Allene Synthesis via Boron-stabilised Alkenyl Carbanions

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A new allene synthesis involving the boron-Wittig reaction of aldehydes with boron-stabilised carbanions is disclosed and its scope and limitations are explored.

We have previously demonstrated the versatility of the boron-Wittig reaction for the synthesis of *E*- and *Z*-alkenes,^{1,2} erythro-1,2-diols³ and ketones.⁴ We have also reported on the ready production of boron-stabilised alkenyl carbanions, and explored their protonation and alkylation.⁵ We have now found that boron-stabilised alkenyl carbanions undergo a facile boron-Wittig reaction with aldehydes to give allenes, according to eqn (1).

$$R^{1}C \equiv CSnMe_{3} \xrightarrow{i,ii} \left[R^{1}CH = \overrightarrow{CBR}_{2}^{2} \right] \xrightarrow{iii,iv} R^{1}CH = C = CHR^{3}$$
(1)
1 2

Reagents: i, R2BH; ii, MesLi; iii, R3CHO; iv, TFAA.

We used 1-trimethylstannyloct-1-yne and 1-trimethylstannyl-2-phenylethyne as typical starting materials. Our results are given in Table 1.

It is clear that the carbanions derived from aryl- or alkyl ethynes behave similarly with either aromatic or aliphatic aldehydes to give allenes 2. Thus the reaction is reasonably general. Substitution of an electron-withdrawing 4-nitro group enhances the reaction (expt. 8, 9) but a far longer reaction than usual is required for 4-methoxybenzaldehyde (expt. 6, 7). The presence of a chlorine or a bromine atom on the 4-position is deleterious to the reaction (expt. 10–13), presumably due to metal-halogen exchange.

Aliphatic aldehydes generally give allenes in acceptable yields, and are not subject to great steric inhibition (expt. 14–22). However, the very readily enolisable phenylacetaldehyde gave low yields (expt. 23–24).

In an effort to overcome the latter restriction, anhydrous salts were added to the solution of the lithio-carbanion. The best salt proved to be cadmium chloride, which strongly enhanced the yields of products from phenylacetaldehyde and led to some improvement of yield in most other cases tried (Table 1).

Thus, a new and general process involving overall the condensation of alk-1-ynes with aldehydes to give 1,3-disubstituted allenes has been uncovered, and this once again illustrates the versatility of the boron-Wittig reaction. Analogies are few, one such being the four-step conversion of alkynylphosphonates into allenes in undisclosed overall yields.⁶ Another is the condensation of 1-lithio-1-triphenylsilylethene with aldehydes, followed by chlorination and elimination to give mono-substituted allenes in moderate yields.⁷

Typical Reaction: Preparation of 1,3-Diphenylpropa-1,2diene.—A freshly prepared solution of 1-trimethylstannyl-1dimesitylboryl-2-phenylethene (4 mmol) in THF⁵ was cooled to -78 °C before dropwise addition of a THF solution of mesityllithium (6 mmol)⁸ with constant stirring. The resultant dark solution was stirred at -78 °C for 30 min before addition of a solution of benzaldehyde (0.918 g, 8.55 mmol) in THF (5 cm³), followed by TFAA (1.80 g, 10 mmol) in THF (5 cm³). The

	R ¹	R ²	Yield (%) of 2 ^{<i>a</i>}		
Expt.			R ³	GC	Isolated
1	Ph	Mes ^b	Ph	72 (75) ^c	61
2	Hex	Chx ^d	Ph	71 (76)	63
3	Hex	Mes	Ph	76	65
4	Ph	Mes	4-MeC ₆ H₄	67	49
5	Hex	Chx	4-MeC ₆ H ₄	69	52
6	Ph -	Mes	4-MeOC ₆ H ₄	41 (52) ^e	22
7	Hex	Chx	4-MeOC ₆ H ₄	50 (59) ^e	29
8	Ph	Mes	4-O ₂ NC ₆ H ₄	74	58
9	Hex	Chx	$4-O_2NC_6H_4$	82	66
10	Ph	Mes	4-BrC ₆ H ₄	7 (9)	
11	Hex	Chx	$4-BrC_6H_4$	4 (7)	
12	Ph	Mes	4-ClC ₆ H₄	11 (10)	
13	Hex	Chx	4-ClC ₆ H ₄	10 (6)	
14	Ph	Mes	C ₉ H ₉	64 (72)	51
15	Hex	Mes	C,H,	74	59
16	Hex	Chx	C ₉ H ₉	68 (75)	61
17	Ph	Mes	Me ₂ CH	71	57
18	Hex	Chx	Me ₂ CH	73	50
19	Ph	Mes	Chx	75	56
20	Hex	Mes	Chx	76	53
21	Ph	Mes	Me ₃ C	61	46
22	Hex	Chx	Me ₃ C	57	48
23	Ph	Mes	PhČH ₂	15 (36)	4
24	Hex	Chx	PhCH ₂	12 (44)	4

^a All yields are for the overall process, and are based on starting alkynes 1. ^b Mes = mesityl (2,4,6-trimethylphenyl). ^c Figures in parentheses are GC yields after addition of CdCl₃ to the lithio-anion. ^d Chx = cyclohexyl. ^e Yields after stirring at room temperature for 12 h.

dark colour faded after *ca.* 10 min and the reaction mixture was allowed to warm to room temperature with stirring and then stirred for a further 30 min. Addition of moist THF was followed by ether extraction and drying (MgSO₄). GC analysis, by comparison with a pure sample of 1,3-diphenylpropa-1,2-diene⁹ showed that this compound was present in 72% yield. Purification was accomplished by chromatography in subdued light on neutral silica using a 1:1 mixture of diethyl ether and light petroleum (b.p. 30–40 °C). This gave pure 1,3-diphenylallene (0.452 g, 61%) identical in all respects with a pure sample.

Acknowledgements

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Table	1	Preparation	of	allenes	from	1-trimethylstannylalkynes
accord	ing	to eqn (1)				

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