ALLYLATION USING ORGANOBORATES AND ACTIVATED ACETALS

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Abstract : Lithium n-butyltriallylborate intermolecularly allylates a range of acetals activated by TMSOTF. The reaction may also be accomplished intramolecularly.

The introduction of an allyl group into an organic molecule has become a reaction of considerable importance[1] in modern synthetic organic chemistry. Several groups[2] have recently placed particular emphasis on the use of allylic organometallic compounds to achieve this transformation, and considerable headway[3] has been made using this approach in meeting the challenges of stereocontrolled construction of acyclic systems. In this regard, boron[4] has been extensively studied as the metal of the allylic organometallic, and both allylboranes[5] and allylboronates[6] have been investigated in their addition to aldehydes. The only study to date of using a Lewis acid-activated acetal as the electrophilic partner has been by Yamamoto and co-workers[3b,7] who have established that allyl-9-BBN allylates acetals using $TiCl_4$ as Lewis acid. In this communication we report on a novel allylation procedure involving lithium n-butyltriallylborate and acetals activated by trimethylsilyl trifluoromethanesulphonate (TMSOTF) and briefly discuss the relevance of this reaction to recent thinking[8] on the importance of compatibility of Lewis acids and organometallic compound, Scheme 1.
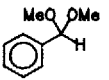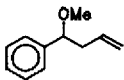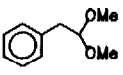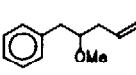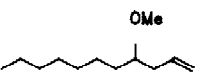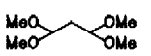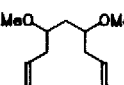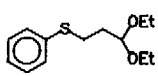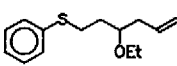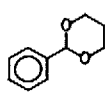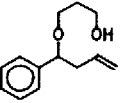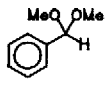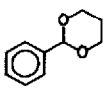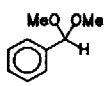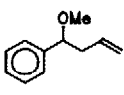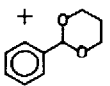
SCHEME 1
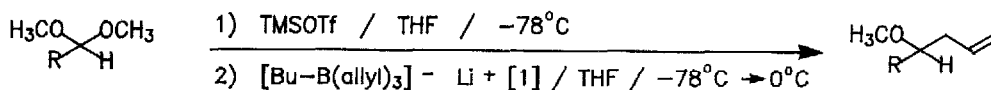
A typical experimental procedure is as follows: To a stirred solution of acetal (1 mmol) in dry tetrahydrofuran (2 mls) at -78°C is added, via syringe, TMSOTf (1.3 mmol) and lithium n-butyltriallylborate (1.2 mmol), formed between n-BuLi (1.2 mmol) and triallylborane (1.2 mmol) in tetrahydrofuran (2 mls) at 0°C. The solution is allowed to warm to 0°C slowly whereupon a solution of H_2O_2 (6 mmol) and KOH (2 mmol) in methanol (3 mls) is added and the mixture left stirring for twenty minutes. Addition of water (10 mls), extraction with ether

(3 x 25 ml), drying ($MgSO_4$) and evaporation of the organic extracts furnishes an oil which affords the homoallylic ether after column chromatography. The yields of the reaction with a variety of acetals are shown in table 1.

TABLE 1

Entry	Acetal	Borate	Product	Yield (%) [a]
1		1		94
2		1		75
3		1		70
4		1		69 [b]
5		1		64
6		1		71
7		2		90
8		3		17
			+	18

a) Isolated yields after column chromatography and based on the acetal as the limiting reagent. b) Two equivalents of both TMSOTf and 1 were used.

$[CH_3(CH_2)_3-B(allyl)_3]^-$ Li$^+$ [1]

Li$^+$ [2]

Li$^+$ [3]
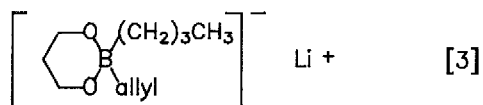
Many of the reactions occurred at –78°C but as a general procedure 0°C proved to be an optimised temperature to terminate the reaction at. Triallylborane could be conveniently prepared from reaction[9] between allylmagnesium chloride and boron trifluoride etherate in ether. The TMSOTf could also be added last to a mixture of the borate and acetal without affecting the allylation, demonstrating that transmetallation between a borate ligand and Lewis acid does not compete with intermolecular carbon-carbon bond formation. $TiCl_4$ proved to be generally unsatisfactory as Lewis acid, promoting reaction with the very reactive benzaldehyde acetal but not with octanal acetal. In the reactions with $TiCl_4$, the solutions took on a dark green colouration with formation of a precipitate, suggesting complex formation between both the borate and Lewis acid. This reaction most likely inhibits activation of the acetal thus preventing allylation. In this regard, the reaction is in stark contrast to Yamamoto's allylation procedure in which $TiCl_4$ functions as a co-ordinator of both acetal and allyl-9-BBN. Another notable aspect is the intermolecular nature of the reaction. Intermolecular reaction[10] (Grignard-type) of organoborates is generally an unattractive procedure for carbon-carbon bond formation, although it can be achieved with reactive electrophiles. Activated orthoformates ($TiCl_4$) have been used as electrophilic partners for alkynylorganoborates[11] via a 1,2-migration reaction, and this current procedure extends the use of activated acetals using organoborate chemistry.

As seen from table 1, yields of the reaction are good. The cyclic acetal of benzaldehyde (entry 6) could also be allylated, opening up the possibility of a diastereoselective allylation procedure[12] using a chiral acetal. In contrast to Hoffmann's successful allylboronate additions to aldehydes, the allylbutyl(1,3-propanediolato)borate(1-) (3) allylated benzaldehyde acetal in competition with a transacetalisation reaction which presumably involves transmetallation of the boron-oxygen bond by TMSOTf as a first step[13]. This reaction supports current thinking[8] on the importance of compatibility between Lewis acid and organometallic in the latter's reaction with an electrophile.

Following this line of thought, attention was focused on the possibility of an intramolecular allylation of an acetal using a proximal hydroxyl group to generate the borate. To this end, hydroxyacetal (4), prepared by condensation between benzaldehyde and the lithium anion of bis(phenylthio)methane followed by transacetalisation ($HgO/BF_3 \cdot Et_2O$/ neopentyl glycol, 38% overall), was reacted with n-BuLi, triallylborane and TMSOTf at –78°C →0°C as usual, Scheme 2. Only starting material was recovered after the normal work up. By comparison, the hydroxyacetal (5), obtained by reduction ($NaBH_4$, MeOH) of pyruvic aldehyde dimethyl acetal, gave a 36% yield of allylated product (6) isolated as the t-butyldimethylsilyl ether as a 1:1 mixture of diastereoisomers, Scheme 2. Intermolecular reaction of the t-butyldimethylsilyl ether of (5) furnished a 33% yield of allylated product as a 1 : 1 ratio of diastereoisomers, Scheme 2. We are currently investigating the scope of the allylation reaction.

SCHEME 2
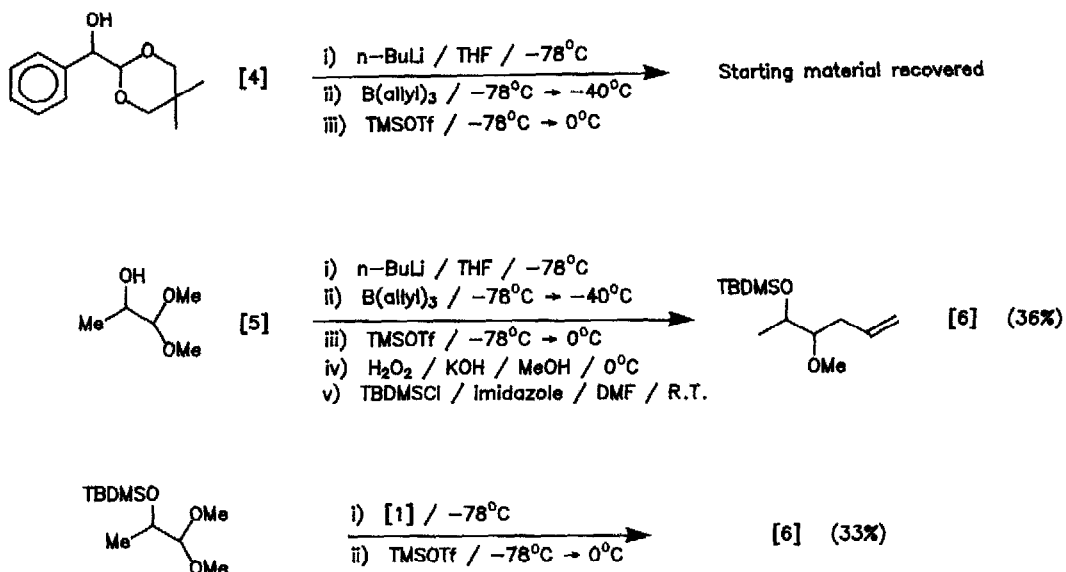
(TBDMSCl = tert-Butyldimethylsilyl Chloride)

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