

Lewis Acid-Mediated Carboxylation of Aryl- and Allylsilanes with Carbon Dioxide

Tetsutaro Hattori,* Yutaka Suzuki, and Sotaro Miyano*

Department of Biomolecular Engineering, Graduate School of Engineering, Tohoku University,
Aramaki-Aoba 07, Aoba-ku, Sendai 980-8579

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Aryl- and allylsilanes are carboxylated with CO₂ with the aid of aluminum-based Lewis acids, to give aromatic and β , γ -unsaturated carboxylic acids in fair to good yields, respectively. Formation of the former is rationalized by an aromatic electrophilic substitution by CO₂ activated by the Lewis acid, while the latter a nucleophilic addition of in situ-generated allyluminum species to CO₂.

Chemical fixation of CO₂ is a topic of growing interest in the field of organic synthesis.¹ Although nucleophilic alkylation or arylation of CO₂ with carbanions, such as organometallic species and phenolic enolates, provides a convenient access to carboxylic acids,¹ there is no established protocol for electrophilic one, in which CO₂ is activated by coordination to a Lewis acid and then attacks to a C=C bond, as is often the case with other carbonyl compounds.^{2,3} Several papers have dealt with the direct carboxylation of aromatic hydrocarbons with CO₂ with the aid of Lewis acids.⁴ We ourselves have recently found that fused aromatic compounds were carboxylated regioselectively by CO₂ in the presence of aluminum-based Lewis acids.^{4e} The reaction mechanism is not clear but may involve attack of the Lewis acid-activated CO₂ to the aromatic ring to form an arenium intermediate, which eliminates a proton to give a carboxylic acid after aqueous workup (the S_EAr mechanism). In this respect, it should be noted that Olah et al. have recently proposed an activation mechanism of CO₂ by AlCl₃ based on ab initio molecular orbital calculations of the conformations of possible complexes between the two.^{4f} On the other hand, it is well known that arylsilanes readily undergo electrophilic displacement of the silyl moiety at the ipso position due to the stabilizing effect in the transition state by the (p- σ) π conjugation between the Si-C bond and the developing positive charge (the β -effect), while the same effect induces allylsilanes to undergo an S_E2'-type displacement at the γ -position to the silyl moiety.³ Herein, we report that aryl- and allylsilanes are readily carboxylated with CO₂ in the presence of aluminum-based Lewis acids. Mechanistic differences between the reactions are discussed.

The general procedure for the carboxylation is as follows: In a 50 cm³ autoclave equipped with a glass inner tube and a magnetic stirring bar were charged a substrate (1.00–1.50 mmol), 2.0 mol equiv. of a Lewis acid, and a solvent (1.0–2.0 cm³) under N₂ and the apparatus was purged with CO₂ by repeated pressurization and subsequent expansion, the final pressure being adjusted to 3.0 MPa. The mixture was stirred at room temperature for 3 h. After aqueous workup, the product was purified by Kugelrohr distillation or column chromatography on silica gel with diethyl ether–hexane (1:1) as the eluent.

First, carboxylation of aryltrimethylsilanes was examined

by using AlBr₃ as the Lewis acid (Table 1). Benzene was employed as the solvent because it remained almost intact when treated with CO₂ under the conditions. Although the carboxylation of phenylsilane and (*p*-fluorophenyl)silane was sluggish, tolylsilanes gave regioisomers of methylbenzoic acid in moderate yields (entries 1–5). The product distribution is rationalized based on the S_EAr mechanism as follows: In *o*-tolylsilane, the ipso carbon of the silyl moiety, which was activated by the *o*-methyl group, underwent the carboxylation to give *o*-methylbenzoic acid. However, steric hindrance between the silyl and the methyl group of the substrate induced protodesilylation⁵ with incidental HBr in the reaction system and subsequent silylation of the resulting toluene at the para-position to give *p*-tolylsilane,⁶ carboxylation of which gave *p*-methylbenzoic acid. Preferential formation of the *p*-substituted product indicates that the latter reaction path was predominant compared with the former (entry 3), which coincides with the fact that *p*-tolylsilane afforded *p*-methylbenzoic acid in high selectivity (entry 5). It is of interest to note that *m*-tolylsilane afforded *o*-methylbenzoic acid in higher yield (up to 30%) than *o*-tolylsilane (8%) (entries 3 and 4). In *m*-tolylsilane, both the methyl and the silyl group activated the ortho- and para-positions to the silyl moiety,⁷ during which the most sterically favorable para-position seemed to undergo the carboxylation to give, after protodesilylation of the resulting silane, *o*-methylbenzoic acid. Naphthylsilanes also afforded naphthoic acids in good yields (entries 6 and 7). It should be recalled that direct carboxylation

Table 1. Carboxylation of arylsilanes^a

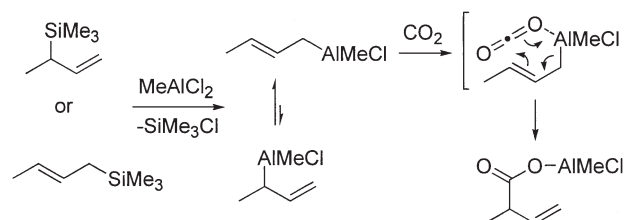
Entry	Substrate	Product (distribution)	Yield / %
1	Ph-SiMe ₃	Ph-CO ₂ H	20
2	<i>p</i> -F-C ₆ H ₄ -SiMe ₃	<i>p</i> -F-C ₆ H ₄ -CO ₂ H	5
3	<i>o</i> -Me-C ₆ H ₄ -SiMe ₃	Me-C ₆ H ₄ -CO ₂ H (<i>o</i> :- <i>p</i> =3:10)	35
4	<i>m</i> -Me-C ₆ H ₄ -SiMe ₃	Me-C ₆ H ₄ -CO ₂ H (<i>o</i> :- <i>m</i> :- <i>p</i> =2:tracel:1)	47
5	<i>p</i> -Me-C ₆ H ₄ -SiMe ₃	Me-C ₆ H ₄ -CO ₂ H (<i>o</i> :- <i>p</i> =1:9)	50
6	1-Naphthyl-SiMe ₃	Naphthyl-CO ₂ H (1:-2=1:trace)	58
7	2-Naphthyl-SiMe ₃	Naphthyl-CO ₂ H (1:-2=5:1)	73
8	Ph-SiCl ₃	Ph-CO ₂ H	15
9	<i>p</i> -Me-C ₆ H ₄ -SiCl ₃	Me-C ₆ H ₄ -CO ₂ H (<i>o</i> :- <i>p</i> =1:2)	54

^aReaction conditions: Substrate, 1.5 mmol; Solvent, 1.0 cm³.

of naphthalene gave 1-naphthoic acid regioselectively but the yield was moderate (38%) even at elevated temperature (40 °C) because of the high tendency of the substrate toward dehydrocoupling to form polyaryls (the Scholl reaction).^{4c} One might suspect that the carboxylation proceeds via arylaluminum intermediates generated in situ from arylsilanes and AlBr_3 . In this respect, however, Austin et al. reported that trichlorophenylsilane on treatment with AlCl_3 did not afford arylaluminum species.⁵ Trichlorophenyl- and trichloro-*p*-tolylsilanes were carboxylated under the standard conditions to give the corresponding carboxylic acids (entries 8 and 9), though the regioselectivity in the latter reaction was reduced compared to that in the reaction of trimethyl-*p*-tolylsilane (entry 5) possibly owing to weaker β -effect of the trichlorosilyl moiety. These observations coincide well with the $\text{S}_{\text{E}}\text{Ar}$ mechanism, though the transmetalation cannot completely be ruled out.

Vinylsilanes were also expected to undergo the carboxylation at the α -carbon owing to the β -effect.^{3,8} However, trimethylvinylsilane polymerized under the conditions, giving no acid product. This led us to examine a weaker Lewis acid, MeAlCl_2 : By using 2.0 mol equiv. of MeAlCl_2 (1.0 M solution in hexane), trimethyl(penta-1,3-dienyl)silane and 1,3-bis(trimethylsilyl)propene were carboxylated to give hexa-2,4-dienoic acid and but-3-enoic acid in 34 and 63% yields, respectively, while other vinylsilanes, including trimethylvinylsilane and bicyclo[2.2.1]hept-2-en-2-yltrimethylsilane, gave only a trace amount of the corresponding carboxylic acids.

Next, carboxylation of allyltrimethylsilanes were examined by using MeAlCl_2 as the Lewis acid (Table 2). Several simple allylsilanes were carboxylated to give allylic acids in moderate yields (entries 1–3). It should be noted that both but-2-enyltrimethylsilane and trimethyl(1-methylallyl)silane gave 2-methylbut-3-enoic acid (entries 2 and 3), formation of which from the latter allylsilane contradicts the $\text{S}_{\text{E}}2'$ mechanism. In addition, allyltrimethylsilane was reported to undergo transmetalation with GaCl_3 to give an allylgallium species.⁹ Therefore, the carboxylation of allylsilanes is likely to proceed via allylaluminum species. Formation of 2-methylbut-3-enoic acid from both the terminal and internal silanes can be explained by the equilibrium between in situ-generated terminal and internal allylaluminum species and nucleophilic addition of the more stable terminal allylaluminum to CO_2 via a six-membered transition



Scheme 1.

state (Scheme 1). However, it seems that allylsilanes are not always converted into allylaluminums under the reaction conditions. For example, trimethyl(penta-2,4-dienyl)silane, when treated with CO_2 in the presence of Me_2AlCl , gave hexa-3,5-dienoic acid (entry 4), while the same treatment of trimethyl(penta-2,4-dienyl)stannum gave 2-vinylbut-3-enoic acid in 67% yield. Although the latter reaction is more likely to proceed via the transmetalation between the allylstannum and Me_2AlCl ,¹⁰ it is difficult to explain the formation of the different products from the same aluminum species.

In conclusion, we have shown here that aryl- and allylsilanes are readily carboxylated with CO_2 in the presence of aluminum-based Lewis acids. Further studies on the reaction mechanisms are in progress.

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Table 2. Carboxylation of allylsilanes^a

$\text{Allyl-SiMe}_3 \xrightarrow[\text{hexane, r.t., 3 h}]{\text{CO}_2, \text{MeAlCl}_2} \text{Allyl-CO}_2\text{H}$			
Entry	Substrate	Product	Yield / %
1			23
2			42
3			43
4 ^b			27

^aReaction conditions: Substrate, 1.00 mmol; Solvent, 2.0 cm³. ^b Me_2AlCl was employed instead of MeAlCl_2 .