第9回ＪＡＩセミナー（1990年11月5日）　日本教育会館／東京

ポリヒドロキシ化合物の反応制御
ー糖類水酸基の位置選択的修飾と変換を例としてー

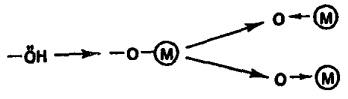
金沢大学 薬学部　　津田 喜典

ポリヒドロキシ化合物（糖　抗生物質など）の特定の位置のみを如何に変換するか？

1　保護と脱保護　　古典的方法

2　特定部位の活性化　　保護一般保護による方法

金属のキレート能の利用



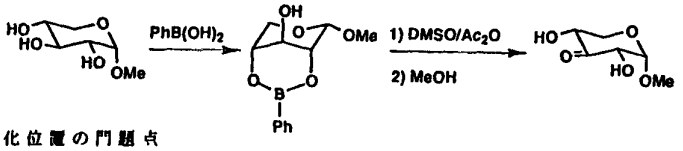
nucleophilic characterの増大

活性化　（As　Sb　Sn etc）

nucleophilic characterの減少

不活性化　（B etc）

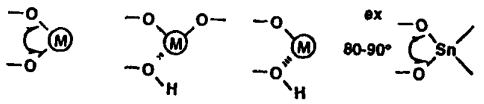
不活性化の例



活性化位置の問題点

Bidentate metalの利用　　Chelationによる安定化

どこに作り易いか　　支配因子は？



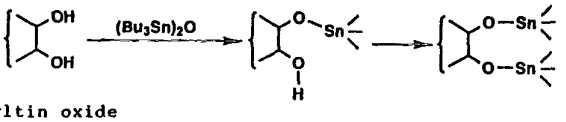
5員環か6員環か？　隣にキレーションしうるグループがあるか？

3　スズ化合物による活性化

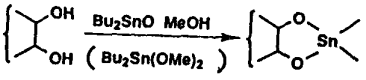
Sn compound is softer acid than Si compound

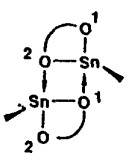
Activation methods

A　bis-Tributyltin oxide



B　Dibutyltin oxide





Dimeric structure

Bipyramidal　but sometimes octahedral

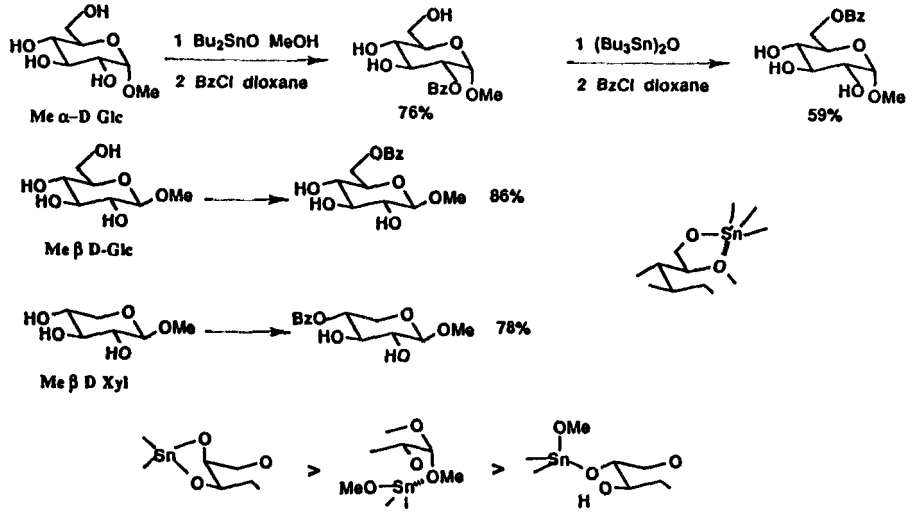
Apical bond is the most reactive?

Presence of a group which is possible to co-ordinate to Sn?

Solvent　Co-ordinating or non-coordinating?

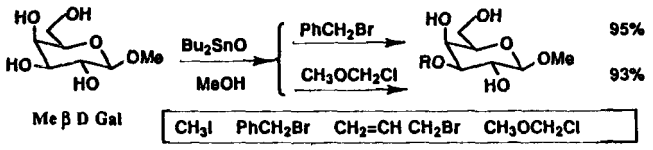
4 実施反応例

4-1 Acylation (R-OH → R-OCOR)



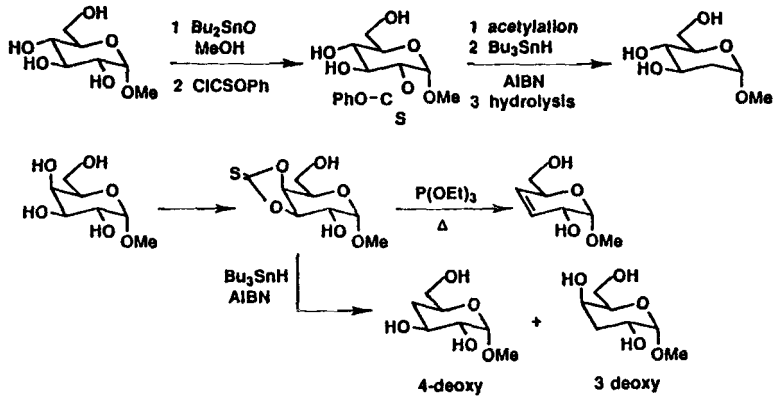
Y Tsuda M E Haque K Yoshimoto Chem Pharm Bull 31 1612 (1983)

4-2 Alkylation (Selective Protection) (R-OH → R-O-R)



M E Haque T Kikuchi K Yoshimoto Y Tsuda Chem Pharm Bull 33 2243 (1985)

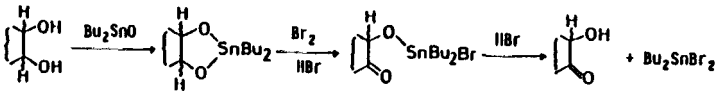
4-3 Thioacylation-Deoxygenation (R-OH → R-H)



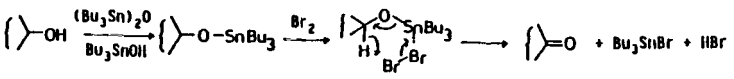
M E Haque T Kikuchi K Kanemitsui Y Tsuda Chem Pharm Bull 35 1016 (1987)

4-6 Oxidation (R-OH → R=O)

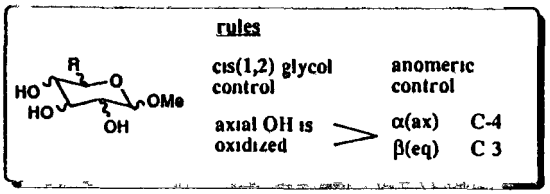
A b m lysis f a d l tylst yl de iv ti e



B l r min ly is f t ibutylst de i ti e

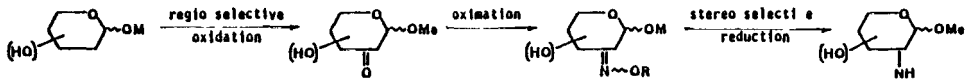


Oxidation of a Hydroxyl Gro p *ia* Tin Intermediates



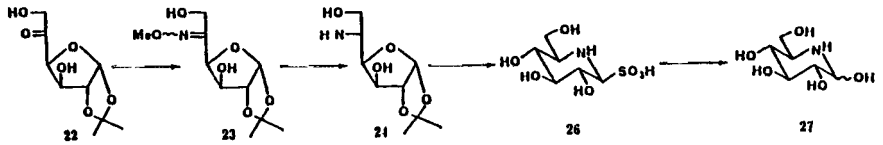
Y Tsuda M Hanajima N Matsuhira Y Okuno h Kanemitsu Chem Pharm Bull 37 2344 (1989)

4-7 Oxidation-Reductive aminaion (R-OH → R-NH$_2$)



Amino-glycosides from Glycosid s (General Sche nc)

Nojirimycin



Y Tsuda Y Okuno M Iwaki K Kanemitsu Chem Pharm Bull 37 2673 (1989)