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Allylation Reactions of Acylsilanes as Synthetic Equivalents of Aldehydes. Application to a Stereocontrolled Synthesis of (1S,2S,5S)-(10S)-and-(10R)-Allyl Myrtanol.

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Abstract: The allylation of acylsilanes with tetraallyltin in the presence of catalytic amounts of $Sc(OTf)_3$ proceeded smoothly to afford the silylated homoallylic alcohols in good yields. Subsequent protiodesilylation gave the formal adducts of the corresponding aldehydes. The homochiral acylsilane **11** gave a reversal of asymmetric induction in the $Sc(OTf)_3$ catalyzed allylation and in the Sakurai reaction.

Keywords: Acylsilanes; allylation; homoallylic alcohols; myrtanol.

Homoallylic alcohols are versatile intermediates in the synthesis of bifunctionalized molecules, due to the presence of both the alcoholic function and the carbon-carbon double bond [1,2]. The most widely used approach to these compounds is the reaction of carbonyl derivatives, particularly aldehydes, with allylmetallic compounds [1]. Among the carbonyl derivatives, acylsilanes are very interesting substrates [3,4] which are known to be the synthetic equivalents of aldehydes due to the possibility of a stereospecific protiodesilylation of the reaction products with fluoride ion. This potential has been exploited by us [5] in the case of chemically and configurationally unstable substrates such as α-amino aldehydes [6]. Moreover, in the case of chiral acylsilanes the degree of stereoselectivity in the addition of nucleophiles is higher than that reached with the corresponding aldehydes, due to the bulkiness of the silyl group [6,7]. Recently Kobayashi introduced the use of $Sc(OTf)_3$ as an effective catalyst in many reactions [8] including the allylation of aldehydes and ketones. This prompted us to use tetraallyltin and catalytic amounts of $Sc(OTf)_3$ for the allylation of acylsilanes **1** leading to the silylated homoallylic alcohols **2**.

The allylation reaction [9] proceeded smoothly and in reasonable times (2-5 h).The results are reported in Table 1. The yields are very good for aromatic **1a** [10] aliphatic **1b** [10], **1g** [11] and cycloalkyl acylsilanes **1c**, **1d** [12]. The acylsilane **1e**, obtained [13] together with the acylsilane **1f** by reaction of glutaryl dichloride with bis(dimethylphenylsilyl)lithium cyanocuprate [14], gave the diallylated adduct **2e** in good yield. It is worthy of note that also the acylsilane **1f**, containing a carboxylic function that is incompatibile with the common Lewis acids, could be successfully employed [15]. The fluorinated acylsilane **1i** [16] was obtained with the same procedure as **1h** [17]. Both products **1h** and **1i** gave the homoallylic alcohols **2h** and **2i** in excellent yields. The protiodesilylation of compounds **2** was performed with 1 equiv. of tetrabutylammonium fluoride (TBAF) in THF at room temperature, to give the homoallylic alcohols **3** in moderate to good yields (Table 1). Problems were encountered only in the protiodesilylation of **2g** where a bromine-fluorine exchange occurred, and in the protiodesilylation of the fluorinated derivatives **2h** and **2i**, which produced a complex mixture of unidentified products.

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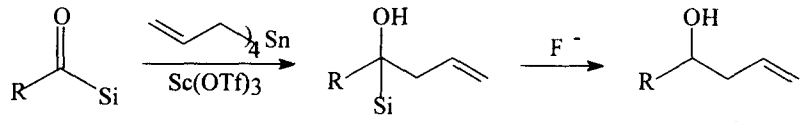
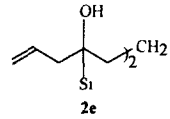
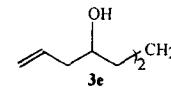
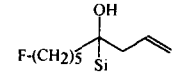


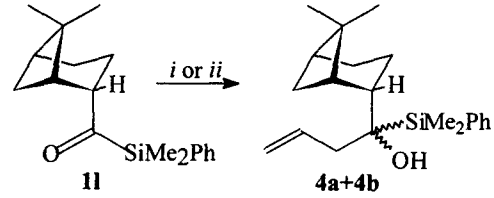
1 2 3

Table 1. Allylation of acylsilanes **1** and protiodesilylation of alcohols **2**.

Acylsilane	R	Si	Product	Yield %	Product	Yield % [ref]
1a	Ph	$SiMe_3$	**2a**	75	**3a**	95 [18]
1b	t-Bu	$SiMe_3$	**2b**	70	**3b**	88 [18]
1c	c-C_3H_5	$SiMe_2Ph$	**2c**	82	**3c**	55[19]*
1d	c-C_6H_{11}	$SiMe_2Ph$	**2d**	88	**3d**	92 [20]
1e	$(CH_2)_3COSi$	$SiMe_2Ph$	 **2e**	60	 **3e**	50 [21]
1f	$(CH_2)_3COOH$	$SiMe_2Ph$	**2f**	93	**3f**	50 [22]
1g	$(CH_2)_5Br$	$SiMe_3$	**2g**	72		60
1h	CF_3	$SiPh_3$	**2h**	76	-	-
1i	CF_3	$SiMe_2Ph$	**2i**	89	-	-

*The lower yield of **3c** was due to the volatility of this compound

This synthetic protocol, allylation-protiodesilylation, has been found particularly useful in the case of the acylsilane **1l**, the synthetic equivalent of myrtanal, which has been reported to be rather unstable at room temperature [23]. The allylation of the homochiral acylsilane **1l** with 0.25 equiv. of tetraallyltin in the presence of 10% mol of $Sc(OTf)_3$ (Scheme 1, *i*) was performed at temperatures ranging from 0 to 30°C. The de values were determined by integration of the signals (^1H NMR) of the methyl of the major isomer **4a** at 0.602 and of the minor isomer **4b** at 0.665. The maximum de value (69%) was obtained at 10 °C (**4a:4b**=84.5:15.5) with a yield of 53%. The reaction was also performed under Sakurai conditions (Scheme 1, *ii*:allyltrimethylsilane in the presence of 1 equiv. of $TiCl_4$ at -70°C). In this case an opposite sense of asymmetric induction was observed and a higher de value (**4a:4b**=10:90) with a 51% yield.



1l **4a+4b**

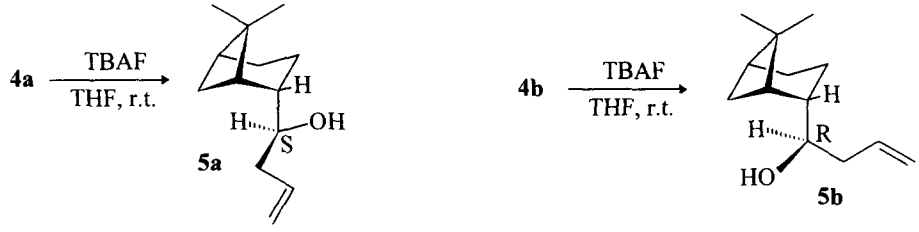
i) $(CH_2{=}CHCH_2)_4Sn$ (0.25 eq.); $Sc(OTf)_3$ (10 % mol);CH_2Cl_2;10°C.

ii) $CH_2{=}CHCH_2SiMe_3$ (2 eq.); $TiCl_4$ (1 eq.); CH_2Cl_2; -70°C.

Scheme 1

The two diastereoisomers **4a** and **4b** [24] were separated by chromatography, but the determination of the configuration of the newly formed carbinol center was unsuccessful. In fact we were unable to form the

Mosher's esters of these very hindered tertiary alcohols, and a n.O.e. study did not provide the necessary resolution. Subsequent protiodesilylation of the two pure epimers **4a** and **4b** occurred stereospecifically giving only product **5a** from **4a**, and **5b** from **4b** (yield 55% and 76% respectively), as indicated by ^{1}H NMR analysis (Scheme 2). Products **5a** and **5b** [25] are the formal adducts of (1S,2S,5S)-myrtanal.



Scheme 2

The absolute stereochemistry of the newly formed stereogenic center in **5a** and **5b** was established by ^{1}H NMR analysis of the corresponding esters of the Mosher's acids (R)-MTPA and (S)-MTPA. From the differences in chemical shifts the S and R configurations were assigned [26] to the carbinol center in **5a** and **5b** respectively. As the fluoride-catalyzed protiodesilylation of α-hydroxysilanes derived from acylsilanes bearing an α–chiral carbon is reported [7] to proceed with complete retention of configuration, we tentatively assign the R and S configuration at the carbinol center of **4a** and **4b**, a consequence of an attack on the Si and Re face of the acylsilane, respectively.

In conclusion the allylation of acylsilanes with tetraallyltin and $Sc(OTf)_3$ is a very easy process if compared with other allylation methods [27]. Subsequent protiodesilylation is a stereospecific process that gives the adducts of the corresponding aldehydes. For the chiral acylsilane **1l**, the sense of asymmetric induction is the opposite in the $Sc(OTf)_3$ catalyzed allylation and in the Sakurai reaction.

Acknowledgements
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References and Notes:

[1] Hoffmann RW. Angew. Chem. Int. Ed. Engl. 1982;21:555-566.
[2] Yamamoto Y. Acc. Chem. Res. 1987;20:243-249.
[3] Ricci A, Degl'Innocenti A. Synthesis. 1989:647-660
[4] Bulman Page PC, Klair SS, Rosenthal S. Chem. Soc. Rev. 1990;19:147-195.
[5] Bonini BF, Comes Franchini M, Mazzanti G, Ricci A, Sala M. J. Org. Chem. 1996;61:7242-7243.
[6] Jurczak J, Golebiowski A. Chem. Rev. 1989;89:149 and references therein.
[7] Nakada M, Urano Y, Kobayashi S, Ohno M. J. Am. Chem. Soc. 1988;110:4826-4827.
[8] Kobayashi S. Synlett. 1994:689-701.
[9] To a suspension of 0.1 mmol of $Sc(OTf)_3$ in CH_2Cl_2 (5ml) purified on a column of alumina, tetraallyltin (0.25 mmol) and the acylsilane (1 mmol) dissolved in CH_2Cl_2 (2ml) were added at -20°C. The mixture was allowed to warm at room temperature and stirred until the starting acylsilane had disappeared (TLC; light petroleum:ethyl ether 20:1) The mixture was then quenched with water and extracted with diethyl ether.The organic layer was dried and concentrated to give the homoallylic alcohols **2**.
[10] Corey EJ, Seebach D, Freedmann R. J. Am. Chem. Soc. 1967;89:434-436.
[11] Bonini BF, Comes Franchini M, Fochi M, Mazzanti G, Ricci A. Tetrahedron. 1997;52:7897-7910.
[12] Bonini BF, Busi F, De-Laet RC, Mazzanti G, Thuring JWJF, Zani P, Zwanenburg B. J. Chem. Soc. Perkin Trans. 1 1993:1011-1018.
[13] Unpublished results of the group.
[14] Fleming I, Newton TW, Roessler F. J. Chem. Soc. Perkin Trans.1. 1991:2527-2532.
[15] **2f**: colourless liquid; I.R. (CCl_4) ν_{max}, cm^{-1}: 3530, 1723; ^{1}H-NMR (300 MHz, $CDCl_3$) δ, ppm: 0.358 (3H, s), 0.364 (3H, s), 1.5-1.65 (5H, m), 2.28 (4H, m), 5.0-5.1 (2H, m), 5.68-5.82 (1H, m), 7.3-7.35 (3H, m), 7 5-7.6 (3H, m); ^{13}C-NMR (50.27

MHz, $CDCl_3$) δ, ppm: -4.61, -4.51, 18.77, 34.10, 36.79, 41.52, 67.94, 118.85, 127.81, 129.31, 133.38, 134.55, 136.42, 179.32; MS (m/z): 293 (M^+ +1), 291 (M^+-1), 275 (M^+-OH).

[16] **1i:** yellow liquid; yield 58%; b.p. 60-65°C (1mmHg); I.R. (CCl_4) ν_{max}, cm^{-1}: 1690; ^{1}H-NMR (300 MHz, $CDCl_3$) δ, ppm: 0.34 (6H, s) 7.00-7.40 (5H, m); ^{13}C-NMR (75 46 MHz, C_6D_6) δ, ppm:-5, 111.28, 115.22, 119.16, 123.09 (q, J = 297 Hz, CF_3), 129.22, 131.50, 135.02, 131.98, 221 83, 222.28, 222.75, 223.21 (q, J = 34.7 Hz, CO); MS (m/z): 232 (M^+) 135 ($SiMe_2Ph$), 99 (CF_3CO), 69 (CF_3).

[17] Jin F, Jiang B, Xu Y. Tetrahedron Lett. 1992;33:1221-1224.

[18] Hoffmann RW, Herold T. Chem. Ber. 1981;114:375-383.

[19] Kirmse W, Rode K. Chem Ber. 1987:839-846.

[20] Davis AP, Jaspars M. J. Chem. Soc., Perkin Trans.1. 1992:2111-2118.

[21] Einhorn C, Luche JL. J. Organomet. Chem. 1987;322:177-183.

[22] Utaka M, Kuriki H, Sakai T, Takeda A. Chem. Lett. 1983:911-912.

[23] Peterson PE, Grant G. J. Org. Chem. 1991;56:16-20.

[24] **4a**: colourless liquid; $[\alpha]_D$ = -1.24 (C = 0.34 g/dL cyclohexane); I.R. (neat) ν_{max}, cm^{-1}: 3500, 1430, 1260, 1110; ^{1}H-NMR (300 MHz,) δ, ppm: 0.39 (3H, s), 0.40 (3H, s), 0.60 (3H, s), 1.15 (3H, s), 1.25 (1H, brs), 1.18-1.60 (3H, m), 1.65-1.75 (3H, m), 1.9 (1H, t, J = 5 14 Hz), 2.0-2.10 (1H, m) 2.20-2.30 (2H, m), 2.41-2.50 (1H, dd, J_1 = 7.06 Hz, J_2 = 7.9 Hz), 5.0-5.12 (2H, m), 5.75-5.90 (1H, m), 7.30-7.42 (3H, m), 7.55-7.65 (2H, m); ^{13}C-NMR (75.46 MHz) δ, ppm: -2.69, -2.51, 16.44, 19.70, 24.26, 24.91, 26.83, 29.89, 39.78, 39.86, 41.54 41.60, 71.93, 118.55, 127.56, 128.91, 134.25, 134.69, 138.2; MS (m/z): 328 (M^+), **4b**: colourless liquid; $[\alpha]_D$ = -11.7 ± (C = 1.23 g/dL cyclohexane); I.R. (neat) ν_{max}, cm^{-1}: 3500, 1430, 1260, 1110; ^{1}H-NMR (300 MHz) δ, ppm: 0.409 (3H, s), 0.415 (3H, s), 0.66 (3H, s), 1.19 (3H, s), 1.30 (1H, brs), 1.32-1.60 (3H, m), 1.70-1.80 (3H, m), 2.0-2.15 (2H, m), 2.20-2.32 (2H, m), 2.45-2.55 (1H, m), 5.00-5.12 (2H, m), 5.70-5.90 (1H, m), 7.30-7.45 (3H, m), 7.55-7.65 (2H, m); ^{13}C-NMR (75.46 MHz) δ, ppm: -3.04, -2.79 , 16.29, 19.83, 24.32, 24.77, 26.79, 29.85, 39.31, 39.86, 41.03, 41.57, 71.98, 118.29, 127.55, 128.92, 134.67, 134.93, 138.06; MS (m/z): 328 (M^+).

[25] **5a**; colourless liquid; $[\alpha]_D$ = -21.6 (C = 1.06 g/dL CH_2Cl_2); I.R. (CCl_4) ν_{max}, cm^{-1}: 3600; ^{1}H-NMR (300 MHz,) δ, ppm: 0.79 (3H, s), 1.19 (3H, s), 1.10-1.35 (2H, m), 1.47-1.54 (1H, m), 1.68-1.95 (4H, m), 1.98-2.08 (2H, m), 2.12 (1H, t, J = 5.9 Hz), 2.30-2.40 (1H, m), 3.33 (1H, 3d), 5.06-5.16 (2H, m), 5.75-5.90 (1H, m); ^{13}C-NMR (75.46 MHz) δ, ppm: 18.24, 20.12, 23.23, 24.25, 26.74, 38.98, 39.24, 40.47, 40.59, 41.47, 72.87, 118.24, 135.23; MS (m/z): 194 (M^+), 193 (M^+-1), 179 (M^+-CH_3), 166 (M^+-CO). **5b**: $[\alpha]_D$ = -10.5 ± 0.5 (C = 0.975 g/dL CH_2Cl_2); I.R. (CCl_4) ν_{max}, cm^{-1}: 3600; ^{1}H-NMR (300 MHz,) δ, ppm: 0.79 (3H, s), 1.18 (3H, s), 1.43 (1H, d, J = 10 Hz), 1.52 (1H, bs) 1.58-1.62 (2H, m), 1.73-1.82 (4H, m), 1.90-1.98 (1H, m,), 2.0-2.1 (2H, m), 2.26-2.36 (1H, m), 3.47 (1H, 4d), 5.05-5.15 (2H, m), 5.7-5.85 (1H, m); ^{13}C-NMR (75.46 MHz) δ, ppm: 17.05, 20.15, 23.97, 24.09, 26.73, 30.03, 39.20, 40.05, 40.42, 43.52, 74.97, 117.95, 135.41; MS (m/z): 194 (M^+), 193 (M^+-1), 179 (M^+-CH_3), 166 (M^+-CO).

[26] Dale JA, Mosher HS. J. Am. Chem. Soc. 1973;95:512-519.

[27] Buynak JD, Geng B, Uang S, Strickland JB. Tetrahedron Lett. 1994;35:985-988.