Stereospecific Synthesis of Allyl Amides by the Cyanoborate Process

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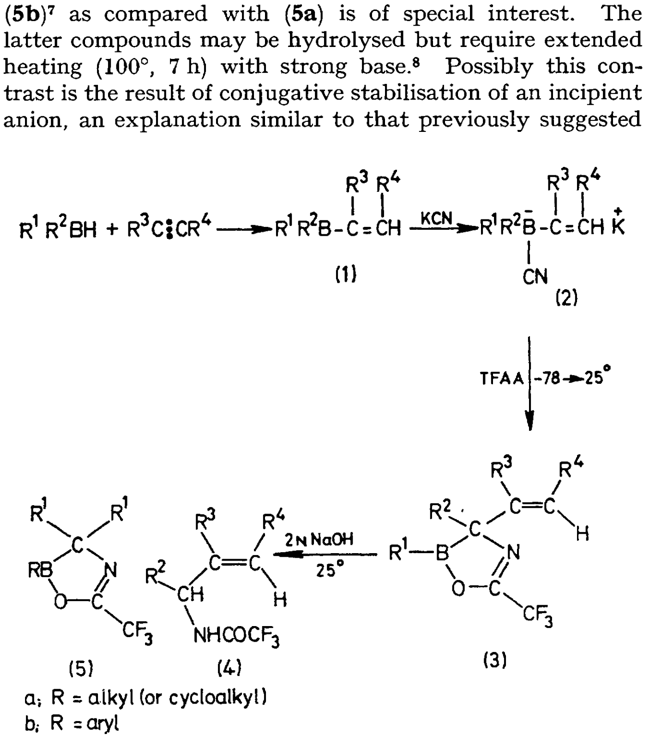
Summary Vinyl groups are shown to migrate readily, with retention of configuration, in the cyanoborate process leading to intermediates that are easily hydrolysed to sterically defined allyl amides.

A potential advantage of the use of cyanide anion as a one carbon insertion unit for organoboranes[1] as compared with carbon monoxide[2] is that the nitrogen atom of the cyanide could be available for incorporation into the migration products. We here report that dialkylalkenylboranes (**1**) made by the stereospecific hydroboration of an alkyne[3] with the readily available dialkylboranes,[4] easily form cyanoborate salts (**2**) which undergo migration on treatment with trifluoroacetic anhydride (TFAA) at low temperatures to yield the intermediate (**3**). These substances are hydrolysed at 25° with 2N NaOH to give the allyl amides (**4**) (Scheme).

The vinyl group migrates with retention of configuration as shown by decoupling of the ^{1}H n.m.r. spectra, and almost certainly is the first group to migrate. We have previously shown that the ease of migration of alkyl groups in all three stages of the cyanoborate process is $p > s > t$[5] and this was utilised so that there should be no wastage of useful alkyl groups. 2,3-Dimethyl-2-butylborane (thexylborane)[6] was used to make fully unsymmetrical boranes. Despite the bulky nature of this group which leads to a marked intensification of the conditions required for carbonylation,[2] no extra difficulties were encountered, even when the migrating group was also large [*c.f.* Table, expt. (vi)]. In no case was migration of a thexyl group observed (Table). The Table shows that alkenyl groups derived from internal alkynes migrate efficiently as do the secondary alkyl groups and the primary group tried.



Scheme

The ready hydrolysis of the intermediates (**3**) and also (**5b**)[7] as compared with (**5a**) is of special interest. The latter compounds may be hydrolysed but require extended heating (100°, 7 h) with strong base.[8] Possibly this contrast is the result of conjugative stabilisation of an incipient anion, an explanation similar to that previously suggested for the ready hydrolysis of benzylborane derivatives.[9] The anion however would never be fully developed as

TABLE. Formation of allyl amides from dialkylvinylboranes

		Organoborane (1)			Product (4)			
	R^1	R^2	R^3	R^4	R^2	R^3	R^4	Yield/%^{a}
(i)	Cyclohexyl	Cyclohexyl	H	Bu^n	Cyclohexyl	H	Bu^n	90
(ii)	„	„	Et	Et	„	Et	Et	76^b
(iii)	2-Methylcyclohexyl	*trans*-2-Methylcyclohexyl	H	Bu^n	*trans*-2-Methylcyclohexyl	H	Bu^n	63
(iv)	Thexyl	Cyclopentyl	„	„	Cyclopentyl	„	„	83
(v)	„	Cyclohexyl	„	„	Cyclohexyl	„	„	82
(vi)	„	„	Et	Et	„	Et	Et	77
(vii)	„	Isobutyl	H	Bu^n	Isobutyl	H	Bu^n	67^b
(viii)	„	„	Et	Et	„	Et	Et	74^b

[a] Isolated yield based on organoborane. [b] Hydrogen peroxide oxidation after hydrolysis.

shown by the regio- and stereo-specificity of the reaction. Allylic rearrangement[10] cannot be occurring as otherwise enamides would result.

The trifluoroacetamides produced can be hydrolysed to the corresponding amines with retention of configuration† and hence a wide variety of allyl amides with known and predictable spatial characteristics becomes available for synthetic and mechanistic studies and as polymer precursors.[11]

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