Formylation of Allylsilanes: A Synthesis of β,γ-Unsaturated Aldehyde Acetals

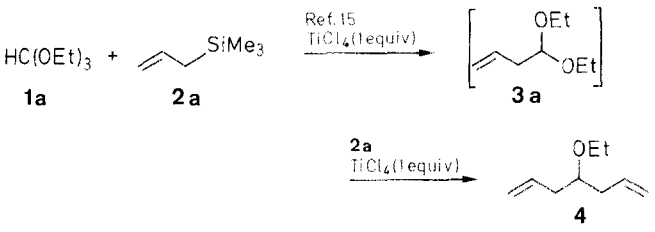
Anton Cambanis, Englbert Bäuml, Herbert Mayr*

Institut für Chemie der Medizinischen Universität zu Lübeck, Ratzeburger Allee 160, D-2400 Lübeck 1, Federal Republic of Germany

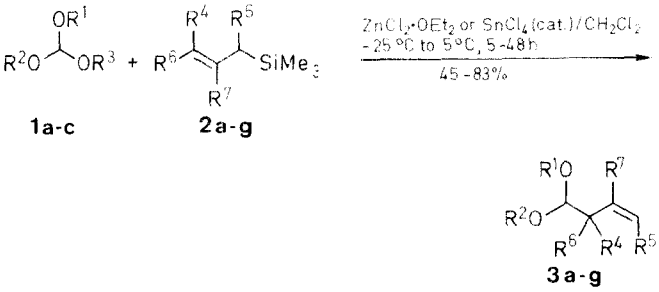
3-Alkenal acetals are synthesized from allylsilanes and orthoformates in the presence of Lewis acids.

Orthoformates have frequently been used for the formylation[1-3] of electron-rich π-systems, e.g., enol ethers and activated aromatic and heteroaromatic compounds.[4-8] Since, on the other hand, allylsilanes are widely used allyl anion equivalents,[9-14] it was surprising to us that a synthetic access to β,γ-unsaturated aldehyde acetals based on the combination of orthoformates and allylsilanes has not been established. Only in two special cases, has the 1:1 reaction between allylsilanes and orthoesters been observed.[23,24]

Hosomi, Endo, and Sakurai investigated the reaction of allyltrimethylsilane **(2a)** with triethyl orthoformate **(1a)** and observed the formation of the bisallylated compound **4** instead of the 3-butenal acetal **3a**.[15] It was concluded that "the reaction of allylsilane with the resulting acetal **(3a)** is apparently faster than the monoallylation of the orthoformate."



This observation is in agreement with the results of model studies,[16] which resulted in the conclusion that, in the presence of equimolar amounts of strong Lewis acids, compound **1a** should be less reactive than **3a**, since **1a** ionizes to a greater extent than **3a**.



1	2, 3	R^1	R^2	R^3	R^4	R^5	R^6	R^7
a	a	Et	Et	Et	H	H	H	H
b	b	CH_3	CH_3	CH_3	H	H	H	CH_3
	c	CH_3	CH_3	CH_3	$-(CH_2)_3-$		H	H
	d	CH_3	CH_3	CH_3	H	H	$-(CH_2)_2-$	
	e	CH_3	CH_3	CH_3	H	H	$-(CH_2)_4-$	
c	f	$-(CH_2)_2-$		CH_3	CH_3	H	CH_3	H
	g	$-(CH_2)_2-$		CH_3	CH_3	H	CH_3	CH_3

In accord with the expectations from our general analysis,[16] we report now that the β,γ-unsaturated acetals **3** can be prepared from **1** and **2** when the weak Lewis acid $ZnCl_2$ or catalytic amounts of $SnCl_4$ are used. Table 1 shows that allylsilanes, which are unsubstituted **(2a, b)** or monosubstituted **(2c–e)** at the site of electrophilic attack, react with the trialkoxymethanes **1a** or **1b**. Probably because of steric reasons, the attempted dialkoxymethylation of the terminally disubstituted allylsilanes

Table 1. β,γ-Unsaturated Aldehyde Acetals **3a–g** from Orthoformates **1a–c** and Allylsilanes **2a–g**

Substrates (mmol)[a]	Time (h)	Product	Yield (%)	bp (°C/mbar)[b]	Molecular Formula[c] or Lit. bp (°C/mbar)
1a (200) + **2a** (40)	15	**3a**[d]	51	42–46/32	44/25[19]
1b (12) + **2b** (4)	12	**3b**	83	95–96/500	$C_7H_{14}O_2$[e] (130.2)
1b (36) + **2c** (15)	18	**3c**[f]	45	80–85/35	$C_8H_{14}O_2$[g] (142.2)
1b (12) + **2d** (4)	6	**3d**	51	80–82/40	$C_9H_{16}O_2$ (156.2)
1b (15) + **2e** (4)	5	**3e**	73	97–102/45	$C_{10}H_{18}O_2$ (170.3)
1c (16) + **2f** (8)	48	**3f**[h]	48	75/45	$C_8H_{14}O_2$ (142.2)
1c (8) + **2g** (2.5)[i]	14	**3g**[h]	81	75–78/45	$C_9H_{16}O_2$ (156.2)

[a] **1a** = $HC(OEt)_3$; **1b** = $HC(OCH_3)_3$; **1c** = 2-methoxy-1,3-dioxolane.
[b] Bulb-to-bulb distillation, bath temperature.
[c] Satisfactory microanalyses obtained: C ±0.38, H ±0.11; except for **3d** (C +0.59).
[d] This reaction was carried out with 4.0 mmol of $SnCl_4$ at −6°C.
[e] In Ref. 21, the bp was not reported.
[f] This reaction was carried out with 3.3 mmol of $SnCl_4$ at −25°C.
[g] In Ref. 22, the bp was not reported.
[h] Compounds **3f, g** were purified by HPLC (RP_{18}/MeOH) prior to distillation.
[i] Because of better accessibility,[20] the triethylsilyl compound was used instead of the trimethylsilyl compound.

Table 2. Spectroscopic Data of the β,γ-Unsaturated Aldehyde Acetals **3a–g**

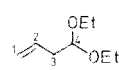
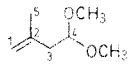
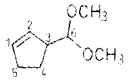
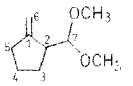
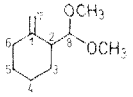
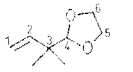
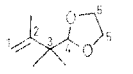
Compound	IR (neat)[a] ν (cm⁻¹)	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS)[b] δ	MS (70 eV)[c] m/z (%)
3a 	3064, 2869, 1640, 1439, 1369, 1342, 1119, 1059, 910	1.21 (t, J = 7.1, 6H, OCH_2CH_3); 2.40 (br t, J ≈ 5.7, 2H, H-3); 3.40–3.75 (m, 4H, OCH_2CH_3); 4.52 (t, J = 5.6, 1H, H-4); 5.0–5.20 (m, 2H, H-1); 5.70–5.95 (m, 1H, H-2)	15.31 (CH_3); 38.48 (C-3); 61.14 (OCH_2); 102.37 (C-4); 117.27 (C-1); 133.51 (C-2)	143 ($M^+ - 1$, 0.2); 103 (58); 99 (50); 75 (41); 71 (42); 47 (100); 43 (41)

Table 2. (continued)

Compound	IR (neat)[a] ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS)[b] δ	MS (70 eV)[c] m/z (%)
3b 	3068, 2938, 2824, 1647, 1447, 1364, 1251, 1228, 1189, 1121, 1074, 1062, 1059, 1055, 890, 845, 805	1.71 (s, 3H, H-5); 2.28 (d, 2H, J = 5.8, H-3); 3.23 (s, 6H, OCH_3); 4.48 (t, 1H, J = 5.8, H-4); 4.73, 4.77 (2br s, 2H, H-1)	22.89 (C-5); 40.90 (C-3); 52.66 (OCH_3); 103.21 (C-4); 112.96 (C-1); 141.21 (C-2)	129 ($M^+ - 1$, 0.4); 99 (19); 84 (5); 75 (100); 67 (10); 58 (4); 55 (5); 47 (16)
3c 	3046, 2929, 2824, 1455, 1373, 1349, 1258, 1190, 1108, 1057, 965	1.68, 1.98 (2 m$_c$, 2H, H-4); 2.38 (m$_c$, 2H, H-5); 3.02 (m$_c$, 1H, H-3); 3.36, 3.38 (2s, 6H, OCH_3); 4.09 (d, 1H, J = 7.6, H-6); 5.66, 5.85 (2 m$_c$, 2H, H-1, H-2)	25.15 (C-4); 32.09 (C-5); 48.61 (C-3); 52.99, 53.60 (OCH_3); 107.77 (C-6); 130.54, 132.93 (C-1, C-2)	141 ($M^+ - 1$, 0.2); 111 (13); 79 (17); 75 (100); 67 (10); 47 (15)
3d 	2940, 2824, 1647, 1446, 1370, 1352, 1189, 1139, 1115, 1066, 1054, 964, 888	1.48–1.90 (m, 4H, H-3, H-4); 2.32 (m$_c$, 2H, H-5); 2.71 (m$_c$, 1H, H-2); 3.36, 3.40 (2s, 6H, OCH_3); 4.23 (d, 1H, J = 6.7, H-7); 4.98, 5.04 (2 m$_c$, 2H, H-6)	24.61, 28.45 (C-3, C-4); 34.27 (C-5); 45.89 (C-2); 53.42, 54.13 (OCH_3); 107.17 (C-6, C-7); 151.92 (C-1)	155 ($M^+ - 1$, 0.3); 125 (9); 93 (4); 75 (100); 47 (11)
3e 	2930, 2855, 2829, 1648, 1446, 1190, 1115, 1100, 1056, 962, 888	1.40–1.80 (m, 6H, H-3, H-4, H-5); 2.16 (m$_c$, 2H, H-6); 2.42 (m$_c$, 1H, H-2); 3.35, 3.37 (2s, 6H, OCH_3); 4.55 (d, 1H, J = 8.0, H-8); 4.70, 4.78 (2 br s, 2H, H-7)	23.77, 28.58, 29.02 (C-3, C-4, C-5); 34.99 (C-6); 45.28 (C-2); 52.93, 53.17 (OCH_3); 104.10 (C-8); 108.65 (C-7); 148.64 (C-1)	139 ($M^+ - OCH_3$, 4); 107 (3); 95 (3); 75 (100); 67 (4); 47 (10)
3f 	2960, 2868, 1638, 1471, 1414, 1387, 1354, 1106, 1045, 1001, 946, 913, 787, 760	1.05 (s, 6H, CH_3); 3.91 (m$_c$, 4H, H-5, H-6); 4.60 (s, 1H, H-4); 5.03–5.14 (m, 2H, H-1); 5.93 (dd, 1H, J = 17.9, 10.5, H-2)	21.49 (CH_3); 40.80 (C-3); 65.35 (C-5, C-6); 109.25 (C-4); 112.84 (C-1); 143.47 (C-2)	141 ($M^+ - 1$, 0.6); 127 (0.3); 73 (100); 69 (2); 45 (26)
3g 	2958, 2869, 1618, 1449, 1370, 1103, 1075, 945, 890	1.09 (s, 6H, 3-CH_3); 1.82 (br s, 3H, 2-CH_3); 3.91 (m$_c$, 4H, H-5, H-6); 4.82 (s, 1H, H-4); 4.88 (br s, 2H, H-1)	20.42 (2-CH_3); 21.36 (3-CH_3); 42.67 (C-3); 65.32 (C-5, C-6); 108.23 (C-4); 111.05 (C-1); 149.70 (C-2)	155 ($M^+ - 1$, 0.5); 141 (0.4); 127 (2); 83 (2); 73 (100); 45 (16)

[a] Recorded on a Shimadzu IR-435 spectrophotometer.
[b] Recorded on a Varian XL 200 spectrometer.
[c] Obtained on a VG 70–250 mass spectrometer.

2f, g with **1b** was not successful, but satisfactory results could be obtained with the cyclic orthoformate **1c**. The Lewis acid catalyzed reaction of orthoformates with allylsilanes, therefore, appears to be a general method for the synthesis of β,γ-unsaturated aldehyde acetals and an alternative to the reaction of orthoformates with allylaluminum compounds.[17]

4,4-Dimethoxy-2-methyl-1-butene (3b); Typical Procedure:
A solution of $ZnCl_2$ (0.55 g, 4.0 mmol) in Et_2O (0.6 mL) and CH_2Cl_2 (1.2 mL)[18] is added to a cooled (5 °C) solution of $HC(OMe)_3$ (**1b**) (1.27 g, 12.0 mmol) in CH_2Cl_2 (15 mL). The allylsilane **2b** (0.51 g, 4.0 mmol) dissolved in CH_2Cl_2 (10 mL) is added dropwise with stirring, and the mixture is stored for 12 h at 5 °C. The solution is washed with cold (5 °C) 3% aq. HCl (10 mL), dried (Na_2SO_4/Na_2CO_3), and the solvent is distilled off at atmospheric pressure. Distillation gives **3b** as a colorless oil; yield: 430 mg (83%); bp 95–96 °C/500 mbar.

We thank Ms. R. Lammers for experimental assistance, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and one referee for bringing Refs. 23 and 24 to our attention.

Received: 26 September 1988

(1) Olah, G.A., Kuhn, S.J., in: *Friedel-Crafts and Related Reactions*, Vol. III, Part II, Olah, G.A. (ed.), Wiley, New York, 1964, p. 1153.
(2) Effenberger, F. *Angew. Chem.* **1980**, *92*, 147; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 151.
(3) Olah, G.A., Ohannesian, J., Arvanaghi, M. *Chem. Rev.* **1987**, *87*, 671.
(4) De Wolfe, R.H. *Carboxylic Ortho Acid Derivatives*, Academic Press, New York, 1970.
(5) Mathieu, J., Weill-Raynal, J. *Formation of C–C Bonds*, Vol. I, Georg Thieme Verlag, Stuttgart, 1973, p. 165.
(6) De Wolfe, R.H. *Synthesis* **1974**, 153.
(7) Meerwein, H., in: *Houben-Weyl*, 4th ed., Vol. VI/3, Georg Thieme Verlag, Stuttgart, 1965, p. 247.
(8) Simchen, G., in: *Houben-Weyl*, 4th ed., Vol. E V, Georg Thieme Verlag, Stuttgart, 1973, p. 117.
(9) Colvin, E.W. *Silicon in Organic Synthesis*, Butterworth, London, 1981.
(10) Weber, W.P. *Silicon Reagents for Organic Synthesis*, Springer, Berlin, 1983.
(11) Fleming, I., in: Barton and Ollis *Comprehensive Organic Chemistry*, Vol. III., Neville Jones, D. (ed.), Pergamon Press, Oxford, 1979, p. 541.
(12) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1.
(13) Schinzer, D. *Synthesis* **1988**, 263.
(14) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.
(15) Hosomi, A., Endo, M., Sakurai, H. *Chem. Lett.* **1976**, 941.
(16) Mayr, H., Schade, C., Rubow, M., Schneider, R. *Angew. Chem.* **1987**, *99*, 1059. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1029.
(17) Picotin, G., Miginiac, P. *Chem. Ber.* **1986**, *119*, 1725.
(18) Mayr, H., Striepe, W. *J. Org. Chem.* **1985**, *50*, 2995.
(19) Barbot, F., Poncini, L., Randrianoelina, B., Miginiac, P. *J. Chem. Res. (S)* **1981**, 343; (*M*) **1981**, 4016.
(20) Wrighton, M.S., Schroeder, M.A. *J. Am. Chem. Soc.* **1974**, *96*, 6235.
(21) Bogdanov, G.M., Lalaev, V.V., Belov, A.P. *Zh. Org. Khim.* **1979**, *15*, 1584.
(22) Murakami, M., Nishida, S. *Chem. Lett.* **1981**, 997.
(23) Chan, T.H., Kang, G.J. *Tetrahedron Lett.* **1982**, *23*, 3011.
(24) Sternbach, D.D., Hobbs, S.H. *Synth. Commun.* **1984**, *14*, 1305.