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THE ALKYLATION OF THEXYLDIALKYLALKYNYLBORATES - A NEW STEREOSELECTIVE TRISUBSTITUTED OLEFIN SYNTHESIS.

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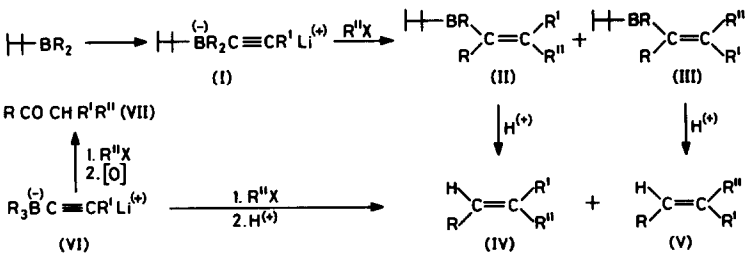
The major product from the alkylation of thexyldialkylalkynylborates is the vinylborane in which the groups derived from the alkylating agent and from migration from boron to carbon are cis to each other.

We have recently defined conditions for the alkylation of trialkylalkynylborates (VI) leading to intermediates which on oxidation give ketones (VII) in excellent yields (see Scheme).[1] The alkylation/migration process however is not stereospecific, and hydrolysis gives mixtures of the olefins (IV) and (V).[1,2,3]



(a) R = R' = Bu^n, R" = Me.
(b) R = R' = Bu^n, R" = Et.
(c) R = R' = Hex^n, R" = Me.
(d) R = R' = Hex^n, R" = Et.
(e) R = R' = Hex^n, R" = Prop^n.
(f) R = Hex^n, R' = Prop^n, R" = Hex^n.
(g) R = Bu^n, R = Amyl^n, R" = Me.
(h) R = R' = Hex^n, R" = Allyl.
(i) R = R' = Hex^n, R" = Benzyl.
(j) R = R' = Hex^n, R" = 4-Pyridinyl.

SCHEME

We now report that alkylation of thexyldialkylalkynylborates (I), readily prepared by the action of lithium alkynyls upon thexyldialkylboranes, is a stereoselective process, which yields olefins (IV) and (V) in a ratio of ca. 9:1 (see Table).

In view of the report[4] that protonation of the salts (I) derived from phenylacetylene (R' = Ph) gives (V) (R" = H) exclusively, whereas our preliminary results indicated that our major component was (IV)(R" = Alkyl), the structures assigned were carefully verified.

Table

Alkynylborate (I) $H-R_2BC\equiv CR'$		Alkylating Agent R''X	Time (hrs)	Temp.	% Yield[1] (IV)+(V)	(IV):(V)
R	R'					
n-Bu	n-Bu	$(CH_3)_2SO_4$	1	$-78^{\circ}\rightarrow 20^{\circ}$	74	83:17
n-Hex	n-Hex	"	"	"	84	85:15
"	"	FSO_2OMe	"	"	55	86:14
"	"	$Et_3\overset{+}{O}BF_4$	"	"	88	91:9
n-Bu	n-Bu	"	"	"	82	88:12
n-Hex	n-Hex	$CH_2{=}CH\,CH_2Br$	96	20°	70	84:16
"	"	$C_6H_5CH_2Br$	120	"	70	92:8
"	"	n-Propyl I	180	40°	69	89:11
"	n-Prop	n-Hexyl I	"	"	68	83:17
"	n-Bu	$N\text{-}PyCOCH_3\overset{+}{Cl}^-$	2	$-78^{\circ}\rightarrow 20^{\circ}$	72	88:12

[1] Isolated, purified product.

Methylation gave (IV) and (V) (a), (c) and (g) arising from the corresponding vinylboranes (II) and (III). The main component (IVa) had a vinyl methyl group which absorbed at τ 8.45, $J_{allylic}$, 0.5 Hz, the minor component showing this group at τ 8.37, J 1.1 Hz. Similarly (IVc) had a signal at τ 8.46, J 0.5 Hz, compared with the minor component (Vc) at τ 8.37, J 1.2 Hz. An authentic sample[¤] of (Vg)[5] exhibited a peak at τ 8.37, J 1.1 Hz, identical with our minor component, the major fraction (IVg) absorbing at τ 8.45, J 0.5 Hz. These results correlate exactly with the many analogies recorded.[6,7,8] Our minor isomer (Vg) ran identically with the authentic sample on g.l.c.

To correlate the products of ethylation, propylation, etc. with the methylation products we adopted the well known g.l.c. technique of plotting log α vs. carbon number,[9] where α is $t'_R/t'_{R\ dodecane}$ and $t'_R = t_R - t_{air}$. Such plots are linear for a particular homologous series at isothermal column temperatures and are widely employed for organic analysis.[10] For the present work the series starting with (IV) and (V) (a) and (b), and also the series starting with (IV) and (V) (c), (d) and (e) were used, under conditions relying entirely upon boiling point separation.[Ø] This situation has been given extensive theoretical treatment. The series (IV) and (V) should lie on separate straight lines which

[¤] We thank Professor Yamamoto for supplying us with this compound.

[Ø] The full chromatographic work will be reported separately.

converge when R'=R", the technique being so accurate that it has been used to correct literature data.[11,12] In fact each series gave the two straight lines expected, all the major components having the longer retention times. Thus the first points having been assigned from n.m.r. data, and with authentic samples of (Vg) and (IVb)[*] (made by the method of Normant[13]) correlating exactly as expected, there could be no doubt as to the consistency shown in the alkylation reactions.

The major components in all cases were the isomers (IV) in which the migrating group and the group introduced by alkylation are on the same side of the double bond.

The reaction of tri-n-hexyloctynylborate (VIb), ($R=R'=hex^n$) with n-propyl iodide gave E- and Z-, 7-n-propyltetradec-7-ene in a ratio of 65:35. When lithium tri-n-hexylpentynylborate (VI), $R = hex^n$, $R' = prop^n$) reacted with hexyl iodide the same compounds were obtained with an E:Z ratio of 35:65. Similar inverse ratios were carried over to the corresponding thexyldialkylalkynylborates when ratios of E:Z of 89:11 and 17:83 were obtained from the propylation and hexylation reactions respectively. Thus, in the main part, the alkylation cannot be controlled by the stability of an equilibrating cation.[4]

Allylation of salts (VI) gave 65:35 mixtures of olefins (IVh) and (Vh), but when the salts (I) were used this ratio became 84:16. The structures were assured by reduction of the terminal olefin group with di-2-methylcyclohexylborane to give the known propyl compounds (IVe) and (Ve).

A similar proportion of benzylated products was obtained (see Table) but in this case neither g.l.c. criteria nor direct correlation are available. The benzyl methylene group of the major isomer shows at τ 6.68, that of the minor at τ 6.76. The corresponding peaks of the allylated olefins (IVh) and (Vh) show at τ 7.30 and 7.47 and this is taken to indicate that benzylation has proceeded in the same manner as other alkylations.

We have previously reported that the salts (VI) attack N-acetylpyridinium chloride at the 4-position in a non-stereospecific way.[14] The ratio of the two readily separable olefins obtained from attack on (I) was 88:12. The major isomer showed a vinyl proton at τ 4.57, t.t. J_1 7.5 Hz, J_2 1.2 Hz whilst the minor product had this proton at τ 4.21 as a broadened triplet, J 7.0 Hz. The cis-proton of 4-vinylpyridine shows at τ 4.10 compared with the trans-proton at τ 4.57.[15] Our major isomer is clearly (IVj), even this complex alkylation having proceeded exactly as did the simple ones.

We shall report separately on the stereospecificity of other complex alkylating agents, including the α-halo-ketones and esters previously noted.[16]

[*] We thank Professor Normant for this sample.

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