Distannoxane-catalysed Transesterification of 1,*n*-Diol Diacetates. Selective Transformation of Either of Chemically Equivalent Functional Groups

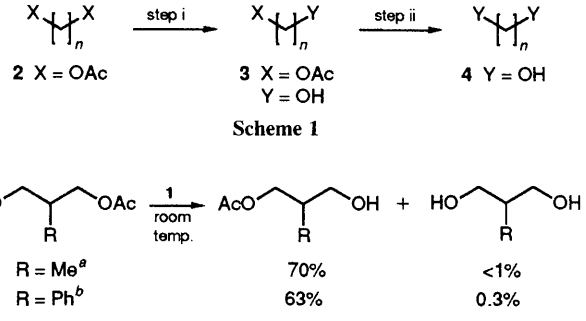
Junzo Otera,* Nobuhisa Dan-Oh and Hitosi Nozaki

Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700, Japan

Using catalysis by 1,3-dichlorotetrabutyldistannoxane, 1,*n*-diol diacetates were selectively converted into the corresponding monoacetates.

Transformation in a selective manner of one of chemically equivalent functional groups is synthetically important but rather difficult to achieve. For instance, attempted monofunctionalisation of 1,*n*-diols and dicarboxylic acids leading to versatile key compounds in natural product synthesis is usually accompanied by difunctionalisation. To this end, the two successive steps in Scheme 1 need to be differentiated, and physical methods have been used: continuous extraction method,[1] use of insoluble polymer supports,[2] and heterogeneously catalysed reaction.[3–5] We report herein a novel, chemically controlled method in which for the first time a homogeneous reaction is shown to be workable for this delicate differentiation.

Bearing in mind the unique template effects[6] resulting from association of distannoxane molecules,[7] we considered the possibility that a template could serve for the above purpose and addressed this issue by investigating transesterification[6a,e,f] of 1,*n*-diol diacetates. A solution of ethylene glycol diacetate (2 mmol) and 1,3-dichlorotetrabutyldistannoxane **1** (0.2 mmol) in MeOH (5 ml)–$CHCl_3$ (0.3 ml) was stirred at room temperature. The presence of $CHCl_3$ or minor amounts of other solvents (*vide infra*) needed to dissolve **1** had no influence on the reaction. As shown in Table 1, the monoacetate was the only product (91% yield based on GLC) after 48 h without any sign of diol formation on TLC monitoring. On further reaction, the yield of the monoacetate decreased while the diol was gradually formed. The generality of this reaction is apparent from Table 1 which summarises the maximum



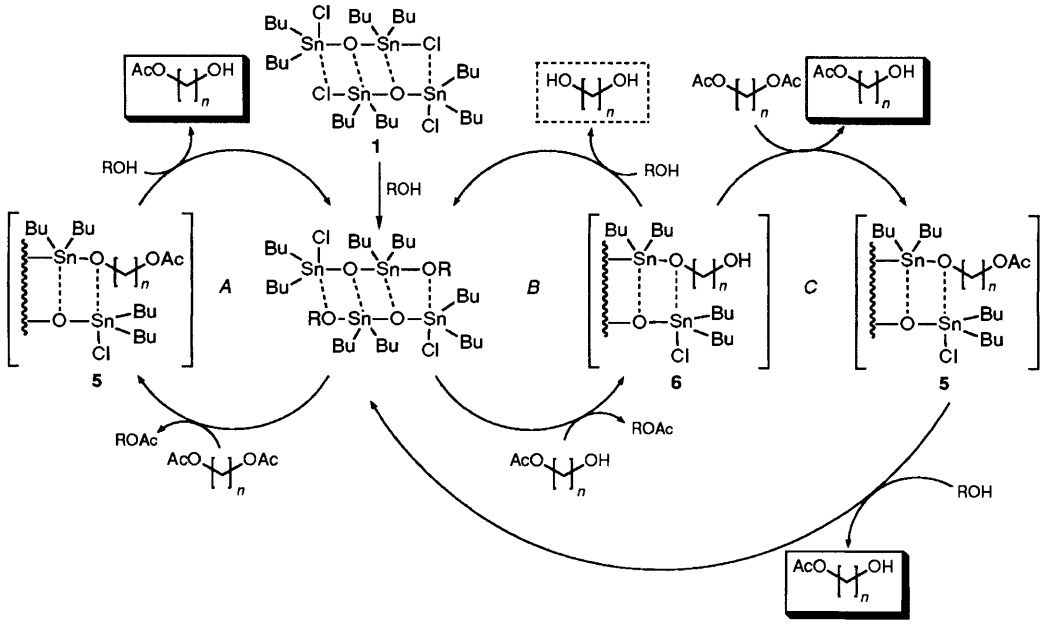
Scheme 1

Scheme 2 [a] $CHCl_3$–MeO, 96 h; [b] Bu^nOH, 288 h

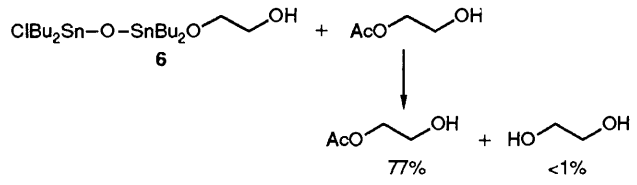
Table 1 Transesterification of 1,*n*-diol diacetates **2** using $Cl_2BuSnOSnBuCl_2$ **1**[a]

n	Solvent	React. time/h	**3**(%)[b,c]
2	MeOH–$CHCl_3$	48	91
	MeOH–CH_2Cl_2	24	69
	MeOH–C_6H_6	24	81
	MeOH–tetrahydrofuran	24	82
	EtOH–$CHCl_3$	216	91
	Bu^nOH[d]	120	85
3	MeOH–$CHCl_3$	48	80
	EtOH–$CHCl_3$	240	78
4	MeOH–$CHCl_3$	48	70
	EtOH–$CHCl_3$	240	72

[a] Reaction conditions: **2** (2 mmol); **1** (0.2 mmol); MeOH (5 ml); $CHCl_3$, CH_2Cl_2, C_6H_6 or THF (0.3 ml). [b] Based on GLC. [c] **4** was not detected on TLC (<1%). [d] Bu^nOH (5 ml).



Scheme 3



Scheme 4 *Conditions*: MeOH–$CHCl_3$, room temp., 21 h

yields† of monoacetates **3** until the stages when diols **4** began to appear. A variety of diacetates **2** exhibited the same proclivity and addition of a second solvent was not necessary when butan-1-ol, a good solvent for **1**, was employed. It is notable that considerable selectivities were also observed with substituted propylene glycol diacetates (Scheme 2).

The first-order rate constants at 25 °C under the conditions described above were measured for conversion of ethylene glycol diacetate to the monoacetate (k_{di}) and of the monoacetate to the diol (k_{mono}), respectively: $10^4 \times k_{di} = 6.7 \pm 0.5\ min^{-1}$ (in MeOH–$CHCl_3$) and $1.4 \pm 0.2\ min^{-1}$ (in EtOH–$CHCl_3$); $10^4 \times k_{mono} = 3.6 \pm 0.3\ min^{-1}$ (in MeOH–$CHCl_3$) and $0.76 \pm 0.05\ min^{-1}$ (in EtOH–$CHCl_3$). Apparently, k_{di} is nearly twice as large as k_{mono}, implying that the reactivity of the acetoxy group in both compounds is virtually identical. We, therefore, conclude that the transesterification of the monoacetate is retarded by the presence of the diacetate. In fact, when an equimolar mixture of the diacetate and monoacetate of ethylene glycol was subjected to the reaction in MeOH–$CHCl_3$, no diol was produced until a 91% total yield of the monoacetate was obtained: 41% from the diacetate and the 50% from the unchanged monoacetate.

A rationale for this anomaly is advanced based on the mechanism illustrated in Scheme 3. In contrast to the smooth process *A* for diacetates consisting of transesterification and subsequent alcoholysis, cycle *B* does not work in the presence of a diacetate. Transesterification between the intermediate **6** and a diacetate predominates over alcoholysis of **6**. Thus, another path *C* gives rise to the transalkoxylation intermediate **5** which undergoes smooth alcoholysis as seen in cycle *A*. The retardation of alcoholysis of **6** was confirmed as follows (Scheme 4). The intermediate **6**, which had been separately prepared by condensation between $ClBu_2SnOSnBu_2OH$ and $HO[CH_2]_2OH$,[6d] was exposed to an equimolar amount of $AcO[CH_2]_2OAc$ in MeOH–$CHCl_3$ at room temperature. After 21 h, 77% of the monoacetate was produced without any diol formation. The transesterification proceeded preferentially even in the presence of a large excess of methanol. The terminal hydroxy group in **6** probably plays a key role for facile transesterification as we have already pointed out in distannoxane-catalysed acetalisation.[6d]

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 03233231 from the Ministry of Education, Science, and Culture, Japan.

Received, 12th September 1991; Com. 1/04741H

† Yields after isolation by column chromatography were almost the same as those determined by GLC to within 5%.

References

1 J. H. Babler and M. J. Coglan, *Tetrahedron Lett.*, 1979, 1971.
2 C. C. Leznoff, *Acc. Chem. Res.*, 1978, **11**, 327.
3 H. Ogawa, T. Chihara and K. Taya, *J. Am. Chem. Soc.*, 1985, **107**, 1365; H. Ogawa, T. Chihara, S. Teratani and K. Taya, *J. Chem. Soc., Chem. Commun.*, 1986, 1337; H. Ogawa, Y. Ichimura, T. Chihara, S. Teratani and K. Taya, *Bull Chem. Soc. Jpn.*, 1986, **59**, 2481.
4 T. Nishiguchi and H. Taya, *J. Am. Chem. Soc.*, 1988, **111**, 9102; T. Nishiguchi and K. Kawamine, *J. Chem. Soc., Chem. Commun.*, 1990, 1766.
5 Reductive cleavage of cyclic acetals of benzaldehyde and cyclic orthoesters gives monoprotected 1,*n*-diols: S. Takano, M. Akiyama, S. Sato and K. Ogasawara, *Chem. Lett.*, 1983, 1593; M. Takasu, Y. Naruse and H. Yamamoto, *Tetrahedron Lett.*, 1988, **29**, 1947.
6 (*a*) J. Otera, T. Yano, A. Kawabata and H. Nozaki, *Tetrahedron Lett.*, 1986, **27**, 2383; (*b*) J. Otera, T. Yano, Y. Himeno and H. Nozaki, *Tetrahedron Lett.*, 1986, **27**, 4501; (*c*) J. Otera and H. Nozaki, *Tetrahedron Lett.*, 1986, **27**, 5743; (*d*) J. Otera, T. Mizutani and H. Nozaki, *Organometallics*, 1989, **8**, 2063; (*e*) J. Otera, S. Ioka and H. Nozaki, *J. Org. Chem.*, 1989, **54**, 4013; (*f*) J. Otera, N. Dan-Oh and H. Nozaki, *J. Org. Chem.*, in the press.
7 For the importance of molecular association in molecular recognition, see J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; 1990, **29**, 1304.