vinylsilanes **2b-d** were dihydroxylated at elevated temperatures, since only slow conversion was observed at lower reaction temperatures. The 5-membered cyclic diol **3b** was transformed into acylsilane **4b**[18] in 76% yield. Its ^{13}C NMR spectrum showed small peaks originating from impurities. Even though **4b** is not as labile as **4a** towards silica gel, flash chromatography of **4b** did not improve the degree of purity (in some experiments it was even degraded). Cleavage of diol **3c** gave **4c** in excellent yield (98%) and good purity as judged by ^{1}H and ^{13}C NMR analysis. Therefore no purification via flash chromatography was necessary. For diol cleavage of **3d**, exclusion of light was necessary during the reaction, aqueous workup, and flash chromatography. Also, evaporation of the solvents was carried out using a rotary evaporator at 25 °C water bath temperature. It is known that acylsilanes represent a quite unstable compound class against heat and light,[1,20] which could be an explanation for the sensitivity of **4d**. Eventually, **4d** was obtained in 90% yield after purification by flash chromatography.



Scheme 2. Synthesis of substrates **3b-d** and subsequent diol cleavage. Reagents and conditions: (a) $TsNH–NH_2$, EtOH, reflux, 2 h; (b) 1. BuLi, pentane/TMEDA, –50 °C to r.t., 4 h; 2. TMSCl, 0 °C to r.t., 19 h; (c) cat. OsO_4, NMO·H_2O, *t*BuOH/H_2O/pyr., 100 °C, 24 h; (d) $NaIO_4$, EtOH/H_2O, r.t., 23 h; (e) 1. KO*t*Bu, BuLi, THF, –78 °C to –45 °C, 80 min; 2. TMSCl, –78 °C to r.t., 21 h; (f) same reaction conditions as (d) plus exclusion of light.

The *cis* diols **3a-d** had already been prepared by Tyagi and Gupta using ozone/aq. NH_4Cl.[21] For all four diols, comparison of our ^{13}C NMR data with the literature values[21] showed significant differences. However, acylsilanes **4a** and **4b** are already known, and our ^{13}C NMR data matched the reported values.[18] This supports the correctness of our ^{13}C NMR data for diols **3a** and **3b**. In addition, we tested our reaction conditions for diol cleavage of cyclic 1,2-dihydroxysilanes on one acyclic substrate as well (Scheme 3). Thus, we converted α-bromostyrene (**7**) to the vinylsilane **2e** by formation of the Grignard reagent and subsequent quenching with TMSCl. Dihydroxylation (unoptimized) of **2e** provided **3e**, which was readily cleaved to give the known acylsilane **4e**[22] in 70% yield.



Scheme 3. Synthesis of acyclic substrate **3e** and subsequent diol cleavage. Reagents and conditions: (a) 1. Mg, THF, reflux to r.t., 2 h; 2. TMSCl, reflux, 18 h, 68%; (b) cat. OsO_4, NMO·H_2O, acetone/*t*BuOH/H_2O, r.t., 26 h, 23%; (c) $NaIO_4$, EtOH/H_2O, r.t., 23 h, 70%.

Conclusions

In conclusion, we found an efficient method for the diol cleavage of cyclic 1,2-dihydroxysilanes to prepare bifunctional acylsilanes in good to excellent yields. We applied our protocol to four cyclic diols and also one acyclic substrate (leading to a monofunctional acylsilane), which are readily prepared from vinylsilanes by *cis* dihydroxylation using catalytic amounts of OsO_4 and NMO. The diol cleavage is characterized by mild reaction conditions, and in some cases simple aqueous workup of the reaction mixture already gave rise to acylsilanes in high purity.

Experimental Section

General remarks: THF and EtOH were dried and purified by passage through a MB-SPS-800 device using molecular sieves. Pentane, CH_2Cl_2, *i*hexane, ethyl acetate, and TMSCl were distilled prior to use. Et_2O was distilled over KOH. All other commercially available reagents were used as received. Reactions were performed under argon atmosphere. Thin layer chromatography was performed on Merck silica gel 60 F254 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm and subsequently developed using anisaldehyde solution or potassium permanganate solution as appropriate. Flash column chromatography was carried out using silica gel (Merck, particle size 40–63 microns). Melting points were measured on a Wagner & Munz PolyTherm A and are uncorrected. Infrared spectra were recorded on a THERMONICOLET Avatar 360 instrument using ATR. NMR spectra were recorded on a Bruker AC 300 P (300 MHz ^{1}H, 75 MHz ^{13}C), on a Bruker DRX 500 P (500 MHz ^{1}H, 125 MHz ^{13}C), or on a Bruker AC 600-P (600 MHz ^{1}H, 151 MHz ^{13}C) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual proton-containing solvent as internal standard[22] ($CDCl_3$ at 7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), quin (quintet), br (broad), m (multiplet). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Mass spectra were recorded with an Agilent 5973N detector coupled with an Agilent 6890N GC (GC-MS, 70 eV) or else with a Bruker Esquire-LC (direct injection as a methanolic NH_4OAc solution, ESI). HRMS spectra were recorded on a Bruker Daltonics "Impact II" (ESI-TOF). Elemental analysis was performed on a Hekatech EA 3000.

Cycloheptanone tosylhydrazone (1c): A mixture of *p*-toluenesulfonyl hydrazide (4.78 g, 25.7 mmol), cyclopentanone (3.05 g, 27.2 mmol), and EtOH (35 mL) was stirred at reflux for 2 h and stored at −32 °C over night without stirring. The precipitate formed was collected by filtration, washed with EtOH (20 mL, cooled to 0 °C) and dried under vacuum to afford cycloheptanone tosylhydrazone (**1c**, 6.48 g, 90%) as a white solid. R_f = 0.37 (pentane/Et_2O, 1:1). m.p. 144–145 °C (Lit.: 144–146 °C).[23] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47–1.62 (m, 6 H), 1.62–1.73 (m, 2 H), 2.23–2.32 (m, 2 H), 2.36–2.49 (m, 5 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.38–7.78 (br. m, 1 H), 7.83–7.93 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.68 (q), 24.37 (t), 27.38 (t), 30.17 (t), 30.31 (t), 30.51 (t), 37.05 (t), 128.04 (d), 129.57 (d), 135.72 (s), 143.89 (s), 164.25 (s) ppm. IR (ATR): $\tilde{\nu}$ = 3235, 2917, 2852, 1629, 1594, 1447, 1384, 1337, 1325, 1290, 1164, 1092, 1028, 928, 803, 718, 662 cm^{-1}. ESI–MS (+25 V): *m*/*z* = 281.1 $[M+H]^+$. The spectra matched previously reported data.[24]

Shapiro reaction of tosylhydrazones 1a-c, representative procedure: To a mixture of cyclohexanone tosylhydrazone (**1a**, 267 mg, 1.00 mmol), pentane (1.4 mL), and TMEDA (1.4 mL) was added butyllithium (1.6 M in hexane, 2.50 mL, 4.00 mmol) over a period of 10 min at −50 °C. After stirring for 80 min at −50 °C and 3 h at room temperature, freshly distilled TMSCl (0.55 mL, 4.3 mmol) was added at 0 °C. After 1 h, the cooling bath was removed, and the reaction mixture was stirred for further 19 h at room temperature. The reaction mixture was poured into a stirred mixture of pentane (20 mL) and water (40 mL). The organic layer was washed with sat. aqueous $CuSO_4$ (20 mL), brine (20 mL) and dried over $MgSO_4$. Cautious removal of the solvent under reduced pressure and flash chromatography over silica gel (pentane) afforded 1-trimethylsilylcyclohexene (**2a**, 104 mg, 67%), which was used for the next step without further purification. Analytically pure material was obtained by distillation.

1-Trimethylsilylcyclohexene (**2a**): yield 67%, colorless liquid. R_f = 0.66 (pentane). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 1.60 (dt, *J* = 6.2, 3.3 Hz, 4 H), 1.98–2.08 (m, 4 H), 5.98 (tt, *J* = 3.5, 1.7 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = −2.07 (q), 22.61 (t), 23.11 (t), 26.63 (t), 26.90 (t), 135.67 (d), 138.85 (s) ppm. IR (ATR): ν = 2952, 2925, 2856, 1614, 1434, 1246, 1063, 938, 854, 826, 747, 719, 688 cm^{-1}. GC–MS: *m*/*z* (%) = 154 (16) $[M]^+$, 139 (68), 111 (6), 79 (48), 73 (100), 59 (40), 45 (12). The spectra matched previously reported data.[17,25]

1-Trimethylsilylcyclopentene (**2b**): yield 48%, colorless liquid. R_f = 0.66 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 1.81 (quin, *J* = 7.5 Hz, 2 H), 2.31–2.42 (m, 4 H), 5.87–6.07 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = −1.52 (q), 24.16 (t), 35.10 (t), 35.90 (t), 140.41 (d), 144.69 (s) ppm. IR (ATR): ν = 3032, 2955, 2845, 1738, 1593, 1398, 1249, 1039, 837, 752, 693 cm^{-1}. ESI–MS (+25 V): *m*/*z* = 163.5 $[M+Na]^+$. The spectra matched previously reported data.[25–27]

1-Trimethylsilylcycloheptene (**2c**): yield 66%, colorless liquid. R_f = 0.77 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 1.43 (ddt, *J* = 8.5, 5.7, 3.0 Hz, 4 H), 1.70–1.81 (m, 2 H), 2.14–2.24 (m, 4 H), 6.17 (t, *J* = 6.3 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = −2.00 (q), 27.01 (t), 27.63 (t), 30.45 (t), 30.55 (t), 33.26 (t), 141.44 (d), 145.92 (s) ppm. IR (ATR): ν = 2917, 2848, 1617, 1448, 1246, 1051, 928, 828, 745, 687 cm^{-1}. GC–MS: *m*/*z* (%) = 168 (19) $[M]^+$, 153 (57), 125 (27), 94 (36), 73 (100), 59 (39), 45 (15). The spectra matched previously reported data.[17,25]

2-Trimethylsilyl-2-norbornene (2d): A solution of norbornene (**6**, 1.34 g, 14.2 mmol) in THF (3 mL) was added to a solution of KO*t*Bu (805 mg, 7.18 mmol) in THF (11 mL) at −78 °C over a period of 15 min. Then butyllithium (1.6 M in hexane, 4.5 mL, 7.2 mmol) was added at the same temperature over 15 min, and the reaction mixture was stirred for 80 min at −45 °C. After addition of freshly distilled TMSCl (514 mg, 4.73 mmol) at −78 °C, the reaction mixture was warmed to room temperature and stirred for 21 h. Water (15 mL) was added at 0 °C, followed by extraction with Et_2O (3×15 mL). The organic layers were combined, dried over $MgSO_4$, concentrated under reduced pressure and purified by flash chromatography (pentane) to afford 2-trimethylsilyl-2-norbornene (**2d**, 495 mg, 63%) as a colorless liquid. R_f = 0.97 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 0.77–0.87 (m, 1 H), 0.89–0.98 (m, 1 H), 1.07–1.14 (m, 1 H), 1.22–1.29 (m, 1 H), 1.51–1.66 (m, 2 H), 2.81–2.90 (m, 1 H), 2.91–3.00 (m, 1 H), 6.28 (d, *J* = 2.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.42 (q), 24.79 (t), 24.84 (t), 43.34 (d), 44.64 (d), 48.93 (t), 145.20 (d), 148.98 (s) ppm. IR (ATR): ν = 3031, 2956, 2915, 2869, 1555, 1447, 1299, 1246, 1210, 1169, 1121, 1038, 850, 834, 817, 749 cm^{-1}. GC–MS: *m*/*z* (%) = 166 (83) $[M]^+$, 151 (90), 138 (100), 123 (100), 95 (78), 83 (86), 73 (100), 59 (52), 45 (45). The spectra matched previously reported data.[19]

α-Trimethylsilylstyrene (2e): To a solution of α-styrylmagnesium bromide, prepared from magnesium turnings (416 mg, 17.1 mmol) and α-bromostyrene (**7**, 3.12 g, 17.0 mmol) in THF (30 mL), was added freshly distilled TMSCl (1.85 g, 17.0 mmol), and the mixture was stirred at reflux for 18 h. The reaction was quenched by addition of sat. aqueous NH_4Cl

(20 mL). After extraction with pentane (3×30 mL), the combined organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography over silica gel (pentane) to afford α-trimethylsilylstyrene (**2e**, 2.05 g, 68%) as a colorless liquid. R_f = 0.64 (pentane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 9 H), 5.61 (d, J = 2.8 Hz, 1 H), 5.82 (d, J = 3.0 Hz, 1 H), 7.14–7.35 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.75 (q), 126.36 (d), 126.85 (d), 127.30 (t), 128.25 (d), 144.93 (s), 153.65 (s) ppm. IR (ATR): ν = 3056, 3025, 2956, 2893, 1944, 1871, 1598, 1490, 1405, 1248, 1071, 1028, 931, 855, 833, 775, 757, 697 cm^{-1}. GC–MS: *m*/*z* (%) = 176 (81) $[M]^+$, 161 (100) $[M–Me]^+$, 145 (35), 135 (95), 103 (37) $[M–TMS]^+$, 77 (35), 73 (75) $[TMS]^+$. The spectra matched previously reported data.[29]

***cis* Dihydroxylation of vinylsilanes 2a and 2e, representative procedure:** A mixture of alkene **2a** (204 mg, 1.32 mmol), acetone (2.3 mL), *t*BuOH (0.13 mL), water (0.23 mL), OsO_4 (0.197 M in toluene, 0.05 mL, 0.01 mmol), and NMO·H_2O (259 mg, 1.91 mmol) was stirred at 45 °C for 26 h. After cooling to room temperature, Et_2O (5 mL) and water (5 mL) were added, and the aqueous layer was extracted with Et_2O (5×5 mL). The combined organic layers were washed with aqueous 2 N HCl (20 mL), aqueous sat. $NaHCO_3$ (20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Flash chromatography of the residue (*i*hexane/ethyl acetate, 3:1) afforded the *cis* diol **3a** (196 mg, 79%) as a white solid.

1-(Trimethylsilyl)cyclohexane-1,2-*cis*-diol (**3a**): yield 79%, R_f = 0.48 (pentane/Et_2O, 1:1). m.p. 85–86 °C (CH_2Cl_2) (Lit.: 85–88 °C).[16] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 9 H), 1.13–1.90 (m, 10 H), 3.60 (dd, J = 9.5, 5.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.03 (q), 19.08 (t), 24.21 (t), 29.73 (t), 32.10 (t), 68.79 (s), 73.46 (d) ppm. IR (ATR): ν = 3414, 3289, 2931, 2858, 1445, 1390, 1243, 1185, 1057, 996, 954, 922, 833, 817, 745, 686 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 171.0 $[M–OH]^+$, 211.1 $[M+Na]^+$. $C_9H_{20}O_2Si$ (188.34): calcd. C 57.40, H 10.70; found C 57.25, H 10.82. ^{1}H NMR analysis matched previously reported data,[16] while ^{13}C NMR analysis showed significant differences to the reported data.[21]

1-Phenyl-1-(trimethylsilyl)ethane-1,2-diol (**3e**): The reaction was carried out at room temperature. Yield 23%, colorless oil. R_f = 0.33 (pentane/Et_2O, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 9 H), 1.99 (br. s, 1 H), 2.73 (br. s, 1 H), 3.93 (d, J = 11.7 Hz, 1 H), 4.15 (d, J = 11.5 Hz, 1 H), 7.15–7.25 (m, 1 H), 7.26–7.40 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.82 (q), 67.44 (t), 73.89 (s), 125.03 (d), 125.89 (d), 128.43 (d), 143.43 (s) ppm. IR (ATR): ν = 3407, 2955, 2896, 1691, 1600, 1445, 1246, 1096, 1056, 1028, 830, 755, 698 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 193.1 $[M–OH]^+$, 228.1 $[M+NH_4]^+$, 443.0 $[2M+Na]^+$. HRMS: calcd. for $C_{11}H_{18}NaO_2Si^+$ $[M+Na]^+$ 233.0968; found 233.09683.

***cis* Dihydroxylation of vinylsilanes 2b-d, representative procedure:** A mixture of alkene **2b** (561 mg, 4.00 mmol), *t*BuOH (8 mL), water (2.4 mL), pyridine (0.32 mL, 4.0 mmol), OsO_4 (0.197 M in toluene, 0.41 mL, 0.081 mmol), and NMO·H_2O (755 mg, 5.58 mmol) was stirred at 100 °C for 24 h. After cooling to room temperature, $Na_2S_2O_5$ (10 g) in buffer pH 7 (10 mL) was added, and stirring was continued for 3 h. The aqueous layer was extracted with Et_2O (3×15 mL), all organic layers were combined and washed with brine (40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane/Et_2O, 1:1) to afford the *cis* diol **3b** (424 mg, 61%) as a white solid.

1-(Trimethylsilyl)cyclopentane-1,2-*cis*-diol (**3b**): yield 61%, white solid. R_f = 0.26 (pentane/Et_2O, 1:1). m.p. 61–62 °C (CH_2Cl_2) (Lit.: 58–60 °C).[28] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 1.37–1.54 (m, 1 H), 1.60–1.78 (m, 3 H), 1.78–1.96 (m, 2 H), 2.17 (br. s, 2 H), 4.01 (t, J = 6.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.89 (q), 20.58 (t), 32.57 (t), 34.57 (t), 73.94 (s), 76.62 (d) ppm. IR (ATR): ν = 3444, 3309, 2961, 2932, 1454, 1423, 1329, 1309, 1246, 1115, 1083, 1030, 988, 830, 749, 688 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 157.0 $[M–OH]^+$, 192.0 $[M+NH_4]^+$, 197.1 $[M+Na]^+$. HRMS: calcd. for $C_8H_{18}NaO_2Si^+$ $[M+Na]^+$ 197.0968; found 197.0972. ^{1}H NMR analysis matched previously reported data,[28] while ^{13}C analysis showed significant differences to the reported data.[21]

1-(Trimethylsilyl)cycloheptane-1,2-*cis*-diol (**3c**): yield 66%, white solid. R_f = 0.43 (pentane/Et_2O, 1:1). m.p. 78–80 °C (CH_2Cl_2) (Lit.: 87–89 °C).[28] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (d, J = 0.4 Hz, 9 H), 1.23–2.14 (m, 12 H), 3.75 (dd, J = 9.7, 1.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.66 (q), 20.63 (t), 23.75 (t), 28.51 (t), 31.63 (t), 34.46 (t), 70.46 (s), 76.19 (d) ppm. IR (ATR): ν = 3438, 3357, 2930, 2856, 1447, 1329, 1244, 1047, 1013, 949, 832, 742, 707, 684 cm^{-1}. ESI–MS (+25 V): *m*/*z* = 225.1 $[M+Na]^+$. HRMS: calcd. for $C_{10}H_{22}NaO_2Si^+$ $[M+Na]^+$ 225.1281; found 225.1283. ^{1}H NMR analysis matched previously reported data,[28] while ^{13}C analysis showed significant differences to the reported data.[21]

exo-2-Trimethylsilyl-norbornane-2,3-*cis*-diol (**3d**): yield 50%, white solid. R_f = 0.38 (pentane/Et_2O, 1:1). m.p. 43–45 °C (CH_2Cl_2) (Lit.: 48–50 °C).[28] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 9 H), 0.98–1.05 (m, 1 H), 1.12 (dq, J = 10.2, 1.5 Hz, 1 H), 1.24–1.32 (m, 1 H), 1.39 (tt, J = 12.8, 4.9 Hz, 1 H), 1.46–1.54 (m, 1 H), 1.92 (ddt, J = 10.3, 3.9, 2.0 Hz, 1 H), 2.12–2.16 (m, 1 H), 2.16–2.20 (m, 1 H), 3.56–3.72 (m, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –2.51 (q), 23.91 (t), 24.77 (t), 33.72 (t), 44.69 (d), 46.86 (d), 73.79 (s), 76.74 (d) ppm. IR (ATR): ν = 3379, 3228, 2947, 2875, 1326, 1246, 1094, 1008, 975, 940, 881, 830, 747, 683 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 218.2 $[M+NH_4]^+$, 401.3 $[2M+H]^+$. $C_{10}H_{20}O_2Si$ (200.35): calcd. C 59.95, H 10.06; found C 60.06, H 10.13. ^{13}C NMR analysis showed significant differences to the reported data.[21] The relative configuration of **3d** was determined using 2D NMR experiments.

Diol cleavage of 1,2-dihydroxysilanes 3a-c and 3e, representative procedure: A mixture of *cis* diol **3a** (43 mg, 0.28 mmol), $NaIO_4$ (97 mg, 0.54 mmol), EtOH (18 mL), and water (4 mL) was stirred at room temperature for 23 h. After addition of CH_2Cl_2 (20 mL) and water (20 mL), the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$, and the solvents were removed under reduced pressure to afford acylsilane **4a** (41 mg, 96%).

1-(Trimethylsilyl)hexane-1,6-dione (**4a**): yield 96%, pale brown liquid. R_f = 0.65 (*i*hexane/EtOAc, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 1.49–1.65 (m, 4 H), 2.44 (td, J = 6.9, 1.6 Hz, 2 H), 2.56–2.73 (m, 2 H), 9.76 (t, J =1.7 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –3.07 (q), 21.63 (t), 21.85 (t), 43.93 (t), 48.05 (t), 202.46 (d), 247.81 (s) ppm. IR (ATR): $\tilde{\nu}$ = 2949, 2869, 2721, 2056, 1722, 1641, 1248, 840, 752 cm^{-1}. GC–MS: *m*/*z* (%) = 186 (4) $[M]^+$, 171 (18), 143 (21), 129 (31), 115 (10), 101 (16), 75 (84), 73 (100), 45 (37). The spectra matched previously reported data.[18]

1-(Trimethylsilyl)pentane-1,5-dione (**4b**): yield 76%, colorless liquid. R_f = 0.36 (pentane/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 9 H), 1.83 (quin, J = 7.0 Hz, 2 H), 2.42 (td, J = 7.1, 1.4 Hz, 2 H), 2.65 (t, J = 7.0 Hz, 2 H), 9.72 (t, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.21 (q), 14.62 (t), 43.20 (t), 47.05 (t), 202.18 (d), 247.33 (s) ppm. IR (ATR): ν = 2957, 2899, 1719, 1640, 1249, 838, 752 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 173.2 $[M+H]^+$. The spectra matched previously reported data.[18]

1-(Trimethylsilyl)heptane-1,7-dione (**4c**): yield 98%, colorless liquid. R_f = 0.48 (pentane/Et_2O, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.19 (s, 9 H), 1.22–1.35 (m, 2 H), 1.46–1.70 (m, 4 H), 2.43 (td, J = 7.3, 1.8 Hz, 2 H), 2.60 (t, J = 7.2 Hz, 2 H), 9.76 (t, J = 1.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.10 (q), 21.81 (t), 21.99 (t), 28.87 (t), 43.77 (t), 48.13 (t), 202.64 (d), 248.19 (s) ppm. IR (ATR): ν = 2937, 2858, 2718, 1722, 1641,

1457, 1406, 1249, 841, 752 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 201.6 $[M+H]^+$, 2018 $[M+NH_4]^+$, 423.2 $[2M+Na]^+$. HRMS: calcd. for $C_{10}H_{21}O_2Si^+$ $[M+H]^+$ 201.1305; found 201.1304.

Phenyl(trimethylsilyl)methanone (**4e**): yield 70% after flash chromatography (*i*hexane:ethyl acetate, 20:1, R_f = 0.39), yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.38 (s, 9 H), 7.41–7.59 (m, 3 H), 7.73–7.93 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.22 (q), 127.62 (d), 128.79 (d), 132.83 (d), 141.49 (s), 235.93 (s) ppm. IR (ATR): ν = 2957, 2924, 1612, 1591, 1447, 1251, 1209, 839, 780, 693 cm^{-1}. GC–MS: *m*/*z* (%) = 178 (11) $[M]^+$, 177 (18), 163 (16), 135 (30), 105 (14) $[PhCO]^+$, 77 (32) $[Ph]^+$, 73 (100) $[TMS]^+$, 51 (17), 45 (21), 43 (13). The spectra matched previously reported data.[22]

Diol cleavage of 1,2-dihydroxysilane 3d: A mixture of *cis* diol **3d** (12.3 mg, 614 µmol), $NaIO_4$ (26.5 mg, 124 µmol), EtOH (4.6 mL), and water (1.2 mL) was stirred at room temperature for 23 h under exclusion of light. After addition of CH_2Cl_2 (20 mL) and water (20 mL), the aqueous layer was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$, and the solvents were removed under reduced pressure using a rotary evaporator (temperature of water bath 25 °C). The residue was purified by flash chromatography (pentane/Et_2O 2:1) to afford *cis*-3-((trimethylsilyl)carbonyl)cyclopentane-1-carbaldehyde (**4d**; 11.0 mg, 90%) as a colorless liquid. Throughout the whole process of aqueous workup and flash chromatography, exposure to light was minimized. R_f = 0.39 (pentane/Et_2O, 3:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 1.77–1.96 (m, 5 H), 2.15 (dt, *J* = 13.4, 7.3 Hz, 1 H), 2.64–2.82 (m, 1 H), 3.26–3.43 (m, 1 H), 9.59 (d, *J* = 2.6 Hz, 1 H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = –2.60 (q), 26.23 (t), 26.81 (t), 27.01 (t), 51.64 (d), 55.58 (d), 203.56 (d), 247.20 (s) ppm. IR (ATR): ν = 2958, 2899, 2866, 1720, 1635, 1451, 1409, 1249, 738, 754, 699 cm^{-1}. ESI–MS (+10 V): *m*/*z* = 199.4 $[M+H]^+$, 414.2 $[2M+NH_4]^+$. HRMS: calcd. for $C_{10}H_{19}O_2Si^+$ $[M+H]^+$ 199.1149; found 199.1143.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (ME 776/20-2).

Keywords: acylsilanes • diol cleavage • 1,2-dihydroxysilanes • oxidation

[1] H.-J. Zhang, D. L. Priebbenow, C. Bolm, *Chem. Soc. Rev.* **2013**, *42*, 8540–8571.

[2] A. F. Patrocínio, P. J. S. Moran, *J. Braz. Chem. Soc.* **2001**, *12*, 7–31.

[3] B. F. Bonini, M. Comes-Franchini, M. Fochi, G. Mazzanti, A. Ricci, *J. Organomet. Chem.* **1998**, *567*, 181–189.

[4] C. Nájera, M. Yus, *Org. Prep. Proced. Int.* **1995**, *27*, 383–456.

[5] P. F. Cirillo, J. S. Panek, *Org. Prep. Proced. Int.* **1992**, *24*, 553–582.

[6] P. C. B. Page, S. S. Klair, S. Rosenthal, *Chem. Soc. Rev.* **1990**, *19*, 147–195.

[7] A. Ricci, A. Degl'Innocenti, *Synthesis* **1989**, 647–660.

[8] L. Capaldo, R. Riccardi, D. Ravelli, M. Fagnoni, *ACS Catal.* **2018**, *8*, 304–309.

[9] K. Ishida, F. Tobita, H. Kusama, *Chem. Eur. J.* **2018**, *24*, 543–546.

[10] W. Cao, D. Tan, R. Lee, C.-H. Tan, *J. Am. Chem. Soc.* **2018**, *140*, 1952–1955.

[11] M. Honda, T. Takatera, R. Ui, K.-K. Kunimoto, M. Segi, *Tetrahedron Lett.* **2017**, *58*, 864–869.

[12] Y. Wang, P. Metz, *Org. Lett.* **2018**, *20*, 3418–3421.

[13] Y. Wang, V. Rogachev, M. Wolter, M. Gruner, A. Jäger, P. Metz, *Eur. J. Org. Chem.* **2014**, 4083–4088.

[14] H. von Wachenfeldt, D. Strand, *J. Org. Chem.* **2013**, *78*, 12268–12273.

[15] P. F. Hudrlik, A. M. Hudrlik, A. K. Kulkarni, *J. Am. Chem. Soc.* **1985**, *107*, 4260–4264.

[16] M. J. Prior, G. H. Whitham, *J. Chem. Soc. Perkin Trans. 1* **1986**, 683–688.

[17] M. G. Banwell, M. Corbett, J. Gulbis, M. F. Mackay, M. E. Reum, *J. Chem. Soc. Perkin Trans. 1* **1993**, 945–963.

[18] T. Chuang, J. Fang, W. Jiaang, Y. Tsai, *J. Org. Chem.* **1996**, *61*, 1794–1805.

[19] P. Mayo, T. Hecnar, W. Tam, *Tetrahedron* **2001**, *57*, 5931–5941.

[20] P. C. B. Page, M. J. McKenzie in *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations Vol. 4: Compounds of Groups 15 (As, Sb, Bi) and Silicon Compounds* (Eds.: H. Adolfsson, D.J. Ager, J.M. Aizpurua, T. Aoyama, K.M. Baines), Georg Thieme Verlag, **2014**, p. 513.

[21] V. Tyagi, A. K. Gupta, *Synth. Commun.* **2013**, *43*, 1915–1919.

[22] F. Mäsing, H. Nüsse, J. Klingauf, A. Studer, *Org. Lett.* **2018**, *20*, 752–755.

[23] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

[24] L. Friedman, H. Shechter, *J. Am. Chem. Soc.* **1961**, *83*, 3159–3160.

[25] R. R. Merchant, D. M. Allwood, D. C. Blakemore, S. V. Ley, *J. Org. Chem.* **2014**, *79*, 8800–8811.

[26] G. Nagendrappa, *Synthesis* **1980**, 704–706.

[27] L. A. Paquette, W. E. Fristad, D. S. Dime, T. R. Bailey, *J. Org. Chem.* **1980**, *45*, 3017–3028.

[28] G. McGaffin, B. Grimm, U. Heinecke, H. Michaelsen, A. de Meijere, R. Walsh, *Eur. J. Org. Chem.* **2001**, 3559–3573.

[29] S.-B. Kim, C.-H. Lee, C.-H. Jun, *Chem. Commun.* **2018**, *54*, 9961–9964.

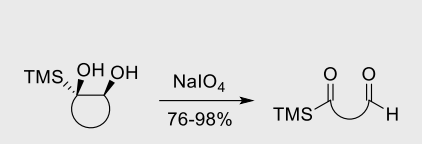
[30] M. N. Mallya, G. Nagendrappa, *Synthesis* **1999**, 37–39.

10.1002/ejoc.201900726

WILEY-VCH

Entry for the Table of Contents

FULL PAPER



Acylsilanes

*Patrick Zimdars, Kristin Böhlig, and Peter Metz**

Page No. – Page No.
Preparation of Functionalized Acylsilanes via Diol Cleavage of Cyclic 1,2-Dihydroxysilanes

We report a study on diol cleavage of cyclic 1,2-dihydroxysilanes for the preparation of functionalized acylsilanes. Sodium periodate turned out to be an efficient reagent for this transformation, resulting in good to excellent yields. The method is characterized by mild reaction conditions, and sometimes simple aqueous workup of the reaction mixture was sufficient to obtain the acylsilanes in high purity. An acyclic 1,2-dihydroxysilane was readily cleaved as well.