Facile Aluminum(III) Chloride Catalyzed Preparation of β,γ-Unsaturated *O*-Aryl Esters from Allylsilanes and Aryl Chloroformates[1]

George A. Olah*, David S. VanVliet, Qi Wang, G.K. Surya Prakash*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, USA

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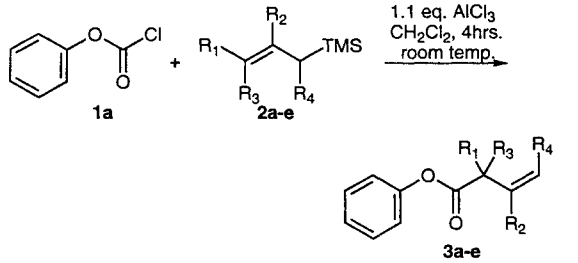
The aluminum trichloride catalyzed reaction of phenyl chloroformate **(1a)** with allylsilanes **2a–e** gives phenyl 3-alkenoates in excellent yields. The reaction with allyltrimethylsilane **2a** also works with a number of *para* substituted aryl chloroformates **1b–f**.

Allylsilanes have been shown to be useful nucleophilic synthons in organic synthesis.[2] Their direct electrophilic carboxylation is of substantial interest. Mayr et al. reported the reaction of allylsilanes with chlorinated phenyl acetals to give the 4-chlorophenyl-3-alkenoates. However, these chlorinated acetals are not readily available and must be prepared first for the reaction.[3] Another approach involves the treatment of allylsilanes with chlorosulfonyl isocyanate to give the carboxamide which subsequently can be hydrolysed to the corresponding carboxylic acid.[4] A third route which gives α,β-unsaturated acids uses 2,2-dichloro-1,3-benzodioxol with excess BCl_3.[5]

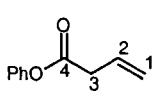
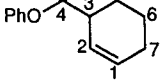
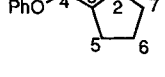
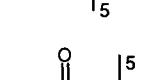
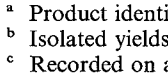
We now would like to report a facile, high-yield preparation of *O*-aryl esters by an intermolecular reaction of



2,3	R_1	R_2	R_3	R_4
a	H	H	H	H
b	H	H	$-(CH_2)_3-$	
c	$-(CH_2)_3-$		H	H
d	H	CH_3	CH_3	H
e	H	CH_3	H	H

Scheme 1

Table 1. Reaction of **2a–e** with Phenyl 3-Alkenoates **3a–e**[a]

Product	Amount of **2** (equiv)	Yield[b] (%)	^{1}H NMR δ ($CDCl_3$/TMS)[c]	^{13}C NMR δ ($CDCl_3$/TMS)[d]	MS (70 eV)[e] *m/z* (%)
 **3a**	1.17	90	3.34 (d, 2H, H-3), 5.27 (d, 2H, H-1), 6.02 (m, 1H, H-2), 7.02–7.42 (m, 5H, H-Ph)	39.3 (t, C-3), 118.9 (t, C-1), 131.2 (d, C-2), 170.3 (s, C-4)	162 (M^+), 94, 77, 68 (100), 51, 41, 39
 **3b**	1.21	91	1.60–2.17 (m, 6H, H-5, H-6, H-7), 3.38 (dt, 1H, H-3), 5.91 (b, 2H, H-1, H-2), 7.06–7.39 (m, 5H, H-Ph)	20.6 (t, C-6), 24.6 (t, C-5), 25.2 (t, C-7), 41.2 (d, C-3), 123.7 (d, C-1), 130.3 (d, C-2), 172.9 (s, C-4)	202 (M^+), 108, 94, 81 (100), 65, 53, 39
 **3c**	1.27	89	1.63–2.53 (m, 6H, H-5, H-6, H-7), 3.53 (t, 1H, H-3), 5.15 (d, 1H, H-1), 5.27 (d, 1H, H-1), 7.06–7.42 (m, 5H, H-Ph)	25.3 (t, C-5), 30.3 (t, C-6), 33.5 (t, C-7), 48.8 (d, C-3), 108.5 (t, C-1), 150.9 (s, C-2), 172.6 (s, C-4)	202 (M^+), 108 (100), 94, 81, 65, 53, 39
 **3d**	1.25	88	1.40 (d, 3H, H-5), 1.87 (s, 3H, H-6), 3.39 (q, 1H, H-3), 4.98 (d, 2H, H-1), 7.05–7.40 (m, 5H, H-Ph)	15.8 (q, C-5), 20.5 (q, C-6), 46.9 (d, C-3), 113.1 (t, C-1), 143.4 (s, C-2), 172.8 (s, C-4)	190 (M^+), 96 (100), 94, 77, 69, 53, 41, 39
 **3e**	1.25	91	1.91 (s, 3H, H-5), 3.27 (s, 2H, H-3), 4.99 (d, 2H, H-1), 7.07–7.40 (m, 5H, H-Ph)	22.5 (q, C-5), 43.4 (t, C-3), 115.2 (t, C-1), 138.0 (s, C-2), 169.8 (s, C-4)	176 (M^+), 133, 105, 94, 83, 82 (100), 66, 55, 39

[a] Product identification is confirmed by comparison of spectral data of the known *p*-chlorophenyl esters.[3]

[b] Isolated yields after purification, purity is 97.2% or better based upon GC/MS analysis.

[c] Recorded on a Varian Unity 300 spectrometer.

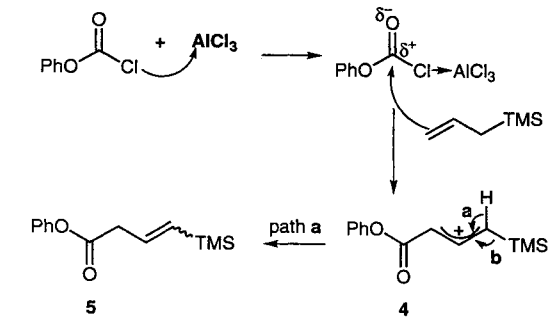
[d] Recorded on a Varian Unity 300 spectrometer operating at 75 MHz; multiplicity is based upon ^{1}H coupled ^{13}C spectra; assignments of phenyl carbons based upon comparison to previously published results:[3] δ (C_{ortho}) = 121.4–122.5; δ (C_{meta}) = 129.3–130.1; δ (C_{para}) = 125.7–126.5; δ (C_{ipso}) = 150.1–151.9.

[e] Taken on a Hewlett Packard gas chromatograph/mass spectrometer model 5971A.

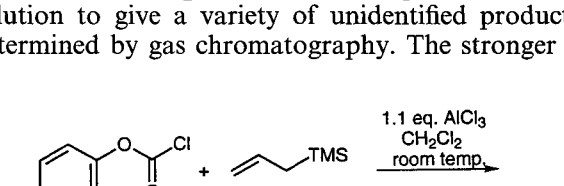
allylsilanes with aryl chloroformates under $AlCl_3$ catalysis. Phenyl chloroformate has been used as a carboxylating agent for aromatic systems under typical Friedel–Crafts conditions.[6] Alkyl haloformates, in contrast, decarboxylate in the presence of strong Lewis acids and act as alkylating agents.[7] More forceful conditions give the diaryl carbonates, or the products of the Fries rearrangement.[8] We surmised that since aryl haloformates do not readily decarboxylate, they could be used as masked electrophilic carboxylate equivalents for allylsilanes. In fact, Kocienski et al. have reported an intramolecular *O*-acylation of a suitably substituted allylsilane in the synthesis of ethyl pederate.[9] The present intermolecular reaction proceeds extremely readily with phenyl chloroformate, and the results obtained are summarized in Table 1 and Scheme 1. The results indicate the formation of only β,γ-unsaturated carboxylic acid esters. While there are many methods to make the α,β-unsaturated moieties,[10] the β,γ-unsaturated systems are much less accessible.[11]

Allylsilanes are known to react in S_E2' manner with many electrophiles, and this also appears to be the case in the present reaction.[2,12] There is clear inversion of the allylic double bond, and all reactions revealed a trace (0.5–2%) as determined by gas chromatography/mass spectrometry) of the deprotonated product **5** (Scheme 2). This would arise from intermediate **4** and pathway **a**. The major product would come from loss of the trimethylsilyl group as shown in path **b**.

Another distinct advantage of this method is the ready availability of several *para* substituted derivatives of phenyl chloroformate. The 4-OMe, 4-Me, 4-Cl, 4-F and 4-NO_2 substituted phenyl chloroformates were all commercially available.[13] While lone pairs of n-donor groups, such as halides, hydroxy, ether, vinylic and carbonyls, in the allylsilane are incompatible with this procedure, these groups present no problems when substituted on the phenyl ring. The results with allyltrimethylsilane **2a** are described in Table 2 and Scheme 3. The yields are consistently high; however, the reaction time varied depending on the nature of the aryl chloroformate. The two exceptions are the 4-F and 4-NO_2 derivatives. The yield is lower for the 4-F compound due to its sluggish reactivity. Attempts to further improve the yield were unsuccessful. The 4-NO_2 derivative decomposes in the $AlCl_3$ solution to give a variety of unidentified products as determined by gas chromatography. The stronger elec-



Scheme 2



Scheme 3

Table 2. The Reaction of **2a** with 4′-substituted phenyl chloroformate derivatives

Product		Yield[a] (%)	Time (h)	Amount of **2a** (equiv)	^{1}H NMR δ ($CDCl_3$/TMS)[b]	^{13}C NMR δ ($CDCl_3$/TMS)[c]	MS (70 eV)[d] *m/z* (%)
X = F[e]	**6c**	65	12	2.50	3.34 (d, 2H, C-3), 5.30 (d, 2H, C-1), 5.95–6.09 (m, 1H, C-2), 7.05–7.27 (m, 4H, C-2′, C-3′)	38.9 (t, C-3), 116.0 (d, C-3′), 119.3 (d, C-2), 122.9 (d, C-2′), 129.4 (t, C-1), 146.4 (s, C-1′), 160.2 (s, C-4′), 170.0 (s, C-4)	180 (M^+), 112 (100), 95, 83, 75, 69, 68, 57, 41, 39
X = Cl	**6d**	95	0.5	1.91	3.33 (d, 2H, C-3), 5.28 (d, 2H, C-1), 5.94–6.09 (m, 1H, C-2), 7.03 (d, 2H, C-2′), 7.32 (d, 2H, C-3′)	39.0 (t, C-3), 119.4 (d, C-2), 122.8 (d, C-2′), 129.3 (t, C-1), 129.4 (d, C-3′), 131.2 (s, C-4′), 149.1 (s, C-1′), 169.7 (s, C-4)	198, 196 (M^+), 130, 128 (100), 111, 99, 73, 69, 68, 41, 39
X = Me	**6e**	86	26	1.52	2.33 (s, 3H, Me), 3.23 (d, 2H, C-3), 5.27 (d, 2H, C-1), 5.96–6.10 (m, 1H, C-2), 6.94–7.25 (m, 4H, C-2′, C-3′)	20.8 (q, Me), 39.1 (t, C-3), 119.1 (d, C-2), 121.1 (d, C-2′), 129.7 (t, C-1), 129.9 (d, C-3′), 135.5 (s, C-4′), 148.4 (s, C-1′), 170.1 (s, C-4)	176 (M^+), 133, 108 (100), 107, 91, 79, 77, 70, 65, 51, 41, 39
X = OMe	**6f**	85	16	1.46	3.32 (d, 2H, C-3), 3.79 (s, 3H, OMe), 5.29 (d, 2H, C-1), 5.96–6.10 (m, 1H, C-2), 6.88–7.00 (m, 4H, C-2′, C-3′)	39.0 (t, C-3), 55.5 (q, Me), 114.4 (d, C-2′), 119.1 (d, C-2), 122.2 (t, C-3′), 129.7 (d, C-1), 144.1 (s, C-1′), 157.2 (s, C-4′), 170.3 (s, C-4)	192 (M^+), 124 (100), 109, 95, 81, 69, 52, 41, 39

[a] Isolated yields after purification, purity is 98.1% or better based upon GC/MS analysis.
[b] Recorded on a Varian Unity 300 spectrometer.
[c] Recorded on a Varian Unity 300 spectrometer operating at 75.4 MHz; multiplicity is based upon ^{1}H coupled ^{13}C spectra.
[d] Taken on a Hewlett Packard gas chromatograph/mass spectrometer model 5971A.
[e] The ^{19}F NMR was taken on the Varian Unity 300 spectrometer operating at 282 MHz; $\delta_F = -117.4$ [ref. δ_F ($CFCl_3$) = 0.00]; $^1J_{CF} = 244.4$ Hz; $^2J_{CF} = 23.4$ Hz; $^3J_{CF} = 8.7$ Hz; $^4J_{CF} = 3.2$ Hz.

tron–withdrawing groups would tend to destabilize the developing positive charge at the carbonyl center and retard the reaction. Being able to include several different functional groups on the ring greatly increases the utility of this novel carboxylation reaction.

The limitations of this new carboxylation are common to many Friedel–Crafts reactions in that relatively few other donor functional groups can be permitted in the allylsilane moiety. This is due to competing coordination of the Lewis acid to the lone pairs of n-donor groups. Milder Lewis acids, such as $SnCl_4$, $TiCl_3$, $TiCl_4$, $ZnCl_2$, and $FeCl_3$, do not catalyze the reaction. To optimize the yields, a slight excess of the silane was used because allylsilanes undergo slow protolytic desilylation in the presence of $AlCl_3$ and other Lewis acids.

Phenyl 3-Alkenoates; General Procedure:
In a dry flask under a slow stream of nitrogen, $AlCl_3$ (1.1 equiv) was mixed with 20 mL of dry CH_2Cl_2 (distilled from CaH). The phenyl chloroformate (1.0 equiv) was slowly added via syringe to the slurry. After 20 min, the silane **2a–e** (1.5–15 mmol, 1.17–1.27 equiv) in 2.0 mL of dry CH_2Cl_2 was gradually added via syringe over 5 min. The reaction mixture was stirred at r.t. for 4 h. It was then quenched in 50 mL of cold distilled water and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried ($MgSO_4$),[14] and the solvent was removed by rotary evaporation. The crude product was then purified by bulb-to-bulb distillation at 0.1 mmHg or silica gel chromatography (eluted with hexanes–EtOAc, 6:1).[15]

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(1) Preliminary results were presented at the ACS Western Regional meeting in Pasadena, California, October 1993. Synthetic Methods and Reactions, 191; for part 190, see: Olah, G.A.; Neyer, G.; Wang, Q. *Org. Synth.*, submitted.
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(13) Purchased from Aldrich Chemical Co., St. Louis, Missouri, USA.
(14) The solutions were cloudy and frequently required a large amount of $MgSO_4$ to completely dry the extract.
(15) For products **3b** and **3c**, silica gel chromatography caused the double bond to isomerize into the α,β position.