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A NEW ROUTE TO DI- AND TRISUBSTITUTED OLEFINS VIA LITHIUM TRIALKYLALKYNYLBORATES

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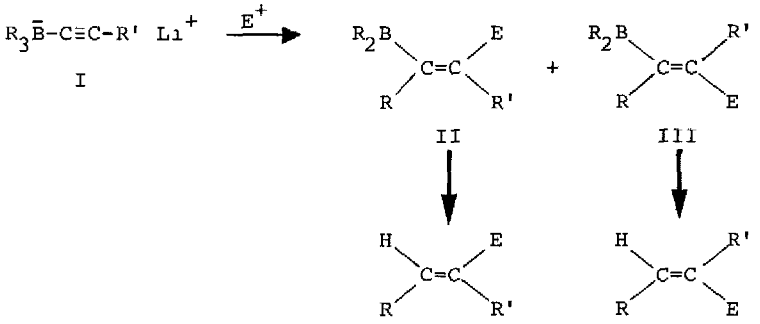
The rearrangement of trialkylalkynylborate salts (I) has been induced by a variety of electrophiles, and the stereochemical outcome is a complex function of several factors, including the nature of the electrophile, the type of organoborane, and the solvent.[1-5] However, direct protonation of I invariably produces a mixture of cis- and trans-vinylboranes (II and III), which leads ultimately to cis-trans olefin mixtures (E = H).[1,6,7]

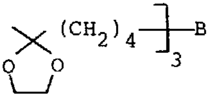
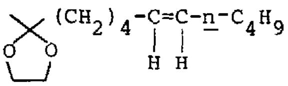


We have investigated the reactions of I with several electrophiles (R_nMX) of Groups III, IV, and VI with a view of forming specifically-substituted vinyl intermediates (II or III, E = MR_n), and determining if the boron-carbon and "metal"-carbon bond can be exploited separately.

Reaction of 1-lithiohexyne (from 5 mmol 1-hexyne and 5 mmol $\underline{n}$-C_4H_9Li (Alfa, hexane)) in 7 ml THF with 5 mmol Et_3B (Alfa) at 0° for 1 hour produced borate I (R = Et, R' = $\underline{n}$-C_4H_9). Then tributyltin chloride (5 mmol, Alfa) was added at room temperature, and the mixture stirred for 1 hour. The precipitate of LiCl was filtered, and solvent removed in vacuo. Mass spectral analysis of the remaining pale amber residue indicated a parent ion, m/e 470 (^{11}B, ^{120}Sn). Oxidation (3N NaOAc, 30% H_2O_2) of the original crude mixture produced 3-octanone (88%), and hydrolysis (formic acid) produced a single olefin shown (vpc, ^1H nmr) to be cis-3-octene (82%). Other hydrolytic media - including HOAc, $EtCO_2H$, pivalic acid, H_2O, aq. NH_4Cl, HCl, CH_3OH and thiophenol - proved less efficient and produced varying amounts (up to 15%) of 3-ethyl-3-octene, the product of "double migration".[8,9]

Thus, the reaction of borates I with Bu_3SnCl specifically produces the isomer in which the migrating group and entering electrophile are trans (II, E = $SnBu_3$). Yields of other olefins (5 mmol scale, HCO_2H hydrolysis) are shown in the Table.

Table

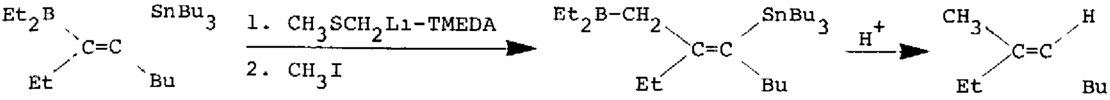
R_3B	R'C≡CH	Olefin[(a)]	Yield[(b)]
Et_3B	hexyne	cis-3-octene	82
Bu_3B	hexyne	cis-5-decene	79
Et_3B	heptyne	cis-3-nonene	77(71)
Et_3B	phenylacetylene	cis-1-phenyl-1-butene	73
Hex_3B	hexyne	cis-5-dodecene	89(70)
	hexyne		(45)

(a) satisfactory ir, pmr, mass spectra and/or vpc comparison with known olefins.

(b) yields in parentheses are isolated, pure material.

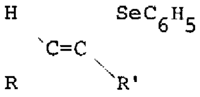
Presumably the bulk of the tributyl tin moiety restricts the olefin synthesis to the use of less branched borates. For example, no olefin was observed with disiamylheptylhexynyl borate, disiamyl-1-hexenylhexynyl borate, (tris)-2-methylpentylhexynyl borate, tricyclohexylhexynyl borate or triethyl-t-butylethynyl borate. Dicyclohexylheptylhexynyl borate gave a mixture of two olefins (50%), 1-cyclohexyl-1-hexene and 5-tridecene, in a 1 3 ratio respectively.

The intermediate mixed vinylorganometallic also serves as a precursor to tri-substituted olefins. Reaction of II (R = Et, R' = n-C_4H_9, E = $SnBu_3$) with thiomethoxymethyllithium-TMEDA[10] (2 equiv dimethyl sulfide, 1 equiv n-$C_4H_9Li\cdot$TMEDA), produced Z-3-methyl-3-octene (52%).



In contrast to Bu_3SnCl, electrophiles such as Et_2AlCl and C_6H_5SCl react with salts I (R = Et, R' = n-C_4H_9) in a non-stereospecific fashion, producing intermediates (presumably II and III, E = $AlEt_2$ and SC_6H_5, respectively) which form cis-trans mixtures on hydrolysis.

Interestingly, reaction of I with C_6H_5SeCl followed by acid hydrolysis gives rise exclusively to vinylselenide IV. The utility of these reagents will be reported separately.



IV

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