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HINDERED ORGANOBORON GROUPS IN ORGANIC SYNTHESIS. 14. STEREOSELECTIVE SYNTHESIS OF ALKENES BY THE BORON-WITTIG REACTION USING ALIPHATIC ALDEHYDES

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Abstract. In the presence of HX, carbanions $Mes_2BCHLiR^1$ react with aliphatic aldehydes to give alkenes. The stereochemistry of the product alkene depends upon the nature of HX.

In our previous paper[1] we showed that in the presence of TFAA or NCS, anions (**1**) ($R^1 \neq H$) yield ketones rather than alkenes when reacted with aliphatic aldehydes (**2**). The exception is anion (**1**) ($R^1=H$) (equation 1), which yields methylene derivatives $R^2CH = CH_2$ (**3**, $R^1 = H$), even in the presence of at least one equivalent of TFAA (Table 1).

$$\underset{(1)}{Li^+ R^1\bar{C}HBMes_2} + \underset{(2)}{R^2CHO} \longrightarrow \underset{(3)}{R^1CH = CHR^2} \qquad (1)$$

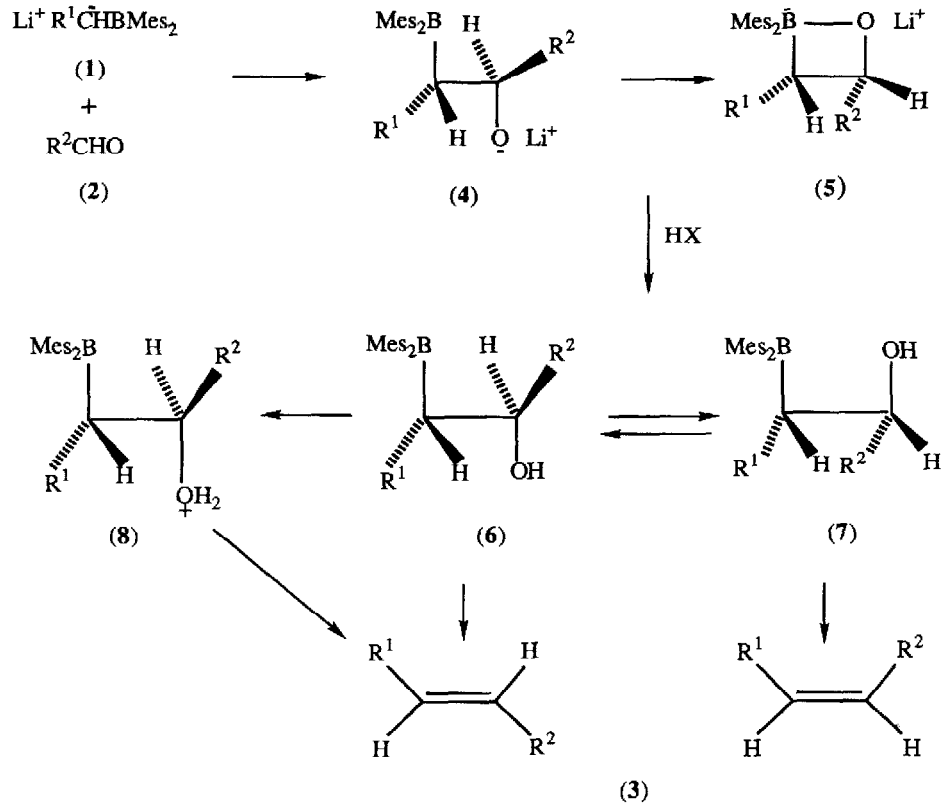
TABLE 1

Reaction of Mes_2BCH_2Li with aliphatic aldehydes, R^2CHO, in the presence of TFAA

Exp. No	R^2	% Yield of $R^2CH:CH_2$[a]
1	Hexyl	91
2	Heptyl	81
3	Nonyl	74
4	Chx[b]	76
5	Bu(Et)CH	79[c]

a) All yields in all Tables are of isolated, purified products unless otherwise stated.
b) Chx = cyclohexyl. c) g.c. yield.

In all cases except when $R^1 = H$, the condensation of anions (**1**) with aliphatic aldehydes gives only poor or no yield of alkene with or without TFAA being present. If ketone production be due to hydride transfer from negatively charged intermediate(s) (**4**)/(**5**)[1] (Scheme 1) then discharge of the anion should inhibit that pathway and allow elimination to yield alkene.



Scheme 1

The obvious candidate for discharge of (**4**)/(**5**) is a protic acid, HX. Of course, it is unusual for reactions of organolithium reagents to be carried out in the presence of a protic acid, but examples exist and we have previously shown that polycondensation of an aldehyde with a carbanion may be controlled by the addition of water.[2] We therefore used (**1**) (R^1 = Hept), which had given no alkene at all with TFAA,[1] for condensation of (**1**) with aliphatic aldehydes containing an acid, initially acetic acid.* *In practise this process gave alkenes in acceptable yields, with no ketone* (Table 1). We believe that the use of protic acids to discharge intermediates produced by the condensation of carbanions with carbonyl compounds may prove widely applicable.

*Subsequent to this work we found brief mention of the use of acetic acid to affect the stereochemistry of condensations of $(MeO)_2P(O)CH_2CO_2Me$/LDA[3].

TABLE 2

Condensation of $Mes_2BCHLiHept$ with R^2CHO in the presence of CH_3CO_2H (1 equiv).

Exp. No	R^2	Yield of (3) (R^2 = Hept) %	E : Z^a
6	Me	52	42 58
7	Et	75	49 51
8	Hept	77	65 35
9	Me_2C	87	69 31
10	Chx	83	10 90
11	Bu^t	79	0[b] 100

a) Ratios were obtained by g.c; response factors were determined using authentic alkenes produced by the Wittig reaction and its Schlosser modification[4] b) Not available by Schlosser modification.

The reaction is not particularly stereoselective, except for hindered aldehydes when *Z*-alkenes predominate (exp. 10, 11). Either the initial condensation is not stereoselective, or there is steric drift,[5] or elimination is both *anti*- (from (**6**)) and *syn*- (from (**7**)).

In the latter event, further protonation to give (**8**), which would take up a conformation such that the protonated hydroxyl group and the electron-deficient boron atom were as far apart as possible, should favour *anti*-elimination to give *E*-alkene. We therefore studied the effect of the nature of HX on the reaction (Table 3).

TABLE 3

Condensation of $Mes_2BCHLiHept$ with R^2CHO in the presence of HX

Exp. No.	R^2	Acid (equiv)	% Yield	E : Z
12	Et	$MeCO_2H$ (1)	75	49 51
13	"	$MeCO_2H$ (2.5)	73	61 39
14	"	CF_3CO_2H (2.5)	71	70 30
15	"	CF_3SO_3H (2.5)	66	78 22
16	"	HCl (2.5)	68	84 16
17	"	HCl (5)	57	86 14
18	Bu^t	HCl (1.2)	72	92 8

As the acid becomes stronger the amount of *E*-alkene increases, as would be expected on the argument given, if the intermediate (**6**) were to have the stereochemistry shown in Scheme 1 and *anti*-elimination predominates, as for aromatic aldehydes.[6] The most striking change came with the use of pivaldehyde (compare exp. 11 and 18)[7]. For this case , in our hands, even the Schlosser modification of the Wittig reaction gave 100% of *Z*-alkene! *It is also important that use of 1-2.5 equiv. of even a strong acid does not materially lower the yield of alkene.*

Both the condensations and the effect of acid on the stereochemistry of the product alkenes are general. Some further results are summarised in Table 4.

TABLE 4

Condensations of $Mes_2BCHLiR^1$ and R^2CHO in the presence of HX

Exp. No.	R^1	R^2	HX (equiv.)	Yield (%)	*E* : *Z*
19	CH_3	$PhCH_2$	$MeCO_2H$ (1)	74	14 : 86
20	"	"	CF_3SO_3H (1.2)	69	93 : 7
21	"	Chx	$MeCO_2H$ (2)	67	63 : 37
22	"	"	HCl (1.2)	72	97 : 3
23	"	Bu(Et)CH	$MeCO_2H$ (1)	52	24 : 76
24	"	"	CF_3SO_3H (1)	57	95 : 5
25	"	Oct	$MeCO_2H$ (1)	77	44 : 56
26	"	"	CF_3SO_3H (1)	48	89 : 11
27	Et	Bu(Et)CH	$MeCO_2H$ (1)	73	4 : 96
28	"	"	CF_3SO_3H (1.2)	59	92 : 8
29	Pr^n	"	$MeCO_2H$ (1)	74	4 : 96
30	"	"	CF_3SO_3H (1)	59	92 : 8
31	"	Chx	$MeCO_2H$ (1)	61	17 : 83
32	"	"	HCl (1)	64	95 : 5

It can be seen (exp. 18, 20, 22, 24, 26, 28, 30, 32) that in the presence of strong acids the products are overwhelmingly the *E*-alkenes and in this way the reaction complements the Wittig-reaction. It is also an acceptable alternative to the Schlosser process,[4] which in our hands frequently gave mixtures of *E*- and *Z*-alkenes, and in one case, as mentioned previously, gave no *E*-isomer at all.

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