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Electrophilic Aromatic Substitution of Arenes with CO_2 Mediated by $R_3SiB(C_6F_5)_4$

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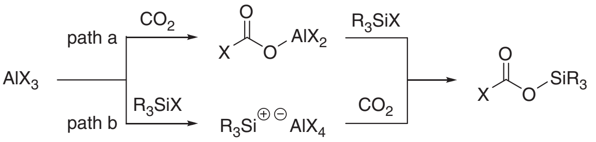
The Friedel–Crafts-type carboxylation of arenes has been achieved by activating CO_2 with silylium borates. The reaction exhibits broader substrate applicability than does our previously reported AlX_3/R_3SiX-mediated carboxylation.

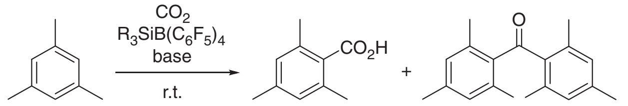
A growing sense of crisis with regard to the exhaustion of fossil resources and global climate change has prompted chemists to develop efficient methods for the utilization of CO_2 as a renewable chemical feedstock.[1] The reaction of CO_2 with carbon nucleophiles has been highlighted recently, and remarkable progress has been made with the development of the transition-metal-catalyzed carboxylation of organometallics bearing weakly polarized metal–carbon bonds,[2] as well as with direct carboxylation via the transition-metal-catalyzed cleavage of an aromatic C–H bond.[3] On the other hand, it has long been known that strong Lewis acids such as aluminum halides mediate the direct carboxylation of aromatic compounds with CO_2.[4] The reaction is believed to proceed via the electrophilic aromatic substitution (S_EAr) mechanism, in which the Lewis acid activated CO_2 serves as an electrophile.[4b] However, the applicability of the electrophilic carboxylation is severely limited because of the low electrophilicity of CO_2 and/or side reactions caused by the strong Lewis acids employed. Recently, we reported that the combined use of $AlBr_3$ and a trialkyl- or triarylsilyl chloride efficiently promotes the electrophilic carboxylation of arenes and halobenzenes.[4d] Mechanistic studies strongly suggested that a silyl halide reacts with CO_2 in cooperation with AlX_3 to give a silylhaloformate-like active species, although its precise structure is not clear at present. The formation of the active CO_2 species can be interpreted by two different mechanistic pathways (Scheme 1). In the first, CO_2 is activated by AlX_3 in such a manner as proposed by Olah et al.[4b] to form an aluminum-haloformate-like species, which then reacts with a silyl halide to give a silyl haloformate (path a). Alternatively, AlX_3 may react with a silyl halide to give a silylium ion, which activates CO_2 to form a silyl haloformate (path b). We are particularly interested in the possibility of the latter path because it may lead to the development of a method for the activation of CO_2 using reagents compatible with acid-sensitive substances. It is well known that the hydrogen atom binds more strongly to carbon than to silicon, which allows the tritylium ion to abstract a hydrogen atom from a triaryl- or trialkylsilane to give a silylium ion.[5] Taking advantage of this property, Kawashima and co-workers have recently reported the successful intramolecular sila-Friedel–Crafts reaction of biphenyl-2-yldiphenylsilanes using $Ph_3CB(C_6F_5)_4$ in the presence of 2,6-lutidine.[6] We envisaged that the electrophilic carboxylation of aromatics may be achieved using silylium borates to activate CO_2.[7]



Scheme 1. Possible mechanisms for the formation of a silyl haloformate-like active species from CO_2 and R_3SiX with the aid of AlX_3. The structures of species are simplified.

First, the carboxylation of mesitylene was tested in the neat substrate in the presence of equimolar amounts of Ph_3SiH and $Ph_3CB(C_6F_5)_4$ under CO_2 pressure at room temperature (Table 1, Entry 1). The reaction actually gave mesitoic acid accompanied by dimesityl ketone. The formation of the ketone is rationalized by the initial carboxylation of mesitylene, followed by the Friedel–Crafts acylation of mesitylene with the resulting triphenylsilyl mesitoate with the aid of $HB(C_6F_5)_4$, which is generated in situ by the carboxylation (vide infra). This could be avoided by the addition of 2,6-di-*tert*-butylpyridine (DTBP), though the yield of mesitoic acid was reduced (Entry 3); the use of the sterically less demanding 2,6-lutidine instead of DTBP disturbed the carboxylation (Entry 2), presumably owing to the formation of an adduct(s) with the silylium ion and/or siloxycarbonylium $Ph_3Si–O–C{\equiv}O^+$ (vide infra). The replacement of Ph_3SiH with Et_3SiH, in expectation of a higher reactivity of the silylium ion of the latter toward CO_2, lowered the product yields (Entry 4); this was attributed to the slow formation of $Et_3SiB(C_6F_5)_4$ under the reaction conditions employed. In relation to this, Lambert et al. reported that $Et_3SiB(C_6F_5)_4$ was prepared quantitatively by immersing $Ph_3CB(C_6F_5)_4$ in an excess of Et_3SiH for two days, while Ph_3SiH gave a complex mixture by the same treatment.[5]

Table 1. Carboxylation of mesitylene with the aid of R_3Si^+ in the neat substrate[a]



Entry	R_3Si^+ source	Base	Acid[b] /%	Ketone[b] /%
1	$Ph_3SiH + Ph_3CB(C_6F_5)_4$	none	52	40
2	$Ph_3SiH + Ph_3CB(C_6F_5)_4$	2,6-lutidine	trace	—
3	$Ph_3SiH + Ph_3CB(C_6F_5)_4$	DTBP	36	—
4	$Et_3SiH + Ph_3CB(C_6F_5)_4$	none	35	31
5	$Et_3SiB(C_6F_5)_4$	none	quant	—
6[c]	$Et_3SiB(C_6F_5)_4$	none	83	—
7[d]	$Et_3SiB(C_6F_5)_4$	none	86	14
8	$Et_3SiB(C_6F_5)_4$	DTBP	66	—

[a] Reaction conditions: mesitylene (5.0 mmol), ether Ph_3SiH and $Ph_3CB(C_6F_5)_4$ (0.20 mmol each) or $Et_3SiB(C_6F_5)_4$ prepared from Et_3SiH and $Ph_3CB(C_6F_5)_4$ (0.20 mmol each), base (0.20 mmol), CO_2 (3.0 MPa), room temp, 18 h. [b] Isolated yield based on the quantity of R_3Si^+. [c] The reaction was carried out under CO_2 (0.1 MPa) atmosphere. [d] Reaction time was extended to 36 h.

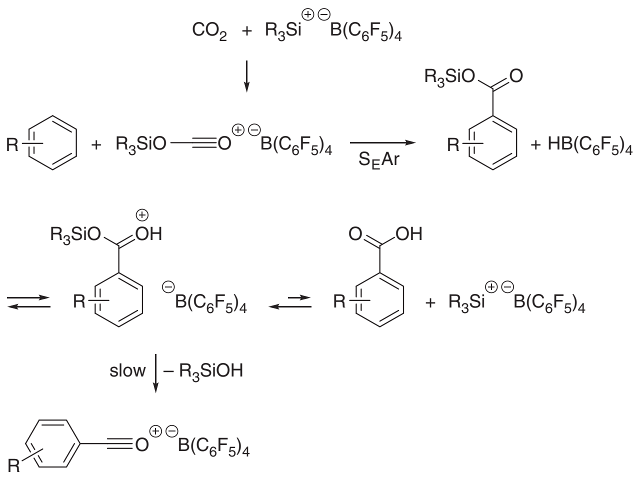
Table 2. Carboxylation of arenes with the aid of $Et_3SiB(C_6F_5)_4$ in chlorobenzene[a]

Entry	Substrate	Product (Distribution)[b]	Yield[c] /%
1	Naphthalene	Naphthoic acid (1-:2- = 18:5)	80
2	Phenanthrene	Phenanthrene-9-carboxylic acid	71
3	Biphenyl	Biphenyl-4-carboxylic acid	81
4	DPE[d]	(2-Phenylethyl)benzoic acid (*o*-:*p*- = 5:14)	73
5	Pyrene	Pyrene-1-carboxylic acid	87
6	Anthracene[e]	Anthracene-9-carboxylic acid	47
7	FL[f]	FL-carboxylic acid (2-:4- = 25:9)	99

[a] Reaction conditions: substrate (5.0 mmol), $Et_3SiB(C_6F_5)_4$ prepared from Et_3SiH and $Ph_3CB(C_6F_5)_4$ (0.20 mmol each), chlorobenzene (1.0 mL), CO_2 (3.0 MPa), room temp, 18 h. [b] Determined by ^1H analysis. [c] Yield of isolated pure product or isomer mixture based on the quantity of Et_3SiH. [d] 1,2-Diphenylethane. [e] Anthracene (3.0 mmol) was employed. [f] FL: 9*H*-Fluorene.

Then, $Et_3SiB(C_6F_5)_4$ was prepared in advance according to this procedure and used for the carboxylation after removal of the excess hydrosilane under reduced pressure. To our pleasure, mesitoic acid was obtained in quantitative yield (Entry 5). The reaction could also be carried out under atmospheric pressure, but the acid yield was reduced (Entry 6). Prolongation of the reaction time resulted in the formation of dimesityl ketone as a by-product at the expense of mesitoic acid (Entry 7). The addition of DTBP again reduced the acid yield (Entry 8). However, such basic conditions, which have never been realized before in the electrophilic carboxylation, would open the applicability of this reaction to acid-sensitive compounds. Toluene could also be carboxylated in the neat substrate (9.4 mmol) under the same conditions as those employed in Entry 5 (Table 1) to give toluic acid in 86% yield as a 1:0.64 mixture of *p*- and *o*-isomers. The addition of dichloromethane (1.0 mL) as a solvent prohibited the reaction,[5] whereas benzene, chlorobenzene, and fluorobenzene were compatible with the silylium borate, giving toluic acid in 39% (*o*-:*p*- = 1:0.62), 80% (1:0.48), and 36% (1:0.68) yields, respectively. Several other arenes were then subjected to the carboxylation, using chlorobenzene as a solvent (Table 2). The reaction was carried out by suspending a large excess of substrate over the silylium borate in the solvent to give the corresponding carboxylic acid in good to excellent yield.[8] It should be noted that anthracene and 9*H*-fluorene are hardly carboxylated with the aid of AlX_3/R_3SiX.[9]

A feasible mechanism for the carboxylation is illustrated in Scheme 2. A siloxycarbonylium species generated in situ from CO_2 and $R_3SiB(C_6F_5)_4$ reacts with an arene through the S_EAr mechanism to yield a silyl ester, which may react with $HB(C_6F_5)_4$ to afford a carboxylic acid, as observed in the AlX_3/R_3SiX-mediated carboxylation.[4d] This should be an equilibrium reaction via a protonated intermediate, but the position of the equilibrium seems not to lie to the right, judging from the fact that $R_3SiB(C_6F_5)_4$ was not recycled during the sequence of the carboxylation, i.e., no catalytic cycle was formed (Table 1, Entry 7). Instead, the protonated ester seems to be slowly decomposed to yield an acylium ion, by which the Friedel–Crafts acylation arises.



Scheme 2. Feasible mechanism for the carboxylation.

In conclusion, the carboxylation of arenes, including those for which the AlX_3/R_3SiX-mediated reaction is not applicable, was achieved with the aid of $Et_3SiB(C_6F_5)_4$ prepared in advance from Et_3SiH and $Ph_3CB(C_6F_5)_4$. The reaction proceeded in the presence of DTBP, which provided the first example of the electrophilic carboxylation under basic conditions.

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8 The carboxylation of naphthalene, using a fivefold excess of substrate (1.0 mmol) over $Et_3SiB(C_6F_5)_4$ (0.2 mmol), or conversely, using a twofold excess of $Et_3SiB(C_6F_5)_4$ (0.4 mmol) over the substrate (0.2 mmol), reduced the acid yield to 59% and 6%, respectively.

9 The carboxylation of pyrene, anthracene, and 9*H*-fluorene (1.0 mmol) with the aid of 1.0 mol equiv of $AlBr_3$ and Ph_3SiCl in chlorobenzene (1.0 mL) under CO_2 pressure (3.0 MPa) at room temperature gave the corresponding carboxylic acids in 56%, 11%, and 12% (2-:4- = 10:1), respectively.