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Efficient Iron-Catalyzed Sakurai–Michael Addition of Allyltrimethylsilane to Chalcones

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Abstract: A general catalytic conjugate addition with allyltrimethylsilane and chalcones is described. Allyltrimethylsilane undergoes the Sakurai–Michael reaction smoothly with high chemoselectivity in the presence of a catalytic amount of $FeCl_3$/TMSCl under very mild and convenient conditions to afford the corresponding Michael adducts in high yields.

Keywords: Enones, iron, Lewis acid, Michael addition, Sakurai reaction

INTRODUCTION

The conjugate addition of allylsilanes to conjugated enones, referred to as the Sakurai–type Michael reaction, has been recognized as one of the most efficient methods of carbon–carbon bond formation and has been extensively applied in organic synthesis, especially in the preparation of some heterocyclic compounds and natural product synthesis.[1] The range of Lewis acids

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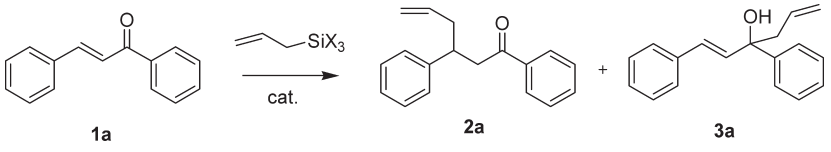
employed in Sakurai–type Michael addition is extensive, among which $TiCl_4$, $AlCl_3$, and BF_3-OEt_2 have been employed as the most effective promoters for these conjugate additions of allylsilanes.[2] However, many of these methods involve the use of highly toxic compounds, expensive reagents, or procedures that require a stoichiometric amount of catalyst to accelerate the reaction. Although a few examples of catalytic Sakurai–type Michael reactions have been reported recently,[3] the development of new and cheap catalyst systems, which are more efficient and lead to convenient procedures with improved yields, is well appreciated.

In our search for an economical, efficient Sakurai–type Michael addition of allylsilane to enones, we became intrigued by the idea of using a catalytic amount of cheap, readily available, and low-toxicity $FeCl_3$ in this reaction. As an extension of these studies of $FeCl_3$-catalyzed organic transformations,[4] herein we report a mild and convenient procedure for the Sakurai–type Michael addition of allyltrimethylsilane to chalcones.

RESULTS AND DISCUSSION

The reaction of chalcone (**1a**) and allyltrimethylsilane was selected as a model in the initial experiments. We screened some metal salts for this reaction. In the first trials, we found many transition-metal salts, such as $InCl_3$, ZnF_2, $FeCl_3$, $Fe(ClO_4)_3$, $PdCl_2(CH_3CN)_2$, and $Mg(ClO_4)_2$, were not effective in this reaction, and only Trace adduct was obtained in the most cases (less than 10% of yield). We also found the product was isomeric in the presence of catalytic $FeCl_3$ (Scheme 1, **2a** and **2b**); even when the amount of $FeCl_3$ was increased to 1.0 equiv., the yield was still low. After the first screening, a test was performed using the strategies of combination of two different Lewis acids and the addition of different additives. As shown in Table 1, $FeCl_3$ was a highly effective catalyst in the presence of TMSCl and gave excellent yields with good chemoselectivity for the desired product **2a** (entry 13). Other types of additives, such as ZnF_2, Brønsted acid (1,1′-Bi-2-naphthol (BINOL)), and Lewis base (hexamethylphosphoramide (HMPA) or amines), were not suitable promoters in the $FeCl_3$-catalyzed Sakurai–Michael reaction (entries 2, 5, 7) (Scheme 2). We reasoned that these results may be due to the activation of Michael acceptors, which should be feasible in the presence of TMSCl or the product of a stronger Lewis acid



Scheme 1. Sakurai–Michael reaction.

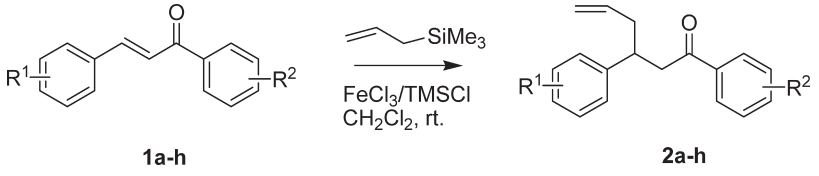
Table 1. Catalytic activity of several Lewis acids in the Sakurai–type Michael reaction

Entry[a]	Allylsilane	Catalysts	Additive	Solvent	Reaction time (h)	Isolated yield (%)
1	$CH_2{=}CHCH_2SiMe_3$	$InCl_3$	—	CH_2Cl_2	4	0
2	$CH_2{=}CHCH_2SiMe_3$	$InCl_3$	BINOL[b]	CH_3NO_2	3	Trace
3	$CH_2{=}CHCH_2SiMe_3$	ZnF_2	—	CH_2Cl_2	12	0
4	$CH_2{=}CHCH_2SiMe_3$	$FeCl_3$	—	CH_2Cl_2	3	Trace
5	$CH_2{=}CHCH_2SiMe_3$	$FeCl_3$	ZnF_2	CH_3NO_2	12	Trace
6	$CH_2{=}CHCH_2SiMe_3$	$Fe(ClO_4)_3$	—	CH_3NO_2	3	Trace
7	$CH_2{=}CHCH_2SiMe_3$	$Fe(ClO_4)_3$	HMPA	CH_2Cl_2	6	NR
8	$CH_2{=}CHCH_2SiMe_3$	$Fe(ClO_4)_3$	—	CH_2Cl_2	3	Trace
9	$CH_2{=}CHCH_2SiMe_3$	$Mg(ClO_4)_2$	—	CH_2Cl_2	12	0
10	$CH_2{=}CHCH_2SiMe_3$	$PdCl_2(CH_3CN)_2$	—	CH_3CN	3	0
11	$CH_2{=}CHCH_2SiMe_3$	L-Proline	—	CH_2Cl_2	24	0
12	$CH_2{=}CHCH_2SiMe_3$	—	TMSCl	CH_2Cl_2	3	Trace
13	$CH_2{=}CHCH_2SiMe_3$	$FeCl_3$	TMSCl	CH_2Cl_2	3	88 (95)[c]
14	$CH_2{=}CHCH_2SiMe_3$	$FeCl_3$	TMSCl	Toluene	4	27[c]
15	$CH_2{=}CHCH_2SiMe_3$	$FeCl_3$	TMSCl	CH_3CN	4	52[c]
16	$CH_2{=}CHCH_2SiMe_3$	$FeCl_3$	TMSCl	THF	12	0
17	$CH_2{=}CHCH_2Si(OEt)_3$	$FeCl_3$	TMSCl	CH_2Cl_2	12	NR
18	$CH_2{=}CHCH_2Si(OEt)_3$	$FeCl_3$	ZnF_2	CH_2Cl_2	24	NR
19	$CH_2{=}CHCH_2Si(OEt)_3$	$Fe(ClO_4)_3$	TMSCl	CH_2Cl_2	12	NR

[a]Reaction conditions: 1.0 mmol of enone, 1.5 mmol of allylsilane, 10 mol% of catalyst, 1.5 equiv. of additive, 3 mL of solvent, at room temperature.
[b]30 mol% of (*S*)-BINOL.
[c]GC yield.

catalyst of $FeCl_3$–TMSCl complex. Further studies indicated that dichloromethane was the best solvent in our experiments (entries 13–16). It is important to note that TMSCl (1.5 eq.) did not show any catalytic activity in the absence of $FeCl_3$ (entry 12). It is well known that the reactivity of allyltrialkloxysilanes was very low, and therefore the Sakurai–Michael reaction of allyltriethoxysilane was also studied (entries 17–19); unfortunately, this reaction did not occur in the presence of catalytic $FeCl_3$ and TMSCl.

The success of the Sakurai–Michael addition between chalcone and allytrimethylsilane prompted us to extend the general scope of the reaction. Under



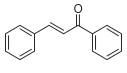
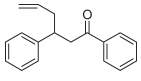
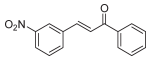
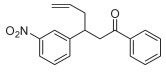
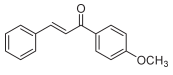
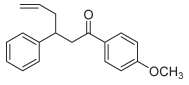
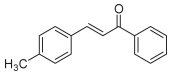
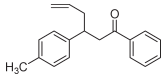
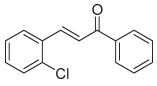
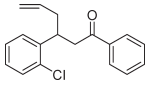
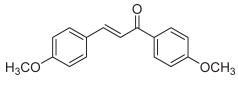
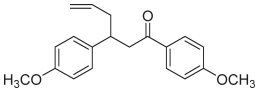
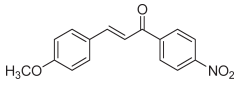
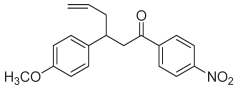
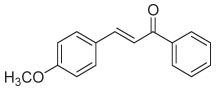
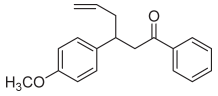
1a-h **2a-h**

Scheme 2. Iron-catalyzed Sakurai–Michael reaction.

the optimized conditions, we were pleased to find that a series of chalcones with allyltrimethylsilane gave the desired Michael adduct in good to excellent isolated yields (Table 2). In this reaction, chalcones with electron-donating groups as CH_3 and Cl (entries 4 and 5) gave better yields, but those with electron-withdrawing groups such as NO_2 afforded lower yields (entry 2). Interestingly, *p*-OCH_3-substituted chalcones worked to give low to moderate isolated yields (entries 3 and 6–8).

With the basic reaction conditions established, questions regarding the mechanism warranted further attention. Although it is known that TMSCl could activate the carbonyl group by the initial interaction of TMSCl with enones to activate the next step of the reaction,[5] the complete reaction mechanism of transition-metal-salt/TMSCl–catalyzed Sakurai–Michael

Table 2. Sakurai–type Michael reactions of allyltrimethylsilane with chalcones catalyzed by $FeCl_3$ in the presence of TMSCl

Entry[a]	Enone	Enone number	Product	Product number	Yield[b]
1		**1a**		**2a**	88
2		**1b**		**2d**	39
3		**1c**		**2c**	55
4		**1d**		**2d**	87
5		**1e**		**2e**	67
6		**1f**		**2f**	21
7		**1g**		**2g**	46
8		**1h**		**2h**	54

[a]Reaction conditions: 1.0 mmol of enone, 1.5 mmol of allylsilane, and 3 mL of solvent at room temperature for 3 h.

[b]Isolated yield (%) by silica column chromatography.

reaction of allyltrimethylsilane with enones was not clear in the past. A series of control experiments with chalcone and allyltrimethylsilane gave some mechanistic insight to better understanding the roles of the catalyst and additive. The results in Tables 1 and 2 show that transition-metal-salt-based Lewis acid and TMSCl should work synergistically in the hetero-Lewis acidic catalyst system. First, the importance of $FeCl_3$ and TMSCl was assessed by carrying out reactions in their absence. As shown in Table 1 (entries 4 and 12), both $FeCl_3$ and TMSCl are required for good reactivity. The results of these experiments were consistent with our working hypothesis based on the enhancement of the activity of $FeCl_3$ in the presence of TMSCl. The activation of Lewis acid by the formation of $Fe^{-}Cl_4 \cdot Si^{+}Me_3$ from $FeCl_3$ and TMSCl,[6,7] resulted in the improvement of catalytic activity of iron in Sakurai–Michael reaction.

In conclusion, we have developed a new catalytic Sakurai–Michael reaction of chalcones and allyltrimethylsilane promoted by the combination of iron(III) salts and TMSCl. This work offers good examples of the combination of Lewis acid and TMSCl catalyst for novel Sakurai–Mchael reactions of allylsilane with chalcones. Further studies are currently under way to expand the application of the reaction to asymmetric catalysis and establish the high reactivity and stereoselectivity with chalcones and allylsilane.

EXPERIMENTAL PART

General

All reaction flasks and solvent were used directly. Flash-column chromatography was performed over silica (100–200 mesh). NMR spectra were recorded on a 400-MHz spectrometer. ^{13}C NMR spectra were obtained with broadband proton decoupling. For spectra recorded in $CDCl_3$, unless noted, chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. IR spectra were recorded using an FTIR apparatus. Thin-layer chromatography (TLC) was performed using silica.

Typical Sakural–Michael Allylation Reaction Procedure

$FeCl_3$ (0.1 mmol), chalcone (1.0 mmol), allyltrimethylsilane (1.1 mmol), and TMSCl (1.5 mmol) in anhydrous CH_2Cl_2 (3 mL) were added to a Schlenk tube under argon. The mixture was stirred for 3 h at room temperature. After completion of the reaction, the mixture was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were washed with 2 N HCl, dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by column chromatography (petroleum ether/EtOAc 10:1) to give the pure products.

Selected Spectra Data of Products

1,3-Diphenylhex-5-en-1-one (**2a**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 7.88$ (m, 2H), 7.52 (m, 1H), 7.42 (m, 2H), 7.17–7.30 (m, 5H), 5.69 (m, 1H), 4.99 (m, 2H), 3.48 (m, 1H), 3.29 (d, $J = 8$ Hz, 2H), 2.46 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 198.78$, 144.20, 137.06, 136.12, 132.79, 128.37, 128.27, 127.87, 127.41, 126.22, 116.64, 44.40, 40.59, 40.54. GC-MS: m/z 250 (M, 4), 130 (58), 105 (100), 77 (39). IR (KBr): 3060, 3022, 2978, 2917, 1678, 1642, 1589, 1449, 1343, 1257, 1217, 984, 906 cm^{-1}.

3-(3-Nitrophenyl)-1-phenylhex-5-en-1-one (**2b**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 8.12$ (s, 1H), 8.04 (d, $J = 12$ Hz, 1H), 7.90 (d, $J = 8$ Hz, 2H), 7.58 (m, 2H), 7.45 (m, 3H), 5.68 (m, 1H), 5.02 (m, 2H), 3.63 (m, 1H), 3.37 (m, 2H), 2.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 197.79$, 148.22, 146.38, 136.62, 135.02, 134.30, 133.14, 129.11, 128.51, 127.80, 122.06, 121.42, 117.63, 43.80, 40.38, 40.13. GC-MS: m/z 295 (M, 3), 120 (37), 105 (100), 77 (41). IR (KBr): 3068, 2978, 2920, 1686, 1597, 1528, 1448, 1349, 1266, 1204, 1098, 1001, 920 cm^{-1}.

1-(4-Methoxyphenyl)-3-phenylhex-5-en-1-one (**2c**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 7.89$ (d, $J = 8$ Hz, 2H), 7.53 (t, $J = 8$ Hz, 1H), 7.42 (t, $J = 8$ Hz, 2H), 7.15 (d, $J = 8$ Hz, 2H), 6.82 (d, $J = 8$ Hz, 2H), 5.69 (m, 1H), 4.98 (m, 2H), 3.76 (s, 3H), 3.42 (m, 1H), 3.26 (m, 2H), 2.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 198.94$, 157.84, 137.08, 136.25, 136.22, 132.76, 128.36, 128.29, 127.87, 116.55, 113.63, 55.02, 44.65, 40.70, 39.85. GC-MS: m/z 280 (M), 160 (13), 105 (100), 77 (24). IR (KBr): 3064, 2998, 2929, 2830, 1684, 1610, 1597, 1513, 1448, 1300, 1248, 1178, 1036, 1001 cm^{-1}.

1-Phenyl-3-*p*-tolylhex-5-en-1-one (**2d**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 7.89$ (d, $J = 12$ Hz, 2H), 7.52 (t, $J = 4$ Hz, 1H), 7.42 (t, $J = 8$ Hz, 2H), 7.11 (m, 4H), 5.69 (m, 1H), 4.97 (m, 2H), 3.43 (m, 1H), 3.26 (m, 2H), 2.44 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 198.87$, 141.15, 137.08, 136.26, 135.65, 132.75, 128.97, 128.36, 127.88, 127.24, 116.54, 44.53, 40.58, 40.18, 20.86. GC-MS: m/z 264 (M), 144 (31), 129 (10), 105 (100), 77 (27). IR (KBr): 3060, 3022, 2978, 2921, 1686, 1597, 1515, 1448, 1360, 1267, 1200, 1114, 1001, 915 cm^{-1}.

3-(2-Chlorophenyl)-1-phenylhex-5-en-1-one (**2e**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 7.93$ (d, $J = 8$ Hz, 2H), 7.53 (t, $J = 4$ Hz, 1H), 7.44 (t, $J = 8$ Hz, 2H), 7.35 (d, $J = 8$ Hz, 1H), 7.24 (m, 1H), 7.13 (t, $J = 4$ Hz, 1H), 5.70 (m, 1H), 4.98 (m, 3H), 4.04 (m, 1H), 3.33 (d, $J = 8$ Hz, 2H), 2.49 (t, $J = 8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 198.28$, 141.20, 136.85, 135.60, 133.87, 132.88, 129.69, 128.41, 127.90, 127.28, 126.67,

116.92, 43.00, 38.92, 36.55. GC-MS: m/z 284 (M), 249 (12), 164 (18), 129 (32), 105 (100), 77(40). IR (KBr): 3072, 2957, 2892, 2827, 1681, 1595, 1476, 1446, 1436, 1350, 1263, 1215, 1034, 985, 924 cm^{-1}.

1,3-Bis(4-methoxyphenyl)hex-5-en-1-one (**2f**): ^1H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 7.88$ (d, $J = 8$ Hz, 2H), 7.14 (d, $J = 8$ Hz, 2H), 6.90 (d, $J = 12$ Hz, 2H), 6.82 (d, $J = 6$ Hz, 2H), 5.68 (m, 1H), 4.98 (m, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 3.41 (m, 1H), 3.20 (m, 2H), 2.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 197.48$, 163.17, 157.81, 136.36, 136.31, 130.21, 130.15, 128.27, 116.43, 113.60, 113.47, 55.27, 55.01, 44.33, 40.65, 40.05. IR (KBr): 3073, 3000, 2920, 2837, 1675, 1639, 1600, 1575, 1511, 1463, 1419, 1363, 1305, 1248, 1169, 1032, 997, 915 cm^{-1}.

3-(4-Methoxyphenyl)-1-(4-nitrophenyl)hex-5-en-1-one (**2g**): ^1H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 8.25$ (d, $J = 8$ Hz, 2H), 8.00 (d, $J = 12$ Hz, 2H), 7.13 (d, $J = 8$ Hz, 2H), 6.81 (d, $J = 8$ Hz, 2H), 5.70 (m, 1H), 5.02 (m, 2H), 3.78 (s, 3H), 3.39 (m, 1H), 3.30 (m, 2H), 2.45 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 197.56$, 158.04, 150.01, 141.51, 135.94, 135.57, 128.83, 128.21, 123.60, 116.89, 113.75, 55.02, 45.12, 40.71, 39.93. IR (KBr): 3064, 2999, 2931, 2835, 1685, 1639, 1611, 1597, 1513, 1448, 1362, 1301, 1248, 1201, 1179, 1036, 1001, 916 cm^{-1}.

3-(4-Methoxyphenyl)-1-phenylhex-5-en-1-one (**2h**): ^1H NMR (400 MHz, $CDCl_3$, ppm), $\delta = 7.88$ (d, $J = 12$ Hz, 2H), 7.51 (t, $J = 4$ Hz, 1H), 7.42 (t, $J = 8$ Hz, 2H), 7.15 (d, $J = 8$ Hz, 2H), 6.81 (d, $J = 12$ Hz, 2H), 5.69 (m, 1H), 4.98 (m, 2H), 3.76 (s, 3H), 3.42 (m, 1H), 3.25 (m, 2H), 2.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 198.93$, 157.86, 137.11, 136.25, 136.23, 132.74, 128.36, 128.29, 127.87, 116.53, 113.64, 55.02, 44.66, 40.69, 39.88. IR (KBr): 3073, 3000, 2920, 2837, 1675, 1639, 1600, 1575, 1511, 1463, 1419, 1363, 1304, 1248, 1169, 1112, 1032, 997, 915 cm^{-1}.

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