In(III)-Mediated Chemoselective Dehydrogenative Interaction of ClMe$_2$SiH with Carboxylic Acids: Direct Chemo- and Regioselective Friedel–Crafts Acylation of Aromatic Ethers
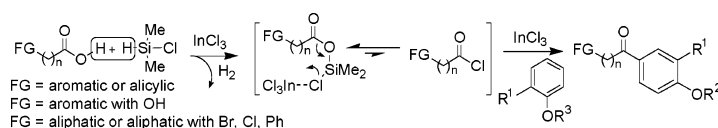
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ABSTRACT

Chemoselective dehydrogenative interaction of ClMe$_2$SiH with a carboxylic acid group in the presence of InX$_3$ is reported. ^{13}C NMR investigation revealed the formation of PhCOOSi(Cl)Me$_2$ as the major transient intermediate. Chemo- and regioselective Friedel–Crafts acylation of aromatic ethers directly from carboxylic acids was established.

Silicon-based reagents have found extensive synthetic applications and are intensively studied in organic syntheses.[1] Indium-mediated reactions are emerging as effective protocols in modern organic chemistry.[2,3] Significantly, the combination of indium and silicon reagents has been found to be exciting in recent synthetic applications.[4]

In the course of applications of indium/silicon-mediated processes, recently we have found the reduction of 1-phenyl-2-propanol into 1-phenylpropane using a ClPh$_2$SiH/InCl$_3$ system, in which elimination of HCl took place.[5a] Surprisingly, addition of benzil changed the reaction path to give

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2-chloro-1-phenylpropane via evolution of H_2 gas instead of 1-phenylpropane (Scheme 1).[5b]

Scheme 1
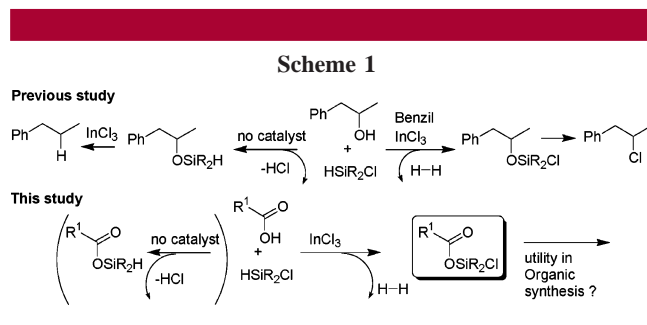
Prompted by the mechanistic illustration of these exciting reactions, we envisioned that evolution of H_2 gas by the interaction of carboxylic acids with $ClMe_2SiH$ in the presence of InX_3 would generate transient silyl intermediates that are applicable in synthetic organic processes. Although preparations of silyl esters have been reported, nevertheless, there exist very rare reports that reveal the utility of silyl esters in organic syntheses.[6] Herein we report the chemoselective interaction of $ClMe_2SiH$ with carboxylic acids in the presence of InX_3 and application of the protocol for the direct Friedel−Crafts acylation of aromatic ethers.[7,8]

Initially, we investigated the interaction of PhCOOH (**1a**, 1 mmol) and $ClMe_2SiH$ (1.2 mmol) in the absence of $InCl_3$. ^{13}C NMR spectra at various intervals showed only the peaks corresponding to PhCOOH and $ClMe_2SiH$ (Figure 1, spectra B). Apparently, neither elimination of HCl nor an interaction of PhCOOH with $ClMe_2SiH$ was detected.

Next, when $InCl_3$ (10−30 mol %) was added to a solution of PhCOOH (**1a**) and $ClMe_2SiH$ in 1,2-dichloroethane, a

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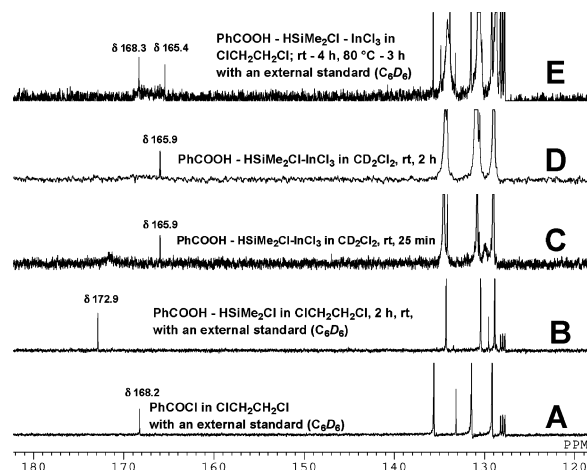
Figure 1. Partial ^{13}C NMR spectra in the investigation of the interaction of PhCOOH with $ClMe_2SiH$.

gradual evolution of H_2 gas was observed,[9a] which ceased within 1 h. Surprisingly, no additive (benzil) was required, unlike in the case of chlorination of an alcohol.[5b] However, the expected PhCOCl generation was not observed. Interestingly, the ^{13}C NMR spectrum revealed the formation of a new peak at 165.9 ppm,[9b] which plausibly corresponds to the carbonyl group of the silyl ester $PhCOOSi(Cl)Me_2$, because a quantitative evolution of H_2 gas was observed (Figure 1, spectra C/D).

Unfortunately, we failed in our attempts to isolate the transient intermediate $PhCOOSi(Cl)Me_2$. Further, a mixture of PhCOOH, $ClMe_2SiH$, and $InCl_3$ in $ClCH_2CH_2Cl$ was heated at 80 °C for 4 h. The ^{13}C NMR spectrum showed the formation of two new peaks at 168.3 and 165.4 ppm, which plausibly correspond to PhCOCl and $PhCOOSi(Cl)Me_2$, respectively (spectra E). In addition, we set up the distillation of the solution (spectra E) under reduced pressure (see Supporting Information for details), which gave PhCOCl in <20% yield.[9c,d] These results possibly revealed that PhCOCl is produced from in situ chlorination of silyl ester ($PhCOOSi(Cl)Me_2$) at high temperature; however, the conversion rate is extremely slow.

Next, we focused our attention on the direct Friedel−Crafts reaction process from carboxylic acids. Initially, the con-

(9) (a) In a separate experiment (carried out with equimolar amounts of reactants), after the addition of $InCl_3$ the evolution of H_2 gas was observed, which was collected into a graduated cylinder (100 mL) inversely kept in a beaker (300 mL). The observed volume change was quantitative. However, employing $ZnCl_2$ failed to afford the evolution of H_2 gas effectively at room temperature under our experimental condition. In the case of $AlCl_3$ the observed volume change was very low (<20%). (b) Based on the kind hint by a referee, using a platinum catalyst (10 mol % of $H_2PtCl_6 \cdot 6H_2O$), the formation of a new peak at δ 165.5 (1,2-DCE, C_6D_6 as an external standard), for the C=O group of $PhCOOSi(Cl)Me_2$ was noted with the evolution of H_2 gas as in the $InCl_3$ system. However, the reaction was incomplete even after a prolonged time. (c) Details of the reaction and ^{13}C NMR spectra are given in Supporting Information. (d) We have not observed the other possible intermediate $(PhCOO)_2SiMe_2$ (**7**) along with PhCOCl during distillation under reduced pressure (150−165 °C/0.2−0.3 mm), as it was (**7**, C=O, 165.7 ppm, 1,2-DCE, C_6D_6 as an external standard) prepared and distilled at a similar temperature under reduced pressure (150−165 °C/0.2−0.3 mm, see Supporting Information). (e) In some of the reactions, traces of regioisomers could be detected in the crude NMR.

ventional benzoylation of anisole with PhCOCl (**1b**) was performed. InCl$_3$ (5 mol %) gave the product **3a** in 89% yield. In contrast, an equimolar amount of AlCl$_3$ was required to obtain a high yield of **3a** (Scheme 1). This was because of the strong oxophilicity that disturbed the dissociation of AlCl$_3$ from produced ketone. The above results strongly encouraged us to envision the InX$_3$-mediated direct acylation of aromatic ethers using carboxylic acids.

Scheme 2

MX$_3$/mol %	**3a**: yield/ %
InCl$_3$ or InBr$_3$ (5)	89
AlCl$_3$ (5)	15
AlCl$_3$ (100)	99
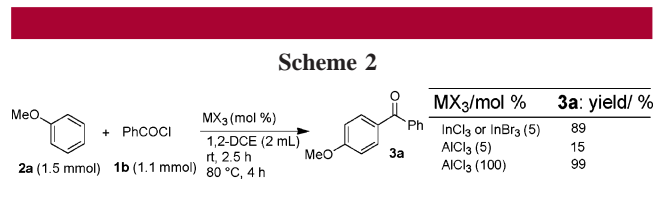
At first, we selected the reaction of 5-phenylvaleric acid (**1c**) with anisole for optimization of the reaction conditions (Table 1). We screened the reactions using InX$_3$ under

Table 1. Optimization of the Reaction Conditions

MX$_3$^{a}	**3b**: yield/ %	MX$_3$	mol %	**3b**: yield/ %	MX$_3$^{a}	**3b**: yield/ %
Yb(OTf)$_3$	0	In(OTf)$_3$	25	28	InCl$_3$	0^d
Sc(OTf)$_3$	<5	InBr$_3$	30	74	InCl$_3$	0^e
BiCl$_3$	0	InBr$_3$	50	83	InCl$_3$	0^f
SnCl$_2$	0	InCl$_3$	10	40	InCl$_3$	0^g
ZnCl$_2$	<20	InCl$_3$	50	62	InBr$_3$	66^h
HfCl$_4$	0	InCl$_3$	50	18^b	InCl$_3$	49^h
AlCl$_3$	0	InCl$_3$	50	50^c		

^{a} 30 mol %. ^{b} Solvent = EtOAc or MeCN. ^{c} Solvent = toluene. ^{d} Solvent = THF or 1,4-dioxane. ^{e} Et$_3$SiH was used instead of HSiMe$_2$Cl. ^{f} (EtO)$_3$SiH was used instead of HSiMe$_2$Cl. ^{g} Ph$_3$SiH was used instead of HSiMe$_2$Cl. ^{h} HSi(^{i}Pr)$_2$Cl was used instead of HSiMe$_2$Cl.

various conditions to afford the product **3b**. Solvents having strong coordination ability such as THF and 1,4-dioxane gave no products. MeCN and EtOAc gave poor results. Nonpolar solvent such as toluene also afforded the product **3b** in moderate yield, and competitive acylation of toluene was not detected. We successfully optimized the conditions whereupon InCl$_3$ or InBr$_3$ (30 mol %) in ClCH$_2$CH$_2$Cl serves as the best system. Under similar conditions, other traditional and water-tolerant Lewis acids such as AlCl$_3$, BiCl$_3$, and Sc-(OTf)$_3$ did not afford the product **3b**. Using Et$_3$SiH or (EtO)$_3$SiH instead of HSiMe$_2$Cl did not promote the reaction, and recovery of the acid was noted even though evolution of H$_2$ gas was observed. However, HSi(^{i}Pr)$_2$Cl gave the product **3b** like HSiMe$_2$Cl. In all runs, the competitive intramolecular acylation product **3b'** from **1c** was not observed.

The generality of this reaction was tested with a variety of functionalized carboxylic acids and aromatic ethers. Interestingly, in all cases, the regioselective carbonylation took place at the *para* position of aromatic ethers (Table 2).[9e] 5-Phenylvaleric acid (**1c**), 3-phenylpropionic acid (**1d**),

Table 2. Friedel−Crafts Acylation Using Carboxylic Acids^a

entry	RCOOH	aromatics	product	yield/ %^{b}
1 2	Ph(CH$_2$)$_4$COOH **1c**	**2b**: R=Me **2c**: R=Ph		**3c**: R=Me; 68 (75) **3d**: R=Ph; 63
3	Ph(CH$_2$)$_2$COOH **1d**	**2d**		**3e**: 72 (74)
4		**2e**		**3f**: 75
5		**2a**		**3g**: 73 (79)
6 7	RX	**2f**: RX=OBu^n **2g**: RX=SMe		**3h**: RX=OBu^n; 77 **3i**: RX=SMe; 58
8 9	**1e**	**2a**: R=H **2b**: R=Me		**3j**: R=H; 78 (82) **3k**: R=Me; 83 (80)
10 11	Cl(CH$_2$)$_5$COOH **1f**	**2b**: R=Me **2h**: R=F		**3l**: R=Me; 78 (83) **3m**:R=F; 72
12		**2d**		**3n**: 73
13	Br(CH$_2$)$_5$COOH **1g**	**2g**		**3o**: 69
14	Br(CH$_2$)$_{10}$COOH **1h**	**2b**		**3p**: 71 (74)
15 16	PhCOOH **1a**	**2i**: X=Cl **2j**: X=Br		**3q**: X=Cl; 67/73^c **3r**: X=Br; 62/70^c
17	*p*-MeOC$_6$H$_4$COOH **1i**	**2a**		**3s**: 70^d
18	CH$_3$(CH$_2$)$_9$COOH **1j**	**2a**		**3t**: 73
19		**2d**		**3u**: 74 (78)
20	**1k**	**2a**		**3v**: 78 (83)
21	**1l**	**2b**		**3w**: 81
22	**1m**	**2b**		**3x**: 81

^{a} Reaction conditions: **2a−j** (1.5−2 mmol), acid (1 mmol), HSiMe$_2$Cl (1.2 mmol), and InCl$_3$ (30 mol %) in ClCH$_2$CH$_2$Cl (2−3 mL) were used; 1 h at rt, then heated at 80 °C for 4 h. ^{b} Yields in parentheses correspond to the reactions in which InBr$_3$ was used instead of InCl$_3$. ^{c} No solvent was used; reaction was carried out in neat condition. ^{d} In the case of **1j**, 6 mL of solvent was used.

and 2-phenylbutyric acid (**1e**) reacted with various phenyl ethers to give the corresponding ketones in good yields. Competitive over-reactions or intramolecular Friedel−Crafts acylation at the terminal phenyl moieties was not observed (entries 1−9). Comparatively higher yields were obtained using InBr$_3$ instead of InCl$_3$. Employing the ω-halo carboxylic acids **1f**, **1g**, and **1h**, the chemoselective acylation of aromatic ethers was observed. However, competitive Friedel−Crafts alkylation of aromatic ethers was not detected (entries 10−14), although this process would be readily promoted by a catalytic amount of Lewis acid. Unfunctionalized aliphatic/aromatic carboxylic acids (**1i−1m** and **1a**) were also reacted to furnish the corresponding ketones (entries 15−22). Interestingly, the reactions were also carried out without any solvent to afford acylation products (e.g., entries 15 and 16).

Though rare reports are available on Friedel−Crafts acylations using acid chlorides having a free hydroxyl moiety,[10] we believed that InX$_3$ would promote the Friedel−Crafts acylations of aromatic ethers with hydroxyl carboxylic

acids because of its mildness and moisture tolerance. The reaction of 4-hydroxybenzoic acid (**1n**) with **2d** gave the product **4a** in 67% yield (Table 3). Other examples of

**Table 3.** Friedel−Crafts Reaction of Hydroxyl Carboxylic Acid[a]

entry	carboxylic acid	aromatics	product	yield/ %[b]
1	**1n**	**2d**		**4a**: 67
2	**1n**	**2c**		**4b**:R^1=Me, R^2= Ph; 63
3		**2b**		**4c**:R^1=Me, R^2= Me; 62
4		**2f**		**4d**:R^1=Bu^n, R^2= H; 60
5	**1o**	**2a**		**4e**: 52 (77)

[a] Conditions: **2a−d,f** (1.5 mmol), **1n,o** (1 mmol), HSiMe$_2$Cl (2.4 mmol), and InCl$_3$ (50 mol %) in ClCH$_2$CH$_2$Cl (6 mL) were used; 1.5−2 h at rt, then heated at 80 °C for 4−5 h. [b] Yield in the parentheses corresponds to the reactions in which InBr$_3$ was used instead of InCl$_3$.

acylation of aromatic ethers using **1n** or 3-(4-hydroxyphenyl)-propionic acid (**1o**) were also developed. These results allowed further expansion of the capability of the Friedel−Crafts acylation directly from free hydroxyl-substituted carboxylic acid.

Next, we checked the scope and limitations of this protocol. At this stage, a limitation of this reaction is the acylation of toluene was not effective. However, 4-phenylbutyric acid (**1p**) successfully afforded the intramolecular Friedel−Crafts acylation product **6a** (67% Scheme 3) without

Scheme 3
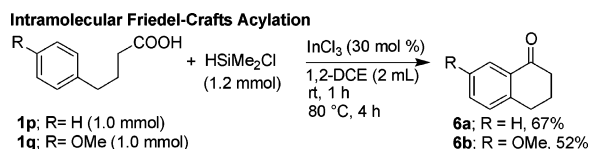
the assitance of alkoxy moiety (OR). Similarly, 4-(4-methoxyphenyl)-butyric acid (**1q**) also afforded the product **6b** (52%).

On the basis of ^{13}C NMR studies on the interaction of PhCOOH with ClMe$_2$SiH and the observed results, the mechanism of direct Friedel−Crafts acylation could be proposed via in situ generated transient species (PhCOOSi-(Cl)Me$_2$, Scheme 4). It might be considered that there is an interaction of InCl$_3$ with the chlorine atom of HSiMe$_2$Cl/

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Scheme 4
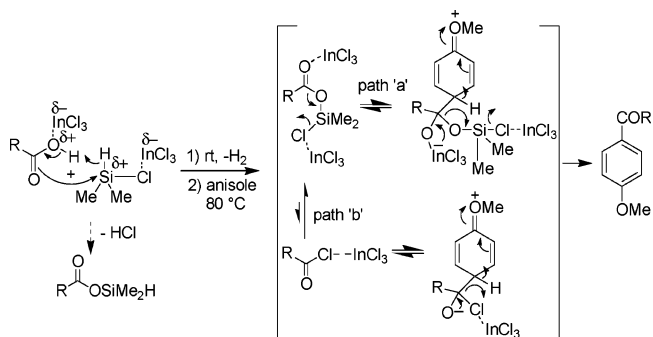
PhCOOSiMe$_2$Cl,[4h] thereby making the silicon center more electropositive. Apparently, this interaction might be important for mediating the dehydrogenative interaction to give the transient species (PhCOOSiMe$_2$Cl) and the successive Friedel−Crafts acylation,[4i] because Et$_3$SiH or (EtO)$_3$SiH were ineffective in the present case. Further, it could be plausibly proposed that the major transient silyl ester PhCOOSi(Cl)-Me$_2$ itself is the predominant acylating agent.[11] This proposal could be supported by an experiment in which the treatment of silyl ester (PhCOO)$_2$SiMe$_2$ (**7**,[9d] 0.8 mmol) with excess amounts of reagents (anisole (2 mmol) and InCl$_3$ (0.4 mmol)) gave the product **3a**, in very low yield (38%). Further, in this stage, perhaps we cannot ignore PhCOCl as the minor intermediate in the present system (though its formation from PhCOOSi(Cl)Me$_2$ is very low at high temperature, Figure 1).

In conclusion, we have discovered a chemoselective dehydrogenative interaction of ClMe$_2$SiH with the carboxylic acid group in the presence of InX$_3$. In view of exploiting the process, chemo- and regioselective direct Friedel−Crafts acylation of aromatic ethers from functionalized carboxylic acids was established. Further work and applications are under investigation.

Supporting Information Available: Experimental procedures, spectral data of products, ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) We sincerely thank the referees for their kind suggestions to improve the proposed mechanism.