

## Synthesis of $\beta,\gamma$ -Unsaturated Carboxylic Acid Esters via Aryloxycarbonylation of Allylsilanes

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The  $\beta,\gamma$ -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  $\alpha,\beta$ -unsaturated carboxylic acids can be synthesized by manifold methods,<sup>1</sup> the corresponding  $\beta,\gamma$ -unsaturated compounds are less readily accessible.<sup>2</sup> 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 ened-adducts.<sup>3,4</sup>

As allylsilanes are known to undergo regioselective  $S_E2'$  reactions with a variety of electrophiles,<sup>5–10</sup> the reaction of allylsilanes with  $\text{HO}_2\text{C}^+$  equivalents can be expected to open a facile access to the title compounds. However, most established  $\text{HO}_2\text{C}^+$  equivalents either have relatively low electrophilicity or tend to react with two equivalents of nucleophiles.<sup>11–13</sup> 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.<sup>14</sup> An alternative carboxylation method, which allows the production of  $\alpha,\beta$ -unsaturated acids from alkenes, employs 2,2-dichloro-1,3-benzodioxol in the presence of excess boron trichloride.<sup>15</sup>

We now report that related conditions can be used to convert allylsilanes into  $\beta,\gamma$ -unsaturated carboxylic acid esters. Recent experiments have shown that alkenes can be carboxylated in better yield<sup>16</sup> when the previously used carboxylating agent,<sup>15</sup> 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.<sup>17</sup>

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

Product	Equiv of <b>2</b>	Reaction Time (h)/Temp. (°C)	Yield <sup>a</sup> (%)	bp <sup>b</sup> (°C/mbar)	Molecular Formula <sup>c</sup>
<b>3a</b>	1.03	72/–78	78	75–80/0.5	C <sub>10</sub> H <sub>9</sub> ClO <sub>2</sub> (196.6)
<b>3b</b>	1.21	4.5/–78	62	100–105/0.5	C <sub>11</sub> H <sub>11</sub> ClO <sub>2</sub> (210.7)
<b>3c</b>	1.50	4/–30	79	110–115/1.5	C <sub>13</sub> H <sub>13</sub> ClO <sub>2</sub> (236.7)
<b>3d</b>	1.23	4/–25	64	125–130/0.09	C <sub>14</sub> H <sub>15</sub> ClO <sub>2</sub> (250.7)
<b>3e</b>	1.00	7/–50	46 <sup>d</sup>	80–85/0.1 <sup>e</sup>	C <sub>12</sub> H <sub>13</sub> ClO <sub>2</sub> (224.7)

<sup>a</sup> Isolated yield based on **1**.


<sup>b</sup> Bulb-to-bulb distillation, bath temperature.

<sup>c</sup> Satisfactory microanalyses obtained: C  $\pm$  0.21, H  $\pm$  0.29.

<sup>d</sup> In addition, **4** (18%) was obtained.

<sup>e</sup> **4**: C<sub>15</sub>H<sub>22</sub>Cl<sub>2</sub>O<sub>2</sub>Si (333.3); bp 120–125°C/0.06 mbar; mp 38–40°C (CH<sub>3</sub>OH).

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

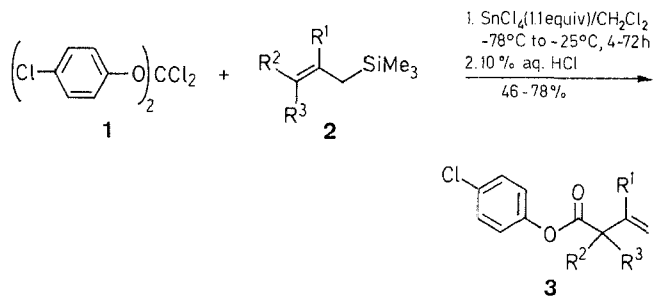
Formula	IR <sup>a</sup> $\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H-NMR (CDCl <sub>3</sub> /TMS) <sup>b</sup> $\delta$ , J (Hz)	<sup>13</sup> C-NMR (CDCl <sub>3</sub> /TMS) <sup>c</sup> $\delta$	MS (70 eV) $m/z$ (%) <sup>d</sup>
Ar = Cl  <b>3a</b>	3074, 1758, 1642, 1485, 1200, 1031, 918, 837	3.34 (dt, 2H, <i>J</i> = 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 <sup>+</sup> , 2, 6); 128 (17, 52); 101, 99 (6, 18); 69 (35); 68 (61); 41 (100)
<b>3b</b>	3073, 2964, 1756, 1649, 1485, 1199, 1161, 1121, 1085, 1015, 910, 835	1.90 (br s, 3H, CH <sub>3</sub> ); 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 <sup>+</sup> , 1, 3); 130, 128 (9, 25); 83 (52); 82 (100); 55 (86)
<b>3c</b>	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 <sub>c</sub> , 1H, H-1); 5.15, 5.24 (2 m <sub>c</sub> , 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 <sup>+</sup> , 0.6, 1.8); 109 (100); 81 (35); 79 (17); 53 (15)
<b>3d</b>	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, <i>J</i> = 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 <sup>+</sup> , 0.5, 1.3); 130, 128 (5, 14); 122 (44); 95 (100); 94 (21); 67 (13)
<b>3e</b>	2962, 1765, 1753, 1486, 1283, 1198, 1160, 1012, 815	1.44 (s, 6H, CH <sub>3</sub> ); 5.18 (d, 1H, <i>J</i> = 10.8, H-4); 5.23 (d, 1H, <i>J</i> = 17.4, H-4); 6.14 (dd, 1H, <i>J</i> = 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 <sup>+</sup> , 1.5, 4.3); 130, 128 (10, 31); 111 (5); 97 (16); 69 (100)
<b>4</b>	2942, 1755, 1485, 1249, 1197, 1123, 1087, 1048, 855	0.09 (s, 9H, SiMe <sub>3</sub> ); 0.97, 1.18 (AB part of an ABX system with <i>J</i> <sub>AB</sub> = 14.4, <i>J</i> <sub>AX</sub> = 1.8, <i>J</i> <sub>BX</sub> = 12.8, 2H, CH <sub>2</sub> ); 1.68, 1.75 (2s, 6H, 2CH <sub>3</sub> ); 3.06 (dd, 1H, X-part, H-2)	–1.52 (SiMe <sub>3</sub> ); 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 <sup>+</sup> , 0.19, 0.31); 321, 319, 317 (0.21, 1.0, 1.4); 283, 281 (0.8, 2.3); 69 (100)

<sup>a</sup> Recorded on a Shimadzu IR-435 spectrophotometer (neat or KBr).

<sup>b</sup> Recorded on a Varian XL 200 spectrometer; *p*-chlorophenyl: AA'BB' system with  $\nu_A = 7.00$ –7.04,  $\nu_B = 7.32$ –7.34, and  $J_{AB} = 8.7$ –9.0 Hz.

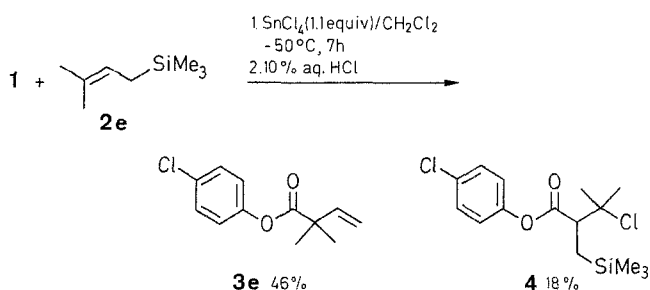
<sup>c</sup> Recorded on a Varian XL 200 spectrometer; assignments based on DEPT spectra;  $\delta$  (*p*-chlorophenyl) = 149.00–149.38 (C-1'); 122.75–122.93 (C-2'); 129.40–129.48 (C-3'); 131.05–131.28 (C-4').

<sup>d</sup> Obtained on a VG 70-250 mass spectrometer.



2, 3	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
a	H	H	H
b	CH <sub>3</sub>	H	H
c	-(CH <sub>2</sub> ) <sub>3</sub> -		H
d	-(CH <sub>2</sub> ) <sub>4</sub> -		H
e	H	CH <sub>3</sub>	CH <sub>3</sub>

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)<sup>18</sup> in dichloromethane at low temperatures (Table 1). Whereas the allylsilanes **2a-d** are regioselectively attacked with intermediate formation of  $\beta$ -silyl stabilized carbenium ions, two modes of addition are observed with the trimethylprenylsilane **2e**. As previously observed for other electrophiles,<sup>19</sup> the double bond of **2e** can be attacked at both termini, resulting in formation of compound **4** in addition to the normal S<sub>E</sub>2' product **3e**.



#### 4-Chlorophenyl 3-Alkenoates **3**; General Procedure:

A solution of **2a-e** (3.0-4.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) is added dropwise to a precooled solution of dichlorobis(4-chlorophenyl)methane (**1**;<sup>17</sup> 1.02 g, 3.0 mmol) and SnCl<sub>4</sub> (0.86 g, 3.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>CO<sub>3</sub> solution (4 × 10 mL). The organic layer is dried (Na<sub>2</sub>SO<sub>4</sub>), 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<sub>2</sub>O, 98:2).

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