Synthesis of β,γ-Unsaturated Carboxylic Acid Esters via Aryloxycarbonylation of Allylsilanes

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The β,γ-unsaturated carboxylic acid 4-chlorophenyl esters **3a–e** *are synthesized from the allylsilanes* **2a–e** *and dichlorobis(4-chlorophenoxy)methane* **(1)** *in the presence of 1.1 equivalents of tin(IV) chloride.*

Whereas α,β-unsaturated carboxylic acids can be synthesized by manifold methods,[1] the corresponding β,γ-unsaturated compounds are less readily accessible.[2] A widely applicable method, recently developed by Salomon, generates allylcarboxylic acids via ene-reaction of alkenes with diethyl oxomalonate and successive oxidative bisdecarboxylation of the ene-adducts.[3,4]

As allylsilanes are known to undergo regioselective S_E2' reactions with a variety of electrophiles,[5–10] the reaction of allylsilanes with HO_2C^+ equivalents can be expected to open a facile access to the title compounds. However, most established HO_2C^+ equivalents either have relatively low electrophilicity or tend to react with two equivalents of nucleophiles.[11–13] A route developed by Fleming involves treatment of an allylsilane with chlorosulfonyl isocyanate to give an allylic carboxamide, which was converted into the corresponding acid by nitrosation.[14] An alternative carboxylation method, which allows the production of α,β-unsaturated acids from alkenes, employs 2,2-dichloro-1,3-benzodioxol in the presence of excess boron trichloride.[15]

We now report that related conditions can be used to convert allylsilanes into β,γ-unsaturated carboxylic acid esters. Recent experiments have shown that alkenes can be carboxylated in better yield[16] when the previously used carboxylating agent,[15] 2,2-dichloro-1,3-benzodioxol, is replaced by dichlorodiphenoxymethane or dichlorobis(4-chlorophenoxy)methane **(1)**, compounds which have become readily available by radical initiated chlorination of formaldehyde acetals.[17]

Table 1. Tin(IV) Chloride Promoted Reactions of Dichlorobis(4-chlorophenoxy)methane **(1)** with the Allylsilanes **2a–e**

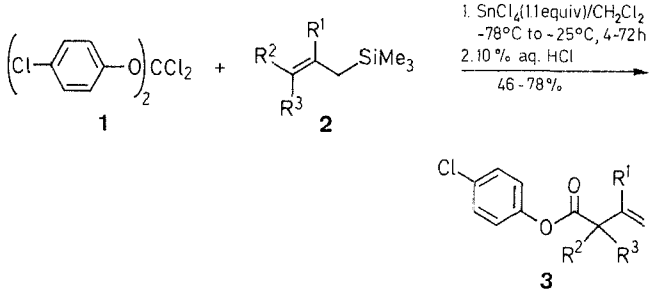
Product	Equiv of **2**	Reaction Time (h)/ Temp. (°C)	Yield[a] (%)	bp[b] (°C/mbar)	Molecular Formula[c]
3a	1.03	72/–78	78	75–80/0.5	$C_{10}H_9ClO_2$ (196.6)
3b	1.21	4.5/–78	62	100–105/0.5	$C_{11}H_{11}ClO_2$ (210.7)
3c	1.50	4/–30	79	110–115/1.5	$C_{13}H_{13}ClO_2$ (236.7)
3d	1.23	4/–25	64	125–130/0.09	$C_{14}H_{15}ClO_2$ (250.7)
3e	1.00	7/–50	46[d]	80–85/0.1[e]	$C_{12}H_{13}ClO_2$ (224.7)

[a] Isolated yield based on **1**.
[b] Bulb-to-bulb distillation, bath temperature.
[c] Satisfactory microanalyses obtained: C ±0.21, H ±0.29.
[d] In addition, **4** (18%) was obtained.
[e] **4**: $C_{15}H_{22}Cl_2O_2Si$ (333.3); bp 120–125°C/0.06 mbar; mp 38–40°C (CH_3OH).

Table 2. Spectral Data of the 4-Chlorophenyl 3-Alkenoates **3a–e** and of **4**

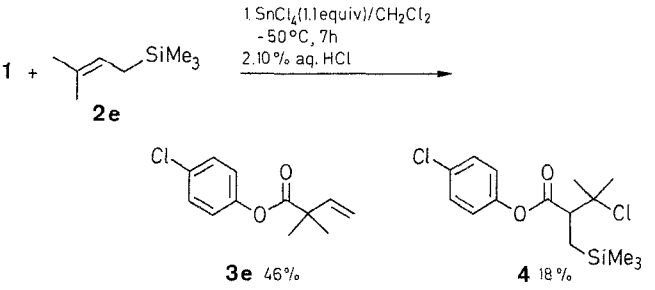
Formula Ar = Cl-C$_6$H$_4$-	IR[a] ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[b] δ, J(Hz)	^{13}C-NMR ($CDCl_3$/TMS)[c] δ	MS (70 eV) m/z (%)[d]
ArO-CH$_2$-CH=CH$_2$ **3a**	3074, 1758, 1642, 1485, 1200, 1031, 918, 837	3.34 (dt, 2H, J = 6.9, 1.4, H-2); 5.20–5.35 (m, 2H, H-4); 5.90–6.13 (m, 1H, H-3)	39.01 (C-2); 119.41 (C-4); 129.36 (C-3); 169.69 (C-1)	198, 196 (M$^+$, 2, 6); 130, 128 (17, 52); 101, 99 (6, 18); 69 (35); 68 (61); 41 (100)
ArO-CH=CH-CH$_3$ **3b**	3073, 2964, 1756, 1649, 1485, 1199, 1161, 1121, 1085, 1015, 910, 835	1.90 (br s, 3H, CH_3); 3.27 (br s, 2H, H-2); 4.97, 5.00 (2 br s, 2H, H-4)	22.49 (C-5); 43.31 (C-2); 115.43 (C-4); 137.73 (C-3); 169.53 (C-1)	212, 210 (M$^+$, 1, 3); 130, 128 (9, 25); 83 (52); 82 (100); 55 (86)
ArO-(cyclohexenone) **3c**	3069, 2949, 1752, 1648, 1485, 1198, 1160, 1115, 1088, 1012	1.55–2.22 (m, 4H, H-4, H-5); 2.40–2.50 (m, 2H, H-3); 3.56 (m$_c$, 1H, H-1); 5.15, 5.24 (2 m$_c$, 2H, H-7)	25.30, 30.25, 33.50 (C-3, C-4, C-5); 48.76 (C-1); 108.65 (C-7); 150.01 (C-2); 172.35 (C-6)	238, 236 (M$^+$, 0.6, 1.8); 109 (100); 81 (35); 79 (17); 53 (15)
ArO-(cyclohexenone) **3d**	2925, 2847, 1755, 1647, 1485, 1210, 1161, 1149, 1112, 1083, 1008, 900, 835	1.52–2.55 (m, 8H, H-3, H-4, H-5, H-6); 3.38 (dd, 1H, J = 4.6, 2.4, H-1); 4.81, 4.91 (2s, 2H, H-8)	23.65, 27.70, 30.18, 34.27 (C-3, C-4, C-5, C-6); 49.43 (C-1); 109.92 (C-8); 145.87 (C-2); 171.91 (C-7)	252, 250 (M$^+$, 0.5, 1.3); 130, 128 (5, 14); 122 (44); 95 (100); 94 (21); 67 (13)
ArO-CH(CH$_3$)-CH=CH$_2$ **3e**	2962, 1765, 1753, 1486, 1283, 1198, 1160, 1012, 815	1.44 (s, 6H, CH_3); 5.18 (d, 1H, J = 10.8, H-4); 5.23 (d, 1H, J = 17.4, H-4); 6.14 (dd, 1H, J = 17.4, 10.8, H-3)	24.53 (C-5); 45.12 (C-2); 113.86 (C-4); 141.67 (C-3); 174.60 (C-1)	226, 224 (M$^+$, 1.5, 4.3); 130, 128 (10, 31); 111 (5); 97 (16); 69 (100)
ArO-(SiMe$_3$, Cl) **4**	2942, 1755, 1485, 1249, 1197, 1123, 1087, 1048, 855	0.09 (s, 9H, $SiMe_3$); 0.97, 1.18 (AB part of an ABX system with J_{AB} = 14.4, J_{AX} = 1.8, J_{BX} = 12.8, 2H, CH_2); 1.68, 1.75 (2s, 6H, $2CH_3$); 3.06 (dd, 1H, X-part, H-2)	–1.52 ($SiMe_3$); 16.21 (C-6); 29.55, 29.74 (C-4, C-5); 54.02 (C-2); 71.79 (C-3); 171.73 (C-1)	334, 332 (M$^+$, 0.19, 0.31); 321, 319, 317 (0.21, 1.0, 1.4); 283, 281 (0.8, 2.3); 69 (100)

[a] Recorded on a Shimadzu IR-435 spectrophotometer (neat or KBr).
[b] Recorded on a Varian XL 200 spectrometer; *p*-chlorophenyl: AA'BB' system with ν_A = 7.00–7.04, ν_B = 7.32–7.34, and J_{AB} = 8.7–9.0 Hz.
[c] Recorded on a Varian XL 200 spectrometer; assignments based on DEPT spectra; δ (*p*-chlorophenyl) = 149.00–149.38 (C-1'); 122.75–122.93 (C-2'); 129.40–129.48 (C-3'); 131.05–131.28 (C-4').
[d] Obtained on a VG 70-250 mass spectrometer.



2, 3	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	$-(CH_2)_3-$		H
d	$-(CH_2)_4-$		H
e	H	CH_3	CH_3

In analogy to these results, the allylsilanes **2a–e** are converted into the allylic carboxylic acid esters **3a–e** with **1** and tin(IV) chloride (1:1.1)[18] in dichloromethane at low temperatures (Table 1). Whereas the allylsilanes **2a–d** are regioselectively attacked with intermediate formation of β-silyl stabilized carbenium ions, two modes of addition are observed with the trimethylprenylsilane **2e**. As previously observed for other electrophiles,[19] the double bond of **2e** can be attacked at both termini, resulting in formation of compound **4** in addition to the normal S_E2' product **3e**.



4-Chlorophenyl 3-Alkenoates 3; General Procedure:
A solution of **2a–e** (3.0–4.5 mmol) in CH_2Cl_2 (10 mL) is added dropwise to a precooled solution of dichlorobis(4-chlorophenyl)methane (**1**;[17] 1.02 g, 3.0 mmol) and $SnCl_4$ (0.86 g, 3.3 mmol) in CH_2Cl_2 (16 mL). The solution is kept at low temperature for the time given in Table 1, and the mixture is then washed with 10% aq. HCl (15 mL). The organic layer is separated, and the solvent is evaporated to give a mixture of **3a–e** and 4-chlorophenol, which is dissolved in petroleum ether (50 mL) and washed with 5% Na_2CO_3 solution (4 × 10 mL). The organic layer is dried (Na_2SO_4), and the solvent is evaporated to give the crude product, which is purified by distillation or by layer chromatography (silica gel 60, petroleum ether/Et_2O, 98:2).

We thank the Deutsche Forschungsgemeinschaft for support of this work.

Received: 20 September 1988

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