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Allylation Using Allylborates

Roger Hunter*

Department of Chemistry, University of Cape Town,
Rondebosch 7700, South Africa.

Joseph P. Michael and Geoffrey D. Tomlinson

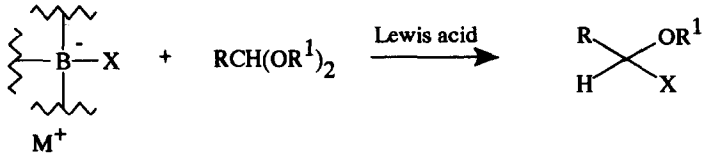
Chemistry Department, University of the Witwatersrand,
P.O. Wits 2050, Johannesburg 2001, South Africa.

Abstract: A study has been carried out on the scope of allylation of a range of acetals activated by trimethylsilyl trifluoromethanesulfonate (TMSOTf) using a number of organoborates. Intermolecular allylation of acyclic acetals proceeds smoothly and in high yield using lithium n-butyltriallylborate or lithium methyltriallylborate in THF at -78°C while 1,3-dioxanes and dioxolanes give rise to some reduction products. Intramolecular allylation may be carried out via anchoring the triallylborane using an alkoxide anion. Mechanistic studies indicate that allyl transfer is from boron and not silicon, while stereoselectivity studies on the crotylation of acyclic acetals as well as the allylation of chiral acetals derived from (2R,4R)-pentanediol indicate moderate levels of diastereoselection.

1. Introduction

In contrast to the well-known[1], intramolecular 1,2 migration reactions of organoborates,intermolecular transfer reactions from boron are far less common[2-8]. Recently, however, a major breakthrough in cross-coupling reactions of organoboron compounds with organic halides and triflates *via* their "ate" complexes has been accomplished using Pd(0) catalysis[9], and we have reported[10] that lithium n-butyltriallylborate allylates Lewis acid activated acetals intermolecularly. In this paper we describe results of a full study of this novel allylation reaction.

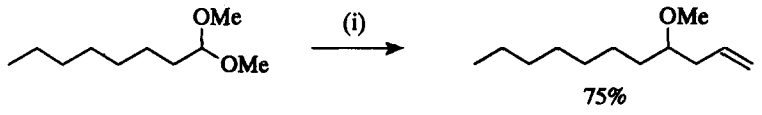
From the outset we were interested in studying the intermolecular migration of a group X to an activated acetal centre[11] as depicted in Scheme 1.



Scheme 1

The first reaction studied was between lithium tetra-n-butylborate and 1,1-dimethoxy-1-phenylmethane activated by trimethylsilyl trifluoromethanesulfonate (TMSOTf) in THF. Substitution occurred at low temperature (-78°C) to give a consistently low yield (20-25%) of 1-methoxy-1-phenylpentane accompanied by varying amounts of the reduction product benzyl methyl ether. Both products were identified by ^{1}H nmr and

gas chromatography relative to known standards. Plausible mechanisms to account for the hydride reduction may be written involving both α-hydride delivery with a 1,2 alkyl migration or β-hydride transfer but further experiments were not carried out to study this aspect. Although this result was not synthetically useful, it suggested that a group such as allyl[12] might be a better alternative. Triallylborane, as the allyl source, was prepared by nucleophilic substitution of boron trifluoride etherate with allylmagnesium chloride in diethyl ether[13]. Reaction of its "ate" complex, formed with butyllithium, with 1,1-dimethoxyoctane and TMSOTf in THF at -78°C afforded the desired homoallyl ether in 75% yield after column chromatography. Scheme 2. The following account describes the scope and limitations of this novel intermolecular transfer reaction.



(i) $Li^{+}BuB^{-}(allyl)_3$ / TMSOTf / THF / -78°C.

Scheme 2

2. **Results and Discussion.**

a) **The scope of acetal.**

Acetals have assumed a pivotal position in dissociative substitution chemistry with various groups now being used in synthesis. Thus, a range of acetals were selected and reacted with lithium *n*-butyltriallylborate and TMSOTf in THF at -78°C to test out the procedure. The results are presented in Table 1. Acyclic acetals generally gave yields of around 70% after chromatography while the less basic dioxane and dioxolane entries gave lower yields, with the 1,3-dioxane of octanal (entry 7) giving a significant amount of the reduction product. The lower yields of the cyclic acetals were later explained by a solvent effect which also accounted for the lack of reactivity of 0,S acetals in THF (see solvent section). Entries 9 and 11 were used to probe the possibility of simple diastereoselection in the reaction. The 1:1 ratio of diastereomers in each case supports an S_N2-like transition state involving an intimate ion-pair over a Cram-type free oxocarbenium ion[14]. 2-Methoxytetrahydropyran (entry 12) reacted to give products of both exocyclic and endocyclic carbon-oxygen bond fission, a result similar to Guindon's[15] findings on the reaction of THP and THF ethers with dimethylboron bromide. By comparison, trans-2-methoxy-3-trimethylsilyloxytetrahydropyran (entry 13), prepared by silylation of the corresponding alcohol with triethylamine and chlorotrimethylsilane, reacted to afford the exocyclic substituted product[45] as a mixture of diastereomers (syn:anti = 2.5:1).

b) **The effect of solvent, counter-ion and Lewis acid.**

From the reactions in Table 1, it became apparent that the choice of solvent for a particular substrate is of crucial importance. For acyclic acetals, THF is the solvent of choice and is convenient for preparing the borate reagent. For substrates of lower Lewis basicity, notably dioxanes and dioxolanes[16], for which THF competes for the Lewis acid, methylene chloride is the preferred solvent. In these cases the THF used to prepare the borate must be removed and replaced. Hexane may also be used for the reaction and progress can be monitored by the dissolution of the insoluble borate reagent. (0,S) Acetals may be allylated in low yield using this solvent. Scheme 3.

TABLE 1

Reactions of acetals with $Li^{+}BuB^{-}(allyl)_3$ (1.3eq) and TMSOTf (1.2eq) in THF at -78°C to 0°

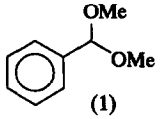
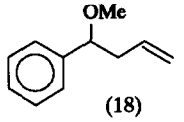
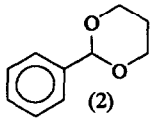
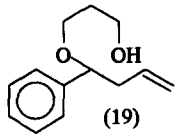
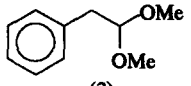
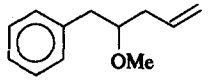
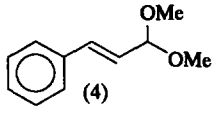
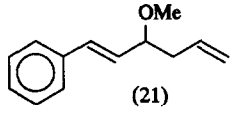
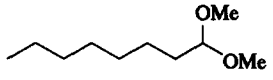
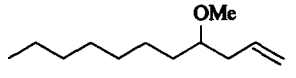
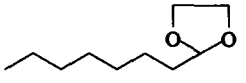
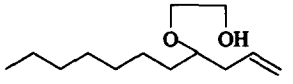
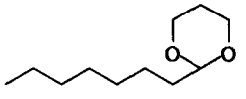
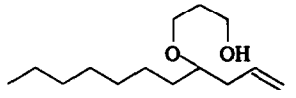
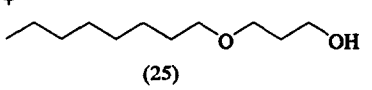
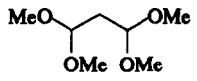
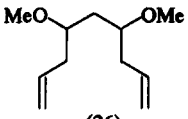
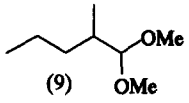
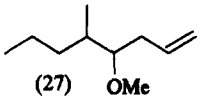
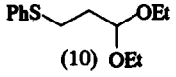
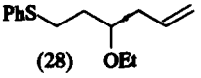
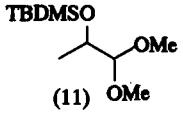
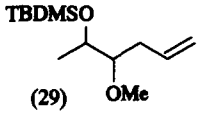
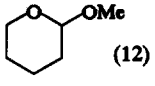
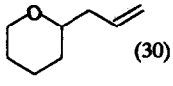
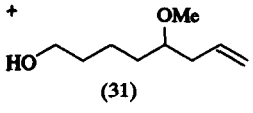
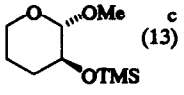
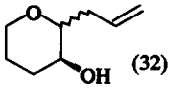
ACETAL	PRODUCT	YIELD[a] %
 (1)	 (18)	94
 (2)	 (19)	71
 (3)	 (20)	75
 (4)	 (21)	22
 (5)	 (22)	75
 (6)	 (23)	61
 (7)	 (24) +  (25)	38 26

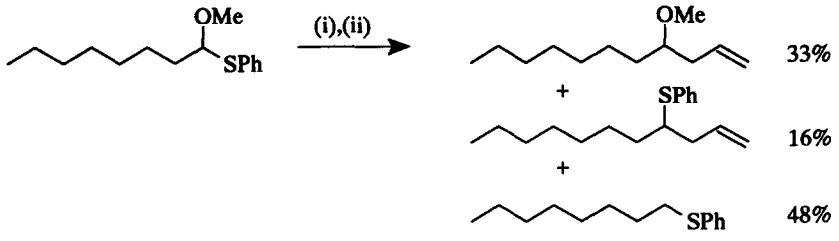
TABLE 1 (cont)

ACETAL	PRODUCT	YIELD %
 (8)	 (26)	69 [b] (1:1)
 (9)	 (27)	70 (1:1)
 (10)	 (28)	64
 (11)	 (29)	33 (1:1)
 (12)	 (30) +  (31)	24 40
 [c] (13)	 (32)	61 (1:2.5)

a: isolated yield after chromatography.

b: two equivalents of TMSOTf and borate were used.

c: prepared insitu from alcohol with TMSCl + NEt_3



(i) $Li^{+}BuB^{-}(allyl)_3$ / TMSOTf / hexane / -78°C to 25°C.

(ii) HOO^{-}.

Scheme 3

Exchange of the lithium cation of lithium methyltriallylborate with benzyltriethylammonium chloride to generate benzyltriethylammonium methyltriallylborate resulted in complete loss of allylation activity emphasizing the importance of the presence of a hard cation to ensure allyl transfer.

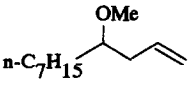
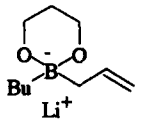
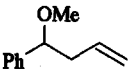
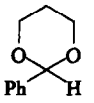
Finally, TMSOTf proved to be the only viable Lewis acid for the reaction. $TiCl_4$ gave rise to dark green solutions with formation of a precipitate and no allylation was observed. $SnCl_4$ did promote reaction but gave a much lower yield of substitution (33% with 1,1-dimethoxyoctane) coupled with demethylation. Other Lewis acids, e.g. $BF_3.Et_2O$ and $AlCl_3$, did not promote the allylation reaction at all.

c) **Ligands on Boron.**

An interesting aspect of the reaction is the range of nucleophiles that can be used to form the borate. Use of lithium methyltriallylborate, formed with methyllithium, resulted in a 90% isolated yield of homoallyl ether from 1,1-dimethoxyoctane compared to 75% with the corresponding butyl reagent. Thus, suppression of hydride reduction appears possible. In this case, if ether is used as the methyllithium solvent, it must be removed and replaced by THF to ensure[17] borate formation. Oxygen nucleophiles such as methoxide may be used to generate the triallylborinate but yields are reduced to around fifty percent. Sodium cyanide may be used to form the cyanoallylborate which still functions as a good allylating agent (75% with 1,1-dimethoxyoctane) without involvement of a Lewis acid promoted 1,2 migration reaction, well known[18] for this class of compound. By comparison, the allylboronate prepared from butyllithium and allyl(1,3-propanedioxy)borane[19] allylated benzaldehyde acetal in competition with a transacetalisation[20] reaction affording 2-phenyl-1,3-dioxane, both products being obtained in low yield. The latter product presumably arises via a transmetallation reaction of the boron-oxygen bond by TMSOTf as the first step. The use of 9-BBN as a blocking group was also investigated. 9-Allyl-9-BBN[19,21] was prepared by nucleophilic substitution of 9-methoxy-9-BBN with allyl Grignard. Conversion to the "ate" complex with n-butyllithium produced the reagent lithium 9-allyl-9-butyl-9-boratabicyclo[3.3.1]nonane, which reacted with 1,1-dimethoxyoctane in THF with TMSOTf at -78°C to 0°C to afford the homoallyl ether in a lower yield compared with using lithium n-butyltriallylborate, although the yield did increase with excess reagent. The results of various borate reactions are summarised in Table 2.

TABLE 2

Reaction of various borates (1eq) with acetals at -78°C to 0°C in THF with TMSOTf (1eq).

ACETAL	BORATE	PRODUCT(S)	YIELD[a] %
$n\text{-}C_7H_{15}CH(OMe)_2$	$Li^+MeB^-(allyl)_3$		90
"	$Li^+BuB^-(allyl)_3$	"	75
"	$Na^+NCB^-(allyl)_3$	"	75
"	$BrMg^+B^-(allyl)_4$[b]	"	66
"	$Li^+BuB^-BBN(allyl)$[c]	"	27
"	"	(1.5eq) "	43
"	$Li^+MeOB^-(allyl)_3$	"	48
$PhCH(OMe)_2$			17
		+ 	18

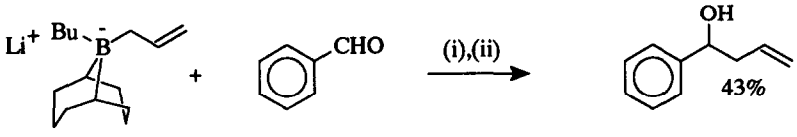
a : yield after chromatography.

b : 1,4 - dioxane as solvent at 25°C.

c : prepared from allyl-9-BBN with n-BuLi.

d) **Mechanistic and stereoselectivity studies.**

A number of experiments were carried out to glean mechanistic information on the reaction as well as to probe the possibility of diastereoselection. Regarding the former, of particular interest was the question of compatibility[22] between organometallic and Lewis acid and whether the allyl group is transferred from boron or silicon during carbon-carbon bond formation. The first experimental observation was that the Lewis acid, borate and acetal may be added in any order without significantly affecting the outcome of the reaction. An experiment was performed based on the fact that allyltrimethylsilane in the presence of a catalytic amount of TMSOTf does not react with benzaldehyde even "under forcing conditions[23]". Lithium 9-allyl-9-butylboratabicyclo[3.3.1]nonane was chosen as the allyl source so as to have only one equivalent of allyl group per equivalent of acetal. Reaction of the borate with benzaldehyde and TMSOTf (1.2 equivalents) did proceed (-78°C to 0°C) to give the corresponding homoallylic alcohol (43%). Thus, since allyltrimethylsilane/TMSOTf does not react with benzaldehyde under these conditions one can conclude that transmetallation does not take place at -78°C in this case and that allyl transfer proceeds from boron and not silicon. Scheme 4.



(i) TMSOTf / THF / -78°C to 0°C.

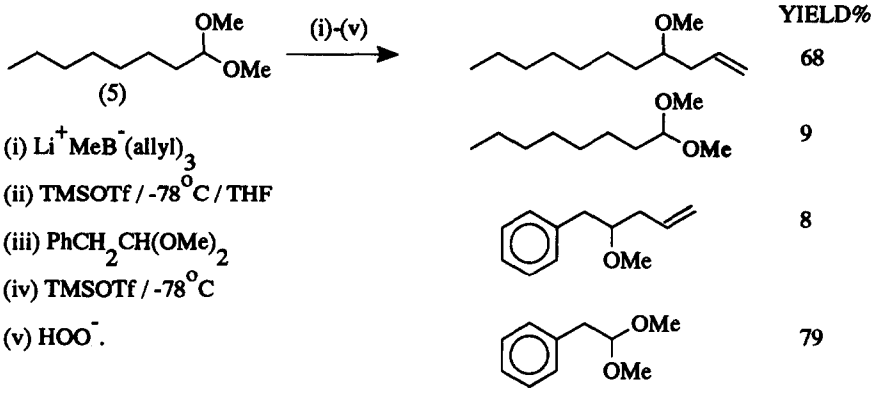
(ii) HOO^-

Scheme 4

As further suppport for this hypothesis, half of an equivalent of TMSOTf was mixed with the same borate at -78°C and stirred for thirty minutes. 1,1-Dimethoxyoctane was then added and the solution warmed to 0°C to afford 21% of isolated homoallylic ether (**22**). The yield compares favourably with that obtained with this borate in previous reactions (27% from Table 2). Thus, one can conclude that no transmetallation consuming the Lewis acid takes place at -78°C and that allyl transfer in this case is from boron and not silicon. Finally, lithium n-butyltriallylborate and TMSOTf were mixed in d_8 THF at -78°C, the mixture left stirring for one hour and the volatile contents then vacuum distilled into a trap at liquid nitrogen temperature (-196°C). However, the reaction flask had to be removed from the acetone/dry-ice bath to ensure complete distillation of the volatile components. Analysis of the distillate by ^1H nmr did reveal the presence of allyltrimethylsilane so one may conclude that transmetallation does take place between -78°C and 0°C in this case. However, there is no evidence to support a transmetallation reaction preceding allyl transfer from boron occurring during acetal substitution. A ^{11}B nmr study of this reaction would establish compatibility unambiguously.

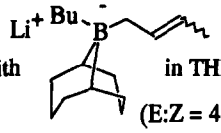
Another pertinent mechanistic aspect is to what extent diallylbutylborane, the product of initial allyl transfer, participates competitively in subsequent allyl transfer. Yamamoto[24] has shown that allyl-9-BBN allylates acetals at low temperature using $TiCl_4$. Therefore, a competition experiment was designed. The reaction between lithium methyltriallylborate and 1,1-dimethoxyoctane activated by TMSOTf

(1.2 equivalents) was allowed to proceed for ninety minutes at -78°C. Subsequently 1,1-dimethoxy-2-phenylethane was added followed by a further 1.2 equivalents of TMSOTf. After a further ninety minutes at 78°C the reaction was quenched with HOO^-. Scheme 5 summarises the products isolated. From the product distribution one may conclude that allylation proceeds at -78°C essentially exclusively from the borate and that diallylbutylborane does not function as an allylating agent at this temperature in competition with the borate.

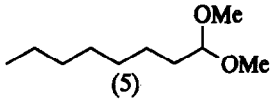
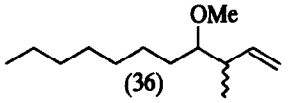
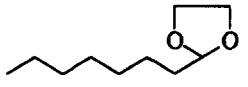
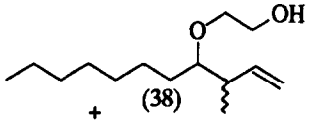


Scheme 5

TABLE 3

Diastereoselectivity study of crotylation with  in THF with TMSOTf at -78°C.

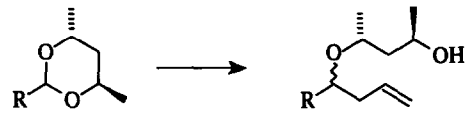
(E:Z = 4:1)

ACETAL	PRODUCT(S)	YIELD %
 (5)	 (36)	62 (1:3)
 (6)	 + (38)	21 (1:2)
	 (37)	35

Stereoselective allylation[25,26] has made a significant contribution in recent years to the construction of natural products. A key feature in this regard has been the successful development of crotylating agents[26,27] which furnish homoallylic compounds with two contiguous chiral centres. Thus, we decided to study the simple diastereoselectivity of the reaction using lithium 9-butyl-9-crotyl-9-boratabicyclo[3.3.1]nonane with 9-BBN as a bulky blocking group and just one crotyl group for transfer. The borate was prepared by crotyl Grignard subsitution of 9-methoxy-9-BBN followed by "ate" formation with butyllithium. The results of crotylation in THF with TMSOTf are presented in Table 3. The yield and simple diastereoselectivity (62% and 3:1 respectively) of the reaction with 1,1-dimethoxyoctane were good, particularly when one takes into account that the E/Z ratio of the borate is 80/20[27] and that the presence of TMSOTf may alter this ratio. As expected, the dioxolane entry gave low yields of substitution and significant amounts of reduction in THF. As observed with other crotylation procedures, transfer proceeded with inversion of double bond configuration. Thus, a degree of simple diastereoselection is observed but it is of little preparative value.

TABLE 4

Allylation of chiral acetals with $Li^+BuB^-(allyl)_3$ and TMSOTf.



(4R , 6R)

(33) R = Ph
(34) R = n-Octyl

GROUP R	SOLVENT / TEMPERATURE	YIELD %	ISOMER RATIO
Ph (14)	Hexane / -78°C to 25°C	83	1:1
Ph	Hexane / -78°C / 15hr then to -20°C	17[a]	1:1.4
Ph	Toluene / -78°C / 17hr	23[b]	1:1.8
n-Octyl (15)	Toluene / -78°C / 17hr	0[c]	--
n-Octyl	CH_2Cl_2 / -78°C / 15hr then to 25°C	25[d]	1:1.9

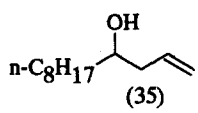
a : 62% starting material recovered.

b : 61% starting material recovered.

c : quantitative recovery of starting material.

d : $Li^+MeB^-(allyl)_3$ used.

+ 28

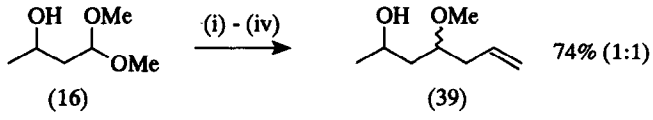


(35)

Chiral acetals derived from (2R,4R)-pentanediol were reacted with lithium n-butyltriallylborate in the hope of effecting a highly diastereoselective transformation which would lead to homoallylic alcohols in high enantiomeric excess after cleavage of the chiral auxiliary. This approach has become a very powerful procedure in asymmetric[28] carbon-carbon bond formation and the mechanistic information to date on the pentanediol system indicates Lewis acid complexation of the oxygen adjacent to the axial methyl group and an intimate ion-pair in the transition state to be crucial features for achieving high stereoselectivity. From the earlier results, we were aware that the low reactivity of dioxanes, particularly in THF, would be a problem. The chiral acetals of benzaldehyde and nonanal were prepared and reacted in a variety of solvents and the results are presented in Table 4. As evidenced by the yields and diastereomer ratios (ascertained by G.C. and nmr) one may conclude that the low reactivity of the borate compared to other nucleophiles results in higher reaction temperatures being required involving "S_N1-like" intermediates[29] resulting, unfortunately, in low levels of diastereoselection.

e) Intramolecular studies.

A further attractive feature of using a borate to deliver an allyl group is the possibility of using a proximal hydroxyl group as its alkoxide anion to trap the borane to its borinate, and then to allylate intramolecularly in the hope of controlling stereoselectivity. As a simple model to achieve this end, the alkoxide of 1,1-dimethoxypropan-2-ol was prepared and reacted with triallylborane to form the borinate complex. Addition of TMSOTf afforded the desired allylated product in 74% yield as a 1:1 mixture of diastereomers after work-up and chromatography. Scheme 6.



(16) (39)

(i) n-BuLi / THF / -78°C

(ii) $B(allyl)_3$

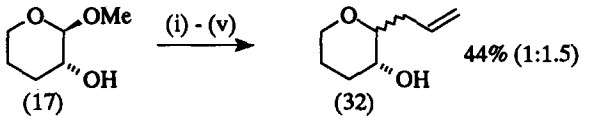
(iii) TMSOTf

(iv) HOO^-.

Scheme 6

As a model for C-glycoside synthesis[30], trans-2-methoxytetrahydropyran-3-ol was subjected to the same sequence as above except that once alkoxide formation had taken place, the THF was replaced by CH_2Cl_2. The desired allylated product was obtained in 44% yield after chromatography as a 1:1.5 ratio of diastereomers with the syn isomer predominating. Although the diastereoselectivity obtained was lower than the intermolecular reaction with 2-methoxy-3-trimethylsilyloxytetrahydropyran (entry 13, Table 1), it does pave the way forward for an in-depth study of this type of approach towards allylated C-glycosides. Scheme 7.

In conclusion, the results of this study, although highlighting the sensitivity of allylation towards substrate and reaction conditions, have extended the scope of borate intermolecular transfer reactions and show promise for the intramolecular allylation of cyclic acetals using a proximal "anchor" site.



(17) (32)

(i) n-BuLi / THF / -20°C

(ii) $B(allyl)_3$ / 0°C

(iii) Replace THF with CH_2Cl_2

(iv) TMSOTf / -78°C to 0°C.

(v) HOO^-.

Scheme 7

Experimental.

All solvents were purified by standard methods before use. The boron reagents; borane-methyl sulphide complex (10M in BH_3), dibromoborane-methyl sulphide complex, 9-borabicyclo[3.3.1]nonane (0.5M solution in hexane), as well as (2R,4R)-pentanediol, benzaldehyde dimethyl acetal (**1**) 1,1-dimethoxy-2-phenylethane (**3**), 1,1,3,3-tetramethoxypropane (**8**) and 2-methylvaleraldehyde were all purchased from Aldrich Chemical Company. n-Butyllithium and methyllithium were purchased from Merck and Fluka chemical companies respectively. 1,1-Diethoxy-3-phenylthiopropane (**10**) was prepared by thiophenoxide substitution of 3-bromo-1,1-diethoxypropane.

Reactions were carried out using dry techniques as described by C.F. Lane and G.W. Kramer[31]. Product separations were carried out by column chromatography using Merck Kieselgel 60 (70-230 mesh). I.R. spectra were recorded on a PYE UNICAM 9512 spectrophotometer and ^1H and ^{13}C nmr spectra recorded on a Bruker AC-200 spectrometer at 200.13 and 50.32 MHz respectively. All spectra were recorded in deuteriochloroform. High resolution measurements were recorded on a Varian MAT 212 at the CSIR, Pretoria.

1. **Synthesis of Acetals.**

Simple acyclic acetals were prepared by treatment of the appropriate aldehyde with methanol and concentrated sulphuric acid. Achiral dioxane and dioxolane derivatives were prepared using the aldehyde, diol and p-toluenesulphonic acid. Chiral acetals were prepared using aldehyde, (2R,4R)-pentanediol and p-toluenesulphonic acid under Dean-Stark conditions. The following acetals were prepared. 2-Phenyl-1,3-dioxane[32] (**2**),(E)-1,1-dimethoxy-3-phenyl-2-propene[33](**4**),1,1-dimethoxyoctane[34](**5**), 1,1-dimethoxy-2-methylpentane[35] (**9**),

a) *2-Heptyl-1,3-dioxolane*[36] (**6**)

δ_H 0.88(3H, t, *J* 6.5 Hz), 1.14-1.52(10H, m), 1.57-1.72(2H, m), 3.77-4.03(4H, m), 4.84(1H, t, *J* 4.8 Hz) ; δ_C 14.0, 22.5, 24.0, 29.1, 29.4, 31.7, 33.8, 64.7 and 104.6.

b) *2-Heptyl-1,3-dioxane*[37] (**7**)

δ_H 0.87(3H, t, *J* 6.4 Hz), 1.16-1.43(12H, m), 1.50-1.68(1H, m), 1.95-2.20(1H, m), 3.75(2H, dt, *J* 2.5 and 11.2 Hz), 4.10(2H, dd, *J* 5 and 10.5 Hz), 4.5(1H, t, *J* 5.0 Hz); δ_C 14.0, 22.5, 23.7, 25.8, 29.1, 29.4, 31.7, 35.2, 66.8 and 102.4.

c) *1,1-Dimethoxypropan-2-ol*[38] (**16**)

Sodium borohydride (1.7 g, 45 mmol) was added slowly to a solution of pyruvic aldehyde dimethyl acetal (5.0 g, 42.3 mmol) in methanol (5 ml) at 0°C. The mixture was stirred for one hour before addition of water (10 ml) and extraction with ether (3 x 20 ml). Drying ($MgSO_4$) and removal of the solvent afforded 1,1-dimethoxypropan-2-ol (2.05 g, 17 mmol, 40%) after vacuum distillation (b.p.70-73°C, 60 mm Hg); δ_H 1.18(3H, d, *J* 5.9 Hz), 3.13(1H, br. s., OH), 3.42(3H, s), 3.45(3H, s), 3.75(1H, dq, *J* 6.2 and 5.9 Hz), 4.08(1H, d, *J* 6.2 Hz); δ_C 17.1, 54.4, 66.8, 107.5.

d) *1,1-Dimethoxy-2-[(1,1-dimethylethyl)dimethylsilyloxy]propane*[10] (**11**)

To a stirred solution of 1,1-dimethoxypropan-2-ol (614 mg, 5.1 mmol) in DMF (3 ml) at room temperature were added t-butyldimethylsilyl chloride (804 mg, 5.4 mmol), imidazole (400 mg, 5.9 mmol) and the mixture left stirring for one hour. After the normal work-up (H_2O/hexane) and chromatography, (**11**) (650 mg, 54%) was obtained as an oil; ν_{max} (CCl_4) 2940, 2845, 1450, 1240 cm^{-1}; δ_H 0.04(6H, s), 0.86(9H, s), 1.10(3H, d, *J* 6.2 Hz), 3.38(3H, s), 3.39(3H, s), 3.73(1H, qd, *J* 6.2 and 5.5 Hz), 3.98(1H, d, *J* 5.5 Hz).

e) *2-Methoxytetrahydropyran*[39] (**12**)

To a stirred solution of 3,4-dihydro-2H-pyran (10 g, 0.12 mol) in dry methanol (100 ml) was added a drop of concentrated hydrochloric acid. An exothermic reaction resulted and the temperature was maintained at 50°C overnight. The reaction mixture was neutralised by the addition of sodium hydroxide (2 g), the methanol removed *in vacuo* and the remaining oil distilled to afford (**12**) (9.3 g, 71%), b.p. 37°-40°C at *ca.* 20 mm Hg ; δ_H 1.50-1.96(6H, m), 3.44(3H,s), 3.49-3.64(2H, m), 4.57(1H, dd, *J* 7 and 3.3 Hz); δ_C 19.0, 25.1, 30.2, 54.5, 62.4, 99.4.

f) *Trans-2-methoxytetrahydropyran-3-ol*[42] (**17**)

To a stirred solution of 3,4-dihydro-2H-pyran (1.23 g, 14.6 mmol) in methanol (10 ml) at -5°C was added magnesium monoperoxyphthalate (8 g, 16 mmol) in methanol (20 ml) dropwise. The reaction was stirred overnight at room temperature whereupon unreacted dihydropyran and methanol were removed *in vacuo* and chloroform added to dissolve the product. The magnesium salts were filtered and the filtrate washed with aqueous sodium carbonate solution. Drying ($MgSO_4$) and evaporation of solvent afforded (**17**) (700 mg, 36%) after vacuum distillation (b.p. 56 °C at 2 mm Hg); ν_{max} (CCl_4) 3620-3100, 2930, 1240 cm^{-1} ; δ_H 1.44-1.82 and 1.92-2.13(4H, m), 2.6-2.73(1H, br. s), 3.39-3.55(2H, m), 3.49(3H, s), 3.84-3.95(1H, m), 4.18(1H, d, *J* 5.6 Hz) ; δ_C 23.0, 28.1, 56.0, 63.7, 68.6, 104.5.

g) *(4R,6R)-4,6-Dimethyl-2-phenyl-1,3-dioxane*[40] (**14**)

δ_H 1.27(3H, d, *J* 6.1 Hz), 1.39(1H, ddd, *J* 1.2, 2.5 and 13.3 Hz), 1.46(3H, d, *J* 6.9 Hz), 1.96(1H, ddd, *J* 6.2, 11.5 and 13.3 Hz), 4.16(1H, ddq, *J* 1.8, 6.1 and 11.5 Hz), 4.97(1H, t, *J ca.* 6.9 Hz), 7.25-7.41(3H, m), 7.46-7.56(2H, m); δ_C 17.1, 21.6, 36.6, 67.9, 68.5, 94.0, 126.1, 128.1, 128.5, 139.1.

h) *(4R,6R)-4,6-Dimethyl-2-octyl-1,3-dioxane*[41] (**15**)

δ_H 0.87(3H, t, *J* 6.4 Hz), 1.08-1.48(14H, m), 1.20(3H, d, *J* 6.2 Hz), 1.35(3H, d, *J* 6.9 Hz)., 1.49-1.64(1H, m), 1.79(1H, ddd, *J* 6.1, 11.6 and 13.1 Hz), 3.93(1H, ddq, *J* 2.4, 6.2 and 11.6 Hz), 4.28(1H, quintet, *J* 6.8 Hz), 4.8(1H, t, *J* 5.1 Hz) ; δ_C 14.0, 17.1, 21.8, 22.6, 24.0, 29.1, 29.4, 31.8, 35.3, 36.7, 67.3, 67.7, 94.2.

2. Preparation of borate solutions for reactions in Table 2.

Lithium n-butyltriallylborate, lithium methyltriallylborate, sodium cyanotriallylborate, lithium methoxytriallylborate and magnesium tetraallylborate were all prepared in THF by addition of the appropriate

nucleophile to triallylborane under nitrogen to afford solutions of known molarity. Lithium 9-allyl-9-butyl-9-boratabicyclo[3.3.1]nonane and lithium 9-crotyl-9-butyl-9-boratabicyclo[3.3.1]nonane were prepared from 9-allyl-9-BBN and 9-crotyl-9-BBN respectively with *n*-butyllithium.

3. **Intermolecular allylation studies with lithium n-butyltriallylborate.**

General procedure

To a stirred solution of acetal (1 mmol) and TMSOTf (0.22 ml, 1.2 mmol) in THF (*ca.* 3 mls) at -78°C was added dropwise a solution of lithium n-butyltriallylborate (3 ml of a 0.43 M solution, 1.3 mmol) in THF. The reaction mixture was allowed to warm slowly to 0°C and then quenched with an alkaline peroxide solution of KOH (80 mg, 1.5 mmol), H_2O_2 (0.5 ml, 9.6 M, 4.8 mmol) and methanol (3 ml). After stirring for one hour at room temperature, the solution was extracted with ether (3 x 30 ml), the combined extracts dried ($MgSO_4$) and the solvents removed under vacuum to afford pure product(s) after column chromatography (eluent: hexane/dichloromethane mixtures).

Results from Table 1

a) Reaction with *1,1-dimethoxyphenylmethane* (**1**) gave 1-methoxy-1-phenyl-3-butene (**18**) 94%; $\nu_{max}(CHCl_3)$ 1650 cm^{-1}; δ_H 2.40(1H, m), 2.57(1H, m), 3.20(3H, s), 4.15(1H, dd, *J* 5.9 and 7.4 Hz), 5.06(2H, m), 5.77(1H, m), 7.24-7.36(5H, m); δ_C 42.5, 56.5, 83.6, 116.7, 126.6, 127.8, 128.2, 134.7, 141.6; HRMS *m/z* *calcd. for* C_8H_9O (M^+-C_3H_5) 121.0653, found 121.0651.

b) *With 2-phenyl-1,3-dioxane* (**2**)

Yield of 4-oxa-5-phenyl-7-octen-1-ol (**19**) = 71%; δ_H 1.78(2H, q, *J* 5.7 Hz), 2.36-2.58(2H, m), 2.76(1H, br. s), 3.37-3.56(2H, m), 3.74(2H, t, *J* 5.7 Hz), 4.28(1H, dd, *J* 5.6 and 7.7 Hz), 5.00-5.11(2H, m), 5.66-5.84(1H, m), 7.23-7.39(5H, m); δ_C 31.9, 42.6, 61.8, 68.0, 82.2, 117.1, 126.5, 127.6, 128.3, 134.5, 141.6; HRMS *m/z* calcd for $C_{10}H_{13}O_2$ (M^+-C_3H_5) 165.0916, found 165.0916.

c) *With 1.1-dimethoxy-2-phenylethane* (**3**)

Yield of 2-methoxy-1-phenyl-4-pentene (**20**) = 75%; ν_{max} ($CHCl_3$) 1620 cm^{-1}; δ_H 2.23(2H, m), 2.77(2H, dd, *J* 7.5 and 7.7 Hz), 3.30(3H, s), 3.43(1H, q, *J* 6.0 Hz), 5.01-5.07 and 5.08-5.14 (2H, m), 5.85(1H, m), 7.13-7.31(5H, m); δ_C 37.4, 39.7, 56.9, 81.6, 117.0, 126.0, 128.1, 129.3, 134.6, 138.8; HRMS *m/z* calcd. for $C_9H_{11}O$ (M^+-C_3H_5) 135.0810, found 135.0807.

d) *With (E)-1,1-dimethoxy-3-phenyl-2-propene* (**4**)

Yield of (E)-3-methoxy-1-phenyl-1,5-hexadiene (**21**) was 22%; ν_{max} ($CHCl_3$) 1615 cm^{-1}; δ_H 2.29-2.53(2H, m), 3.32(3H, s), 3.77(1H, m), 5.03-5.17(2H, m), 5.84(1H, ddt, *J* 7.0, 10.1 and 17.2 Hz), 6.07(1H, dd, *J* 7.9 and 16.0 Hz), 6.55(1H, d, *J* 16.0 Hz), 7.19-7.43(5H, m); δ_C 40.2, 56.3, 82.0, 117.1, 126.5, 127.7, 128.6, 129.6, 132.5, 134.4, 136.5; HRMS *m/z* calcd. for $C_{10}H_{11}O$ (M^+-C_3H_5) 147.0810, found 147.0807.

e) *With 1,1-dimethoxyoctane* (**5**)

Yield of 4-methoxy-1-undecene (**22**) = 75%; δ_H 0.88(3H, t, *J* 6.7 Hz), 1.11-1.63(12H, m), 2.26(2H, t, *J* 5.8 Hz), 3.20(1H, t, *J* 2.9 Hz), 3,34(3H, s), 5.01-5.13(2H, m), 5.72-5.92(1H, ddt, *J* 7.1, 10.2 and 17.1 Hz); δ_C 14.1, 22.6, 25.3, 29.3, 29.7, 31.8, 33.4, 37.7, 56.5, 80.5, 116.7, 135.0; HRMS *m/z* calcd. for $C_9H_{19}O$ (M^+-C_3H_5) 143.1436, found 143.1434.

f) *With 2-heptyl-1,3-dioxolane* (**6**)

Yield of 4-heptyl-3-oxa-6-hepten-1-ol (**23**) = 61%; ν_{max} (CCl_4) 3700-3200, 1635 cm^{-1}; δ_H 0.88(3H, t, *J* 6.4 Hz), 1.12-1.63(12H, m), 2.20-2.33(2H,m), 2.49(1H, br. s), 3.35(1H, quintet, *J* 5.8 Hz), 3.49-3.61(2H, m),

3.61-3.76(2H, m), 5.00-5.16(2H, m), 5.69-5.95(1H, m); δ_C 14.0, 22.5, 25.3, 29.2, 29.6, 31.7, 33.8, 38.3, 61.9, 69.9, 79.4, 116.7, 134.9; HRMS *m/z* calcd. for $C_{10}H_{21}O_2$ (M^+-C_3H_5) 173.1542, found 173.1529.

g) *With 2-heptyl-1,3-dioxane* (**7**)

Yield of 5-heptyl-4-oxa-7-octen-1-ol (**24**) = 38%; ν_{max} (CCl_4) 3700-3400, 1630 cm^{-1}; δ_H 0.88(3H, t, *J* 6.5 Hz), 1.17-1.61(12H, m), 1.81(2H, quintet, *J* 5.6 Hz), 2.18-2.33(2H, m), 2.79(1H, br.s), 3.31(1H, quintet, *J* 5.8 Hz), 3.55-3.62(2H, m), 3.76(2H, t, *J* 5.5 Hz), 5.03-5.13(2H, m), 5.71-5.92(1H, m); δ_C 14.0, 22.6, 25.2, 29.2, 29.6, 31.8, 32.1, 33.6, 39.2, 62.2, 68.4, 79.5, 116.9, 134.9; HRMS *m/z* calcd. for $C_{11}H_{23}O_2$ (M^+-C_3H_5) 187.1698, found 187.1700.

Yield of 3-octyloxypropan-1-ol (**25**) = 26%; ν_{max} (CCl_4) 3700-3200, 1645 cm^{-1}; δ_H 0.88(3H, t, *J* 6.5 Hz), 1.08-1.54(10H, m), 1.46-1.64(2H, m), 1.83(2H, quintet, *J* 5.7 Hz), 2.74(1H, br.s), 3.43(2H, t, *J* 6.6 Hz), 3.61(2H, t, *J* 5.7 Hz), 3.77(2H, t, *J* 5.6 Hz); δ_C 14.0, 22.6, 26.1, 29.2, 29.4, 29.6, 31.8, 31.9, 62.2, 70.2, 71.4.

h) *With 1,1,3,3-tetramethoxypropane* (**8**)

Yield of 4,6-dimethoxy-1,8-nonadiene[10] (**26**) = 69% as a 1:1.2 mixture of diastereomers; ν_{max} ($CHCl_3$) 1635 cm^{-1}; δ_H 1.53(2H, dd, *J* 5.6 and 7.2 Hz), 1.60(1H, t, *J* 5.9 Hz), 1.75(1H, t, *J* 6.8 Hz), 2.24-2.33(2 x 4H, m), 3.28-3.52(2 x 2H, m), 3.33(2 x 3H, s), 3.36(2 x 3H, s), 5.03-5.14(2 x 4H, m), 5.70-5.92(2 x 2H, m); δ_C 37.1, 37.6, 38.0, 39.3, 56.3, 56.7, 76.8, 77.3, 117.0, 117.1, 134.4, 134.5.

i) *With 1,1-dimethoxy-2-methylpentane* (**9**)

Yield of 4-methoxy-5-methyl-1-octene[43] (**27**) = 70% as a 1:1.1 mixture of diastereomers; δ_H 0.70-0.97(2 x 6H, m), 1.02-1.47(2 x 5H, m), 2.13-2.32(2 x 2H, m), 2.99-3.09(2 x 1H), 3.34(3H, s), 3.35(3H, s), 5.01-5.13(2 x 2H, m), 5.73-5.97(2 x 1H, m).

j) *With 1,1-diethoxy-3-phenylthiopropane* (**10**)

Yield of 4-ethoxy-6-phenylthio-1-hexene (**28**) = 64%; δ_H 1.17(3H, t, *J* 7.0 Hz), 1.78(2H, m), 2.25(2H, m), 3.00(2H, m), 3.32-3.64(3H, m), 5.05(2H, m), 5.87(1H, ddt, *J* 7.1, 10.3 and 16.9 Hz), 7.08-7.18(1H, m), 7.19-7.34(4H, m); δ_C 15.4, 29.4, 33.4, 38.2, 64.4, 77.0, 117.0, 125.5, 128.7, 128.8, 134.4, 136.6; HRMS *m/z* calcd. for $C_{14}H_{20}OS$ (M^+) 236.1235, found 236.1230.

k) *With 1,1-dimethoxy-2-[(1,1-dimethylethyl)dimethylsilyloxy]propane* (**11**)

Yield of 4-methoxy-5-[(1,1-dimethylethyl)dimethylsilyloxy]-1-hexene (**29**) = 33% as a 1:1 mixture of diastereomers; δ_H 0.07 (2 x 6H, s),0.89(2 x 9H, s), 1.09(3H, d, *J* 6.4 Hz), 1.15(3H, d, *J* 6.2 Hz), 2.03-2.46(2 x 2H, m), 3.02-3.13(2 x 1H, m), 3.39(3H, s), 3.42(3H, s). 3.72-3.85(1H, m), 3.85-3.98(1H, m), 4.99-5.16(4H, m), 5.76-6.00(2H, m); HRMS *m/z* calcd. for $C_{12}H_{23}OSi$ (M^+-CH_5O) 211.1519, found 211.1510.

l) *With 2-methoxytetrahydropyran* (**12**)

Yield of 2-(2-propenyl)tetrahydropyran[44] (**30**) = 24%. Yield of 5-methoxy-7-octen-1-ol (**31**) = 40%; δ_H 1.14-1.70(6H, m), 1.88-2.13(1H, broad s,), 2.20-2.38(2H, m), 3.33(3H, s), 3.39-3.63(3H, m).4.99-5.17(2H, m), 5.70-5.94(1H, m); δ_C 21.5, 31.6, 33.0, 37.6, 56.5, 62.6, 80.4, 116.8, 134.8.

m) *With trans-2-methoxy-3-trimethylsilyloxytetrahydropyran* (**13**).

Reaction carried out in CH_2Cl_2 to afford 2-(2-propenyl)tetrahydropyran-3-ol[45] (**32**) in 82% yield as a 1:2.5 mixture of diastereomers; δ_H (major diastereomer) 1.26-1.47(2H, m), 1.81-2.16(2H, m), 2.17-2.52(2H, m), 2.46-2.64(1H, br.s,) 3.25-3.56(2H, m), 3.61-3.75(1H, m), 3.84-4.05(1H, m), 5.02-5.19(2H, m), 5.72-6.03(1H, m); δ_C 19.9, 30.5, 36.2, 65.8, 68.4, 79.5, 116.9, 134.4. δ_H (minor diastereomer) 1.50-2.16(4H, m), 2.17-2.52(1H, m), 2.62-2.70(1H, m), 2.66-2.96(1H, broad, s). 3.05-3.16(1H, ddd, *J* 3.4, 7.9 and 8.8 Hz), 3.42-3.56(2H, m). 3.84-4.05(1H, m), 5.02-5.19(2H, m), 5.72-6.03(1H, m); δ_C 25.4, 32.6, 36.6, 67.5, 69.7, 81.7, 116.5, 135.1.

n) *With (4R,6R)-4,6-dimethyl-2-phenyl-1,3-dioxane* (**14**)

Yield of (2R,4R)-4-methyl-5-oxa-6-phenyl-8-nonen-2-ol (**33**) in hexane was 83% as a 1:1 mixture of diastereomers; δ_H (2 diastereomers) 1.02(3H, d, *J* 6.4 Hz), 1.09(3H, d, *J* 6.3 Hz), 1.18(2 x 3H, d, *J* 6.2 Hz), 1.41-1.82(2 x 2H, m), 2.27-2.63(2 x 2H, m), 3.01(1H, br.s), 3.28(1H, broad s), 3.53-3.68(1H, m), 3.68-3.85(1H, m), 3.98-4.23(2 x 1H, m), 4.40(1H, t, *J* 5.6 Hz). 4.44(1H, t, *J* 5.4 Hz), 4.98-5.13(2 x 2H, m), 5.62-5.87(2 x 1H, m), 7.16-7.46(2 x 5H, m); δ_C (2 diastereomers) 18.1, 20.3, 23.1, 23.6, 42.5, 42.8, 43.4, 44.7, 63.9, 64.1, 69.5, 72.4, 78.4, 80.3, 117.0, 117.4, 126.5, 126.7, 127.3, 127.7, 128.1, 128.3, 134.4, 134.5, 141.5, 141.7; HRMS *m/z* calcd. for $C_{12}H_{17}O_2$ (M^+-C_3H_5) 194.1229, found 194.1231.

o) *Reaction of (4R,6R)-4,6-dimethyl-2-octyl-1,3-dioxane* (**15**) *with lithium methyltriallylborate in dichloromethane/* -78°C to RT.

Yield of (2R,4R)-4-methyl-6-octyl-5-oxa-8-nonen-2-ol[46] (**34**) was 25% as a 1:1.9 mixture of diastereomers. Yield of 1-dodecen-4-ol[47] (**35**) was 28%; δ_H 0.88(3H, t, *J* 6.3 Hz), 1.18-1.61(14H, m), 1.65-1.78(1H, s, OH), 2.05-2.38(2H, m), 3.58-3.70(1H, m), 5.08-5.19(2H, m), 5.73-5.94(1H, m); δ_C 14.1, 22.7, 25.7, 29.3, 29.6, 29.7, 31.9, 36.6, 41.9, 70.7, 118.0, 134.9.

4. **Diastereoselectivity studies with lithium-9-butyl-9-crotyl-9-boratabicyclo[3.3.1]nonane. (Table 3)**

a) *Reaction with 1,1-dimethoxyoctane.*

To a stirred solution of 1,1-dimethoxyoctane (186 mg, 1.06 mmol) in THF (*ca.* 2 ml) at -78°C were added dropwise a solution of lithium 9-butyl-9-crotyl-9-boratabicyclo[3.3.1]nonane (3 ml of a 0.43 M solution, 1.3 mmol) in THF followed by TMSOTf (0.23 ml, 1.27 mmol). The reaction mixture was allowed to warm slowly to 0°C and then quenched with an alkaline peroxide solution of KOH (80 mg, 1.5 mmol) in H_2O_2 (0.5 ml, 9.6 M, 4.8 mmol) and methanol (3 ml). After stirring for one hour at room temperature, water (20 ml) was added and the solution was extracted with ether (3 x 30 ml), the combined extracts dried ($MgSO_4$) and the solvent removed to afford 4-methoxy-3-methyl-1-undecene (**36**) (130 mg, 0.66 mmol, 62%) after column chromatography as a 1:3 mixture of diastereomers; ν_{max} (CCl_4) 1640 cm^{-1}; δ_H (2 diastereomers) 0.88(2 x 3H, t, *J* 6.5 Hz), 1.00(3H, d, *J* 6.8 Hz), 1.01(3H, d, *J* 6.9 Hz), 1.16-1.49(2 x 12H, m), 2.31-2.55(2 x 1H, m), 2.93-3.08(2 x 1H, m), 3.36(2 x 3H, s), 4.95-5.09(2 x 2H, m), 5.7-5.90(2 x 1H); δ_C 14.1, 14.8, 15.4, 22.6, 25.6, 25.9, 29.3, 29.8, 30.5, 30.7, 31.8, 40.1, 40.5, 57.5, 57.7, 74.6, 85.0, 114.1, 114.3, 140.9, 141.1.

(b) *With 2-heptyl-1,3-dioxolane.*

The same procedure was used as above to afford 2-octyloxyethanol[48] (**37**) in 35% yield and 4-heptyl-5-methyl-3-oxa-6-hepten-1-ol (**38**) in 21% yield as a 1:2 mixture of diastereomers; δ_H (2 diastereomers) 0.88(2 x 3H, t, *J* 6.5 Hz), 1.01(3H, d, *J* 6.9 Hz), 1.02(3H, d, *J* 6.9 Hz), 1.18-1.54(2 x 12H, m), 2.25(2 x 1H, dd, *J* 6 and 11.6 Hz, OH), 2.34-2.53(2 x 1H, m), 3.11-3.23(2 x 1H, m), 3.52-3.63(2 x 2H, m), 3.65-3.77(2 x 2H, m), 4.97-5.12(2 x 2H, m), 5.69-5.93(2 x 1H, m); δ_C (2 diastereomers) 14.1, 15.1, 15.2, 22.6, 25.7, 29.3, 29.8, 30.8, 31.1, 31.8, 40.7, 40.8, 62.4, 70.8, 70.9, 83.8, 114.4, 114.6, 141.1; HRMS *m/z* calcd. for $C_{10}H_{21}O_2$ (M^+-C_4H_7) 173.1542, found 173.1561.

5. **Competition experiment involving two acetals**

To a stirred solution of 1,1-dimethoxyoctane (179 mg, 1.03 mmol) in THF (*ca.* 2 ml) at -78°C were added dropwise a solution of lithium methyltriallylborate (3 ml of a 0.4M solution, 1.2 mmol) in THF followed by TMSOTf (0.22 ml, 1.2 mmol). The reaction mixture was stirred at -78°C for ninety minutes whereupon a solution of 1,1-dimethoxy-2-phenylethane (162 mg, 0.97 mmol) in THF (*ca.* 2 ml) was then added dropwise at

-78°C, followed by more TMSOTf (0.22 ml, 1.2 mmol). The reaction mixture was stirred at -78°C for a further ninety minutes and then quenched with an alkaline peroxide solution of KOH (160 mg, 3 mmol) and H_2O_2 (1 ml, 9.6 M, 9.6 mmol) in methanol (6 ml). After stirring for one hour followed by the normal work-up, the reaction mixture was chromatographed to give 4-methoxy-1-undecene (**22**) (128 mg, 0.7 mmol, 68%), 2-methoxy-1-phenyl-5-pentene (**20**) (14 mg, 0.08 mmol, 8%) and recovered starting materials, 1,1-dimethoxyoctane (9%) and 1,1-dimethoxy-2-phenylethane (79%). The spectral characteristics of the products were consistent with those obtained previously.

6. **Intramolecular allylation studies**

a) *With 1,1-dimethoxy-2-propanol* (**16**)

To a stirred solution of 1,1-dimethoxy-2-propanol (123 mg, 1.02 mmol) in THF (2 ml) at -78°C was added n-butyllithium (0.64 ml, 1.03 mmol) and the mixture was stirred for ten minutes before adding triallylborane (0.2 ml, 1.12 mmol). The solution was allowed to warm slowly to -40°C before being recooled to -78°C whereupon TMSOTf (0.22 ml, 1.2 mmol) was added. The reaction mixture was allowed to warm to 0°C before being quenched with alkaline peroxide consisting of KOH (80 mg, 1.5 mmol), H_2O_2 (0.5 ml, 9.6 M, 4.5 mmol)and methanol (5 ml). After thirty minutes, water (20 ml) was added and the solution extracted with ether (3 x 20 ml). Drying ($MgSO_4$) and removal of solvent afforded 3-methoxy-5-hexen-2-ol (**39**) (98 mg, 0.75 mmol, 74%) after column chromatography as a 1:1 mixture of diastereomers; δ_H (2 diastereomers) 1.04 (2 x 3H, d, *J* 6.0 Hz), 1.98-2.30 (2 x 2H, m), 3.08-3.28 (2 x 1H, m), 3.30(3H, s), 3.32(3H, s), 3.58(2 x 1H, m), 3.92(2 x 1H, d, OH), 4.72-5.16(2 x 2H, m), 5.36-6.13(2 x 1H, m). Silylation of (**39**) with t-butyldimethylsilyl chloride and imidazole in DMF gave a compound with identical spectral characteristics to (**29**) obtained from the intermolecular route.

b) *With trans-2-methoxytetrahydropyran-3-ol* (**17**)

To a stirred solution of trans-2-methoxytetrahydropyran-3-ol (149 mg, 1.13 mmol) in THF (2 ml) at -20°C was added n-butyllithium (0.75 ml, 1.65 M, 1.25 mmol) in hexane. The reaction mixture was stirred for 30 mins and then neat triallylborane (0.2 ml, 1.3 mmol) added. The mixture was allowed to warm slowly to 0°C and the THF removed *in vacuo* using a double manifold system. Dichloromethane (4 ml) was introduced into the flask, the mixture cooled to -78°C and TMSOTf (0.25 ml, 1.4 mmol) added. The mixture was allowed to warm to 0°C then quenched with a mixture of KOH (80 mg, 1.5 mmol) and $NaBO_3$ (0.8 g, 5 mmol) in H_2O (5 ml). After stirring for thirty minutes at room temperature, water (20 ml) was added and the solution extracted with ethyl acetate (3 x 30 ml). After drying ($MgSO_4$) and removal of solvent, 2-(2-propenyl)tetrahydropyran-3-ol[45] (**32**) (70 mg, 44%) was obtained after column chromatography as a 1:1.5 mixture of diastereomers. The spectral characteristics were identical with those obtained for the compound from the intermolecular pathway.

References

1. a) March, J. *Advanced Organic Chemistry* 3rd Edition ; J. Wiley and Sons, **1985**; p 995-1002 b) Pelter A.; Smith, K. *Comprehensive Organic Chemistry*; Ed. D. Neville Jones; Pergamon Press: Oxford, **1979**; Vol 3, p 892.
2. Brown, H.C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, 83, 3834.
3. Larock, R.C. *Intra-Sci. Chem.Rep.* **1973**, 7, 95.
4. Brown, H.C.; Campbell, J.B. Jr. *J. Org. Chem.* **1980**, 45, 389.
5. Negishi, E.I.; Chiu, K.W.; Yosida, T. *J. Org. Chem.* **1975**, 40, 1676.
6. Negishi, E.I. *Organometallics in Organic Synthesis* **1974**, 1, 286.
7. (a) Miyaura, N.; Sasaki, N.; Itoh, M.; Suzuki, A. *Tetrahedron Lett.* **1977**, 3369; (b) Miyaura, N.; Itoh, M.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1977**, 50, 2199; (c) Yamada, K.; Yano, T.; Miyaura, N.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1979**, 52, 275.
8. Negishi, E.I. *J. Organometallic Chem.* **1976**, 108, 281.
9. Oh-e, T.; Miyaura, N.; Suzuki, A. *J. Org. Chem.* **1993**, 58, 2201.
10. Hunter, R.; Tomlinson, G.D. *Tetrahedron Lett.* **1989**, 30, 2013.
11. Mukaiyama, T.; Murakami, M. *Synthesis* **1987**, 1043.
12. (a) Pelter, A. *Chem. Soc. Rev.* **1982**, 11, 191;. (b) Mikhailov, B.M. *Organomet. Chem. Rev. Sec. A.* **1972**, 8, 1.
13. Brown, H.C.; Racherla, U.S. *J. Org. Chem.* **1986**, 51, 427.
14. Mori, I.; Ishihara, K.; Flippin, L.A.; Nozaki, K.; Yamamoto, H.; Bartlett, P.A.; Heathcock, C.H. *J. Org. Chem.* **1990**, 55, 6107.
15. (a) Guindon, Y.; Bernstein, M.A.; Anderson, P.C. *Tetrahedron Lett.* **1987**, 28, 2225; (b) Guindon, Y.; Anderson, P.C. *Tetrahedron Lett.* **1987**, 28, 2485.
16. Denmark, S.E.; Willson, T.M.; Almstead, N.G. *J. Am. Chem. Soc.* **1989**, 111, 9258.
17. Brown, H.C.; Racherla, U.S. *Organometallics* **1986**, 5, 391.
18. Pelter, A.; Smith, K. *Comprehensive Organic Chemistry*; Ed. D. Neville Jones; Pergamon Press: Oxford, **1979**; vol 3, p 888.
19. Pelter, A.; Smith, K.; Brown, H.G. *Borane Reagents*; Academic Press: London, **1988**.
20. Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, 21, 1357.
21. Kramer, G.W.; Brown, H.C. *J. Organometallic Chem.* **1974**, 73, 1.
22. Yamamoto, Y. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 947.
23. Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, 21, 71.
24. (a) Yamamoto, Y.; Komatsu, T.; Maruyama, K. *J. Organometallic Chem.* **1985**, 285, 31; (b) Yamamoto, Y.; Nishii, S.; Yamada, J. *J. Am. Chem. Soc.* **1986**, 108, 7116.
25. Yamamoto, Y.; Nishii, S. *J. Org. Chem.* **1988**, 53, 3597.
26. Hoffmann, R.W. *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 489.
27. Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, 103, 1969.
28. Alexakis, A.; Mangeney, P. *Tetrahedron: Asymmetry* **1990**, 1, 477.
29. Denmark, S.E.; Almstead, N.G. *J. Am. Chem. Soc.* **1991**, 113, 8089.
30. a) Postema, M.H.D. *Tetrahedron* **1992**, 48, 8545; b). Armstrong, R.W.; Beau, J-M.; Cheon, S.H.; Christ, W.J.; Fugioka, H.; Ham, W-H.; Hawkins, L.D.; Jin, H.; Kang, S.H.; Kishi, Y.; Martinelli, M.J.;

McWhorter, W.W.Jr.; Mizuno, M.; Nakata, M.; Stutz, A.E.; Talamas, F.X.; Taniguchi, M.; Tino, J.A.; Ueda, K.; Uenishi, H-i.; White, J.B.; Yonaga, M. *J. Am. Chem. Soc.* **1989**, 111, 7525.

31. Lane, C.F.; Kramer, G.W. *Adrichimica Acta* **1977**, 10, 11.
32. Takano, S.; Akiyama, M.; Sato, S.; Ogasawara, K. *Chem. Lett.* **1983**, 1593.
33. *Dictionary of Organic Compounds 5th Edn.*; Ed. J. Buckingham; Chapman and Hall, London; **1982**; Vol 5, p 4664.
34. Stork, G.; Colvin, E. *J. Am. Chem. Soc.* **1971**, 93, 2080.
35. Hildebrand, U. *Spez. Ber. Kernforschungsanlage Juelich* **1988**, Juel-Spez-432, 88 pp.
36. Rosenthal, I.; Elad, D. *J. Org. Chem.* **1968**, 33, 805.
37. Bergmann, E.D.; Pinsky, I.; Aizenshtat, Z.; Bar-Zeev, M. *Isr. J. Entomol.* **1976**, 11, 15.
38. Ando, W.; Suzuki, J.; Arai, T.; Migita, T. *Tetrahedron* **1973**, 29, 1507.
39. Diner, U.E.; Brown, R.K. *Can. J. Chem.* **1967**, 45, 2547.
40. Normant, J.F.; Alexakis, A.; Ghribi, A.; Mangeney, P. *Tetrahedron* **1989**, 45, 507.
41. Lindell, S.D.; Elliott, J.D.; Johnson, W.S. *Tetrahedron Lett.* **1984**, 25, 3947.
42. Sweet, F.; Brown, R.K. *Can. J. Chem.* **1966**, 44, 1571.
43. Sakurai, H.; Sasaki, K.; Hayashi, J.; Hosomi, A. *J. Org. Chem.* **1984**, 49, 2808.
44. Sakurai, H.; Sakata, Y.; Hosomi, A. *Chem. Lett.* **1983**, 409.
45. Kozikowski, A.P.; Ghosh, A.H. *J. Org. Chem.* **1985**, 50, 3017.
46. Johnson, W.S.; Crackett, P.H.; Elliott, J.D.; Jagodzinski, J.J.; Lindell, S.D.; Natajaran, S. *Tetrahedron Lett.* **1984**, 25, 3951.
47. Otera, J.; Yoshinaga, Y.; Yamaji, T.; Yoshioka, T.; Kawasaki, Y. *Organometallics* **1985**, 4, 1213.
48. Kropp, P.J.; Poindexter, G.S.; Pienta, N.J.; Hamilton, D.C. *J. Am. Chem. Soc.* **1976**, 98, 8135.

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