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Direct Carboxylation of Arenes and Halobenzenes with CO_2 by the Combined Use of $AlBr_3$ and R_3SiCl

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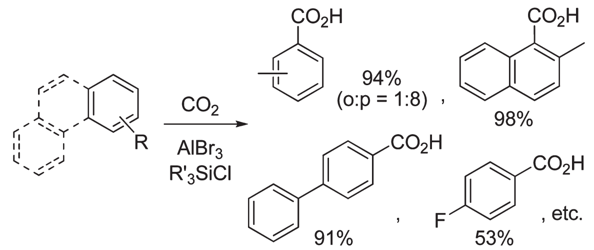
Received September 14, 2010



The Lewis acid-mediated direct carboxylation of aromatic compounds with CO_2 is efficiently promoted by the addition of silyl chlorides bearing three alkyl and/or aryl substituents in total on the silicon atom. Thus, toluene, xylenes, mesitylene, and some other alkylbenzenes are treated with a 1:1 mixture of $AlBr_3$ and Ph_3SiCl in neat substrates under CO_2 pressure (3.0 MPa) at room temperature, to give the corresponding carboxylic acids in 60−97% yields, based on $AlBr_3$. Polycyclic arenes, including naphthalene, phenanthrene, and biphenyl, are regioselectively carboxylated in 91−98% yields with the aid of 1 molar equiv of $AlBr_3$ and Ph_3SiCl in an appropriate solvent, chosen from benzene, chlorobenzene, and fluorobenzene. These solvents, as well as bromobenzene, resist carboxylation; however, they are also carboxylated in moderate yields when treated with a 1:5 mixture of $AlBr_3$ and ^{i}PrSiCl at elevated temperatures. The FT-IR spectrum of a mixture prepared by exposing a suspension of $AlBr_3$ and Ph_3SiCl in cyclohexane to CO_2 exhibits an absorption band around 1650 cm^{-1}, assigned to the C=O stretching vibration of a species consisting of CO_2, $AlBr_3$, and Ph_3SiCl, which suggests that the silyl chlorides activate CO_2 in cooperation with $AlBr_3$. ^1H NMR analysis of unworked-up reaction mixtures reveals that the products merge as aluminum carboxylates. The mass balance concerning silicon indicates that the silyl chlorides are recycled during the reaction sequence. On the basis of these observations, a feasible mechanism is proposed for the present carboxylation.

Introduction

There has been a growing interest in the development of efficient methods for the chemical fixation of CO_2, which is an abundant, inexpensive, nontoxic, and renewable carbon source.[1] The carboxylation of carbon nucleophiles with CO_2 is one of the most fundamental processes for CO_2 fixation. Because of the relatively low reactivity of CO_2, the reaction generally requires strong nucleophiles, such as organolithium and Grignard reagents, which devalues this transformation with regard to functional group compatibility. However, remarkable progress has been made with the development of the transition metal-catalyzed insertion of CO_2 into less polarized metal−carbon bonds of organometallics such as allylstannanes,[2] organozincs,[3] and organoboronic

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DOI: 10.1021/jo101808z

esters.[4] It is also a recent important finding that alkali metals can mediate metalation,[5−10] transmetalation,[11] and metal insertion into carbon−halogen bonds;[12−15] this finding provides an otherwise difficult access to functionalized organomagnesium,[5,6,11,12] aluminum,[7,13] zinc,[6,8,14] copper,[9] cadmium,[10] and indium reagents,[15] which can be used for the nucleophilic carboxylation, either by itself or in combination with the catalytic metal−carbon bond insertion.[16] The transition metal-mediated or catalyzed hydrocarboxylation[17] and alkylative carboxylation[18] of unsaturated C−C bonds are also promising approaches for obtaining carboxylic acids.

On the other hand, it has been known that aromatic compounds can be directly carboxylated with CO_2 with the aid of aluminum-based Lewis acids.[19,20] The reaction is believed to be an electrophilic fixation of CO_2, in which a Lewis acid-activated CO_2 molecule electrophilically attacks an aromatic nucleus, according to the electrophilic aromatic substitution (S_EAr) mechanism.[21] Carboxylic acids are generally obtained in poor yields using this procedure because of the low electrophilicity of CO_2 and/or side reactions caused by the strong Lewis acidity of aluminum-based compounds. Recently, the research group of Olah and Prakash has reported that the yield of carboxylic acids can be improved by the addition of aluminum powder together with $AlCl_3$.[21] This increase in the yield was attributed to the ability of metallic aluminum to scavenge HCl liberated by carboxylation to give $AlCl_3$. The in situ-generated $AlCl_3$ initiates further carboxylation, while HCl disturbs the reaction. Therefore, the aluminum powder acts in two distinct capacities for promoting carboxylation. In the same paper,[21] the authors proposed an activation mechanism of CO_2 using $AlCl_3$ based on DFT calculation. Munshi and Beckman have reported that the carboxylation of toluene proceeds efficiently by incubating $AlCl_3$ under CO_2 pressure prior to the reaction and that this manipulation enables weaker Lewis acids, such as $SnCl_4$, $MoCl_5$, and $TiCl_4$, to replace $AlCl_3$ without appreciable loss of the product yield.[22] These observations indicate that the complexation between a Lewis acid and CO_2 is important for the present carboxylation, which supports Olah's mechanism.

It is known that a trialkylsilyl group on an aromatic nucleus promotes the S_EAr reaction and that it directs the reaction to the ipso position. This is because the silyl moiety stabilizes the transition state, leading to the formation of a benzenonium intermediate by the $(p\text{-}\sigma)_\pi$ conjugation between the Si−C bond and developing positive charge (the β-effect).[23] We reported that trimethylsilyl-substituted benzene, toluene, and naphthalene underwent Lewis acid-mediated carboxylation more efficiently than the corresponding arenes.[24] During this study, we have found that the carboxylation of arenes is significantly promoted by the addition of trialkyl- or triarylsilyl chlorides. Herein, we wish to report in detail the beneficial effect of silyl chlorides in the Lewis acid-mediated carboxylation of arenes, as well as halobenzenes.[25]

Results and Discussion

Carboxylation of Arenes and Halobenzenes. First, toluene was carboxylated under CO_2 pressure at room temperature with various silyl halides acting as promoters (Table 1). The initial CO_2 pressure was adjusted to 3.0 MPa and $AlBr_3$ was employed as a Lewis acid, according to our previous study.[19g] The reaction was carried out in the neat substrate, and the yield of toluic acid was calculated on the basis of the amount of $AlBr_3$, assuming that 1 mol of $AlBr_3$ is consumed per mole of toluic acid produced (vide infra). Carboxylation carried out with 1.0 molar equiv of Me_3SiCl to $AlBr_3$ gave a 1:3 mixture of *o*- and *p*-toluic acid in a 21% yield (entry 2), while the yield dropped to 10% (o:p = 1:33) in the absence of Me_3SiCl (entry 1). Other trimethylsilyl halides were less effective than Me_3SiCl (entries 3 and 4). The replacement of the methyl groups of Me_3SiCl with long chains or branched alkyl groups favorably affected the yield of toluic acid; the introduction of one such substituent increased the yield to 30% (entries 10 and 11), whereas the introduction of three such substituents increased the yield to 40% (entries 14 and 15). The phenyl group was more effective, giving yields of 51%, 75%, and 94% by replacing one through three of the methyl groups, respectively (entries 19, 21, and 24). The difference in magnitude of the promoting effect of the silyl chlorides seems to originate from the difference in magnitude of the electron-donating effect

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TABLE 1. Carboxylation of Toluene in the Presence of Various R_3SiX in the Neat Substrate[a]

entry	R_3SiX	$R_3SiX/AlBr_3$[b]	yield (%)[c]	o:p ratio[d]
1	none		10	1:33
2	Me_3SiCl	1.0	21	1:3
3	Me_3SiBr	1.0	11	1:3
4	Me_3SiI	1.0	5	1:4
5	Me_3SiCl	2.0	45	1:4
6	Me_3SiCl	3.0	63	1:4
7	Me_3SiCl	4.0	73	1:5
8	Me_3SiCl	5.0	80	1:5
9	Me_3SiCl	10.0	96	1:6
10	$[CH_3(CH_2)_{17}]Me_2SiCl$	1.0	30	1:3
11	$^tBuMe_2SiCl$	1.0	27	1:3
12	$^tBuMe_2SiCl$	2.0	55	1:3
13	$^tBuMe_2SiCl$	3.0	79	1:4
14	$[CH_3(CH_2)_5]_3SiCl$	1.0	39	1:5
15	$^iPr_3SiCl$	1.0	40	1:6
16	$^iPr_3SiCl$	2.0	73	1:6
17	$^iPr_3SiCl$	3.0	83	1:8
18	$(Me_3Si)_3SiCl$	1.0	43	1:4
19	$Me_2PhSiCl$	1.0	51	1:5
20	$Me_2PhSiCl$	2.0	84	1:5
21	$MePh_2SiCl$	1.0	75	1:5
22	$MePh_2SiCl$	2.0	93	1:5
23	$^tBuPh_2SiCl$	1.0	89	1:6
24	Ph_3SiCl	1.0	94	1:8

[a] Reaction conditions: substrate (2.0 mL), CO_2 (initial pressure, 3.0 MPa), $AlBr_3$ (1.00 mmol), rt, 3 h. [b] Molar ratio. [c] Yield of isomer mixture based on the quantity of $AlBr_3$. [d] Determined by ^1H NMR analysis.

of the substituents, stabilizing a silyl cation (vide infra). Increasing the amount of silyl chlorides also improved the product yield with varying efficiency, depending on the substituents on the silicon atom. For example, toluic acid was obtained in a synthetically useful yield (80%) by employing 5.0 molar equiv of Me_3SiCl (entry 8), whereas the amount could be reduced to 3.0 molar equiv for $^tBuMe_2SiCl$ and $^iPr_3SiCl$ (entries 13 and 17) and to 2.0 molar equiv for $Me_2PhSiCl$ (entry 20) without losing the yield. There is a loose but steady tendency in regioselectivity that the bulkier the silyl chloride is, the more selectively the reaction proceeds at the para position (entries 2, 10, 11, 14, and 15; entries 19, 22, and 24). It is interesting to note that increasing the amount of the silyl chloride also improves the para selectivity (entries 2−9; entries 11−13; entries 15−17). This fact may suggest that the molar ratio of the silyl chloride to $AlBr_3$ affects the composition of active species generated from the silyl chloride, $AlBr_3$, and CO_2 during the reaction (vide infra).

Several other alkylbenzenes were carboxylated with the aid of Ph_3SiCl or Me_3SiCl (Table 2); these silyl chlorides were chosen as promoters, on the basis of their performance observed in the carboxylation of toluene (vide supra) and their practical usefulness. Olah et al. reported that ethylbenzene and *tert*-butylbenzene, on treatment with $AlCl_3$ and aluminum powder under CO_2 pressure at 20−40 °C, preferentially underwent disproportionation rather than carboxylation to give benzene and 1,4-dialkylbenzene, the latter of which was in situ carboxylated to give 2,5-dialkylbenzoic acid.[21] In contrast, these compounds were successfully carboxylated under our conditions to give monoalkylbenzoic acids in good yields (entries 1 and 2). The reaction of xylenes proceeded with the regioselectivity rationalized by the S_EAr mechanism to produce a mixture of dimethylbenzoic acids (entries 3−8). In the case of *o*- and *p*-xylene, 2,4-dimethylbenzoic acid was also obtained as a minor product (entries 3, 4, 7, and 8), indicating that a portion of the substrates isomerized to thermodynamically more stable *m*-xylene, prior to the carboxylation, under the Lewis acidic conditions.[26] The Lewis acid-mediated carboxylation often affords diaryl ketones, the formation of which can be rationalized by the initial carboxylation of a starting aromatic compound, followed by the Friedel−Crafts acylation between the resulting carboxylic acid and another molecule of the starting aromatic, to the corresponding diaryl ketone. In fact, the carboxylation of mesitylene with the aid of Me_3SiCl produced dimesityl ketone as a minor product, in addition to 2,4,6-trimethylbenzoic acid (entry 9). However, the use of Ph_3SiCl could suppress the formation of the ketone, giving the desired acid in an almost quantitative yield (entry 10). This means that Ph_3SiCl hastened the carboxylation so efficiently that the subsequent acylation could be ignored. Another benzene derivative, which we supposed to undergo the carboxylation, is anisole. However, the reaction of anisole carried out under the same conditions as those employed for alkylbenzenes using 1.0 molar equiv of Ph_3SiCl did not give any acidic products, recovering the substrate almost unchanged (97%).

It is difficult to successfully apply the Lewis acid-mediated carboxylation to fused aromatic compounds, because they have a marked tendency to dehydrocouple, to form polyaryls, in the presence of Friedel−Crafts catalysts (the Scholl reaction).[27] We reported that the carboxylation of naphthalene, carried out in benzene with the aid of $AlBr_3$ at 40 °C, gave naphthoic acid in a moderate yield (43%), accompanied by many neutral byproduct, consuming the entire substrate.[19g] We have attempted the carboxylation of naphthalene using 1.0 molar equiv of Ph_3SiCl as a promoter in various solvents (Table 3, entries 1−6). Fortunately, the reaction proceeded smoothly in carbon disulfide and halobenzenes to produce naphthoic acid in good to excellent yields (entries 2, 4, and 5). On the other hand, cyclohexane and benzene were less effective as solvents (entries 1 and 3). The superiority of carbon disulfide and halobenzenes over cyclohexane seems to be largely attributable to their high solvency toward the substrate, as well as the reagents. However, another reason for the carboxylation to proceed smoothly in these solvents is derived from the fact that halobenzenes are superior to benzene, despite both being good solvents for the reactants, and that the performance of the aromatic solvents occurs in the following order: fluorobenzene > chlorobenzene > benzene. Mechanistic studies of S_EAr reactions are revealing that, in the course of the interaction between a substrate and an electrophile, they first form a π complex and it is then converted into an arenium ion.[28] The order of the performance of aromatic solvents may therefore be interpreted as indicating that the more the aromatic ring of a solvent is electron deficient, the more difficult it is for the solvent molecule to form a π complex and, as a result, to a lesser extent, the solvent disturbs the complexation between a substrate and an electrophile. However, an attempt to employ highly electron-deficient nitrobenzene as a solvent failed; it decomposed under the reaction conditions (entry 6). Other fused polycyclic aromatic compounds, as well as nonfused ones, were carboxylated in benzene and/or halobenzenes using 1.0 molar equiv of Ph_3SiCl as a promoter (entries 7−19). By choosing a proper solvent

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TABLE 2. Carboxylation of Alkylbenzenes in the Presence of Ph$_3$SiCl or Me$_3$SiCl in Neat Substrates[a]

entry	substrate	R$_3$SiCl	R$_3$SiCl/AlBr$_3$[b]	product (distribution)[c]	yield (%)[d]
1	ethylbenzene	Ph$_3$SiCl	1.0	ethylbenzoic acid (o:p = 1:20)	61
2	*tert*-butylbenzene	Ph$_3$SiCl	1.0	*p-tert*-butylbenzoic acid	72
3	*o*-xylene	Me$_3$SiCl	5.0	dimethylbenzoic acid (3,4:2,3:2,4 = 15:1:1)	51
4	*o*-xylene	Ph$_3$SiCl	1.0	dimethylbenzoic acid (3,4:2,3:2,4 = 17:2:1)	60
5	*m*-xylene	Me$_3$SiCl	5.0	dimethylbenzoic acid (2,4:2,6 = 1:trace)	50
6	*m*-xylene	Ph$_3$SiCl	1.0	dimethylbenzoic acid (2,4:2,6 = 20:1)	67
7	*p*-xylene	Me$_3$SiCl	5.0	dimethylbenzoic acid (2,5:2,4 = 5:1)	53
8	*p*-xylene	Ph$_3$SiCl	1.0	dimethylbenzoic acid (2,5:2,4 = 10:1)	65
9	mesitylene	Me$_3$SiCl	5.0	2,4,6-trimethylbenzoic acid dimesityl ketone	87 6
10	mesitylene	Ph$_3$SiCl	1.0	2,4,6-trimethylbenzoic acid	97

[a] Reaction conditions: substrate (2.0 mL), CO$_2$ (initial pressure, 3.0 MPa), AlBr$_3$ (1.00 mmol), rt, 3 h. [b] Molar ratio. [c] Determined by ^{1}H NMR analysis. [d] Yield of isomer mixture or isolated pure product based on the quantity of AlBr$_3$.

TABLE 3. Carboxylation of Polycyclic Aromatic Compounds in the Presence of Ph$_3$SiCi in Solution[a]

entry	substrate	solvent	product (distribution)[b]	yield (%)[c]
1	naphthalene	cyclohexane	naphthoic acid (1:2 = 1:trace)	13
2	naphthalene	CS$_2$	naphthoic acid (1:2 = 12:1)	80
3	naphthalene	benzene	naphthoic acid (1:2 = 12:1)	68
4	naphthalene	chlorobenzene	naphthoic acid (1:2 = 14:1)	87
5	naphthalene	fluorobenzene	naphthoic acid (1:2 = 11:1)	93
6	naphthalene	nitrobenzene		0
7	1-methylnaphthalene	benzene	4-methyl-1-naphthoic acid	97
8	1-methylnaphthalene	chlorobenzene	4-methyl-1-naphthoic acid	99
9	2-methylnaphthalene	benzene	2-methyl-1-naphthoic acid	89
10	2-methylnaphthalene	chlorobenzene	2-methyl-1-naphthoic acid	98
11	2,7-dimethylnaphthalene	chlorobenzene	2,7-dimethyl-1-naphthoic acid	95
12	phenanthrene	benzene	phenanthrene-9-carboxylic acid	73
13	phenanthrene	chlorobenzene	phenanthrene-9-carboxylic acid	89
14	phenanthrene	fluorobenzene	phenanthrene-9-carboxylic acid	91
15	biphenyl	benzene	biphenylcarboxylic acid (4:2 = 12:1)	68
16	biphenyl	chlorobenzene	biphenyl-4-carboxylic acid	91
17	4-methylbiphenyl	benzene	4′-methylbiphenyl-4-carboxylic acid	73
18	4-methylbiphenyl	chlorobenzene	4′-methylbiphenyl-4-carboxylic acid	97
19	1,2-diphenylethane	chlorobenzene	*p*-(2-phenylethyl)benzoic acid	98

[a] Reaction conditions: substrate (1.00 mmol), CO$_2$ (initial pressure, 3.0 MPa), AlBr$_3$ (1.00 mmol), Ph$_3$SiCl (1.00 mmol), solvent (1.0 mL), rt, 3 h. [b] Determined by ^{1}H NMR analysis. [c] Yield of isolated pure product or isomer mixture based on the quantity of substrate.

according to the reactivity of individual substrates, the corresponding carboxylic acids could be obtained in excellent yields with high regioselectivity. It should be noted that an attempt to carboxylate ethylbenzene in chlorobenzene did not improve the yield of ethylbenzoic acid [65% (o:p = trace:1)] as compared to that achieved by the reaction carried out in the neat substrate (Table 2, entry 1). Indeed, halobenzenes are suitable solvents for dissolving solid substrates, presumably due to not disturbing the complexation between a substrate and an electrophile (vide supra), but this seems not to mean that halobenzenes positively assist a substrate to form a π complex with an electrophile. It also should be noted that the aromatic solvents employed for the carboxylation of polycyclic arenes would have been carboxylated, to some extent, under the reaction conditions, if there had been no substrate (vide infra). Much higher reactivity of the polycyclic arenes seems to have prevented the solvents from suffering from carboxylation.

It was found that chlorobenzene was carboxylated with Ph$_3$SiCl as a promoter, to give 4-chlorobenzoic acid, though in a poor yield (Table 4, entry 1). Increasing the reaction temperature to 80 °C improved the yield; however, it caused the formation of a small amount of benzoic acid, which was attributed to the carboxylation of Ph$_3$SiCl at the ipso carbon bearing the ClPh$_2$Si moiety (entry 2). The replacement of Ph$_3$SiCl with ^{i}Pr$_3$SiCl required the use of a larger amount of the promoter and more severe reaction conditions, but this produced the desired acid in a moderate yield without generating 2-methylpropionic acid as a byproduct (entries 3 and 4). Under similar conditions, fluorobenzene, bromobenzene, and benzene also produced the desired carboxylic acids in moderate yields (entries 6, 8, and 10). In this context, Olah et al. reported that bromobenzene was exclusively disproportionated under their carboxylation conditions with the aid of AlCl$_3$ and aluminum powder.[21] Under our conditions, the disproportionation of bromobenzene was significant above 100 °C, judging from the emergence of benzoic acid, the formation of which is rationalized by the disproportionation of bromobenzene into dibromobenzene and benzene, followed by the carboxylation of the latter.

Mechanistic Considerations. In the beginning of this study, we supposed that the reaction would proceed via the silylation of an aromatic substrate with R$_3$SiX, along with the aid of AlX$_3$, according to the S$_E$Ar mechanism, followed by the carboxylation of the resulting arylsilane with AlX$_3$-activated CO$_2$ (Scheme 1).[25] This was assumed because we had found that aryltrimethylsilanes were efficiently carboxylated with CO$_2$ in the presence of AlBr$_3$, and our experiments had suggested that the trimethylsilyl moiety of a starting arylsilane could migrate on the aromatic nucleus before being replaced with CO$_2$.[24,29] There are only a few reports on the electrophilic silylation of aromatic compounds. Silylation

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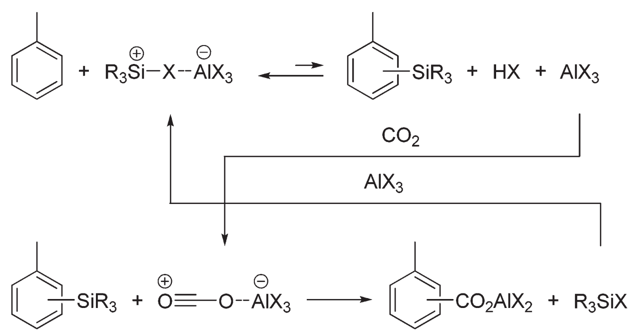
TABLE 4. Carboxylation of Halobenzenes and Benzene in Neat Substrates at Various Temperatures

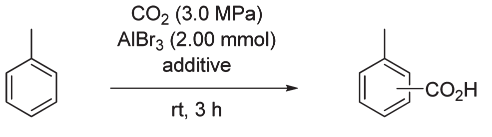
entry	substrate	R_3SiCl	$R_3SiCl/AlBr_3$[a]	temp (°C) [time (h)]	product	yield (%)[b]
1	chlorobenzene	Ph_3SiCl	1.0	rt (3)[c]	4-chlorobenzoic acid	9
2	chlorobenzene	Ph_3SiCl	1.0	80 (3)[d]	4-chlorobenzoic acid	29 (5)[e]
3	chlorobenzene	$^iPr_3SiCl$	3.0	80 (24)[d]	4-chlorobenzoic acid	31
4	chlorobenzene	$^iPr_3SiCl$	5.0	120 (48)[d]	4-chlorobenzoic acid	45
5	fluorobenzene	Ph_3SiCl	1.0	rt (3)[c]	4-fluorobenzoic acid	12
6	fluorobenzene	$^iPr_3SiCl$	5.0	80 (48)[d]	4-fluorobenzoic acid	53
7	bromobenzene	Ph_3SiCl	1.0	rt (3)[c]	4-bromobenzoic acid	8
8	bromobenzene	$^iPr_3SiCl$	5.0	80 (48)[d]	4-bromobenzoic acid	40
9	benzene	Ph_3SiCl	1.0	rt (3)[c]	benzoic acid	11
10	benzene	$^iPr_3SiCl$	5.0	80 (48)[d]	benzoic acid	61

[a]Molar ratio. [b]Isolated yield based on the quantity of $AlBr_3$. [c]Reaction conditions: substrate (2.0 mL), CO_2 (initial pressure, 3.0 MPa), $AlBr_3$ (1.00 mmol). [d]Reaction conditions: substrate (6.0 mL), CO_2 (initial pressure, 3.0 MPa), $AlBr_3$ (2.00 mmol). [e]Isolated yield of benzoic acid based on the quantity of $AlBr_3$.

SCHEME 1. Tentative Mechanism for Carboxylation via an Arylsilane Generated in Situ by a Friedel−Crafts-Type Silylation

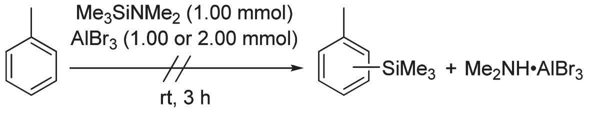


necessitates reaction conditions under which no Brønsted acid is liberated during the reaction, because the resulting arylsilanes exhibit a marked tendency to undergo protolytic desilylation. The combinations of reagents, Me_3SiOTf−Et_3N,[30] Ph_3SiNMe_2−$AlCl_3$,[31] and R_3SiCl−$AlCl_3$−Hunig's base,[32] have only been employed for the silylation of highly nucleophilic ferrocene and nitrogen-containing heteroaromatics, thus far. The silylation of arenes is more difficult[33] and no synthetically useful yield has been achieved, until the recent report by Kobayashi and co-workers;[34] they disclosed that 4,4′-di-*tert*-butyl-2-(diphenylsilyl)biphenyl, upon treatment with tritylium in the presence of 2,6-lutidine, successfully undergoes intramolecular silylation to afford the corresponding silafluorene. We attempted the silylation of toluene, as well as its carboxylation, using $(Me_3Si)NMe_2$ and $AlBr_3$. It was found that $(Me_3Si)NMe_2$ promoted carboxylation in cooperation with $AlBr_3$ (eq 1), but gave no arylsilane under similar conditions in the absence of CO_2 (eq 2). A more straightforward finding that contradicts this tandem silylation−carboxylation mechanism arose from the carboxylation of triphenyl(*p*-tolyl)silane carried out in benzene with 1.0 molar equiv of $AlBr_3$ (eq 3); the silane produced a poor yield of toluic acid (8%), with a lesser amount of benzoic acid, despite being the expected intermediate for the carboxylation of toluene with the aid of Ph_3SiCl, which had previously exhibited the highest performance in promoting the reaction (vide supra). In contrast, toluene produced toluic acid in 92% yield (o:p = 1:10) under similar conditions, with the aid of 1.0 molar equiv, each, of Ph_3SiCl and $AlBr_3$. Therefore, we concluded that this mechanism was not reasonable for the present carboxylation.

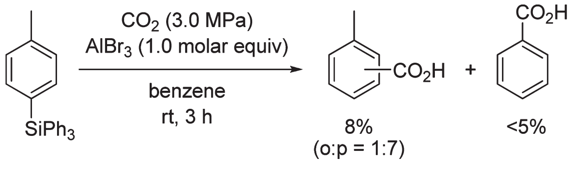


(1)

additive	Yield[a] (o:p ratio)
none	8% (trace:1)
Me_3SiCl (1.00 mmol)	36 (1:6)
Me_3SiNMe_2 (1.00 mmol)	17% (1:6)
Me_3SiNMe_2 (2.00 mmol)	0%



(2)



(3)

Another plausible mechanism by which carboxylation may take place is that a species generated from CO_2, R_3SiX, and AlX_3 directly attacks the substrate via the S_EAr mechanism (Scheme 2). Figure 1 shows the FT-IR spectrum of a mixture prepared by exposing a suspension of $AlBr_3$ and Ph_3SiCl in cyclohexane to 3.0 MPa of CO_2 (Figure 1a). This spectrum is compared with the spectra of a mixture prepared by a similar treatment in the absence of Ph_3SiCl (Figure 1b), a mixture prepared by treating $AlBr_3$ with Ph_3SiCl in cyclohexane under nitrogen (Figure 1c), and a suspension of Ph_3SiCl in cyclohexane (Figure 1d). In Figure 1a, a small but distinct absorption is observed at 1623 cm^{-1}, which can be assigned to the C=O stretching vibration ($\nu_{C=O}$) of a species generated from $AlBr_3$, Ph_3SiCl, and CO_2, as evidenced by the fact that the signal is absent in samples b−d in Figure 1. To date, the structures of many complexes between acyl halides and Lewis acids have been determined via mechanistic studies of Friedel−Crafts acylation. It has been reported that the $\nu_{C=O}$ value of a complex

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(31) Sollott, G. P.; Peterson, W. R., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 5054.

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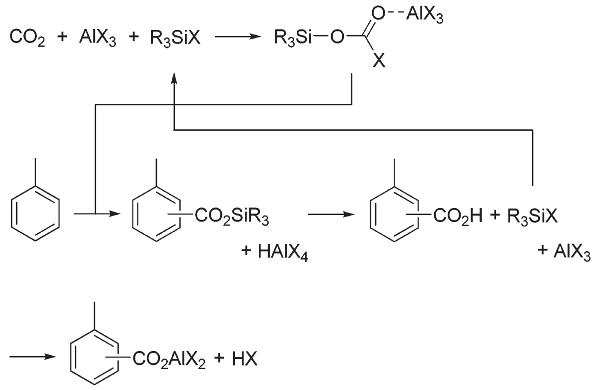
SCHEME 2. Direct Carboxylation with CO$_2$ Activated by R$_3$SiX and AlX$_3$



in which an acyl halide coordinates to AlX$_3$ with the carbonyl oxygen falls within a range of 1550−1650 cm^{-1} whereas that of a complex consisting of an acylium cation and AlX^{4-} lies within 2200−2300 cm^{-1}.[35,36] Although the structure of the active CO$_2$ species seems to vary with the molar ratio of R$_3$SiCl to AlBr$_3$, as suggested in the carboxylation of toluene (vide supra), its most simple picture would therefore be a complex in which a silyl haloformate coordinates to AlX$_3$ (Scheme 2), judging from the $\nu_{C=O}$ value. In this context, ethyl chloroformate, on treatment with AlBr$_3$ in cyclohexane, exhibited a strong absorption at 1630 cm^{-1}, which supports this assignment. The enhanced promoting effect observed upon replacing the methyl groups of Me$_3$SiCl with phenyl groups or other alkyl groups (vide supra) can be explained by the notion that the more stable the silyl cation (R$_3$Si$^+$) is, the more readily the silyl haloformate-like intermediate is formed. It should be noted that the treatment of toluene with carbon disulfide in the presence of AlBr$_3$ afforded,[37] after aqueous workup, dithio-*p*-toluic acid in a 24% yield, but the addition of Me$_3$SiCl did not promote the reaction (eq 4). This may indicate that silyl halides can activate CO$_2$, owing to silicon's strong affinity for oxygen.

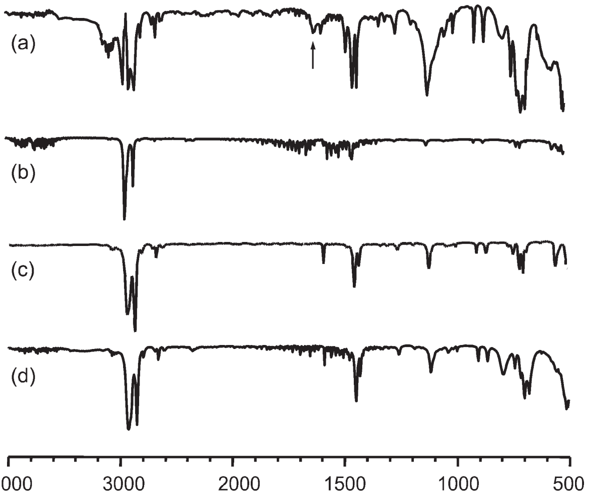
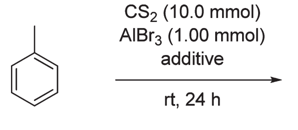


FIGURE 1. FT-IR spectra measured as liquid films. Sample: (a) A mixture prepared by exposing a suspension of AlBr$_3$ and Ph$_3$SiCl in cyclohexane to 3.0 MPa of CO$_2$, (b) a mixture prepared by a similar treatment to that for part a in the absence of Ph$_3$SiCl, (c) a mixture prepared by treating AlBr$_3$ with Ph$_3$SiCl in cyclohexane under nitrogen, and (d) a suspension of Ph$_3$SiCl in cyclohexane. For details, see the Experimental Section.



(4)

additive	Yield
none	24%
Me$_3$SiCl (1.0 mmol)	5%
Me$_3$SiCl (5.0 mmol)	trace

According to the direct carboxylation mechanism (Scheme 2), the initial product of the carboxylation should be a silyl ester. To ascertain this point, we carried out carboxylation of toluene using Ph$_3$SiCl and ^{i}Pr$_3$SiCl and analyzed the reaction mixtures by ^{1}H NMR spectroscopy, without aqueous workup (Figure 2). It was revealed that the products obtained via the two runs were identical; the compound exhibited two doublets (2H each) at 8.15 and 7.40 ppm and one singlet (3H) at 2.52 ppm (Figure 2a,b). In addition, the spectrum was also identical with that of the species prepared by the treatment of *p*-toluic acid with AlBr$_3$ (Figure 2c), suggesting that it is an aluminum carboxylate.[38] On the other hand, the authentic sample of triisopropylsilyl *p*-toluate exhibited two doublets (2H each) at 7.95 and 7.23 ppm and one singlet (3H) at 2.41 ppm for the *p*-tolyl unit (Figure 2d). The signals of the silyl ester, on treatment with 1.0 molar equiv of AlBr$_3$, shifted downfield (Figure 2e), which was attributed to the coordination of the carbonyl oxygen to the aluminum center. Further, the introduction of gaseous HCl to the mixture of the silyl ester and AlBr$_3$ made the spectrum compatible with the aforementioned species, which we believe to be an aluminum carboxylate (Figure 2f). Therefore, it was concluded that a silyl ester initially produced by the electrophilic substitution of the active CO$_2$ species is decomposed in situ with the concomitantly generated superacid HAlX$_4$ to give the corresponding carboxylic acid, which then reacts with AlX$_3$ to afford an aluminum carboxylate (Scheme 2). This means that the silyl halide is reproduced during the decomposition of the silyl ester. This issue was examined for Me$_3$SiBr and Ph$_3$SiCl as follows: The carboxylation of toluene was first carried out with AlBr$_3$ (1.00 mmol) and Me$_3$SiBr (5.33 mmol). After volatile materials were collected in vacuo into liquid-nitrogen-cooled tandem traps, the reaction mixture was worked up and purified by column chromatography to obtain 0.317 mmol of toluic acid. On the other hand, GC analysis of the distillate revealed that it included 5.10 mmol of Me$_3$SiBr. The fact that the crop of toluic acid (0.317 mmol) exceeded the amount of unrecoverable Me$_3$SiBr (0.23 mmol) indicates that the silyl halide is not stoichiometrically consumed during the sequence of the carboxylation. The incomplete recovery of the silyl halide is attributed to an inevitable loss in the vacuum distillation, considering the fact that this compound is highly volatile and that no silylated

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(35) (a) Susz, B. P.; Wuhrmann, J. J. *Helv. Chim. Acta* **1957**, *40*, 722. (b) Susz, B. P.; Wuhrmann, J. J. *Helv. Chim. Acta* **1957**, *40*, 971. (c) Susz, B. P.; Cassimatis, D. *Helv. Chim. Acta* **1961**, *44*, 395.

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(38) Puri, J. K.; Vats, V. K.; Miglani, A. *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.* **2001**, *31*, 1063.

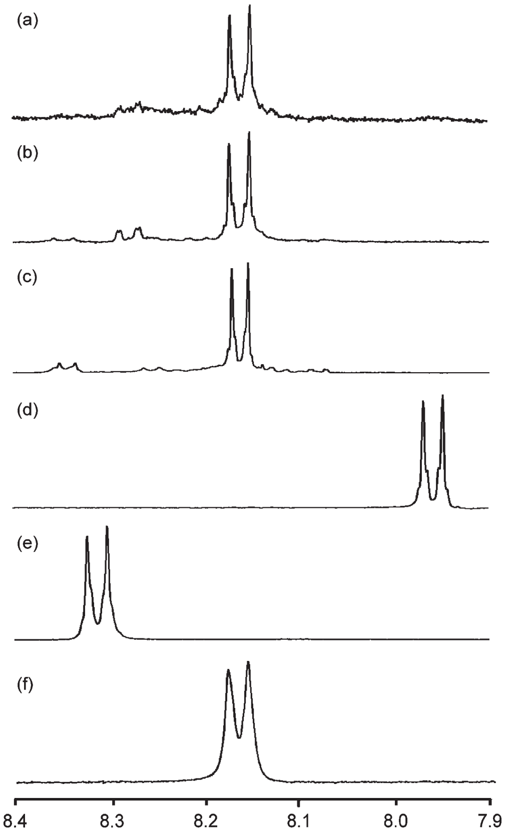

FIGURE 2. Expanded ^{1}H NMR spectra (400 MHz) measured in $CDCl_3$. Sample: (a) A mixture prepared by the carboxylation of toluene with the aid of $AlBr_3$ and Ph_3SiCl, (b) a mixture prepared by a similar treatment to that for part a by using ^{i}Pr$_3$SiCl instead of Ph_3SiCl, (c) a mixture prepared by treating *p*-toluic acid with $AlBr_3$ in toluene, (d) authentic triisopropylsilyl *p*-toluate, (e) a mixture prepared by treating triisopropylsilyl *p*-toluate with $AlBr_3$ in toluene, and (f) a mixture prepared by passing gaseous HCl into a solution of triisopropylsilyl *p*-toluate and $AlBr_3$ in toluene. For details, see the Experimental Section.

byproducts were detected in the residue, as well as the distillate, by ^{1}H NMR analysis. In the case of low volatile Ph_3SiCl, after carboxylation was carried out with $AlBr_3$ (1.00 mmol) and Ph_3SiCl (1.00 mmol), silicon compounds, as well as toluic acid, were isolated from the reaction mixture by extraction (see the Experimental Section), which gave Ph_3SiCl (0.319 mmol), triphenylsilanol (0.590 mmol), and toluic acid (0.940 mmol). The recovery of Ph_3SiCl again indicates that the silyl halide is not stoichiometrically consumed during the sequence of the carboxylation. In a separate experiment, it was revealed that Ph_3SiCl resisted hydrolysis under the extraction conditions, because it was recovered almost unchanged (99%). However, when mixed with an equimolar amount of $AlBr_3$, Ph_3SiCl was severely decomposed by the same operations to produce triphenylsilanol in 48% yield with the recovery of Ph_3SiCl (46%). It therefore seems that the silanol isolated from the reaction mixture was formed during the extraction. These observations may indicate that the silyl halides act as catalysts in the carboxylation, although 1 molar equiv or an excess amount of the reagents is required to achieve good product yields.

Conclusion

The Lewis acid-mediated carboxylation of arenes and halobenzenes was efficiently promoted by the addition of silyl chlorides bearing three alkyl and/or aryl substituents on the silicon atom. Among the silyl chlorides examined, Ph_3SiCl exhibited the best performance. The fact that polycyclic arenes could be carboxylated almost quantitatively with high regioselectivity, with the aid of each 1 molar equiv of $AlBr_3$ and Ph_3SiCl, is of practical use. Trialkylsilyl chloride ^{i}Pr$_3$SiCl could be a good alternative to Ph_3SiCl for reactions that require heating, as it produced no acidic byproduct under heated reaction conditions. Mechanistic studies strongly suggested that the silyl chlorides promote carboxylation by reacting with CO_2 in cooperation with $AlBr_3$ to give haloformate-like active species coordinating to AlX_3. In addition, it was revealed that the silyl chlorides are reproduced during the sequence of carboxylation.

Experimental Section

General. Melting points were taken using a micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with tetramethylsilane as an internal standard and $CDCl_3$ as a solvent unless otherwise noted. Silica gel (63−200 μm) was used for column chromatography and TLC. Benzene and toluene were distilled from sodium diphenyl ketyl before use. Ethylbenzene, *tert*-butylbenzene, *o*-, *m*-, and *p*-xylene, mesitylene, fluorobenzene, chlorobenzene, and bromobenzene were distilled from calcium hydride and stored under nitrogen. Triphenyl(*p*-tolyl)silane was prepared as described in the literature.[39] $AlBr_3$ was well ground with a mortar under nitrogen before use. Other materials were used as purchased.

Typical Procedure for the Carboxylation (Entry 24 in Table 1). In a 50 mL autoclave equipped with a glass inner tube and a magnetic stirring bar were charged toluene (2.0 mL), powdered $AlBr_3$ (267 mg, 1.00 mmol), and Ph_3SiCl (294 mg, 1.00 mmol) under nitrogen, and the apparatus was purged with CO_2 by repeated pressurization and subsequent expansion, the final pressure being adjusted to 3.0 MPa. After the mixture was stirred at room temperature for 3 h, the reactor was depressurized and the mixture was quenched with 2 M HCl and extracted with diethyl ether. The organic layer was extracted with 0.5 M Na_2CO_3 and the extract was acidified with concentrated HCl to liberate the free acid, which was extracted with diethyl ether. The extract was dried over $MgSO_4$ and evaporated to leave a residue, which was purified by TLC with hexane−diethyl ether (1:1) as a developer to give a mixture of *o*- and *p*-toluic acid (128 mg, 94%).[16] ^{1}H NMR analysis of the sample differentiated well the methyl signals of the ortho and para isomers (2.67 and 2.43 ppm, respectively), integration of which determined the o:p ratio to be 1:8. Repeated TLC with hexane−diethyl ether (2:1) as a developer allowed us to separate a small amount of each isomer from the mixture.

***o*-Toluic acid:** as crystals, mp 103.3−104.6 °C (lit.[40] mp 103−104 °C); IR (ATR) 2788, 1681, 1410, 1276, 1180, 923, 746, 665 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.67 (3H, s), 7.29 (2H, m), 7.46 (1H, td, J = 7.5, 1.4 Hz), 8.09 (1H, dd, J = 8.4, 1.4 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.4, 125.9, 130.4, 130.6, 131.6, 131.8, 139.2, 168.9.

***p*-Toluic acid:** as crystals, mp 183.2−184.0 °C (lit.[41] mp 179−181.5 °C); IR (ATR) 2580, 1681, 1424, 1281, 1188, 981, 840, 753 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.43 (3H, s), 7.28 (2H, d, J = 8.1 Hz), 8.01 (2H, d, J = 8.1 Hz); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.2, 128.2, 129.2, 129.5, 143.1, 167.5.

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The carboxylation of other compounds was carried out by a similar procedure unless otherwise noted. See Tables 1−4 and eqs 1 and 3 for the reaction conditions and product yields, and Supporting Information for the characterization data of compounds synthesized. The following are some comments on individual experiments: The reaction mixture obtained by the carboxylation of polycyclic aromatic compounds was extracted with chloroform instead of diethyl ether (Table 3). When the reaction was carried out at elevated temperature (Table 4), a larger amount of substrate (6.0 mL) was required to prevent the reaction mixture from drying up; as our autoclave was equipped with a glass inner tube, a part of the evaporated substrate condensed outside the tube when the apparatus was heated. The carboxylation of toluene in the presence of $AlBr_3$ and Me_3SiNMe_2, as well as its control reactions, was carried out in the neat substrate (2.0 mL) (eq 1). The carboxylation of triphenyl(*p*-tolyl)silane was carried out in benzene (2.0 mL) (eq 3).

Attempted Silylation of Toluene with $(Me_3Si)NMe_2$. A solution of $(Me_3Si)NMe_2$ (d = 0.750; 156 μL, 1.00 mmol) and $AlBr_3$ (267 mg, 1.00 mmol or 534 mg, 2.00 mmol) in toluene (2.0 mL) was stirred at room temperature for 3 h. The mixture was quenched with water and extracted with diethyl ether. The organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated. ^1H NMR analysis of the residue revealed that it did not contain trimethyl(*p*-tolyl)silane.

Dithiocarboxylation of Toluene. A solution of carbon disulfide (d = 1.261; 604 μL, 10.0 mmol) and $AlBr_3$ (267 mg, 1.00 mmol) in toluene (2.0 mL) was stirred at room temperature for 24 h. The mixture was quenched with 2 M HCl and extracted with diethyl ether. The organic layer was extracted with 1 M NaOH and the extract was acidified with concentrated HCl to liberate the free acid, which was extracted with diethyl ether. The extract was dried over $MgSO_4$ and evaporated to leave a residue, which was purified by TLC with hexane−diethyl ether (2:1) as a developer to give dithio-*p*-toluic acid as crystals (40.4 mg, 24%), mp 95.3−96.0 °C (lit.[42] mp 98 °C); IR (ATR) 2630, 1599, 1317, 1265, 1178, 1030, 858, 827, 770 cm^{-1}; ^1H NMR (400 MHz) δ 2.39 (3H, s), 7.19 (2H, d, J = 8.5 Hz), 7.98 (2H, d, J = 8.5 Hz); ^{13}C NMR (100 MHz) δ 21.7, 127.8, 129.4, 141.4, 144.4.

FT-IR Analysis of a Mixture Prepared by Exposing a Suspension of $AlBr_3$ and Ph_3SiCl in Cyclohexane to CO_2. In a 50 mL autoclave, a suspension of powdered $AlBr_3$ (267 mg, 1.00 mmol) and Ph_3SiCl (294 mg, 1.00 mmol) in cyclohexane (1.0 mL) was exposed to CO_2 (3.0 MPa) at room temperature for 3 h in a similar manner to that described for the carboxylation. Referential samples were similarly prepared in the absence of Ph_3SiCl or under atmospheric pressure of nitrogen. After these reactions, a portion of each reaction mixture was sandwiched between NaCl windows under nitrogen and analyzed by FT-IR spectroscopy under air. A suspension of Ph_3SiCl in cyclohexane was also analyzed by FT-IR spectroscopy as a liquid film.

^1H NMR Analysis of Unworked-Up Reaction Mixtures Obtained by the Carboxylation of Toluene. Toluene was carboxylated according to the typical procedure in the presence of $AlBr_3$ (267 mg, 1.00 mmol) and either Ph_3SiCl (294 mg, 1.00 mmol) or $^iPr_3SiCl$ (d = 0.910; 212 μL, 1.00 mmol) in the neat substrate (2.0 mL). On the other hand, referential samples c, e, and f in Figure 2 were prepared as follows: (c) *p*-Toluic acid (68.0 mg, 0.499 mmol) was allowed to react with $AlBr_3$ (267 mg, 1.00 mmol) in toluene (2.0 mL) at room temperature for 3 h under nitrogen. (e) Triisopropylsilyl *p*-toluate (292 mg, 1.00 mmol) was allowed to react with $AlBr_3$ (267 mg, 1.00 mmol) in toluene (2.0 mL) at room temperature for 3 h under nitrogen. (f) To a stirred solution of triisopropylsilyl *p*-toluate (292 mg, 1.00 mmol) and $AlBr_3$ (267 mg, 1.00 mmol) in toluene (2.0 mL) was introduced gaseous HCl generated by adding concentrated H_2SO_4 (d = 1.840; 533 μL, 10.0 mmol) dropwise to powdered NaCl (584 mg, 10.0 mmol), and stirring was continued for 3 h. After each reaction, most of the toluene was evaporated under reduced pressure as an azeotropic mixture with hexane. The resulting residues, as well as authentic triisopropylsilyl *p*-toluate, were analyzed by ^1H NMR spectroscopy.

Determination of the Mass Balance Concerning Silicon in the Carboxylation of Toluene with the Aid of $AlBr_3$ and Me_3SiBr. Toluene was carboxylated according the typical procedure using $AlBr_3$ (267 mg, 1.00 mmol) and Me_3SiBr (816 mg, 5.33 mmol) in toluene (2.0 mL). Volatile materials were collected in vacuo in liquid-nitrogen-cooled tandem traps and the residue was worked up as before to give a mixture of *o*- and *p*-toluic acid (43.2 mg, 0.317 mmol) after purification by TLC. The ratio of ortho and para isomers was determined to be 1:6 by ^1H NMR analysis. On the other hand, the distillate was combined and subjected to GC analysis [column, Quadrex MPS-10 (0.32 mm i. d. × 25 m); oven temperature, 40 °C; detector, FID], using ethyl acetate as an internal standard to reveal that it included Me_3SiBr (781 mg, 5.10 mmol).

Determination of the Mass Balance Concerning Silicon in the Carboxylation of Toluene with the Aid of $AlBr_3$ and Ph_3SiCl. Toluene was carboxylated according the typical procedure using $AlBr_3$ (267 mg, 1.00 mmol) and Ph_3SiCl (294 mg, 1.00 mmol) in the neat substrate (2.0 mL). The reaction mixture was quenched with 2 M HCl and extracted with diethyl ether. The organic layer was extracted first with 0.5 M Na_2CO_3 (layer A) and then with 1 M NaOH (layer B). The resulting organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was recrystallized from diethyl ether−hexane to recover Ph_3SiCl (94.1 mg, 0.319 mmol). The sample was not contaminated with Ph_3SiBr as evidenced by the elemental analysis for halogens; it included 12.05% of chlorine (calculated value 12.02%) and no bromine. On the other hand, layer A was acidified with concentrated HCl to liberate the free acid, which was extracted with diethyl ether. The extract was dried over $MgSO_4$ and evaporated to leave a residue, which was purified by TLC with hexane−ethyl acetate (2:1) as a developer to give a mixture of *o*- and *p*-toluic acid (128 mg, 0.940 mmol). The ratio of ortho and para isomers was determined to be 1:8 by ^1H NMR analysis. The same treatment of layer B as that of layer A gave triphenylsilanol (163 mg, 0.590 mmol).

Acknowledgment. This study was supported in part by a Grant-in-Aid for Scientific Research on a Priority Area "Advanced Molecular Transformations of Carbon Resources" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Preparation of triisopropylsilyl *p*-toluate, characterization data for some compounds, and ^1H and ^{13}C NMR spectra of all compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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