Stereoselective Synthesis of *E*- and *Z*-Alkenes by the Boron–Wittig[1] Reaction†

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Reactions of dimesitylboryl stabilised carbanions with aromatic aldehydes produce *erythro*-intermediates, which can be trapped by trimethylsilylation or trifluoroacetylation to give products which can yield *E*- or *Z*-alkenes in good overall yields in new and controllable boron–Wittig reactions.

Stereochemical control of the Wittig reaction has been an area of intense interest for many years.[2] Some understanding of the various processes involved has been obtained by investigation of the intermediate phosphetanes[3] and, in the case of the silicon–Wittig (Peterson) reaction,[4] by examination of the reactions of the intermediate β-hydroxysilanes and their salts.[5]

When we introduced the boron–Wittig reactions of carbonyl compounds with dimesitylboryl stabilised carbanions,[1] we expected that the reactions would proceed through anionic oxaboretanes (**3**) and (**4**) (Scheme 1) and that these intermediates would be more sterically compressed than the corresponding phosphorus or silicon analogues. We predicted therefore that *threo*-oxaboretanes (**4**) would be favoured and would undergo the usual *syn*-elimination to yield *E*-alkenes, in contrast to the Wittig reaction itself.

Apparent confirmation of this reasoning was the production of *E*-1-phenylnon-1-ene, (**8aa**)‡ from the condensation of (**1a**) and (**2a**).[1] However, in contrast with the reactions of aromatic ketones, the yield was only 40%, and products due to protiodeboronation[6] and Canizzaro reactions were present.

However, when we condensed either (**1a**) or (**1b**) with aromatic aldehydes at −78 °C or below and then carried out oxidation, also at low temperature, good yields of *erythro*-1,2-diols were obtained.[7] To confirm that the same intermediates are involved in *E*-alkene and *erythro*-1,2-diol product, a divided experiment was done with (**1a**) and (**2a**) to give 1-phenylnon-1-ene (*E*:*Z* 90:10) and 1-phenyl-1,2-dihydroxynonane in 80% yield with an *erythro*:*threo* ratio of 92:8. Alkaline hydrogen peroxide oxidation of organoboranes proceeds with retention of configuration, and hence, in contradiction to our expectation, the *E*-alkene arises from (**3**) and not (**4**)!

This interesting result could be explained by unusually strong stereochemical drift[8] or by the assumption that (**3**) actually exists in the acyclic form (**5**) which undergoes an *anti*-elimination. The latter is unprecedented in direct Wittig reactions, though well precedented in organoboron chemistry.[9] We therefore undertook to trap and characterise the intermediates involved in these boron–Wittig reactions, and then to study their further reactions.

Condensation of (**1a**) and (**2a**) at −78 °C followed by addition of chlorotrimethylsilane gave (**6aa**) as the sole product in 78% isolated yield. Compound (**6aa**) is a white solid, m.p. 81—82 °C, readily handled in air, difficult to hydrolyse, and readily purified by alumina chromatography. It was fully characterised by elemental analysis and the usual physical measurements. In particular in the ^{1}H n.m.r. spectrum it has a $J_{1,2}$ of 11 Hz, this being characteristic of 1,2-*erythro* compounds.[10]

In addition to confirming that *erythro*-intermediates are in fact the sole products of the low-temperature condensation of (**1**) and (**2**),§ this experiment gave us a salt-free, unequivocally

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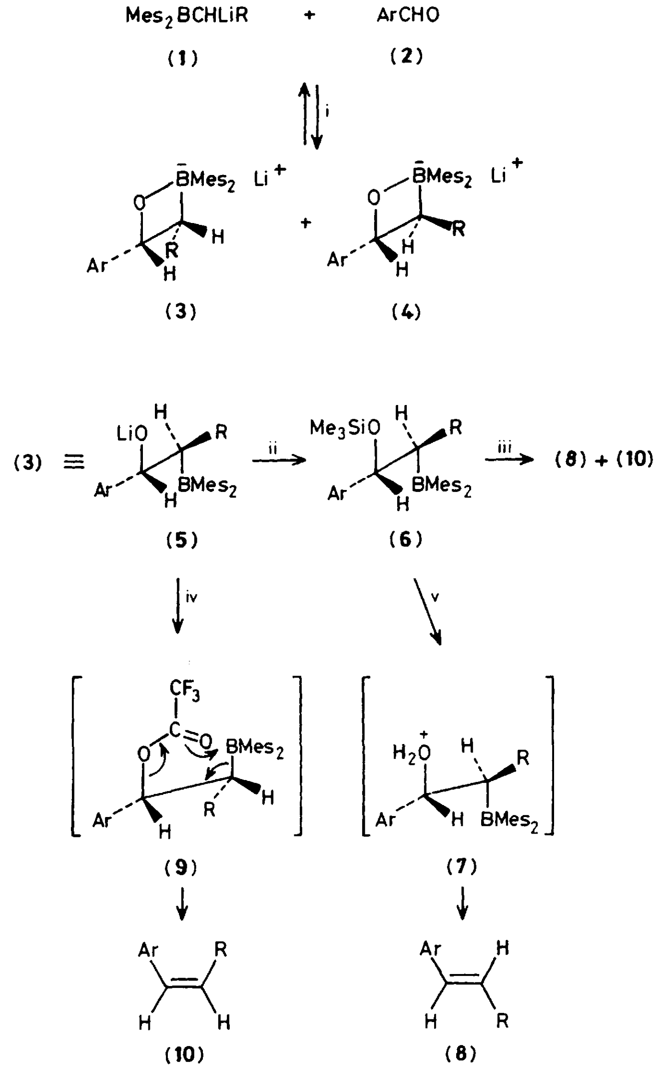
† For Part 10 of the series 'The Dimesitylboryl Group in Organic Synthesis,' see A. Pelter and A. Keating, *Tetrahedron Lett.*, 1986, **27**, 5037.

‡ The nomenclature for products is a combination of that of reactants, *e.g.* (**1a**) + (**2a**) $\twoheadrightarrow$ (**8aa**).

§ We have carried out similar experiments with other aromatic aldehydes and (**1a**) and (**1b**) with similar results.



For anions (1):
a; R = Hept
b; R = Me

For aldehydes (2):
a; Ar = Ph
b; Ar = 4-MeC$_6$H$_4$
c; Ar = 4-ClC$_6$H$_4$
d; Ar = 4-MeOC$_6$H$_4$
e; Ar = 4-O$_2$NC$_6$H$_4$
f; Ar = mesityl
Mes = mesityl

Scheme 1. *Reagents and conditions:* i, −78 °C, tetrahydrofuran; ii, Me$_3$SiCl, −78 °C; iii, 150 °C; iv, TFAA, −110 °C, 2 h; v, aq. HF–MeCN, 30 min, room temp.

acyclic intermediate (**6aa**) for further study. Desilylation of (**6aa**) with tetrabutylammonium fluoride[11] was slow and gave the same product mix (alkene ∼43%) as in the original, untrapped condensation reaction.

Reaction of pure (**6aa**) with aqueous HF in acetonitrile[12] was rapid and gave alkene (73% isolated) with an E : Z ratio of 95 : 5, presumably through the protonated intermediate (**7aa**). If (**6aa**) was not isolated but the desilylation reagent added directly to the reaction mixture containing (**6aa**) the yield of alkene increased to an overall 95% but the E : Z ratio dropped to 84 : 16. Thus in this case there was a deleterious salt effect on stereoselectivity. Hence the isolation of (**6aa**) was optimised (90%) as was its elimination (93%) and the conditions so established became our procedure B (Table 1). In some cases (Table 1, expts. 4 and 6) the one-pot process (procedure A) was stereospecific to give only (**8ad**) and (**8af**) respectively, and procedure B was unnecessary. Substitution of the 4-position of the aromatic aldehyde by electron-withdrawing or -donating groups caused little variation in yield or stereoselectivity. These also proved invariant to the use of a very hindered aromatic aldehyde (expt. 6) or to a variation in the alkyl group attached to boron (expt. 7). Experiment 7 was of particular interest as we had been unable to obtain any alkene at all by use of (**1b**) in the direct boron–Wittig reaction. *Hence our new process to give* E*-alkenes is general* and complements the usual Wittig reaction.

Table 1. Production of alkenes by the boron–Wittig reaction.

			Yield, %[a]			E : Z Ratio[b]		
Expt.	Ar	R	A	B	C	A	B	C
1	Ph	Hept^n	95	84	77	84 : 16	97 : 3	10 : 90
2	p-MeC$_6$H$_4$	Hept^n	86	83	74	89 : 11	95 : 5	4 : 96
3	p-ClC$_6$H$_4$	Hept^n	87	84	73	74 : 26	97 : 3	20 : 80
4	p-MeOC$_6$H$_4$	Hept^n	84	—	76	100 : 0	—	9 : 91
5	p-NO$_2$C$_6$H$_4$	Hept^n	65	74	72	93 : 7	98 : 2	69 : 31
6	Mesityl	Hept^n	80	—	75	100 : 0	—	7 : 93
7	Ph	Me	93[c]	78[c]	77[c]	84 : 16	98 : 2	7 : 93

[a] Procedure A: trapping at −78 °C with Me$_3$SiCl, reaction with HF–MeCN without isolation of (**6**); B: trapping at −78 °C with Me$_3$SiCl, isolation of (**6**), reaction with HF–MeCN; C: trapping at −110 °C with TFAA. Yields are of isolated, characterised product. [b] Determined by g.c. [c] G.c. yield using an authentic sample of β-methylstyrene.

We next attempted to convert (**5**) into Z-alkenes and for this we required a *syn*-elimination. Pyrolysis of (**6aa**) gave a 60% yield of a 59 : 41 mixture of (**10aa**) and (**8aa**). We then argued that acylation of (**5**) should produce derivatives such as (**9**) which might exist in the required conformation as the attraction between the carbonyl oxygen and boron atoms could overcome the unfavourable steric interactions. A novel cyclic elimination process involving boron would then yield Z-alkenes (**10**).

Reaction with benzoyl chloride at −78 °C was slow and reaction with acetyl chloride was complicated by ketene formation. However, addition of trifluoroacetic anhydride (TFAA) at −110 °C to (**5aa**) followed by allowing the temperature to rise to 20 °C gave 77% of alkenes (**8aa**) and (**10aa**) in the ratio of 10 : 90. At −78 °C the ratio was slightly less favourable. Use of 2 mol. equiv. of TFAA gave an E : Z ratio of 45 : 55! Optimum conditions are ratios of (**1**) : (**2**) : TFAA of 1.2 : 1 : 1.2 and these must be carefully observed as even small variations can lead to a lowering of stereoselectivity. The reaction was carried out on a series of aromatic aldehydes (Table 1), with yields somewhat lower than the corresponding reactions to give E-alkenes but generally of comparable selectivity. However, two experiments proceeded with low stereoselectivity. Experiment 3 indicated that elimination may be subject to a strong salt effect (compare 3A and 3B) but it is difficult to understand the low stereoselectivity in the production of (**10ae**) (expt. 5C). Once more it was pleasing to note that when (**1b**) is used, alkene (**10ba**) is produced in good yield.

In summary the carbon–carbon bond forming step in the reactions between aromatic aldehydes and dimesitylboryl stabilised carbanions gives *erythro*-intermediates (**5**), which are the central point for a complex series of reactions which include elimination, protiodeboronation, and reversion to components followed by Canizzaro reactions. However, reaction with chlorotrimethylsilane at low temperature prevents reversion, protiodeboronation, and elimination, and the products give E-alkenes in good yields on treatment with

HF. Trapping (**5**) with TFAA leads directly to *Z*-alkenes by a cyclic *syn*-elimination of the trifluoroacetyl derivative also in good yields. When it is remembered that (**5**) undergoes oxidation to give *erythro*-1,2-diols it is clear that the boron–Wittig reaction is a versatile and controllable process that should be of synthetic use. Further work on the boron–Wittig reactions of other classes of carbonyl compounds is in hand.

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