

Reactivity of Carbon Dioxide with *n*-Butyl(phenoxy)-, (alkoxy)-, and (oxo)stannanes: Insight into Dimethyl Carbonate Synthesis

Danielle Ballivet-Tkatchenko,^{*,†} Olivier Douteau, and Stefanie Stutzmann

Institut de Recherches sur la Catalyse, CNRS-UPR 5401 Liée par Convention à l'Université Claude Bernard Lyon 1 et à l'École Normale Supérieure de Lyon, 2 Avenue Albert Einstein, 69626-Villeurbanne Cedex, France

Received May 10, 2000

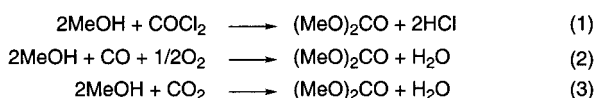
The CO₂ insertion into Sn–O bonds of a series of butyl(phenoxy)-, (alkoxy)-, and (oxo)-stannanes has been investigated. The tributyl derivatives Bu₃SnOR (**2a**, R = Me; **3a**, R = ⁱPr; **4a**, R = ^tBu; **5a**, R = SnBu₃)¹ give quantitatively Bu₃Sn(OCO₂R), **2b–5b**; the analogous tributylphenoxystannane, **1**, is less reactive. For the dibutyl series, Bu₂Sn(OR)₂, steric effects of ^tBu groups in OR (**8a**) suppress carbonation under atmospheric pressure. With R = Me (**6a**) or R = ⁱPr (**7a**), only one Sn–OR bond reacts, resulting in Bu₂Sn(OR)(OCO₂R), **6b** or **7b**. Treating **6a** with 2-propanol affords under CO₂ the mixed compound Bu₂Sn(OMe)(OCO₂ⁱPr), selectively. Facile deinsertion of CO₂ is a common property of all compounds, occurring more readily in the dibutyl series. The stoichiometric transformation of the carbonato ligand in **2b**, **5b**, or **6b** to dimethyl carbonate (DMC) on reaction with MeI requires nucleophilic assistance by F[–] to proceed. In the presence of MeOH, **2b** and **5b** are almost inactive for DMC formation, in contrast with **6b**. The best yield is obtained under supercritical CO₂–methanol conditions.

Introduction

Dimethyl carbonate (DMC) has a number of specialty chemical applications,² but its primary use to date is in the production of polycarbonates.³ It is now considered as an option for fuel additives.⁴ This potential market constitutes a challenge for DMC production via environmentally friendly processes to avoid the use of phosgene and formation of the coproduct HCl (eq 1). More generally, new applications for organic carbonates can be anticipated through safer synthetic methods.⁵ In this context, the catalytic oxidative carbonylation of methanol was studied and is now operative on a commercial scale (eq 2).⁶ However, substitution of phosgene by carbon dioxide is more appealing, through the carbonation of alcohols (eq 3).⁷ Dibutyldialkoxy-

their low activity is a problem. To circumvent this drawback, an important step is an understanding of the reaction mechanism. Since the first reports of CO₂ insertion into the Sn–O bond of Bu₃SnOMe, (Bu₃Sn)₂O,¹¹ and Bu₂Sn(OMe)₂,¹² only bis(trialkyltin)carbonates were characterized by X-ray structure determination,^{13,14} until very recently, when the structure of Me₂Sn(OMe)(OCO₂Me) was published.¹⁵

In this paper we report a detailed study focused on key steps of reaction 3 to proceed in the presence of organostannane derivatives by (i) the evaluation of carbon dioxide insertion reactivity into the Sn–O bond according to the nature of the R groups in the series Bu₃SnOR (R = Ph, Me, ⁱPr, ^tBu, SnBu₃) and Bu₂Sn(OR)₂ (R = Me, ⁱPr, ^tBu)¹ and (ii) the conditions of DMC formation from the corresponding carbonato species. Our approach employs ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy, volumetric experiments, and reaction either with methanol in supercritical CO₂ or with methyl iodide. IR spectroscopy was also used to monitor the presence of absorption bands of the carbonato moieties.¹⁶



stannanes are known to promote reaction 3,^{8–10} but

* Corresponding author. Fax: +33 3 80 39 37 72. E-mail: ballivet@u-bourgogne.fr.

[†] Present address: LSEO, Université de Bourgogne, Faculté des Sciences Mirande, BP 47870, 21078 Dijon Cedex, France.

(1) In all cases where Bu is written, it is *n*-C₄H₉ groups that are present.

(2) Mauri, M.; Romano, U.; Rivetti, F. *Ing. Chim. Ital.* **1985**, *21*, 6.

(3) *Chem. Br.* **1994**, 970.

(4) Pacheco, M. A.; Marshall, C. L. *Energy Fuels* **1997**, *11*, 2.

(5) Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951, and references therein.

(6) Romano, U.; Tessei, R.; Massi Mauri, M.; Rebora, P. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 396.

(7) Aresta, M.; Quaranta, E. *CHEMTECH* **1997**, March, 32.

(8) Yamazaki, N.; Nakahama, S. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 249.

(9) Genz, J.; Heitz, W. Ger. Offen. DE 3 203 190, 1983; *Chem. Abstr.* **1983**, *99*, 139320s.

(10) Kizlink, J.; Pastucha, I. *Collect. Czech. Chem. Commun.* **1994**, *59*, 2116.

(11) Bloodworth, A. J.; Davies, A. G.; Vasishtha, S. C. *J. Chem. Soc. (C)* **1967**, 1309.

(12) Davies, A. G.; Harrison, P. G. *J. Chem. Soc. (C)* **1967**, 1313.

(13) Tieckink, E. R. T. *J. Organomet. Chem.* **1986**, *302*, C1.

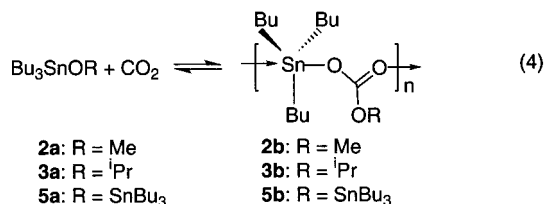
(14) Kümmerlen, J.; Sebald, A.; Reuter, H. *J. Organomet. Chem.* **1992**, *427*, 309.

(15) Choi, J.-C.; Sakakura, T.; Sako, T. *J. Am. Chem. Soc.* **1999**, *121*, 3793.

(16) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651.

Results and Discussion

Reaction of CO₂ with Bu₃SnOR. To systematically investigate the reactivity of Sn–OR bonds toward CO₂, we prepared a series of compounds for which the R group may influence the reactivity through electronic and steric effects: R = Ph, **1**; Me, **2a**; ⁱPr, **3a**; ^tBu, **4a**; SnBu₃, **5a**. These tributylstannane derivatives are colorless liquids at room temperature and monomeric, as evidenced by ¹¹⁹Sn NMR spectroscopy.^{17,18} The insertion of CO₂ into the Sn–O bond has been known for a long time for **2a** and **5a**.^{11,12} In our study, volumetric experiments showed no significant reaction with **1** (CO₂:Sn ≈ 0.1) over several hours of exposure under atmospheric pressure of CO₂ at room temperature, neither in toluene or DMF, nor in the presence of pyridine or 2,2'-bipyridine. However, a progressive CO₂ uptake occurred for the other compounds, either as neat samples or in solution (heptane, toluene, or THF); the equilibrium was reached within 30 min for **2a** and **3a**, but needed a longer time, 18 h, for **4a**. The maximum uptake corresponded to a CO₂:Sn molar ratio of 1. The difference of reactivity observed between **1** and **2a** (or **5a**) follows the basicity of the oxygen atom as previously reported,¹⁹ whereas for **4a** steric hindrance of the *tert*-butyl substituent causes a decrease in the rate of CO₂ fixation. The neat CO₂ adducts, denoted **2b**, **3b**, and **4b**, exhibited a strong ν(C=O) IR band between 1610 and 1590 cm⁻¹, while for **5b** the absorption was centered at 1525 cm⁻¹. The ¹³C{¹H} NMR spectra showed a new resonance in the carbonato region at δ 158.4, 157.7, 157.3, and 162.7 for **2b**, **3b**, **4b**, and **5b**, respectively. The corresponding ¹³C NMR resonance revealed ³J_{C,H} couplings for **2b** (q, 3.7 Hz) and **3b** (d, 2.7 Hz) and none for **5b**, which agrees with the presence of Bu₃Sn–OC(O)–OR species. The signals OCH₃ (δ 53.5) and OCH(CH₃)₂ (δ 69.7) appeared as a quartet and a doublet of multiplet, respectively. The ¹H resonance of OCH(CH₃)₂ was a septet centered at δ 4.57. The ¹¹⁹Sn{¹H} NMR spectrum recorded for **3b** exhibited one broad signal at δ –28 (*W*_{1/2} = 850 Hz), shifting upfield to –45 (*W*_{1/2} = 680 Hz) upon cooling to –30 °C. These values are close to those already reported for **2b**, indicating the presence of five-coordinate tin atoms due to the bidentate character of the carbonate monoester ligand.²⁰ This ligand is probably better described as a bridging one, by comparison with the carbonate analogue **5b**. For the latter compound, two ¹¹⁹Sn{¹H} NMR signals of equal intensity belonging to four- and five-coordinate tin atoms were found (eq 4).¹⁶ At room temperature, line broadening was observed for the resonances of the α carbon atom of the butyl groups, Sn–CH₂–C₃H₇, and of dissolved CO₂, arising from an exchange process on the NMR time scale involving reversible insertion of CO₂ into the Sn–OR bond. Under vacuum, **2a** was quantitatively recovered at room temperature, while **3a**, **4a**, and **5a** were recovered at higher temperatures: 36, 40, and 65 °C, respectively. Further experiments by



variable-temperature ¹³C{¹H} NMR spectroscopy are needed to obtain a better insight into the exchange phenomena, by the determination of the energy barrier as a function of the nature of R.

Reaction of CO₂ with Bu₂Sn(OR)₂. Substitution of one butyl group by alkoxy results in dimeric structures with five-coordinate tin atoms for R = Me, **6a**, and ⁱPr, **7a**, whereas for ^tBu, **8a**, steric hindrance favors the monomeric form.¹⁶ In our work, the carbonation reaction was found to depend on the nature of R; the adducts were less stable than those of Bu₃SnOR, which correlates with the basicity of the oxygen atoms reported for the series Bu₃SnOPh < Bu₂Sn(OMe)₂ < Bu₃SnOMe.¹⁸ The uptake of CO₂ by **6a** and **7a** corresponded to a maximum CO₂:Sn = 0.90 at room temperature and atmospheric pressure of CO₂, in solvents such as toluene, heptane, THF, and acetonitrile. When the adsorption proceeded at 0 °C, the ratio CO₂:Sn increased to only 1.0 and never approached 2 as reported earlier.¹² This observation is in full agreement with very recently published results on Me₂Sn(OMe)₂.¹⁵ Under the same conditions, **8a** did not fix CO₂. However, exposure of neat **8a** to 30 bar of CO₂ at room temperature for 16 h provided a CO₂:Sn ratio of 0.4, determined by back-titration under acidic hydrolysis. Clearly, steric effects are involved with the *tert*-butoxy groups, as was found in the Bu₃SnOR series (*vide supra*).

As neat liquids, **6a** and **7a** were transformed into white solids, **6b** and **7b**, under atmospheric CO₂ at room temperature, the reaction being reversible under vacuum. The IR spectra showed ν(C=O) IR bands centered between 1640 and 1620 cm⁻¹. Multinuclear NMR revealed the disappearance of the starting compound with the following features: for **6b**, two methoxy resonances were present in the ¹H spectrum (δ 3.66 and 3.53; 1:1 ratio) and in the ¹³C{¹H} spectrum (δ 54.09 and 52.71). In addition, there was a carbonato signal at δ 158.9, and the α carbon atom of the butyl groups appeared as a broad resonance at δ 24.03. Similarly for **7b**, the OCH(CH₃)₂ appeared as two septets (δ 4.62, ³J_{H,H} = 6.2 Hz and 4.12, ³J_{H,H} = 6.1 Hz) in a 1:1 ratio, and two OCH(CH₃)₂ signals were found at δ 69.9 and 67.4 in the ¹³C{¹H} spectrum. The resonance of the carbonato group was at δ 158.1, and that for the α carbon atom of the butyl groups at 21.8 (broad). The identification of **6b** and **7b** as Bu₂Sn(OR)(OCO₂R) species is strengthened by a very recent single-crystal X-ray diffraction study of Me₂Sn(OMe)(OCO₂Me).¹⁵ The compound is dimeric through OMe bridges with a monodentate methyl carbonato ligand. Comparison of the NMR data with those of **6b** shows very close OCH₃ chemical shifts, the higher field signal being assigned to the methoxy ligands.

To gain further insight into the reactivity of **6a** toward substitution of the methoxy ligands, exchange with 2-propanol followed by CO₂ absorption was carried out. When **6a** was dissolved in 2-propanol at room temperature for 3 h, then treated under vacuum, and finally

(17) Smith, P. J.; White, R. F. M.; Smith, L. J. *Organomet. Chem.* **1972**, *40*, 341.

(18) Nadvornik, M.; Holecek, J.; Handlir, K.; Lycka, A. J. *Organomet. Chem.* **1984**, *275*, 43.

(19) Marchand, A.; Mendelsohn, J.; Lebedeff, M.; Valade, J. J. *Organomet. Chem.* **1969**, *17*, 379.

(20) Blunden, S. J.; Hill, R.; Ruddick, J. N. R. J. *Organomet. Chem.* **1984**, *267*, C5.

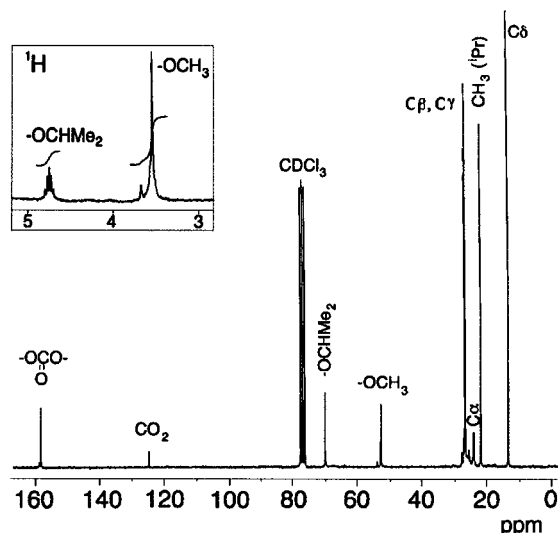
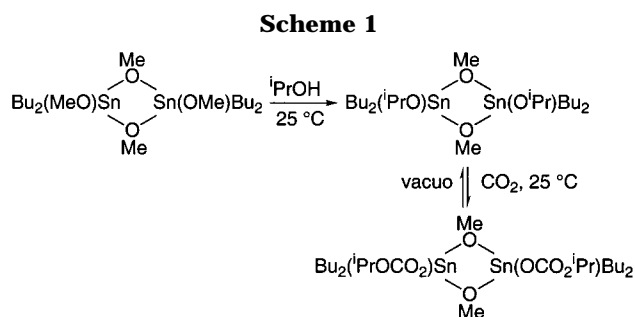


Figure 1. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Bu}_2\text{Sn}(\text{OMe})(\text{O}^i\text{Pr})$ under CO_2 , and ^1H NMR spectrum of the alkoxy region.



submitted to CO_2 at room temperature for 1 h, only one compound was present. Interestingly, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showed that it is neither **6b** nor **7b**, but a mixed species resulting from the substitution of one OMe by O^iPr . Besides the ^1H multiplets of the alkyl moieties, only one septet for $\text{OCH}(\text{CH}_3)_2$, δ 4.72 ($J(\text{H},\text{H}) = 6.2$ Hz), and one singlet for OCH_3 , δ 3.52, were present in a 1:3 ratio. In the ^{13}C resonance region of the alkyl moieties, one signal was observed for (i) each carbon atom of the butyl groups (C_α , br, 24.16; C_β , 26.97; C_γ , 26.69, $^3J(^{13}\text{C}, ^{119}\text{Sn}) = 112$, $^3J(^{13}\text{C}, ^{117}\text{Sn}) = 108$ Hz; C_δ , 13.48) and (ii) $\text{OCH}(\text{CH}_3)_2$, δ 21.97. The resonances at δ 70.04, 52.77, and 158.2 were attributed to $\text{OCH}(\text{CH}_3)_2$, OCH_3 , and $\text{OC}(\text{O})\text{O}$, respectively (Figure 1). By comparison with **6b** and **7b** data, only the low-field ^1H and ^{13}C resonances of OCHMe_2 were present, with the concomitant high-field resonances of OCH_3 . On the basis of previous assignments for $\text{Me}_2\text{Sn}(\text{OMe})(\text{OCO}_2\text{Me})$,¹⁵ the existence of only the higher field methoxy signal leads us to propose that CO_2 has been selectively inserted into the $\text{Sn}-\text{O}^i\text{Pr}$ bond, according to the following steps (Scheme 1). Selective bridging of the methoxy versus the isopropoxy ligand can originate from steric effects, coupled with the higher stability of the isopropoxy carbonate fragment as found in the tributyl series (vide supra).

Reactivity of 2b, 5b, and 6b. The formation of DMC resulting from electrophilic attack of MeI on the oxygen atom linked to tin, $\text{Sn}-\text{OC}(\text{O})\text{OMe}$, was studied first. Exposure of **2b** (1 equiv) to MeI (2 equiv) at 19 °C either in methanol, dichloromethane, 1,2-dimethoxyethane (DME), acetone, 1-methyl-2-pyrrolidinone (NMP), or

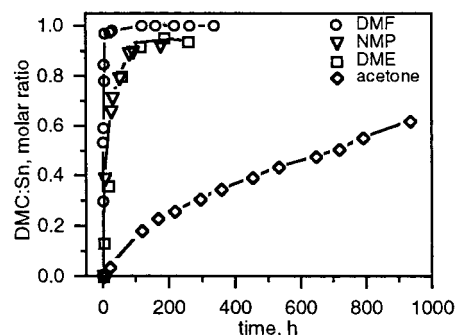


Figure 2. Rate of production of DMC from **2b** (1 equiv) in the presence of MeI (2 equiv) and CsF (1.4 equiv) at 19 °C in DMF, NMP, DME, and acetone.

N,N-dimethylformamide (DMF) failed to afford DMC. This lack of reactivity was circumvented by the addition of CsF (1.4 equiv) to the reaction medium. DMF turned out to be the best solvent for rate enhancement, in agreement with previous reports on the etherification of alcohols²¹ and esterification of carboxylic acids²² mediated by tin compounds. DMC was quantitatively formed within 6 h, whereas a longer time was needed in DME, NMP, or acetone in the following order: $\text{DMF} < \text{NMP}$, $\text{DME} \ll \text{acetone}$. The initial rate of formation is quite similar in DMF, NMP, or DME and much slower in acetone (Figure 2). Changing the fluoride source to KF led to an induction period linked to solubility problems: addition of 18-crown-6 gave a kinetic curve very similar to that of CsF . When the molar ratio $\text{CsF}:\text{2b}$ was < 1 , the yield of DMC was equal to the amount of CsF introduced. The selective formation of the organic carbonate versus dialkyl ether was confirmed with the system $\text{Bu}_3\text{SnOC}(\text{O})\text{OEt}/\text{EtI}/\text{CsF}/\text{DMF}$, because diethyl ether could be more easily quantified than dimethyl ether, if any. Diethyl carbonate was formed in stoichiometric amount, whereas no diethyl ether was detected. On the basis of these results, the behavior of **5b** and **6b** was studied in DMF at 19 °C with a $\text{Sn}:\text{MeI}:\text{CsF}$ molar ratio = 1:2:1.4. The molar ratio $\text{DMC}:\text{Sn}$ reached a maximum value after 23 h of 0.48 or 0.94, respectively. Interestingly, addition of 2.6 equiv of CsF to **6b** increased the value $\text{DMC}:\text{Sn}$ to 1.7 after 22 h, which indicates that both methoxy groups of the starting compound **6a** can react.

The driving force for the alkylation of organotin carbonates to form DMC may originate from the interaction of fluoride anion with the tin atom by increasing the nucleophilicity of the masked alkyl carbonate. To corroborate this hypothesis, the $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **2b**/DMF revealed one resonance at δ -19 characteristic of five-coordinate tin. After 5 h of reaction at room temperature with 2 equiv of CsF , the signal shifted to δ -48, and upon a further 2 h of reaction to -62 (an authentic sample of $\text{Bu}_3\text{SnF}/\text{DMF}$ exhibited a single resonance at δ -79). In the presence of MeI, after 23 h of reaction (stoichiometric amount of DMC formed), evaporation of the organics and extraction of the residue with toluene allowed us to identify Bu_3SnF as the only tin product, by comparison of the ^{13}C NMR and IR spectra with those of an authentic sample (eq 5).

(21) Ando, T.; Yamawaki, J.; Kawate, T.; Sumi, S.; Hanafuda, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2504.

(22) Sato, T.; Otera, J.; Nozaki, H. *J. Org. Chem.* **1992**, *57*, 2166.

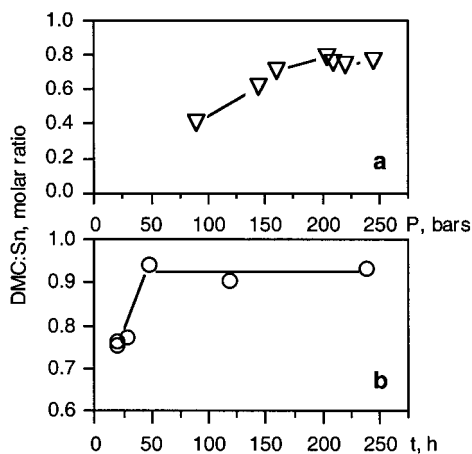
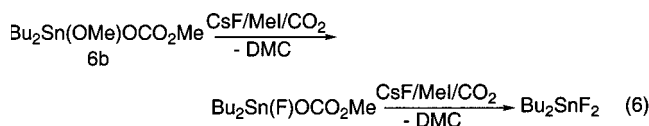
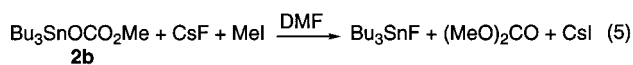


Figure 3. DMC formation from **6b** (4 mmol) in the presence of MeOH under CO₂ pressure (MeOH:CO₂ = 0.8) at 145 °C as a function of (a) pressure and (b) reaction time.

Accordingly, we propose that the two methoxy groups of **6a** are carboxylated stepwise in the presence of fluoride as depicted in eq 6. No tin compounds could be extracted with toluene, which is not surprising if Bu₂SnF₂ is formed.



A second approach for DMC formation was to study reaction 3 under catalytic conditions, i.e., replacing MeI by MeOH. In contrast with the identical behavior of **2b**, **5b**, and **6b** toward MeI, we found that species **2b** and **5b** treated under 75 bar (148 °C, 20 h) with an excess of MeOH/CO₂ mixture afforded a DMC:Sn molar ratio that did not exceed 0.1; addition of CsF had no effect. Interestingly, **6b** was found much more effective. This observation was surprising, since the CO₂ adduct is less stable (vide supra). At 145 °C and for 20 h of reaction, the DMC:Sn ratio increased with CO₂ pressure to a value of 0.8, which remained constant between 200 and 250 bar (Figure 3a). Addition of CsF (1 equiv) has no effect on the yield. Under these supercritical conditions, the DMC:Sn ratio was found to increase to ~1 with reaction time during the first 50 h (Figure 3b). To check if methanol was a reactant, it was replaced by toluene. DMC did form, but the DMC:Sn ratio remained constant at a value of 0.4 with an increase in CO₂ pressure from 80 to 190 bar. These results show that an intramolecular pathway is operative with Bu₂Sn(OMe)(OCO₂Me). However, methanol plays a role in the reaction mechanism. We also observed that dibutyl(oxo)stannane, (Bu₂SnO)_n, led to DMC under supercritical CO₂ in the presence of methanol (210 bar, 140 °C, 20 h). The DMC:Sn value was equal to 0.6 versus 0.8 for **6b**, under the same experimental conditions.

Conclusion

We have shown that the CO₂ insertion into Sn–O bonds is facile in the alkoxide series Bu₃SnOR and Bu₂–

Sn(OR)₂ for R = Me and ⁱPr, forming 1:1 adducts even in the case of dialkoxides. With the latter compounds, reversibility occurs more readily. The selective formation of Bu₂Sn(OMe)(OCO₂ⁱPr) shows that the isopropoxy is prompt to (i) insert CO₂ and (ii) stabilize the alkyl carbonate ligand, a situation also encountered with the monoalkoxide compounds **2a** and **3a**. The transformation of the carbonate ligand to dimethyl carbonate is feasible with MeI, through the assistance of fluoride anion to increase the nucleophilicity of the alkyl carbonate ligand. The difference in reactivity between mono- and dimethoxy species is better seen by running the reaction in methanol: DMC is formed only with **6b**. The best yield is obtained under a supercritical CO₂–methanol mixture. Although an intramolecular pathway produces DMC, methanol enhances the yield. It is noteworthy that dibutyl(oxo)stannane, (Bu₂SnO)_n, has a comparable reactivity.

Experimental Section

General Comments. All reactions were carried out under dry argon using Schlenk tube techniques. Chemicals were purchased from Aldrich and Acros Chimica. Bu₃SnX (X = F, Cl, I), Bu₂SnCl₂, (Bu₃Sn)₂O, and (Bu₂SnO)_n were used as received. The anhydrous fluorides were treated under vacuum at 140 °C for 20 h, just before use. CO₂ N45 was purchased from Air Liquide. The solvents were purified by standard methods. ¹H NMR spectra were recorded on a Bruker AC 100 (100.130 MHz), Bruker AM 250 (250.133 MHz), or Bruker AMX 400 (400.132 MHz) spectrometer. ¹³C NMR spectra were run on a Bruker AC 100 (25.178 MHz), Bruker AC 200 (50.323 MHz), Bruker AM 250 (62.896 MHz), or Bruker AMX 400 (100.623 MHz) spectrometer. Chemical shifts (δ, ppm) were determined relative to the solvent (¹H, CHCl₃ δ 7.24; ¹³C, CDCl₃ δ 77.00) and converted to the δ scale downfield from Me₄Si. Additional DEPT experiments allowed identification of methyl and methylene resonances, when needed. ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker AMX 400 (149.207 MHz) spectrometer. Chemical shifts (δ, ppm) are reported downfield from Me₄Sn. Infrared spectra were obtained with a Perkin-Elmer 597 spectrometer, the sample being placed between KBr windows either as neat or dispersed in Nujol. Elemental analysis was performed at the Laboratoire de Synthèse et Electrosynthèse Organométalliques, Université de Bourgogne, Dijon.

Bu₃SnOPh (1). The synthesis was adapted from ref 23. Hexabutylidistannoxane, (Bu₃Sn)₂O (16.4 g, 27.5 mmol), was mixed with phenol (5.2 g, 55.2 mmol) in 100 mL of heptane. After heating under reflux for 2 h, water, heptane, and the excess phenol were removed under vacuum, leaving a colorless oil. Anal. Calcd for C₁₈H₃₂OSn: C, 56.43; H, 8.42. Found: C, 56.64; H, 8.40. ¹H NMR (100 MHz, CDCl₃): δ 7.3–6.6 (m, 5 H), 1.8–0.7 (m, 27 H). ¹³C{¹H} NMR (25 MHz, CDCl₃): δ butyl Cα 15.8 (¹J(¹³C, ¹¹⁹Sn) = 353, ¹J(¹³C, ¹¹⁷Sn) = 338 Hz), Cβ 27.6 (²J(¹³C^{119,117}Sn) = 20 Hz), Cγ 26.9 (³J(¹³C, ¹¹⁹Sn) = 63; ¹J(¹³C, ¹¹⁷Sn) = 60 Hz), Cδ 13.5, phenyl 162.0, 129.1, 119.5, 118.2.

Bu₃SnOR (2a–4a) and Bu₂Sn(OR)₂ (6a–8a). The synthesis was adapted from ref 24. Butylalkoxystannanes were prepared from the corresponding butylchlorostannanes and sodium alkoxide.

Typical procedure for **2a**: tributyltin chloride (18 g, 55.3 mmol) in dry toluene (30 mL) was added dropwise to sodium methoxide (sodium, 1.5 g) in methanol (25 mL) at 0 °C. After the addition, the reaction mixture was heated at reflux for 6

(23) Sasin, G. S.; Sasin, R. *J. Org. Chem.* **1955**, *20*, 770.

(24) Mehrotra, R. C.; Gupta, V. D. *J. Organomet. Chem.* **1965**, *4*, 145.

h. The sodium chloride formed was centrifuged, leaving a supernatant solution from which toluene and methanol were removed under vacuum. Distillation of the crude oil with a Büchi GKR51 operating under reduced pressure (100 °C, 5 10^{-2} mbar) gave tributylmethoxystannane (13.3 g, yield 75%).

All compounds were characterized by elemental analysis and NMR spectroscopy; the ^{13}C data for **5a** are also included.

2a. Anal. Calcd for $\text{C}_{13}\text{H}_{30}\text{OSn}$: C, 48.63; H, 9.42. Found: C, 48.60; H, 9.30. ^1H (100 MHz, CDCl_3): δ 3.5 (s, 3H), 1.8–0.7 (27H). $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 14.1 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 360$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 344$ Hz), C β 28.3 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 21$ Hz), C γ 27.3 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 57$ Hz), C δ 13.7, methoxy 54.3.

3a. Anal. Calcd for $\text{C}_{15}\text{H}_{34}\text{OSn}$: C, 51.60; H, 9.82. Found: C, 50.93; H, 9.50. ^1H (100 MHz, CDCl_3): δ 3.9 (sept, $J(\text{H},\text{H}) = 6$ Hz, 1H), 1.8–0.7 (33H). $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 14.7 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 363$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 347$ Hz), C β 27.5, C γ 27.1, C δ 13.5, isopropoxy C β' 66.5, C γ' 28.0.

4a. Anal. Calcd for $\text{C}_{16}\text{H}_{36}\text{OSn}$: C, 52.92; H, 9.99. Found: C, 52.89; H, 9.94. ^1H (100 MHz, CDCl_3): δ 1.7–0.75. $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 16.1 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 365$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 349$ Hz), C β 28.1 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 17$ Hz), C γ 27.1, C δ 13.6, *tert*-butoxy C β' 70.5, C γ' 33.6 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 13$ Hz).

5a. Anal. Calcd for $\text{C}_{24}\text{H}_{54}\text{OSn}_2$: C, 48.36; H, 9.13. Found: C, 48.78; H, 9.07. $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 16.3 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 366$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 350$ Hz), C β 28.1 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 19$ Hz), C γ 27.2 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 63$ Hz), C δ 13.5.

6a. Anal. Calcd for $\text{C}_{10}\text{H}_{24}\text{O}_2\text{Sn}$: C, 40.72; H, 8.20. Found: C, 40.61; H, 8.41. ^1H (100 MHz, CDCl_3): δ 3.52 (s, 6H), 1.8–0.6 (18H). $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 19.2 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 636$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 608$ Hz), C β 27.3 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 30$ Hz), C γ 26.9 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 96$ Hz), C δ 13.5, methoxy 51.9.

7a. Anal. Calcd for $\text{C}_{14}\text{H}_{32}\text{O}_2\text{Sn}$: C, 47.89; H, 9.19. Found: C, 48.27; H, 9.32. ^1H (100 MHz, CDCl_3): δ 4.11 (sept, $J(\text{H},\text{H}) = 6.0$ Hz, 2H), 1.8–0.7 (30H). $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 18.4 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 498$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 478$ Hz), C β 27.1, C γ 26.9, C δ 13.4, isopropoxy C β' 66.6, C γ' 27.5.

8a. Anal. Calcd for $\text{C}_{16}\text{H}_{36}\text{O}_2\text{Sn}$: C, 50.69; H, 9.57. Found: C, 50.37; H, 9.46. ^1H (100 MHz, CDCl_3): δ 1.7–0.75. $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 21.4 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 489$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 467$ Hz), C β 27.2, C γ 26.7 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 85$ Hz), C δ 13.4, *tert*-butoxy C β' 71.5, C γ' 33.6 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 15$ Hz).

Carbonation Reaction. The tin compounds were dissolved in CDCl_3 , then CO_2 was admitted into the Schlenk tube, at room temperature. After the solution was stirred under CO_2 for at least 2 h, it was transferred into the NMR tube for analysis.

2b. ^1H (100 MHz, CDCl_3): δ 3.4 (s, 3H), 1.8–0.7 (27H). $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 18.1 (br), C β 28.1 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 26$ Hz), C γ 27.1 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 79$ Hz), C δ 13.6, methoxy 53.5, carbonato 158.4.

3b. ^1H (400 MHz, CDCl_3): δ 4.57 (sept $J(\text{H},\text{H}) = 4.8$ Hz, 1H), 1.8–0.7 (33H). $^{13}\text{C}\{^1\text{H}\}$ (100 MHz, CDCl_3): δ butyl C α 18.92 (br, $^1J(^{13}\text{C}, ^{119}\text{Sn}) = 483.4$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 462.3$ Hz), C β 28.18 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 26.6$ Hz), C γ 27.32 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) =$

83.0 Hz), C δ 13.73, isopropoxy C β' 69.68, C γ' 22.06, carbonato 157.72. $^{119}\text{Sn}\{^1\text{H}\}$ (149 MHz, CDCl_3): δ –28.

5b. $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 17.4 ($^1J(^{13}\text{C}, ^{119}\text{Sn}) = 412$, $^1J(^{13}\text{C}, ^{117}\text{Sn}) = 403$ Hz), C β 28.1 ($^2J(^{13}\text{C}, ^{119,117}\text{Sn}) = 23$ Hz), C γ 27.3 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 76$ Hz), C δ 13.7, carbonato 162.7.

6b. ^1H (250 MHz, CDCl_3): δ 3.66 (s, 3H), 3.53 (s, 3H), 1.8–0.8 (18H). $^{13}\text{C}\{^1\text{H}\}$ (63 MHz, CDCl_3): δ butyl C α 23.93 (br), C β 26.94, C γ 26.72 ($^3J(^{13}\text{C}, ^{119,117}\text{Sn}) = 107$ Hz), C δ 13.51, methoxy 54.02, 52.69, carbonato 158.87.

7b. ^1H (100 MHz, CDCl_3): δ 4.62 (sept, $J(\text{H},\text{H}) = 6.2$ Hz, 1H), 4.12 (sept, $J(\text{H},\text{H}) = 6.1$ Hz, 1H), 1.8–0.6 (30H). $^{13}\text{C}\{^1\text{H}\}$ (25 MHz, CDCl_3): δ butyl C α 25.9 (br), C β 26.8, C γ 26.5, C δ 13.3, isopropoxy C β' 69.9, 67.4, C γ' 21.8, carbonato 158.2.

Gasometry. A Schlenk tube containing 1 mmol of the tin compound in 1 mL of solvent was connected to a pressure transducer and to a CO_2 reservoir of known pressure. The volumes of each part of the apparatus were determined, and the amount of CO_2 gas absorbed was calibrated by the reference experiment in the absence of the tin compound. The calculated CO_2 :Sn molar ratio was at ± 0.05 .

Reaction of 2b, 5b, and 6b with MeI. Compound **2a**, **5a**, or **6a** was submitted to an atmospheric pressure of CO_2 at 19 °C for 2 h. Then, a 0.3 M solution was prepared with the appropriate solvent under CO_2 , followed by the addition of toluene (internal standard, 1 equiv), methyl iodide (2 equiv), and CsF (1.4 equiv). The identification of dimethyl carbonate was performed by GC–MS (Fisons MD 800, EI 70 eV, J&W Scientific DB-1 60 m capillary column), and the quantitative analysis was done by GC (Shimadzu 14 A, FID detector, J&W Scientific DB-WAX 15 m megabore column).

Reaction under CO_2 Pressure. In a 100 mL stainless steel batch reactor was introduced a methanolic solution or suspension (10–30 mL) of the tin compound (~ 4 mmol). The reactor was pressurized with CO_2 to a $\text{MeOH}:\text{CO}_2$ molar ratio of 0.8 and heated to the desired temperature controlled by an internal thermocouple. At the end of the reaction, the reactor was cooled to 0 °C and depressurized, and the condensed phase was transferred to a Schlenk tube for analysis by GC (Fisons 8000, FID detector, J&W Scientific DB-WAX 15 m megabore column) and identification by GC–MS (Fisons MD 800, EI 70 eV, J&W Scientific DB-1 60 m capillary column). Evaporation of the volatiles under vacuum at room temperature allowed the characterization of the residue by NMR.

Acknowledgment. We are grateful for financial support of this work from the Centre National de la Recherche Scientifique under the program “Catalyse et catalyseurs pour l’industrie et l’environnement”. The authors wish to thank S. Mangematin for technical assistance.

Supporting Information Available: ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for **2b**, **3b**, **5b**, **6b**, and **7b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000397F