Carbonylation of Butylstannyl Alkoxides with Five-membered Cyclic Carbonates

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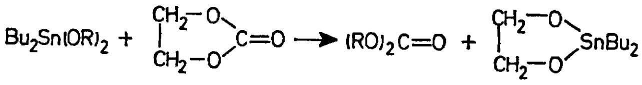
Summary Reaction of dibutylstannyl alkoxides with ethylene carbonate gives dialkyl carbonates without elimination of CO_2.

Ethylene carbonate, readily prepared from ethylene oxide and CO_2, would be a useful carbonylation reagent and intermediate for CO_2 fixation, if CO_2 were not evolved in its reactions. However, its reactions with metal alkoxides or oxides are reported to afford the corresponding β-hydroxyethyl derivatives and CO_2.[1]

We now report that dibutylstannyl dialkoxides (**1**) react readily with ethylene carbonate (**2**) under dry nitrogen at atmospheric pressure to give dialkyl carbonates (**3**) and the dimer of the organostannyl alkoxide (**4**) in relatively good yields.



(1) (2) (3) (4)

Although the reactions of equimolar amounts of (**1**) and (**2**) without solvent are heterogeneous, $Bu_2Sn(OMe)_2$ reacted instantaneously with (**2**) at room temperature to precipitate (**4**). Alkylene carbonates (**1**) can thus be converted into dialkyl carbonates (**3**), and decarboxylation is not observed. The data in the Table for homogeneous reactions in dry benzene or toluene show that the more bulky alkoxides are less reactive, suggesting that there is a strong steric effect.

Tributylstannyl alkoxides unexpectedly were less reactive towards (**2**) than the dibutylstannyl compounds (**1**) (Table). Triorganostannyl alkoxides are reported to react easily with lactones at 60°,[2] and bis(tributylstannyl) glycolate reacts with CS_2 to form a spiro-orthocarbonate under much milder conditions than for the corresponding dibutylstannyl derivative.[3] The fact that tributylstannyl alkoxides react with (**2**) only under severe conditions to give (**3**), (**4**), and Bu_4Sn suggest that Bu_3SnOR disproportionates to Bu_4Sn and (**1**), followed by a fast reaction of (**1**) with (**2**) to form (**3**) and (**4**).

TABLE

Starting alkoxide	Temp./°C	Time/h	Yield (%)[a] (**3**)	(**4**)
$Bu_2Sn(OMe)_2$	Room temp.	2	70(92[b])	83
$Bu_2Sn(OEt)_2$	40	4	73(93[b])	82
$Bu_2Sn(OPr^n)_2$	100	8	51(30[b])	45
$Bu_2Sn(OBu^n)_2$	120	16	35(0[b])	42
$Bu_2Sn(OPr^i)_2$	100	8	61(99[c])	48
$Bu_2Sn(OBu^s)_2$	120	16	27(20[c])	31
$Bu_2Sn(OBu^t)_2$	120	16	62(0[c])	57
Bu_3SnOMe	185	2(13[d])	70(59[d])	68(30[d])
Bu_3SnOEt	185	24	28	24
Bu_3SnOPr^i	185	24	20	—
Bu_3SnOBu^t	185	48	47	45

[a] In a typical experiment (**1**) and (**2**) (10 mmol each) were heated for several hours without solvent under dry nitrogen and distilled to afford (**3**). Compound (**4**) was separated from the distillate by recrystallization from toluene. The dialkyl carbonates obtained were identified by comparison (b.p. and i.r. and ^1H n.m.r. spectra) with authentic samples. [b] Reaction for 24 h in benzene under reflux. [c] Reaction for 26 h in refluxing toluene. [d] Reaction with 1,2-propylene carbonate.

Carbonylations of organostannyl derivatives of amines and thiols by reaction with (**2**) failed; the reaction of $R_2Sn(NEt_2)_2$ (R = Bu, Me) with (**2**) for 12 h at 70—80° gave only $R_2Sn(NEt_2)OC_2H_4OCONEt_2$;† $Bu_2Sn(SMe)_2$ had not reacted with (**2**) after 20 h at 150° and starting materials were recovered in good yields.

$Bu_2Sn(OPh)_2$ reacted with (**2**) at 180° for 30—60 h, and the i.r. and ^1H n.m.r. spectra of the reaction mixture indicate the formation of $(PhO)_2CO$ (ν_{CO} 1758 cm^{-1}), followed by its decarboxylation.

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† Not isolated; structure assumed from the i.r. and ^1H n.m.r. spectra.

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