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Communication

Reactivity of γ-benzyloxyallyltins with cyclohexylidene glyceraldehydes

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Abstract

Benzyloxyallyltributyltins were obtained in 50–80% yield by S_N2' reaction of alkyl-cyanocuprates with 3,3-dibenzyloxy-1-tributylstannylprop-1-ene in the presence of boron trifluoride. They reacted with cyclohexylidene glyceraldehyde in the presence of different Lewis acids and the obtained diastereomeric adducts were unambiguously identified after an ozonolysis/deprotection sequence by comparison with authentic aldopentoses. The mechanisms are briefly discussed as well as the relationship of the configuration of the reagents to the selectivity of the allylstannation reaction.

Keywords: β-Tributylstannylacrolein dibenzyloxyacetal; Benzyloxyallyltributyltins; Cyclohexylidene glyceraldehyde; Allylstannation; Aldopentoses

1. Introduction

The addition of α- and γ-alkoxyallyltins to aldehydes has been extensively studied in recent years [1,2]. While α-alkoxycrotyltins have been shown to react with aldehydes upon heating, this type of reactivity has been scarcely used because of the lack of reactivity of the *Z*-isomer due to the higher energy of the cyclic chair-like transition state when compared to the *E*-isomer [3–5]. Attempts of activation using Lewis acids can lead to different possibilities depending on the nature of the Lewis acid.

In the case of a Lewis acid unable to transmetallate the $Sn–C_{allyl}$ bond (for instance BF_3), the addition occurs through an opened transition state where the reacting species are often γ-alkoxyallyltins whatever the position of the alkoxy group on the allyl unit since α-alkoxyallyltins isomerize very easily, in a stereospecific fashion, into γ-alkoxyallyltins under these experimental conditions [6,7].

When Lewis acids are able to give transmetallation of the Sn–C bond, γ-alkoxyallylmetals (stabilized by chelation of the metal on the oxygen) obtained from α-alkoxyallyltins react with aldehydes through a cyclic transition state. This is the actual trend when $InCl_3$ is used as Lewis acid [8]. The use of $SnCl_4$ is expected to give similar results on the basis of studies on allyltins bearing a remote alkoxy functionality [9] on the condition that allylstannation occurs before destruction of the reagents [10].

The use of $TiCl_4$ may involve both of these processes depending on the order of addition of the reagents [11]. Nonetheless in the oxygenated series, the nature of the functional group is of importance because examples of destruction of the reagents have been mentioned [10] as well as expected allyltitanation [12].

In the present paper, we wish to report recent results obtained in the γ-alkoxyallyltin series using a Lewis acid unable to give the transmetallation reaction. The early studies in these series achieved with non functionalized crotyltins have shown a high *syn* selectivity whatever the geometry of the crotyltin [13] and a similar trend was observed for γ-alkoxyallyltins [1,2].

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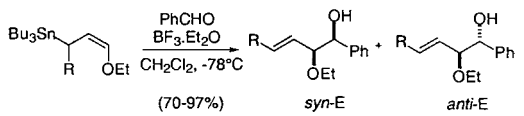
The *syn* selectivity was initially explained by an antiperiplanar transition state [13]. The possibility of a synclinal transition state was shown in an intramolecular allylstannation [14]. Subsequently the balance between antiperiplanar and synclinal transition states has been shown to be very subtle and dependent on secondary effects such as an inside alkoxy effect [15,16], the geometry of the double bond [17] or steric hindrance of the α substituent or of the β substituent when α- or β-substituted γ-alkoxyallyltins are involved [18,19].

Due to the easy preparation of differently α-substituted γ-ethoxyallyltins by reaction of RCu(CN)MgX with β-tributylstannylacrolein acetals [20], we have been able to test this parameter and to obtain reversed selectivities as a function of the size of the α-substituent for reactions on benzaldehyde or 2-furaldehyde [18].



The *syn*/*anti* ratios (93/7 for R = Me and 3/97 for R = *t*-Bu) were explained by an antiperiplanar transition state in the first case (R = Me) and by a synclinal transition state in the second case (R = *t*-Bu).

On the basis of this preliminary study it seems possible to obtain aldopentoses from glyceraldehyde and appropriately substituted γ-oxygenated allyltins (the alkoxy groups being easily removable groups like BnO and R_3SiO).

Accordingly, γ-benzyloxyallyltributyltins and γ-siloxyallyltributyltins were prepared from β-tributylstannylacrolein acetals [21] according to Scheme 1.

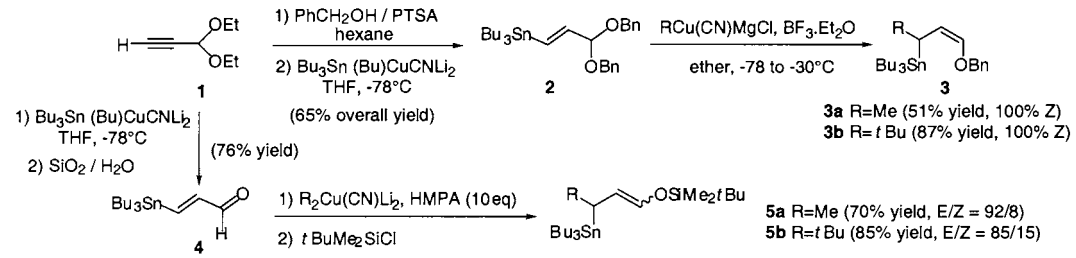
Allyltins **3a** and **3b** were obtained easily as clean *Z* isomers according to our previously described procedure [20] while **5a** and **5b** were obtained via conjugate addition of higher order lithium alkylcyanocuprates to β-tributylstannylacrolein **4**.

The γ-benzyloxyallyltins seem the more interesting reagents because they could give *syn* or *anti* adducts with aldehydes depending on the size of the R group. With γ-siloxy derivatives, *syn* selectivity is obtained even in the presence of α-bulky groups (for instance R = $SnBu_3$) [25]. Indeed, **3b** has been shown to react with benzaldehyde to give the *anti* adduct (98% yield, *syn*/*anti* = 2/98).

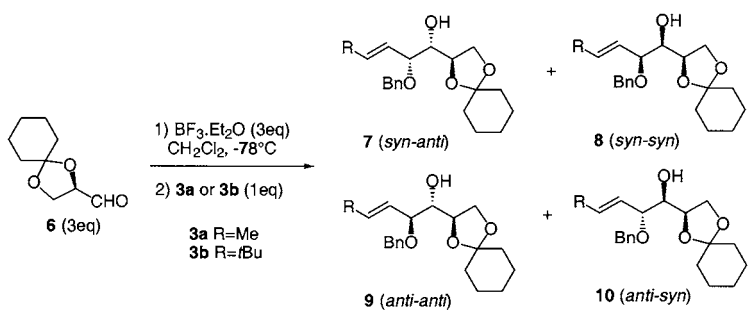
In order to evaluate the validity of the above assumptions and to prepare precursors of aldopentoses, **3a** and **3b** were reacted with (*R*)-cyclohexylidene glyceraldehyde (which has been recently used for the synthesis of 2-C branched 2-deoxypentofuranoses [26]) in the presence of boron trifluoride etherate (Scheme 2).

With $BF_3{\cdot}Et_2O$ (3eq) as Lewis acid (at −78°C in CH_2Cl_2), **3a** affords a mixture 39/37/24 of **7**, **8**, **9** in 48% yield while **3b** affords a 49/41/6/4 mixture of **7**, **8**, **9** and **10** in 98% yield (these values were obtained on the basis of HPLC analysis assuming that the four diastereomers have similar ε values for the benzyloxy group).

The identification of the diastereomers **7**–**10** has been made after separation by liquid chromatography and further transformation into aldopentoses according to the Scheme 3.



Scheme 1.



Scheme 2.

Each diastereomer (**7**–**10**) was transformed according to this scheme and identified by comparison with authentic samples of aldopentoses (comparison of the ^{1}H-NMR spectra). The following correlation can be established:

Diastereoisomer **7** $\xrightarrow{(89\%)}$ arabinose (*syn-anti*)

Diastereoisomer **8** $\xrightarrow{(63\%)}$ xylose (*syn-syn*)

Diastereoisomer **9** $\xrightarrow{(70\%)}$ ribose (*anti-anti*)

Diastereoisomer **10** $\xrightarrow{(75\%)}$ lyxose (*anti-syn*)

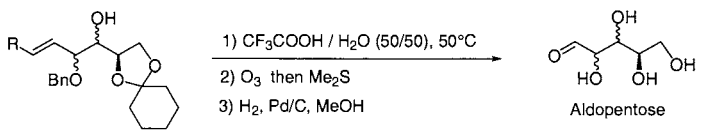
It is worth noting that the correlation sequence must be done from purified diastereomers since significant difference in reactivity can be observed between two diastereomers (for instance **7** and **8**).

Obviously the size of the R group has not the expected effect on the diastereoselection since *syn* selectivity appears to be the major addition mode in both cases with a higher preference for R = *t*-Bu (**7** + **8**/**9** + **10** = 90/10) when compared with R = Me (77/23 for the similar ratio)!

This result is in disagreement with the trends previously observed with benzaldehydes [18]. In order to obtain more information about the reaction mechanisms, two reactions have been conducted in the presence of Lewis acids which can be doubly coordinated (cf. Table 1). With $ZnCl_2$, **7** remains the major product while $MgBr_2$ (reaction at −20°C, in CH_2Cl_2, 15 h) induces a preference for the *anti* diastereomer **7** + **8**/**9** + **10** = 24/76 for R = *t*-Bu (30% yield). It is worth noting that side products were obtained in both cases.

The second test which has been conducted was a comparative study between (*R*) and (*S*) cyclohexylidene glyceraldehyde (*R*)-**6** or (*S*)-**6** which were allowed to react with racemic **3b** under conditions in which starting materials were recovered (**3b**/**6** = 1/1, $BF_3{\cdot}Et_2O$ = 1.2 eq, CH_2Cl_2, −78°C, 2 h) (see Table 1). After flash chromatography, the recovered organotin exhibits an uncorrected '$[\alpha]_D$' value of −27.9 (C_6H_6, c = 1.4) starting from (*R*)-**6** and +32.8 starting from (*S*)-**6**. On the basis of the known $[\alpha]_D$ values for pure α-*n*-alkyl-γ-alkoxyallyltins (between +70 and +120 for the (*S*) enantiomers [6,20]), taking into account the similarity of polarisabilities of the bonds around the asymmetric centre, enrichment of the (*S*)-allyltin seems likely in the first case ('$[\alpha]_D$' = −27.9) and of the (*R*)-allyltin in the second case ('$[\alpha]_D$' = +32.8) since priority of the substituents around the chiral centre is modified (*n*-Bu < γ-alkoxyvinyl < *t*-Bu).

For α-*t*-butyl-γ-benzyloxyallyltributyltin, the (*R*) enantiomer is more reactive than the (*S*) enantiomer with (*R*)-cyclohexylidene glyceraldehyde; this result is corroborated by a reverse trend with (*S*)-cyclohexylidene glyceraldehyde.



Scheme 3.

Table 1
Reaction of γ-benzyloxyallyltin **3b** on cyclohexylidene glyceraldehydes (*R*)-**6** and (*S*)-**6**

Aldehyde [a]	Experimental conditions [b]	Adducts [d]					Remaining allyltin
		Overall yield	**7**	**8**	**9**	**10**	$[\alpha]_D$
(*R*)-6 (3eq)	$BF_3{\cdot}Et_2O$ (3eq); −78°C	98	49	41	6	4	
(*R*)-6 (1.5eq)	$MgBr_2$ (1.5eq); −20°C	30	6	18	10	66	n.d.
(*R*)-6 (1.5eq)	$ZnCl_2$ (2eq); −25°C to rt	24	66	15	18	1	n.d.
(*R*)-6 (1eq)	$BF_3{\cdot}Et_2O$; (1.2eq)[c]	36	72	24	0 [e]	4	−27.9 [f]
(*S*)-6 (1eq)	$BF_3{\cdot}Et_2O$; (1.2eq) [c]	45	65 (**ent-7**)	28 (**ent-8**)	0 [e] (**ent-9**)	7 (**ent-10**)	+32.8 [f]

[a] (*R*)-**6** and (*S*)-**6** were obtained according to litterature [32].

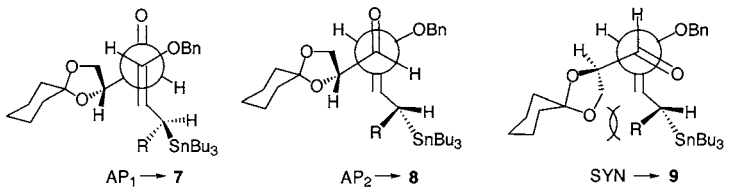
[b] Experimental conditions: in a Schlenk reactor containing **6** in dry degased CH_2Cl_2 (10 ml) were added Lewis acid (*x*eq) at the above-mentioned temperature before addition of **3b** (0.4 mmol, 1eq) in CH_2Cl_2 (2 ml). The obtained mixture is allowed to react at the desired temperature until complete disappearance of **6** (TLC monitoring). After hydrolysis ($NaHCO_3$) and usual treatments, compounds **7**–**10** were purified by flash chromatography on silica gel using hexane/ether = 85/15 [33].

[c] Same procedure as (b) but the mixture is allowed to react only for 2 h at −78°C in order to have an incomplete reaction.

[d] HPLC separation of **7**–**10** was performed on hypersil (5 μ, 25 × 0.45 cm, eluent = ether/hexane = 15/85, 1 ml min^{-1}). The retention times were the following ones: **7** (10.6 min), **8** (9.8 min), **9** (13.3 min), **10** (7.4 min).

[e] Due to its longer retention time, a small amount of **9** (ca. 3%) might be omitted.

[f] These values were determined on crude remaining allyltin and therefore cannot be considered as specific optical rotation because remaining allytin is polluted with non-chiral organotins.



Scheme 4.

2. Comments

Though not complete enough to allow a detailed discussion, these results offer some interesting insight on stereochemical trends of this allylstannation. The stereochemical results appear to be consistent with Marshall's reports concerning the addition of enantioenriched γ-alkoxyallyltins to chiral α-alkoxy aldehydes [2] with matched and mismatched effects [27].

In the present case, among the possible transition states, compound **7** is believed to come from an antiperiplanar transition state AP_1 (reaction of (*R*)-**3b** on (*R*)-**6**) while compound **8** and **9** might be due mainly to the addition of (*S*)-**3b** to (*R*)-**6** through an antiperiplanar transition state AP_2 or a synclinal transition state (which is less disfavoured when R = Me instead of R = *t*-Bu because of the difference in steric hindrance) (Scheme 4).

Similar effects can also account for formation of **ent-7** to **ent-10** when (*S*)-**6** reacts with **3b** in the presence of boron trifluoride.

However, these explanations are unable to rationalize the observed stereochemistry when bidentate Lewis acids like $ZnCl_2$ or $MgBr_2$ are used. In these cases, the situation appears to be much more complicated and probably involves chelations both on the α-alkoxy and on the β-alkoxy groups of the aldehyde [28].

3. Conclusion

In spite of their limited application for the preparation of the aldopentoses, the above results demonstrate that the diastereoselectivity of allylstannanes additions observed with aromatic aldehydes cannot be applied to glyceraldehyde derivatives.

Furthermore these preliminary results suggest that significant improvements can be expected in terms of selectivity using γ-alkoxyallyltins with appropriate configuration. For this purpose the previously described enantioselective synthesis of γ-alkoxyallyltins [20] or γ-aminoallyltins [29] through S_N2' opening of β-tributylstannylacrolein derivatives can bring tools of interest to prepare differently protected sugars or azasugars, the allylstannation being possible on α-alkoxy or α-amino aldehydes [2] as well as aldimines [9,30,31].

Acknowledgements

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3a: ^{1}H-NMR δ (ppm): 0.7–1.7 (m, 30H); 2.52 (ddq, 1H, $^3J = 7.6$, $^3J = 10.8$, $^4J = 0.9$, $^2J_{SnH} = 60$); 4.45 (dd, 1H, $^3J = 10.8$, $^3J = 6.0$, $^3J_{SnH} = 20$); 4.7 and 4.77 (syst. AB, 2H, $^2J = -12.7$); 5.85 (dd, 1H, $^3J = 6.0$, $^4J = 0.9$, $^4J_{SnH} = 20$); 7.2–7.4 (m, 5H); ^{13}C-NMR δ (ppm): 8.7 (3C, $^1J_{SnC} = 298/285$); 13.7 (3C); 16.6; 18.7; 27.5 (3C, $^3J_{SnC} = 54$); 29.3 (3C, $^2J_{SnC} = 20$); 73.5; 114.6; 127.4–128.3 (5C); 138.0; 139.4; ^{119}Sn-NMR δ (ppm): −15.7.

3b: ^{1}H-NMR δ (ppm): 0.7–1.7 (m, 36H); 2.65 (dd, 1H, $^3J = 12.4$, $^4J = 0.6$, $^2J_{SnH} = 64$); 4.52 (dd, 1H, $^3J = 12.4$, $^3J = 6.2$, $^3J_{SnH} = 22/27$); 4.71 and 4.79 (syst. AB, 2H, $^2J = -12.5$); 5.92 (dd, 1H, $^3J = 6.2$, $^4J = 0.6$, $^4J_{SnH} = 19$); 7.2–7.4 (m, 5H); ^{13}C-NMR δ (ppm): 10.7 (3C, $^1J_{SnC} = 283/295$); 13.7 (3C); 27.6 (3C, $^3J_{SnC} = 57$); 29.3 (3C, $^2J_{SnC} = 13$); 30.6 (3C, $^3J_{SnC} = 26$); 33.8 (1C, $^2J_{SnC} = 13$); 39.9 (1C, $^1J_{SnC} = 297/312$); 73.4; 109.5 (1C, $^2J_{SnC} = 38$); 127.3–128.3 (5C); 138.1; 141.1 (1C, $^3J_{SnC} = 48$); ^{119}Sn-NMR δ (ppm): −29.0. Found: C, 63.23; H, 9.58. $C_{26}H_{46}OSn$ (492.26) requires C, 63.30; H, 9.40.

5a: see [34].

5b: *E* isomer: ^{1}H-NMR δ (ppm): 0.1 (s, 6H); 0.7–1.0 (m, 24H); 0.9 (s, 9H); 1.15–1.6 (m, 12H); 1.86 (d, 1H, $^3J = 12.6$, $^2J_{SnH} = 60.1$); 5.09 (dd, 1H, $^3J = 12.6$, $^3J = 11.6$, $^2J_{SnH} = 24.1$); 6.08 (d, 1H, $^3J = 11.6$, $^2J_{SnH} = 20.6$); ^{13}C-NMR δ (ppm): −5.1 (2C); 10.5 (3C, $^2J_{SnH} = 280/301$); 13.7 (3C); 18.2; 25.7 (3C); 27.6 (3C, $^2J_{SnH} = 60$); 29.3 (3C, $^2J_{SnH} = 18$); 30.7 (3C, $^2J_{SnH} = 20$); 33.8; 42.5; 112.9 (1C, $^2J_{SnH} = 36$); 137.5.

7: ^{1}H-NMR δ (ppm): 1.05 (s, 9H); 1.3–1.65 (m, 10H); 2.5 (d, OH, $^3J = 6.3$); 3.57 (ddd, 1H, $^3J = 3.9$, $^3J = 6.3$, $^3J = 6.4$); 3.88 (dd, 1H, $^3J = 3.9$, $^3J = 8.4$); 3.95 (dd, 1H, $^3J = 6.3$, $^2J = -8.3$); 4.01 (dd, 1H, $^3J = 6.2$, $^2J = -8.3$); 4.11 (ddd, 1H, $^3J = 6.2$, $^3J = 6.3$, $^3J = 6.4$; 4.38 and 4.60 (syst. AB, 2H, $^2J = -10.8$); 5.43 (dd, 1H, $^3J = 8.4$, $^3J = 15.8$); 5.73 (d, 1H, $^3J = 15.8$); 7.25–7.40 (m, 5H); ^{13}C-NMR δ (ppm): 23.7–36.3 (5C); 29.4 ($C(\underline{C}H_3)_3$); 33.1 ($\underline{C}(CH_3)_3$); 66.0; 69.8 (Bn); 75.0; 75.3; 79.6; 109.4; 121.5; 127.5–128.2 (5C); 138.6; 147.1.

8: ^{1}H-NMR δ (ppm): 1.05 (s, 9H); 1.2–1.8 (m, 10H); 2.60 (d, OH, $^3J = 5.3$); 3.53 (ddd, 1H, $^3J = 4.3$, $^3J = 5.3$, $^3J = 5.6$); 3.76 (dd, 1H, $^3J = 7.6$, $^2J = -7.8$); 3.78 (dd, 1H, $^3J = 5.6$, $^3J = 8.7$); 3.90 (dd, 1H, $^3J = 6.3$, $^2J = -7.8$); 4.17 (ddd, 1H, $^3J = 4.3$, $^3J = 6.3$, $^3J = 7.6$); 4.34 and 4.60 (syst. AB, 2H, $^2J = -11.9$); 5.32 (dd, 1H, $^3J = 8.7$, $^3J = 15.9$); 5.77 (d, 1H, $^3J = 15.9$); 7.25–7.40 (m, 5H); ^{13}C-NMR δ (ppm): 23.8–36.0 (5C); 29.4 ($C(\underline{C}H_3)_3$); 33.2 ($\underline{C}(CH_3)_3$); 65.8; 69.9 (Bn); 73.0; 75.0; 81.5; 109.6; 121.1; 127.5–128.3 (5C); 138.3; 148.2.

9: ^{1}H-NMR δ (ppm): 1.05 (s, 9H); 1.3–1.65 (m, 10H); 2.38 (s, OH); 3.85 (dd, 1H, $^3J = 3.7$, $^3J = 6.3$); 3.91 (dd, 1H, $^3J = 3.7$, $^3J = 8.4$); 3.92 (dd, 1H, $^3J = 6.6$, $^2J = -8.2$); 3.96 (dd, 1H, $^3J = 6.1$, $^2J = -8.2$); 4.04 (ddd, 1H, $^3J = 6.1$, $^3J = 6.3$, $^3J = 6.6$); 4.37 and 4.59 (syst. AB, 2H, $^2J = -11.9$); 5.42 (dd, 1H, $^3J = 8.4$, $^3J = 15.8$); 5.78 (d, 1H, $^3J = 15.8$); 7.25–7.40 (m, 5H); ^{13}C-NMR δ (ppm): 23.8–36.3 (5C); 29.5 ($C(\underline{C}H_3)_3$); 33.3 ($\underline{C}(CH_3)_3$); 65.9; 69.8 (Bn); 74.1; 75.0; 80.9; 109.2; 122.9; 127.5–128.3 (5C); 138.3; 148.2.

10: ^{1}H-NMR δ (ppm): 1.05 (s, 9H); 1.2–1.7 (m, 10H); 2.30 (d, OH, $^3J = 5.2$); 3.53 (ddd, 1H, $^3J = 5.2$, $^3J = 5.2$, $^3J = 6.4$); 3.69 (dd, 1H, $^3J = 6.4$, $^3J = 8.1$); 3.77 (dd, 1H, $^3J = 7.3$, $^2J = -8.1$); 3.98 (dd, 1H, $^3J = 6.4$, $^2J = -8.1$); 4.22 (ddd, 1H, $^3J = 5.2$, $^3J = 6.4$, $^3J = 7.3$); 4.34 and 4.58 (syst. AB, 2H, $^2J = -11.9$); 5.36 (dd, 1H, $^3J = 8.1$, $^3J = 15.9$); 5.73 (d, 1H, $^3J = 15.9$); 7.20–7.40 (m, 5H); ^{13}C-NMR δ (ppm): 22.6–36.1 (5C); 29.5 ($C(\underline{C}H_3)_3$); 33.3 ($\underline{C}(CH_3)_3$); 66.0; 69.8 (Bn); 73.8; 75.7; 81.0; 109.5; 121.5; 127.5–128.3 (5C); 138.2; 148.1.

7–**10**: Found: C, 74.17; H, 9.24. $C_{23}H_{34}O_4$ (374.25) requires C, 73.76; H, 9.15.

[34] J.A. Marshall, G.S. Welmaker, J. Org. Chem. 57 (1992) 7158.