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Effective synthesis of dialkyl carbonate from CO_2 and alcohols using dibutyltin(IV) oxide catalyst and dehydrating agents

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Materials

The $(Bu_2SnO)_n$ (98%) catalyst was purchased from Sigma-Aldrich. Super dry methanol (99%), ethanol (99%), 1-propanol (99%), 1-butanol (99%) were purchased from Wako Pure Chemical Industries. Dimethyl carbonate (>98%), diethyl carbonate (>98%), dipropyl carbonate (>98%), dibutyl carbonate (>98%), 2,2-diethoxypropane (>98%), 1,1-diethoxycyclohexane, tetramethyl orthosilicate (99%), tetraethyl orthosilicate (>97%), tetrapropyl orthosilicate (>98%), tetrabutyl orthosilicate (>98%) and triethyl orthoacetate (96%) were purchased from Tokyo Chemical Industries Co., Ltd. All compounds were used without further purification.

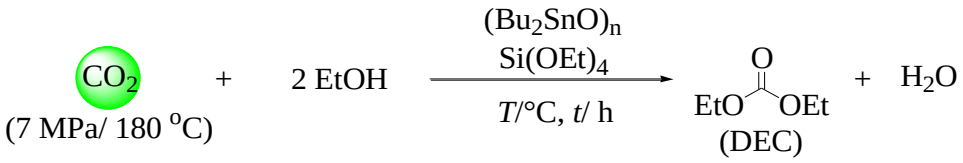
Catalytic activity studies

All reactions and operations involving air-sensitive compounds were performed in an N_2-filled glove box. General dialkyl carbonate syntheses from CO_2 and alcohols in the presence of $(Bu_2SnO)_n$ catalyst and dehydrating agents were carried out in a 10 ml autoclave. As a representative example: a magnetic stirrer bar, $(Bu_2SnO)_n$ (0.21 g), ethanol (42.8 mmol), and triethyl orthoacetate (10.7 mmol) were placed into the autoclave in the indicated order. The autoclave was sealed and purged three times with 5 MPa CO_2, and then pressurized to 6-7 MPa CO_2 at the reaction temperature (100-200 °C). The autoclave was kept heating at the reaction temperature (100-200 °C) for the specific reaction time. In the study of CO_2 pressure effect, the autoclave is pressurized by CO_2 at 1, 3 and 5 MPa at room temperature. In the synthesis of dialkyl carbonates with alcohols, 5 MPa of CO_2 is inserted at room temperature. At the end of the reaction, the autoclave was cooled to room temperature using an ice bath. The reaction mixture was analyzed by GC using a Shimadzu GC-2014 instrument equipped with a flame ionization detector and a TC-1 column with *p-tert*-butyl toluene as the internal standard. DEC yield and TON number were calculated using the following equations:

DEC yield (based on OE)/% = [mol of detected DEC/mol of initial OE] × 100%

TON = mol of detected DEC / initial mol of $(Bu_2SnO)_n$ catalyst

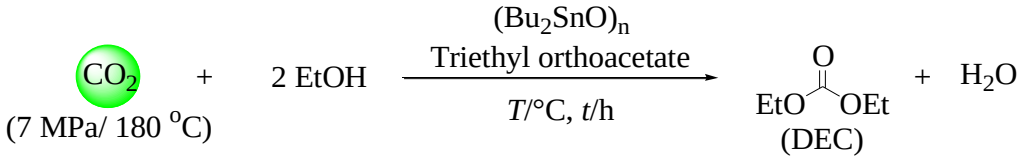
Table S1 Details of time profile for the reaction of CO_2 and ethanol with $Si(OEt)_4$.



Entry	*t* / h	*T* / °C	DEC / mmol	Yield[a] / %	Yield[b] / %	TON
1	3	180	0.81	4	15	0.9
2	6	180	1.27	6	23	1.5
3	16	180	1.85	9	35	2.2
4	24	180	2.46	11	45	2.9
5	48	180	2.14	10	40	2.5
6	72	180	2.30	11	42	2.7

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol $Si(OEt)_4$, 7 MPa CO_2 at 180 °C. [a]DEC yield based on ethanol. [b]DEC yield based on ortho ester.

Table S2 Details of time profile for the reaction of CO_2 and ethanol with ortho ester.



Entry	*t* / h	*T* / °C	DEC / mmol	Yield[a] / %	Yield[b] / %	TON
1	3	180	1.77	8	16	2.1
2	6	180	3.00	14	26	3.5
3	16	180	6.42	30	57	7.5
4	24	180	7.81	36	68	9.1
5	48	180	8.46	42	75	9.8
6	72	180	8.80	42	78	10.2

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol triethyl orthoacetate, 7 MPa CO_2 at 180 °C. [a]DEC yield based on ethanol. [b]DEC yield based on triethyl orthoacetate.

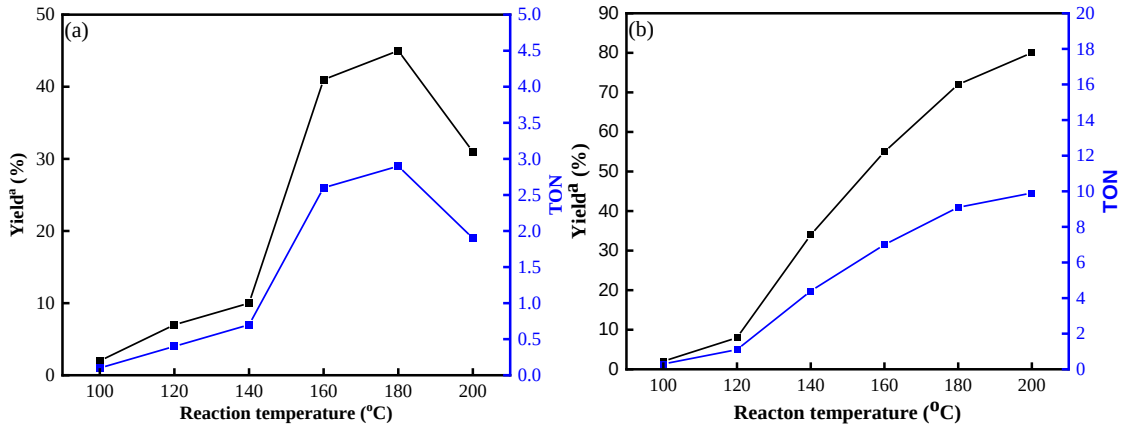
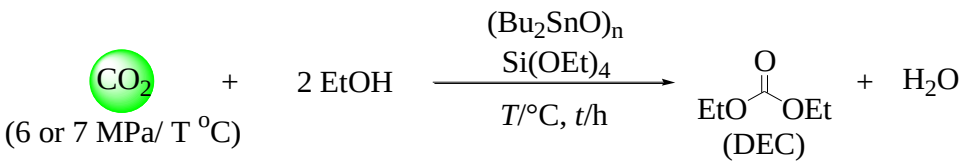


Figure S1 Effect of temperature on DEC yield and TON using (*a*) $Si(OEt)_4$, and (*b*) ortho ester as dehydrating agent. *Reaction conditions*: 42.8 mmol ethanol, 10.7 mmol dehydrating agent, 6 or 7 MPa CO_2 at the reaction temperature, 0.86 mmol $(Bu_2SnO)_n$ catalyst, 24 h. [a] Yield was determined by GC using an internal standard method, based on dehydrating agent.

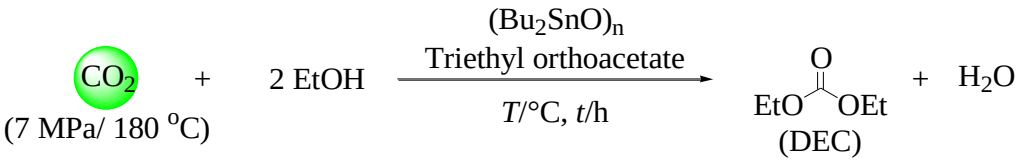
Table S3 Details of temperature effect for the reaction of CO_2 and ethanol with $Si(OEt)_4$.



Entry	*T* / °C	P_{CO2} at *T* / MPa	DEC / mmol	Yield[a] / %	Yield[b] / %	TON
1	100	6	0.08	0.4	2	0.1
2	120	6	0.36	2	7	0.4
3	140	7	0.56	3	10	0.7
4	160	7	2.20	10	41	2.6
5	180	7	2.46	11	45	2.9
6	200	7	1.66	8	31	1.9

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol $Si(OEt)_4$, 6 or 7 MPa CO_2 at reaction temperature, 24 h. [a]DEC yield based on ethanol. [b]DEC yield based on triethyl orthoacetate.

Table S4 Details of temperature effect for the reaction of CO_2 and ethanol with ortho ester.



Entry	*T* / °C	P_{CO2} at *T* / MPa	DEC / mmol	Yield[a] / %	Yield[b] / %	TON
1	100	7	0.28	1	2	0.3
2	120	7	0.91	4	8	1.1
3	140	7	3.78	17	34	4.4
4	160	7	6.02	28	55	7.0
5	180	7	7.81	36	68	9.1
6	200	7	8.53	40	80	9.9

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol triethyl orthoacetate, 7 MPa CO_2 at reaction temperature, 24 h. [a]DEC yield based on ethanol. [b]DEC yield based on triethyl orthoacetate.

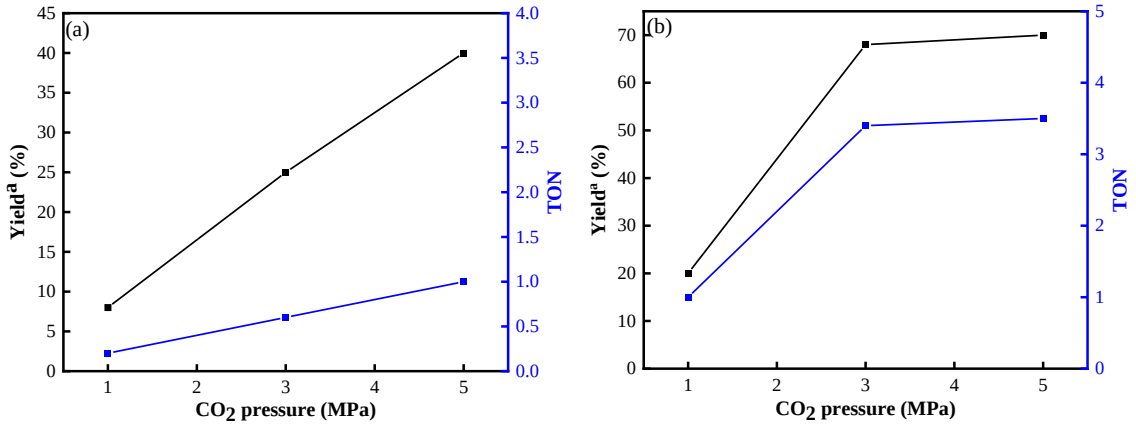
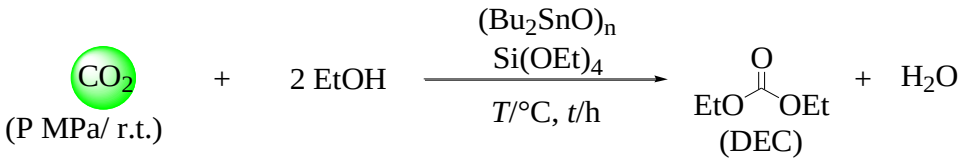


Figure S2 Effect of CO_2 pressure on DEC yield and TON using (*a*) $Si(OEt)_4$ and (*b*) ortho ester as dehydrating agent. *Reaction conditions*: 42.8 mmol ethanol, 10.7 mmol dehydrating agent, 0.86 mmol $(Bu_2SnO)_n$ catalyst, 180 °C, 24 h. [a] Yield was determined by GC using an internal standard, based on dehydrating agent. The pressure values indicated in the graph are the pressure at room temperature.

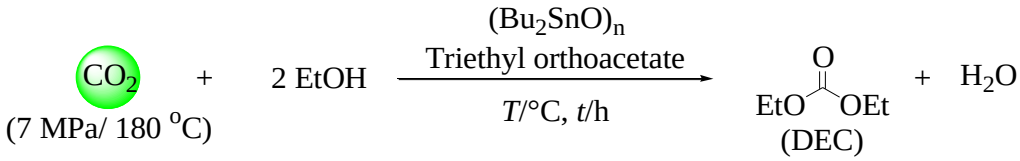
Table S5 Details of pressure effect for the reaction of CO_2 and ethanol with $Si(OEt)_4$.



Entry	P_{CO2} at r.t / MPa	P_{CO2} at 180 °C / MPa	DEC / mmol	Yield[a] / %	Yield[b] / %	TON
1	1	2.2	0.43	2	8	0.2
2	3	6	1.32	6	25	0.6
3	5	10	2.13	10	40	1.0

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol $Si(OEt)_4$, 180 °C, 24 h. [a]DEC yield based on ethanol. [b]DEC yield based on $Si(OEt)_4$.

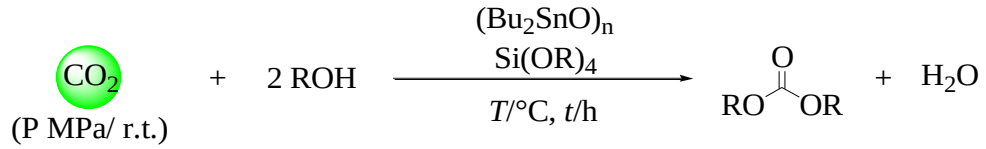
Table S6 Details of temperature effect for the reaction of CO_2 and ethanol with ortho ester.



Entry	P_{CO2} at r.t / MPa	P_{CO2} at 180 °C / MPa	DEC / mmol	Yield[a] / %	Yield[b] / %	TON
1	1	2	2.18	10	20	1.0
2	3	5	7.26	35	68	3.4
3	5	10	7.48	36	70	3.5

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol triethyl orthoacetate, 180 °C, 24 h. [a]DEC yield based on ethanol. [b]DEC yield based on triethyl orthoacetate.

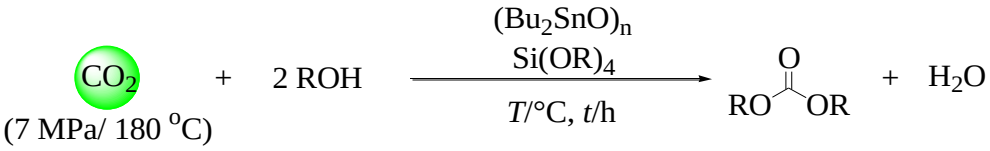
Table S6 Details of direct dialkyl carbonates synthesis with 5 MPa CO_2 at room temperature.



Entry	Alcohol	P_{CO2} at r.t / MPa	P_{CO2} at 180 °C / MPa	$(RO)_2CO$/ mmol	Yield[a] / %	Yield[b] / %	TON
1	MeOH	5	10	2.53	12	47	2.9
2	EtOH	5	10	2.13	10	40	2.5
3	^{n}PrOH	5	9	1.09	5	20	1.3
4	^{n}BuOH	5	8	0.84	3	16	1.0

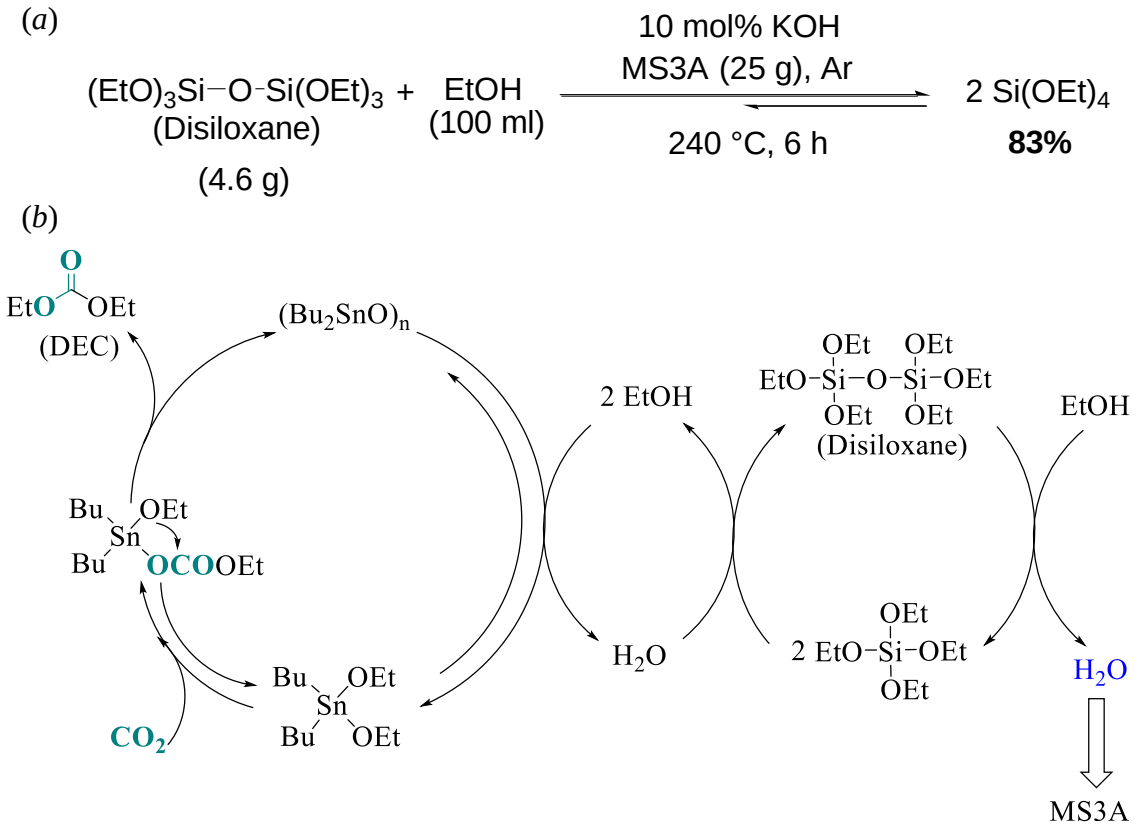
Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol alcohol, 10.7 mmol $Si(OR)_4$, 180 °C, 24 h. [a]$(RO)_2CO$ yield based on alcohol. [b]$(RO)_2CO$ yield based on $Si(OR)_4$.

Table S7 Details of direct dialkyl carbonates synthesis with 7 MPa CO_2 at 180 °C.



Entry	Alcohol	P_{CO2} at 180 °C / MPa	$(RO)_2CO$/ mmol	Yield[a] / %	Yield[a] / %	TON
1	MeOH	7	1.86	9	35	2.2
2	EtOH	7	2.46	11	45	2.9
3	^{n}PrOH	7	2.07	10	39	2.4
4	^{n}BuOH	7	1.79	8	33	2.1

Reaction conditions: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol alcohol, 10.7 mmol $Si(OR)_4$, 180 °C, 24 h. [a]$(RO)_2CO$ yield based on alcohol. [b]$(RO)_2CO$ yield based on $Si(OR)_4$.



Scheme S1 (*a*) The regeneration of $Si(OEt)_4$ from the corresponding disiloxane. (b) General illustration of the direct synthesis of DEC from CO_2 and ethanol using $(Bu_2SnO)_n$ catalysts and $Si(OEt)_4$ dehydrating agent [S1,S2].

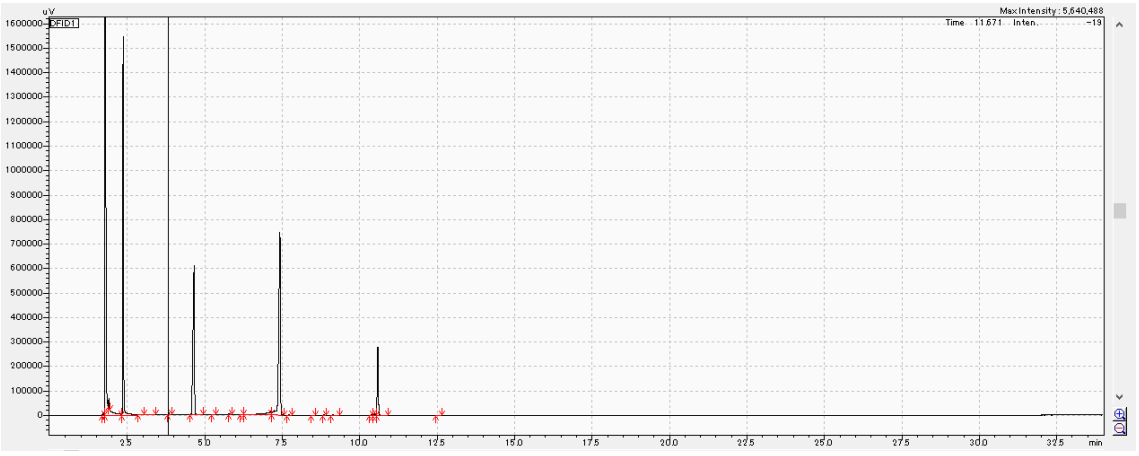


Figure S3. Typical GC chart of DEC synthesis from CO_2 and ethanol in the presence of ortho ester (triethyl orthoacetate) with $(Bu_2SnO)_n$. *Reaction conditions*: 0.86 mmol $(Bu_2SnO)_n$, 42.8 mmol ethanol, 10.7 mmol triethyl orthoacetate, 7 MPa CO_2 at 180 °C, 180 °C, 24 h.

Table S7. The assignment in the typical GC chart for DEC synthesis from CO_2 and ethanol using $(Bu_2SnO)_n$ and ortho ester (triethyl orthoacetate)

Retention time (min)	Compound
1.789	Ethanol
2.364	Ethyl acetate
4.453	Diethyl carbonate
7.425	Triethyl orthoacetate
10.585	*p-tert*-Butyltoluene

References

[S1] K. Kohno, J. C. Choi, Y. Ohshima, A. Yili, H. Yasuda and T. Sakakura, *J. Organomet. Chem.*, 2008, **693**, 1389–1392.

[S2] J. C. Choi, T. Sakakura and T. Sako, *J. Am. Chem. Soc.*, 1999, **121**, 3793–3794.