Group 4 Organometallic Reagents Part 6.[1] The Organotin-mediated Monofunctionalization of Diols: an Insight into the Selective Monoesterification with Acyl Chlorides

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The monoesterification of ethylene glycol with acyl chlorides through its dibutylstannylene derivative (**1**) has been selected as a model reaction to investigate, by n.m.r. spectroscopy, the origin of the organotin-mediated selective monofunctionalization of diols. The reaction has been found to take place in two separate steps, namely, an initial fast formation of a stannylated diol monoester followed by a slower intermolecular transesterification. The latter affords diester products and regenerates the starting dioxastannolane (**1**). Thus, the success of monoesterification depends on the timing of quenching the intermediate and is ensured by the large rate difference between the two steps. The above transesterification is an equilibrium reaction, shifted towards (**1**), that eventually leads to complete formation of diesters. Dynamic phenomena exhibited by n.m.r. spectra reveal that such a transesterification equilibrium also takes place intramolecularly at a much faster rate, showing intramolecularity factors of the order of 10^7 with respect to its intermolecular counterpart. Dibutyltin dichloride (**3**), which forms in the reaction, exerts a catalytic effect enhancing the reactivity of dioxastannolane toward the ester functionality. Such a catalytic effect may be accounted for by the very fast and strongly biased equilibrium reaction that occurs between (**1**) and (**3**), leading to ring-opening of the highly stable dioxastannolane. The generality of the stannylation method is further confirmed by monosilylation, carried out with silyl chlorides.

In recent years, considerable attention has been focused on the use of organotin derivatives to achieve selective monofunctionalization of diols and polyols.[2] Indeed, polyhydroxy compounds have been efficiently alkylated, acylated, oxidized, *etc.* at a single hydroxy site with excellent mono- and regioselectivities by simple activation through their alkyltin derivatives in one-pot procedures.[2]

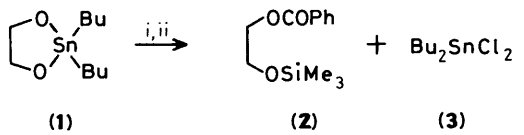
Surprisingly, the origin of selectivity of the organotin-mediated method has received very little attention up to now, despite its wide synthetic application: the only available hypothesis rests on structural considerations based on the well established dimerization of stannoxane reagents.[3] In dimeric dioxastannolanes, for example, one pair of oxygen atoms is co-ordinated to tin, hence, they have been suggested to be less reactive toward electrophilic reagents than the unco-ordinated pair.

Although the structure of dioxastannolane in solution has been elucidated[4] and the selective enhancement of oxygen reactivity by co-ordination can be considered plausible,[5] no information on the actual reaction path is available yet. Indeed, a better knowledge of the mechanism would enable the optimization of the method and would shed light on its scope and limitations.

In this context, the monoesterification of ethylene glycol with acyl chlorides, through the corresponding dibutylstannylene derivative, was selected as a model reaction for an investigation by n.m.r. spectroscopy and the results are reported in the present paper.

Results

Ethylene glycol is converted into 2,2-dibutyl-1,3,2-dioxastannolane (**1**) by azeotropic dehydration in the presence of dibutyltin oxide. Reaction of (**1**) with 1 equivalent of acyl chloride, followed by hydrolytic work-up, affords monoester products. As a standard procedure, a concentrated solution of acyl chloride (2 mmol ml^{-1} of $CHCl_3$) is added dropwise at 5 °C to a solution of (**1**) (1 mmol ml^{-1} of $CHCl_3$). Complete reaction is generally obtained in a few minutes by simply allowing the mixture to warm to room temperature. Although the monoester products can then be obtained by acidic or neutral hydrolytic treatment, better selectivities are achieved upon quenching the reaction at 5 °C with chlorotrimethylsilane (Me_3SiCl), that affords silyl-protected diol monoesters. The reaction with benzoyl chloride (PhCOCl) was chosen as a reference in the present investigation (Scheme 1). Final



(**1**) (**2**) (**3**)

Scheme 1. *Reagents:* i, PhCOCl; ii, Me_3SiCl

mixtures were analysed by ^1H n.m.r. spectroscopy: besides monoesters, only disilyl and diester derivatives of ethylene glycol could usually be detected.

Monoesterification Selectivity.—The influence of varying the reaction conditions on monoester yields was investigated (Table 1). The results show that yields are fairly insensitive to temperature and concentration variations, except when operating at room temperature without cooling the exothermic reaction (entry 7). Interestingly, reversing the order of addition of PhCOCl and Me_3SiCl (entry 6) does not appear to affect monoester's yield to any extent (*cf.* entry 5).

A deeper insight required a detailed analysis of stannylated intermediates before quenching. Immediately after the addition

Table 1. Influence of reaction conditions on monoester yield for Scheme 1

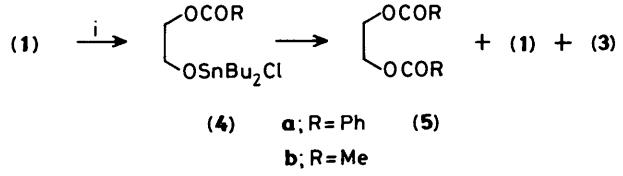
Entry	Temp. °C	Conc.[a]	Yield(%)
1	−50	1.05	86
2	−50	0.35	87
3	−30	2.00[b]	86
4	5	0.33	86
5	5	2.00[b]	80
6[c]	5	2.00[b]	81
7	22[d]	1.00	61

[a] Concentration of reagents solutions in mmol ml^{-1} of $CHCl_3$. [b] Concentration of the solution of (**1**) is 1.00. [c] Run with reversed addition order of the chloride reagents. [d] Run without cooling during the addition of reagents.

Table 2. Progress of the transesterification of (**4a**) (Scheme 2) at 22 °C detected by ^1H n.m.r. spectroscopy[a]

t/h	(**5a**) (%)	(**4a**) (%)	(**1**) (%)
0.5	12	82	6
6	13	79	8
18	15	76	9
30	19	70	11
56[b]	21	65	14
103[c]	25	56	19
148[c]	28	50	22
462	35	36	29

[a] Spectra were run at 300 MHz; concentrations as in Table 1 entry 5. [b] Spectrum run at 90 MHz. [c] Spectrum run at 200 MHz.



Scheme 2. *Reagents:* i, RCOCl

of PhCOCl, the formation of the stannylated diol monoester (**4a**) was observed in 90% yield (Scheme 2). Performing the reaction at temperatures lower than 5 °C merely increased the time required for the complete formation of (**4a**) without appreciably affecting the final amount. However, allowing the mixture to stand at room temperature caused the amount of (**4a**) slowly to decrease, while a corresponding increase of dioxastannolane (**1**) and dibenzoate (**5a**) was observed. After having refluxed the solution for 14 h, only 22% of (**4a**) was left, together with 38% of (**1**) and 40% of (**5a**). Apparently, fast formation of the monoester with good selectivity is followed by a slower transesterification that produces bis-derivatives at its expense (Scheme 2).

The progress of the transesterification was followed at 22 °C by ^1H n.m.r. spectroscopy (Table 2). Under these conditions, the intermediate (**4a**) was consumed with an estimated half-life of *ca.* 10 days.

Analogous results were obtained for monoacetylation with acetyl chloride. The initial formation of the stannylated monoacetate (**4b**), detected in 74% amount after *ca.* 20 min, was followed by a reorganization to compound (**1**) and to the diacetate (**5b**) with a half-life of 5 h at 22 °C under the same conditions.

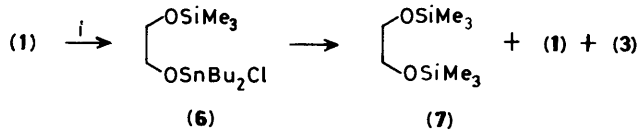
According to the above results, the observed insensitivity of

Table 3. ^1H N.m.r. chemical-shift and linewidth values relative to the CH_2O resonance for mixtures of (**1**) and (**3**) in different ratios[a]

Entry	(**1**):(**3**)	δ[b]	Linewidth[c]	Normalized linewidth[d]
1	1:0	3.526	1.9	1.9
2	3:1	3.613	6.7	6.7
3	2:1	3.660	7.9	7.7
4	1:1	3.743	16.7	16.5
5	1:1[e]	3.737	3.6	3.3
6	1:10	3.763	23.9	23.5
7	1:20	3.722	2.4	1.8
8	1:50	3.724	1.9	1.8

[a] Data obtained at 300 MHz and 22 °C by mixing 0.85M-solutions (1 mmol ml^{-1} of solvent) of reagents in $CDCl_3$. The chemical-shift and linewidth variations of the internal $CHCl_3$ resonance in the set of spectra investigated were $\Delta\delta = 0.003$ p.p.m. and $\Delta LW = 0.6$ Hz, respectively. [b] Chemical-shift values in p.p.m. from external $SiMe_4$. [c] Half-height linewidth values in Hz. [d] Half-height linewidth values normalized to the value of 0.6 Hz of the $CHCl_3$ resonance in the spectrum of pure (**1**). [e] Spectrum run at 50 °C.

the benzoylation reaction to the reversal of reagent addition (Table 1, entry 6) is somewhat unexpected. The addition of 1 equivalent of Me_3SiCl to (**1**) afforded the stannylated monosilyldiol (**6**), which, after 20 min at 22 °C, was detected in 71% amount, together with 29% of (**7**) and (**1**) (Scheme 3). An



Scheme 3. *Reagents:* i, Me_3SiCl

almost complete transformation of (**6**) into (**7**) and (**1**) was obtained when the mixture was allowed to stand for 20 h at room temperature. The overall picture is consistent with a much faster disappearance of (**6**) with respect to the benzoylated intermediate (**4a**). Thus, the observation of the same yield of monoester by reversed reagent addition appears to be a serendipitous result due to the timing of quenching, but shows that monofunctionalization can be achieved analogously with silyl chlorides.

Dynamic Processes.—Dynamic processes are evident in the behaviour of the n.m.r. signals of (**1**). To support this point, spectra of mixtures of (**1**) and (**3**) prepared independently were recorded at 22 °C in mole ratios ranging from pure (**1**) to (**1**):(**3**) = 1:50 (Table 3). The main feature is a broad single line, for the CH_2O signal, that shifts downfield on increasing the amount of (**3**), to the chemical shift value for the 1:1 mole ratio (entry 4), after which no further shift is observed; smaller mole ratios only induced narrowing of the signal. Line narrowing was also observed when the spectrum of the 1:1 mixture was run at 50 °C (entry 5). Spectra of the 1:1 mixture at various concentrations (Table 4) showed remarkable variation in linewidth, but small fluctuations of chemical shift; only a single signal was observed in all cases, except for the lowest concentration (entry 6), in which case splitting into close lines of unequal intensity occurred. A frequency difference $\Delta\nu = 67$ Hz between the single resonance at its minimum linewidth and that of (**1**) was measured.

In the ^1H n.m.r. spectrum of the benzoylation mixture signals belonging to (**4a**) are broad and badly resolved [Figure 1(A)]. The same mixture at 50 °C exhibits narrower lines [Figure

Table 4. ^{1}H N.m.r. chemical-shift and linewidth values relative to the CH_2O resonance for a 1:1 mixture of (**1**) and (**3**) at different concentrations[a]

Entry	Concentration[b]	δ[c]	Linewidth[d]	Normalized linewidth[e]
1	7×10^{-1}	3.731	14.4	14.4
2	5×10^{-1}	3.742	16.7	16.4
3	1×10^{-1}	3.775	12.7	12.5
4	1×10^{-2}	3.746	1.6	1.3
5	1×10^{-3}	3.748	5.5	5.2
6	1×10^{-4}	3.736	*ca.* 1.5	*ca.* 1
		3.742	*ca.* 1.5	*ca.* 1
		3.746	*ca.* 1.5	*ca.* 1

[a] Data obtained at 300 MHz and 22 °C in $CDCl_3$ solution. The chemical-shift and linewidth variation of the internal $CHCl_3$ resonance in the whole concentration range were $\Delta\delta = 0.002$ p.p.m. and $\Delta LW = 0.6$ Hz, respectively. [b] Molar concentration of the (**1**)–(**3**) adduct. [c] Chemical-shift values in p.p.m. from external Me_4Si. [d] Half-height linewidth values in Hz. [e] Half-height linewidth values normalized to the value of 0.6 Hz of the $CHCl_3$ resonance in the spectrum of pure (**1**).

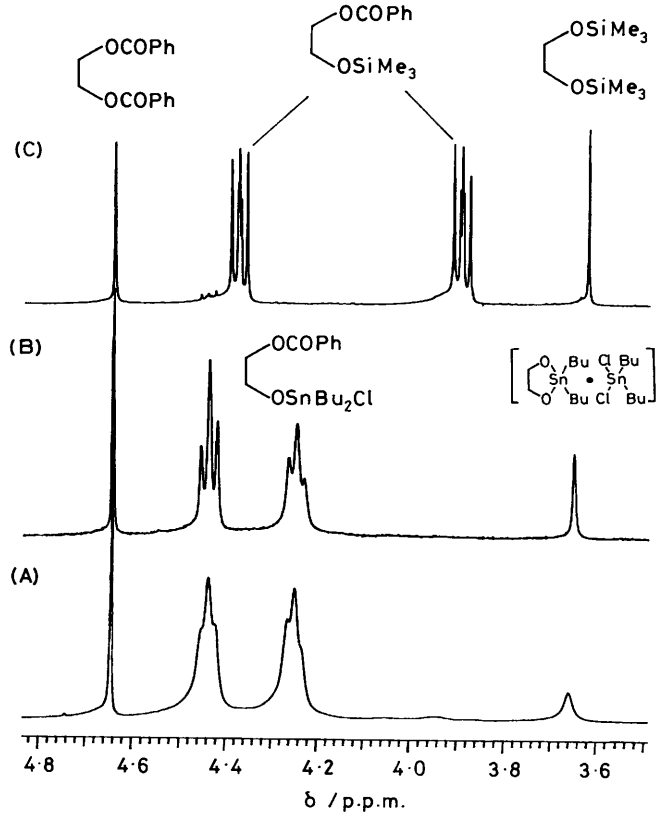


Figure 1. ^{1}H N.m.r. spectra (300 MHz) of the benzoylation mixture of 2,2-dibutyl-1,3,2-dioxastannolane: (A) at 22 °C, after the addition of 1 equivalent of PhCOCl; (B) same mixture at 50 °C; (C) at 22 °C, after quenching with 1 equivalent of Me_3SiCl. Only the CH_2O spectral region is shown

1(B)], that broaden again at 22 °C. In contrast, after having been quenched, the silylated monobenzoate (**2**) exhibits sharp signals [Figure 1(C)] as does dibenzoate (**5a**) at all temperatures. This evidence suggests the occurrence of intramolecular exchange processes within the stannylated monoester (**4a**). However, coalescence of signals for (**4a**) could not be achieved because of the low boiling point of the solvent.

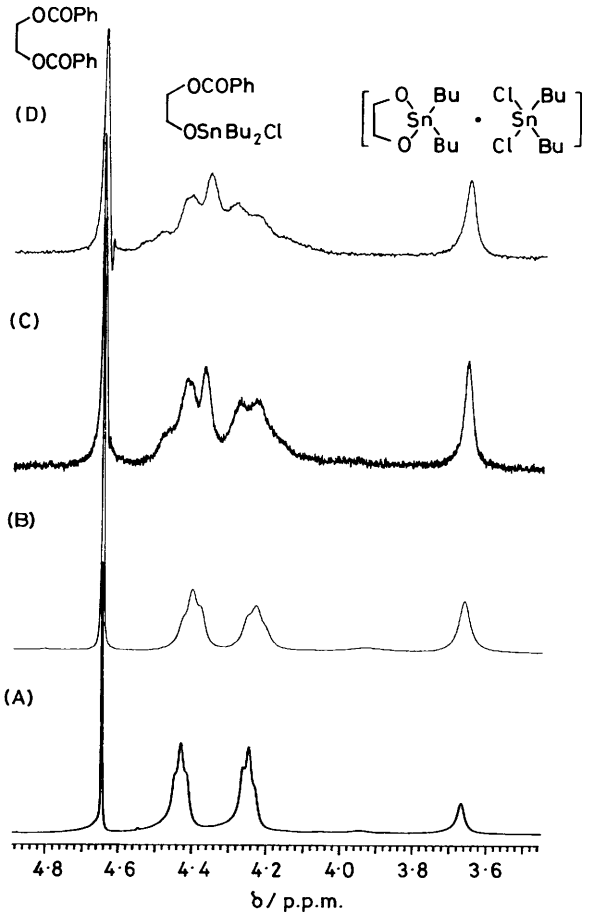


Figure 2. Room-temperature (22 °C) ^{1}H n.m.r. spectra of the benzoylation mixture of 2,2-dibutyl-1,3,2-dioxastannolane at different magnetic field values: (A) at 300 MHz; LW: 0.95 Hz (**5a**), 9.6 Hz (**1**); (B) at 200 MHz; LW: 0.73 Hz (**5a**), 7.2 Hz (**1**); (C) at 90 MHz; LW: 1.0 Hz (**5a**), 2.2 Hz (**1**); (D) at 60 MHz; LW: 0.9 Hz (**5a**), 1.8 Hz (**1**). Only the CH_2O moiety spectral region is shown

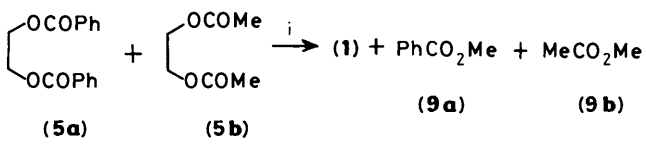
To overcome this limit, room-temperature ^{1}H n.m.r. experiments were run at decreasing magnetic field values. The resulting spectra (Figure 2) show the approaching coalescence for signals of (**4a**), while a narrowing from 9.6 to 1.8 Hz for the line of (**1**) and a constant value for the linewidth of (**5a**) in the whole field range are observed. Analogous behaviour was observed for the acetyl monoester (**4b**).

The above results support the existence of two independent dynamic processes involving the stannylated species, the dioxastannolane (**1**), and the monoester (**4**).

Equilibration.—The transesterification reaction of stannoxyesters has been shown to be a fast equilibrium in the case of macrocyclic polyesters.[1] Thus, a basic question is whether the final products are kinetically or thermodynamically controlled.

First, two reaction mixtures quenched with Me_3SiCl, containing widely differing amounts of (**2**) (23 and 84%), (**5a**), and (**7**), were refluxed for 10 h, after which time the resulting product distribution was essentially unaltered. Diol monoesters are known to isomerize;[6] the present results verify that silyl-protected derivatives are stable in the reaction medium.

Next, a 1:1 mixture of ethylene glycol dibenzoyl ester (**5a**) and diacetyl ester (**5b**) in chloroform was refluxed in the presence of 1 equivalent of (**1**). After 18 h, only trace amounts of the mixed acetate–benzoate diester were detected. Instead, by addition of 1 equivalent of Bu_2SnCl_2 (**3**) to the latter solution,



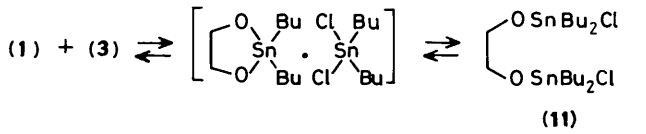
Scheme 4. *Reagents:* i, 2 $Bu_2Sn(OMe)_2$ (**8**)

equilibration was observed and a 1:1:1 mixture of (**5a**), (**5b**), and the mixed diester was detected after a 15 h reflux.

A faster initial rate of stannoxane-reagent decay was observed when a 1:1 mixture of (**5a**) and (**5b**) was treated at room temperature with 1 equivalent of dibutyldimethoxystannane [$Bu_2Sn(OMe)_2$ (**8**)], the open-chain analogue of (**1**) (Scheme 4): the reaction leads to the formation, besides the starting dioxastannolane, of methyl benzoate (**9a**) and methyl acetate (**9b**), with a much faster rate for the former ($t_{\frac{1}{2}}$ = 1 h) than for the latter (20% product formation in 15.5 h). Notably, this reaction occurred in the absence of (**3**).

Discussion

The Role of Dibutyltin Dichloride.—Concerning dynamic processes involving (**1**), it has been shown previously[1] that the single resonance observed for the CH_2O moiety is actually an average signal from species participating in the fast equilibrium of Scheme 5, in which (**3**) reacts with (**1**) to produce the mixed



Scheme 5.

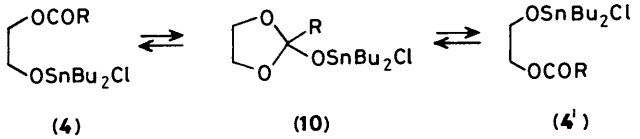
species (**11**). It is now apparent that such exchange processes are independent of those involving stannylated monoesters. Furthermore, the dependence of the chemical shift and linewidth on mole ratio, temperature, and field strength confirms that the equilibrium (5) is fast and that the line is above coalescence. The saturation effect on chemical shift indicates that for a 1:1 reagent ratio a complete formation of (**11**) is achieved, *i.e.* the equilibrium is strongly biased. As a matter of fact, for high dilution (slow intermolecular processes) only the resonance of (**11**) could be detected, coincident with that obtained for very low (**1**):(**3**) ratios [greatly reduced amount of exchanging (**1**)]. For such a dynamic system, the considerably larger linewidths observed cannot be due only to the (**1**) $\rightleftharpoons$ (**11**) exchange and are attributed to concurrent fast aggregation equilibria analogous to those occurring with (**1**).[4] Chemical-shift fluctuations and splitting with concentration are in line with this interpretation. Although the analysis of the system is complicated by association phenomena, an estimate of lifetime τ of the species involved as $2 \times 10^{-3} > \tau > 10^{-4}$ s under the monofunctionalization conditions shows that this equilibrium is the fastest of the whole reaction pattern.

Dibutyltin dichloride (**3**) has been observed to take part in transesterification reactions in the macrocyclic series, but its role is still unclear.[1] The much slower reactions exhibited by the open-chain counterparts in equilibration experiments ascertained that (**3**) plays a catalytic role in the reaction of (**1**) with esters, in that it enhances its otherwise low reactivity. Considering that transesterifications are actually carried out by chlorostannylated species, the equilibrium (5) might explain the catalytic effect exerted by (**3**) with the fast formation of the more reactive species (**11**). Thus (**1**) appears to be a much more efficient transesterification catalyst in the presence of dibutyltin dichloride, probably because of ring-opening of the highly stable[1] dioxastannolane. Indeed, the uncatalysed reaction of the open-chain dioxastannane (**8**) with esters proceeds at rates comparable to those of the catalysed reaction of (**1**), but much larger than those of the corresponding uncatalysed one.*

The Monoesterification Reaction Pattern.—A two-step pathway has been suggested for the monoesterification of ethylene glycol *via* the dibutylstannylene derivative. In the first step, a stannylated monoester is produced with high selectivity from 1 equivalent of acyl chloride; in the second, a rearrangement to afford bis-derivatives takes place through a transesterification. Thus, the reaction outcome depends not only on selectivity of formation of the intermediate, but also on the timing of the quenching. Benzoyl and acetyl chloride have been observed to react with (**1**) under the given conditions with a $t_{\frac{1}{2}}$ of 16 and 5 s, respectively;[5] on the other hand, subsequent transesterfication takes place with $t_{\frac{1}{2}}$ of 10 days and 5 h, respectively;† thus, the large reactivity difference ensures a clear-cut separation between the two steps and essentially no loss of selectivity upon quenching. In contrast, it was not possible to improve upon the 90% yield of (**4**) in the first step: this might represent the selectivity limit obtainable in the monoesterification of ethylene glycol with the acyl chlorides used. However, it is still unclear how the monoester formation actually occurs: although dioxastannolane oxygens might be selectively activated by co-ordination, preferential formation of diester derivatives would be expected from the larger reactivity (ascertained from equilibration experiments) of the chlorostannoxy group formed after the first event with respect to the starting dioxastannolane.

Equilibration experiments also showed that transesterification is indeed an equilibrium reaction for open-chain stannoxy esters, but the reverse reaction is so slow that the final products can by no means be considered as being thermodynamically controlled, *i.e.* the equilibrium is too slow to compete with quenching.

In contrast, transesterification takes place intramolecularly at a much faster rate. Dynamic processes relative to (**4**), observed in the ^1H n.m.r. spectra, are attributed to the equilibrium of Scheme 6, in which virtual exchange of the acyl group between



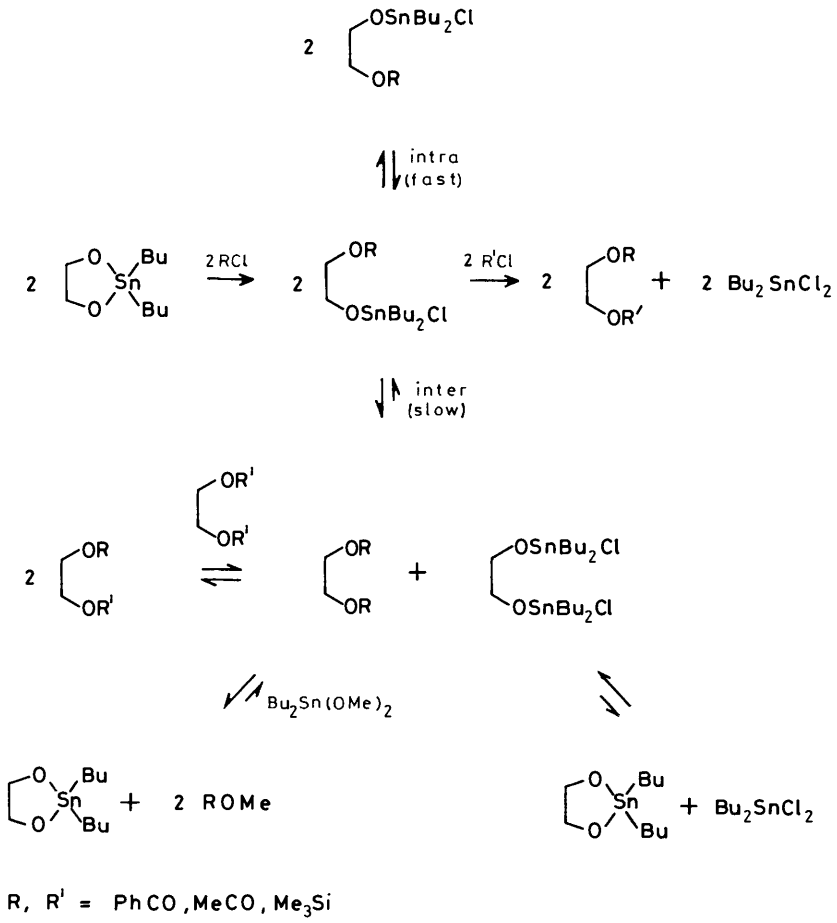
Scheme 6.

the diol oxygen atoms occurs through the tetrahedral intermediate (**10**). For the benzoyl derivative, for example, the lifetime τ of species taking part to this equilibrium is estimated from n.m.r. parameters as $10^{-1} > \tau > 5 \times 10^{-2}$ s at 22 °C. Considering the half-life 10 d for its intermolecular counterpart (Scheme 2), intramolecularity factors of the order of 10^7 are encountered, that compare very well with values described for analogous systems involving five-membered-ring tetrahedral intermediates.[7]

Finally, a major feature common to open-chain and cyclic systems is that intermolecular transesterification equilibria are

* The same effect was observed in the macrocyclic series,[1] where equilibration of polyesters occurred at a much slower rate in the absence of dibutyltin dichloride.

† With both stannoxane reagents (**1**) and (**8**), benzoyl esters appeared to react between 1 and 2 orders of magnitude slower than acetyl esters.



Scheme 7. Monofunctionalization reaction path

constantly shifted toward the complete formation of (**1**). A transesterification equilibrium biased in the same manner is observed in the presence of (**8**) as well (see Scheme 4). This evidence supports the previous conclusion[1] that the driving force of transesterification equilibria is the formation of (**1**)—which is strongly favoured because of the chelate effect of ethylene glycol on tin—eventually leading to quantitative production of di- or poly-esters.

Conclusions

The complete reaction pattern illustrated in Scheme 7 summarizes the findings regarding the monoesterification of ethylene glycol with acyl chlorides. Further, the outcome of the reaction by reversed reagent addition indicates that monofunctionalization can be carried out with silyl chlorides as well. Thus, with appropriate tuning of experimental conditions, the stannylation method can be regarded as a quite general synthetic procedure for diol monoderivatization.

Experimental

Preparation[8] and purification[9] of 2,2-dibutyl-1,3,2-dioxastannolane, monofunctionalization procedure,[10] materials, instruments, and techniques[1] have been described. Acetyl chloride was a commercial sample (Carlo Erba), purified by fractional distillation. Ethylene glycol dibenzoyl ester (**5a**) and diacetyl ester (**5b**) were prepared and purified from benzoyl and acetyl chloride by conventional literature methods. ^{1}H N.m.r. spectra at 60 and 200 MHz were recorded on Varian EM 360 and Bruker MSL 200 instruments, respectively. Dynamic n.m.r. experiments were run on a Varian VXR 300 instrument, equipped with a variable-temperature apparatus.

Selected ^{1}H n.m.r. data in $CDCl_3$ at 300 MHz and 22 °C (δ values in p.p.m. from Me_4Si, using $CHCl_3$ as internal secondary reference at δ = 7.26) are as follows: 2-*trimethylsilyloxyethyl benzoate* (**2**), 3.90 (2 H, m, CH_2OSi) and 4.38 (2 H, m, CH_2OCOPh); 2-*dibutyl(chloro)stannyloxyethyl benzoate* (**4a**), 4.25 (2 H, br m, CH_2OSn) and 4.44 (2 H, br m, CH_2OCOPh); 2-*dibutyl(chloro)stannyloxyethyl acetate* (**4b**), 4.09 (2 H, br m, CH_2OSn) and 4.12 (2 H, br m, CH_2OCOMe); 1,2-*bisbenzoyloxyethane* (**5a**), 4.64 (4 H, s, CH_2OCOPh); 1,2-*bisacetyloxyethane* (**5b**), 4.22 (4 H, s, CH_2OCOMe); 1-*dibutyl(chloro)stannyloxy-2-trimethylsilyloxyethane* (**6**), 3.62 (2 H, br m, CH_2OSi) and 4.10 (2 H, br m, CH_2OSn); 1,2-*bis(trimethylsilyloxy)ethane* (**7**), 3.61 (4 H, s, CH_2OSi); *methyl benzoate* (**9a**), 3.86 (3 H, s, OCH_3); *methyl acetate* (**9b**), 3.60 (3 H, s, OCH_3); 1-*acetyloxy-2-benzoyloxyethane*, 4.38 (2 H, m, CH_2OCOMe) and 4.46 (2 H, m, CH_2OCOPh).

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