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ORGANOBORANES
XIII. THE MERCURATION OF VINYLBORANES. A CONVENIENT STEREOSPECIFIC PROCEDURE FOR THE CONVERSION OF ACETYLENES INTO VINYLMERCURY SALTS VIA HYDROBORATION–MERCURATION

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SUMMARY

Vinylboranes derived from terminal and internal acetylenes via hydroboration with dicyclohexylborane undergo an instantaneous reaction with mercuric acetate at 0° to give the corresponding vinylmercury acetates. Treatment with aqueous sodium chloride provides a convenient stereospecific synthesis of vinylmercury chlorides. This reaction is accompanied by a "side reaction" leading to cyclohexyl olefins and elemental mercury. The extent of this "side reaction" is apparently determined by the steric requirements of the vinylborane. Greater than 85% isolated yields of isomerically pure *trans*-vinylmercury chlorides can be obtained from terminal acetylenes. The yields of isomerically pure *cis*-vinylmercury chlorides from internal acetylenes are somewhat lower.

INTRODUCTION

The mercuration of organoboranes derived from terminal olefins provides a highly convenient synthesis of primary alkylmercuric salts[1] (eqn. 1). Organoboranes containing secondary alkyl groups are much less reactive[2]. These reactions

$$(RCH_2CH_2)_3B + 3\,Hg(OAc)_2 \rightarrow 3\,RCH_2CH_2HgOAc \qquad (1)$$

exhibit all the characteristics of an electrophilic substitution reaction. Since aryl and vinyl groups are generally much more reactive towards electrophilic substitution than alkyl groups, we were interested in studying the mercuration of vinylboranes, now readily available via hydroboration of acetylenes, in the hope of providing a possible general route to vinylmercurials of established stereochemistry.

There are scattered reports of the conversion of vinylboron compounds to organomercurials. Thus, *cis*- and *trans*-1-propenyl-[3], ω-styryl-[4] and (*trans*-2-chlorovinyl)mercury[5] halides have been obtained from the corresponding vinylboronic acids upon treatment with mercuric halides (eqn. 2). It has also been reported that

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trivinyl-, tri-1-hexenyl-, and tri-1-octadecenylboranes react with mercuric oxide or

$$\mathrm{RCH{=}CHB(OH)_2 + HgX_2 \rightarrow RCH{=}CHHgX} \qquad (2)$$

mercuric chloride in water to give the corresponding divinylmercury compounds[6]. Similarly, treatment of trivinylborane with mercuric chloride in the presence of divinylboron chloride reportedly gives divinylmercury[7]. Even a *gem*-dimercurial has been obtained from a vinylboron ester[8] (eqn. 3). These reactions apparently proceed

$$\mathrm{(CH_3)_2C{=}C[B(OCH_3)_2]_2 + 2\,HgCl_2 \rightarrow (CH_3)_2C{=}C(HgCl)_2} \qquad (3)$$

with retention of configuration in the group being transferred[3,5]. Unfortunately, experimental details on most of these reactions are lacking.

Until the discovery of hydroboration in 1956, the conversion of the vinylboranes to vinylmercurials was of little practical synthetic utility due to the fact that the vinylboranes must themselves first be prepared from the corresponding organolithium or magnesium compounds. Since the vinylmercurials could be obtained directly from these reagents, there was no advantage to using the intermediate vinylborane. Now, however, vinylboranes of known stereochemistry are readily available via hydroboration of acetylenes and we have established that they are extremely valuable for the convenient synthesis of vinylmercurials of known stereochemistry.

RESULTS AND DISCUSSION

Synthesis of vinylboranes

Trivinylboranes are readily available through the reaction of internal acetylenes and "borane"[9] (eqn. 4). However, the reaction of "borane" with terminal acetylenes leads to preferential dihydroboration of the acetylene[9]. The use of hydroborating agents of large steric requirements, such as disiamylborane [bis(3-methyl-2-butyl)borane] or dicyclohexylborane, permits the conversion of both internal and terminal acetylenes to the corresponding vinylboron compounds in essentially quantitative yields[9,10] (eqn. 5). The boron adds to the less hindered position of the triple bond in unsymmetrical internal acetylenes[10]. The ability of the hydroboration reaction to accommodate functional groups[11] and the high stereochemical purity of the result-

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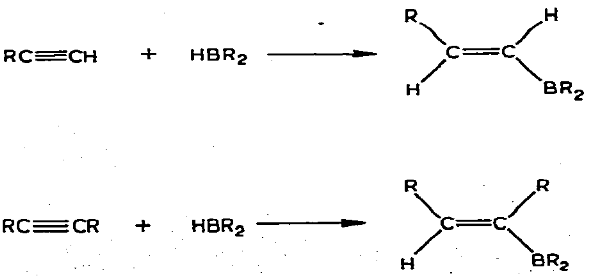

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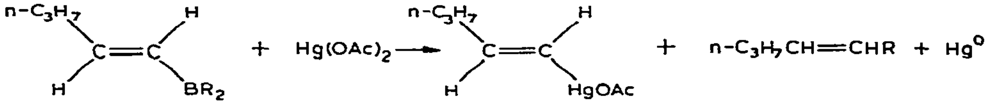
ing vinylboranes[10] offer many advantages over use of the standard vinyllithium or magnesium routes to the vinylmercurials[12]. Consequently, a systematic study of the reaction of vinylboranes with mercuric salts was undertaken to help extend the hydroboration–mercuration reaction to the synthesis of vinylmercuric salts.

TABLE 1

MERCURATION OF *trans*-1-PENTENYLDIALKYLBORANES



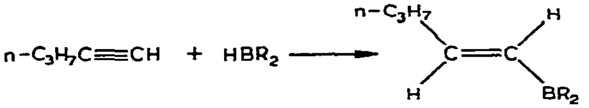
Alkyl in *trans*-1-pentenyl-dialkylborane	Temp. (°C)	Olefin [a](%) n-$C_3H_7CH{=}CHR$	*trans/cis*	Hg° (%)
Cyclohexyl	30	20	5	14
Cyclohexyl	−78	30	1	19
Siamyl	30	52		55
Siamyl	−78	66		73

[a] GLC analysis.

Mercuration of vinylboranes.

The mercuration of tri-*cis*-3-hexenylborane (from 3-hexyne and "borane")[9] with mercuric acetate (3 equivalents) and subsequent work-up with aqueous sodium chloride resulted in the formation of considerable amounts of elemental mercury and no solid *cis*-3-hexenylmercury chloride could be isolated. We chose then to study the mercuration of vinylboranes derived from dialkylboranes.

1-Pentyne was chosen as a typical acetylene and treated with both disiamyl- and dicyclohexylboranes (eqn. 6). Treatment of the resulting vinylboranes with mercuric chloride or mercuric oxide (followed on work-up by hydrochloric acid) leads to immediate reaction and formation of a high melting white precipitate. This solid was not, however, the expected *trans*-1-pentenylmercury chloride. Mercuric acetate also gave an instantaneous reaction even at −78°. Treatment with aqueous sodium chloride provided an excellent yield of *trans*-1-pentenylmercury chloride. This reaction was accompanied, however, by a "side reaction" resulting in metallic mercury and coupled olefin (eqn. 7). The extent of this "side reaction" varied slightly from run to



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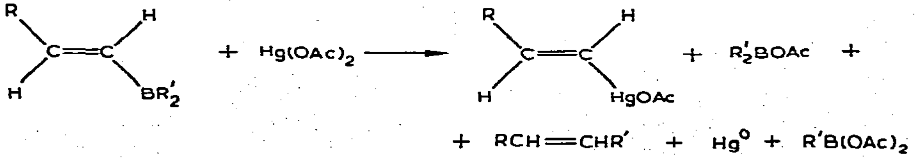

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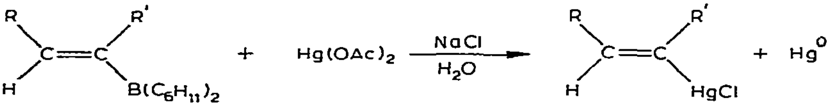
run and appeared to depend upon the manner of addition of the mercuric acetate. The yields of olefin and mercury were generally comparable and depended greatly on the dialkylborane used in the reaction. The more sterically hindered disiamylborane gave 2,3-dimethyl-4-octene and elemental mercury as the predominant products. Lowering the temperature of the reaction appeared to lead to increasing amounts of olefin and mercury and altered the stereochemistry of the olefin formed. Some typical results are listed in Table 1.

Clearly, dicyclohexylborane is the superior reagent for the synthesis of vinylmercurials. In order to determine the scope of this reaction for the synthesis of vinylmercury salts, we hydroborated a number of representative acetylenes with dicyclohexylborane. The resulting vinylboranes were treated with mercuric acetate at 0°. Any mercury formed was filtered from the reaction mixture and the remaining solution was treated with aqueous sodium chloride. The yields of vinylmercury chlorides

TABLE 2

MERCURATION OF DICYCLOHEXYLVINYLBORANES



Vinyl in Dicyclohexylvinylborane	Formula		Vinylmercury chloride (%)	Hg^0 (%)
	R	R'		
trans-1-Pentenyl	n-C_3H_7	H	85	8
trans-Cyclohexylethenyl	C_6H_{11}	H	87	6
trans-3,3-Dimethyl-1-butenyl	t-C_4H_9	H	96	1
trans-Styryl	C_6H_5	H	98[a]	[a]
cis-3-Hexenyl	C_2H_5	C_2H_5	59	27

[a] Small amount of mercury(0) present.

TABLE 3

PHYSICAL CHARACTERISTICS OF VINYLMERCURY CHLORIDES

Compound	M.p.[a](°C)	Analysis, found (calcd.) (%)		
		C	H	Hg
trans-1-Pentenylmercury chloride	130–130.5	19.66 (19.68)	3.07 (2.97)	65.71 (65.73)
trans-Cyclohexylethenylmercury chloride	134–135	27.72 (27.83)	3.80 (3.79)	58.00 (58.10)
trans-3,3-Dimethyl-1-butenylmercury chloride	89.5– 90.0	22.53 (22.58)	3.63 (3.47)	63.00 (62.85)
trans-Styrylmercury chloride	216–217[b]			
cis-3-Hexenylmercury chloride	47.5– 48.0	22.31 (22.58)	3.63 (3.47)	62.70 (62.85)

[a] Recrystallized from 95% ethanol. [b] Lit.[4] m.p. 216.5–217.5.

derived from terminal acetylenes were excellent in all cases. As the steric bulk of the terminal acetylene was increased, the yield of vinylmercurial also increased. Internal acetylenes lead to decreased yields of the desired product. This is apparently due to greater steric hindrance to attack at the boron–carbon bond. Some typical results are indicated in Table 2.

The melting points and elemental analyses of all new compounds are included in Table 3.

Stereochemistry

The stereochemical course of the mercuration of vinylboranes has been examined by NMR and infrared spectroscopy.

The NMR spectra of all vinylmercury chlorides are consistent with retention of the stereochemistry present in the vinylborane itself. The vinylmercury chlorides derived from tert-butyl- and phenylacetylenes were clearly *trans* compounds with vinyl proton–proton coupling constants $J(H_1–H_2)$ 18–19 Hz indicative of *trans* vinyl hydrogens. The organomercurials derived from 1-pentyne and cyclohexylacetylene both gave complicated spectra in the vinyl hydrogen region from which proton–proton coupling constants could not readily be determined. ^{199}Hg–H Coupling constants, however, clearly showed these compounds to be *trans*. Although it has been reported that vinylmercuric bromide itself exhibits no pattern corresponding to ^{199}Hg–H coupling[13], all of the vinylmercury chlorides prepared during the course of this study exhibited ^{199}Hg–H coupling. In *trans*-1-pentenylmercury chloride and (*trans*-cyclohexylvinyl)mercury chloride the satellites due to *gem* ^{199}Hg–H and *cis* ^{199}Hg–H coupling were found to overlap. Integration of the satellite areas gave 16–17% of the total vinyl hydrogen area (^{199}Hg has a relative abundance of 16.86%). This fact plus the magnitude of the coupling constants $J(^{199}Hg–H)$ ≈292 and ≈296 Hz respectively is only consistent with a *trans* configuration. The ^{199}Hg–H coupling constants $J(^{199}Hg–H)$ 260–308 Hz present in all compounds rule out the possibility of these compounds containing vinyl hydrogens *trans* to mercury. For comparison, the corresponding *cis* ^{199}Hg–H coupling constant in vinylmercury acetate itself is 331 Hz[13]. The *trans* ^{199}Hg–H coupling was found to be 658 Hz[13]. Large coupling with the *trans* proton is also observed in (*cis*-2-chlorovinyl)mercury chloride [$J(^{199}Hg–H)$ 474 Hz][13]. No ^{199}Hg–H coupling of this magnitude was observed in any of the vinylmercuric chlorides. The ^{199}Hg–H coupling constants for di-*trans*-propenylmercury have also been reported[14]. *cis* ^{199}Hg–H coupling constants of 140 Hz were observed here. However, it has been observed that the coupling constants [$J(^{199}Hg–H)$] are reduced by approximately a factor of 2.2 on proceeding from compounds RHgX to R_2Hg[13]. Thus, we might expect coupling constants of approximately $2.2 \times 140 = 308$ Hz for coupling between ^{199}Hg and its *cis* proton, and this is indeed found.

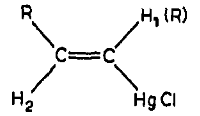
Geminal ^{199}Hg–H coupling constants in the range $J(^{199}Hg–H)$ 279–304 Hz were also observed for the vinylmercurials derived from terminal acetylenes. Vinylmercuric acetate has a *gem* ^{199}Hg–H coupling constant of $J(^{199}Hg–H)$ 291 Hz. Our values are consistent with these results.

The NMR data is summarized in Table 4.

The infrared spectra of the vinylmercury chlorides derived from terminal acetylenes further confirm the assignment of a *trans* configuration. Chumaevskii and

TABLE 4

NMR OF VINYLMERCURY CHLORIDES

Compound	Formula			$J(H_1–H_2)$ (Hz)	$J(^{199}Hg–H_1)$ (Hz)	$J(^{199}Hg–H_2)$ (Hz)
		δ_1 (ppm)	δ_2 (ppm)			
trans-1-Pentenylmercury chloride	$n\text{-}C_3H_7CH{=}CHHgCl$	≈5.8	≈5.8		296[a]	296[a]
trans-Cyclohexylethenylmercury chloride	$C_6H_{11}CH{=}CHHgCl$	≈5.8	≈5.8		292[a]	292[a]
trans-3,3-Dimethyl-1-butenyl mercury chloride[b]	$t\text{-}C_4H_9CH{=}CHHgCl$[b]	6.02	5.65	18.5	304	284
trans-Styrylmercury chloride[b]	$C_6H_5CH{=}CHHgCl$[b]	6.93	6.57	18	279	260
cis-3-Hexenylmercury chloride	$C_2H_5CH{=}C(C_2H_5)HgCl$		5.43			308

[a] It is clear from the multiplet patterns that these coupling constants are not truly identical. [b] The chemical shifts are assigned in analogy to those of vinylmercury bromide[13] and the isomeric dipropenylmercurials[14]. This gives rise to the unusual case of ^{199}Hg–H coupling constants with $J_{gem} > J_{cis}$. However, we are not sure enough of this assignment to make such an unequivocal statement.

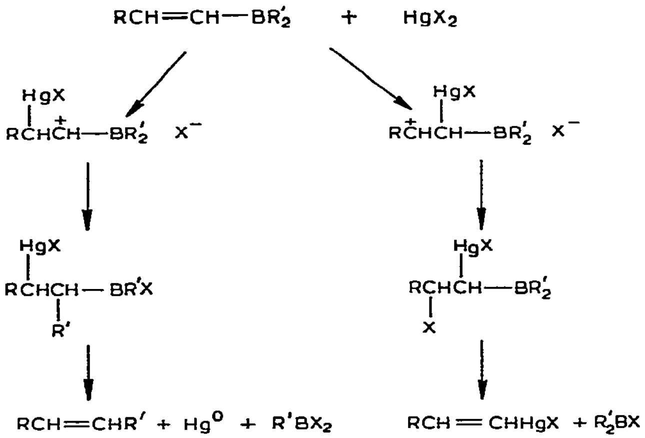
Borisov have reported the infrared absorption spectra of *cis*- and *trans*-propenylmercury chlorides[15]. These compounds could be distinguished by the difference in intensities of the in-plane (1200–1300 cm^{-1}) and out-of-plane (920–970 cm^{-1}) C–H vibrations. The *trans* compound exhibits a particularly strong band in the 920–970 cm^{-1} region. The vinylmercury chlorides derived from terminal acetylenes also exhibit a very strong band in this region. Infrared spectra for vinylmercurials of the type *cis*-RCH=CR'HgCl have not yet been reported.

The NMR and infrared spectra of all compounds provide further proof that the mercuration of dicyclohexylvinylboranes proceeds with strict retention of configuration.

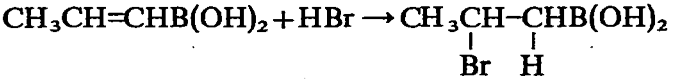
Mechanism

Several mechanistic pathways can account for the mixture of products obtained in the reaction of dicyclohexylvinylboranes with mercuric acetate. The products might arise by an addition–elimination sequence in which mercuric acetate adds to the double bond in two different directions (Scheme 1).

SCHEME 1

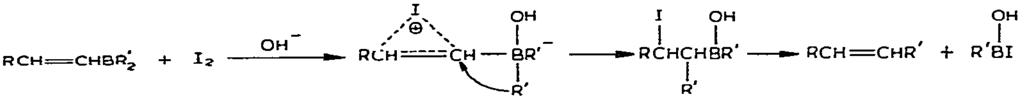


Might electrophilic attack in two directions be expected? Unfortunately, electrophilic additions to dialkylvinylboranes have not been studied. Matteson, however, has reported that addition of hydrogen bromide to dibutyl 1-propene-1-boronate proceeds to place the proton α to the boron[16] (eqn. 8). The more highly electron donating dialkylboron moiety might be expected to reverse this mode of addition. Thus, it is not inconceivable that addition in two directions might occur.



$$CH_3CH{=}CHB(OH)_2 + HBr \rightarrow CH_3\underset{Br}{\underset{|}{C}}H{-}\underset{H}{\underset{|}{C}}HB(OH)_2 \qquad (8)$$

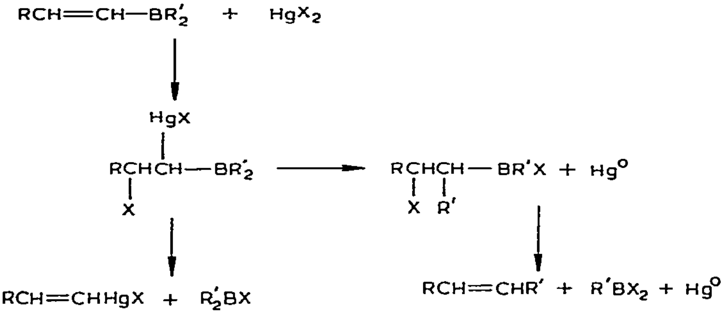
The formation of olefin according to Scheme 1 is analogous to the mechanism proposed for the formation of olefins in the iodination of vinylboranes[17] (eqn. 9). Although boron–mercury elimination reactions have never been observed previously, there are several examples of mercury(0) acting as a leaving group. Thus, mercury(0)


(9)

has been shown to be a good leaving group in solvolysis[18] and substitution[19] reactions. Loss of stereospecificity in the olefin can occur in either of the last two steps leading to its formation. Retention of configuration in the vinylmercurial requires presumably *trans* addition of the mercuric acetate to the double bond followed by a *cis* elimination of the elements $R'_2B{-}OAc$. β-Acetoxyboranes are known to undergo such a *cis* β-elimination[11c]. All steps in this scheme are consistent with previously observed chemistry.

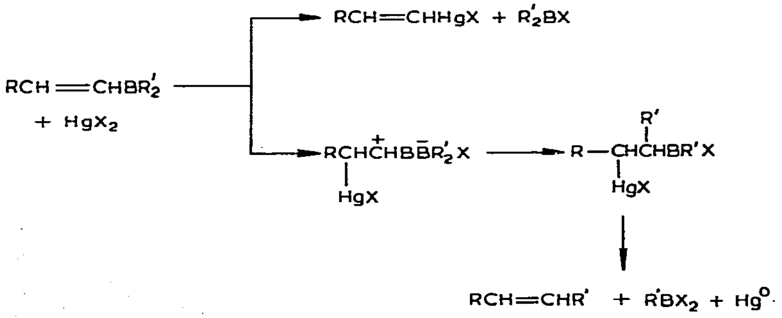
An alternate pathway to the products also involving addition of the mercuric acetate to the double bond is conceivable. This pathway involves addition of the mercuric acetate in only one direction (Scheme 2). Again, a *trans* addition of mercuric acetate to the vinylborane followed by a *cis* elimination of R'_2BOAc leads to *trans*-vinylmercury acetate. Competitive α-transfer of an alkyl group from boron to the α-carbon resulting in the elimination of mercury(0) could lead after subsequent β-elimination of $R'B(OAc)_2$ to the olefin. α-Transfer reactions of this type are well known for α-haloboranes[20], but α-acetoxymercuriboranes have not been previously prepared.

SCHEME 2



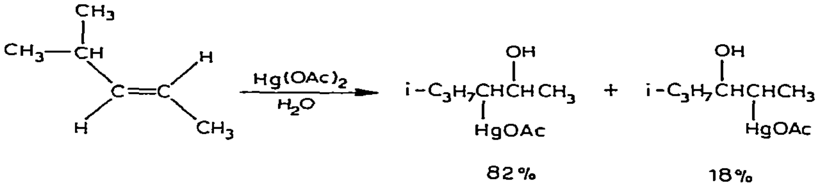
Lastly, a third scheme can be envisioned involving attack of the mercuric acetate at two different sites within the vinylborane (Scheme 3). Direct electrophilic cleavage of the boron–carbon bond could occur as suggested for the protonolysis

SCHEME 3



of organoboranes by acetic acid[9]. A vinylmercurial of retained configuration would then result. Attack of the mercuric acetate on the double bond as outlined in Scheme 1 would account for the olefin product and metallic mercury.

Are all three schemes consistent with the observations on the role of steric effects and the role of the dialkylborane? In Scheme 1 one might expect the addition of the mercuric salt to the double bond of the vinylborane to exhibit directive effects similar to the oxymercuration of unsymmetrical olefins[21]. The oxymercuration of olefins proceeds to place the mercury atom on the end of the double bond containing the more bulky alkyl groups (eqn. 10). This would then predict that in changing from

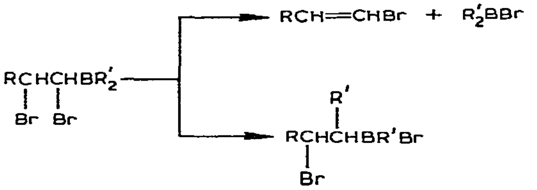


(10)

the less hindered dicyclohexylborane to the more hindered disiamylborane, more of the mercury should add α to the boron and lead to more vinylmercurial and less olefin. This is exactly opposite of what is indeed found (see Table 1). Similarly, increasing the steric requirements of the acetylene should result in decreasing amounts of vinylmercurial. Again this is not found (see Table 2).

If, however, the mercuric acetate should add in such a manner so as to place the mercuric acetate groups at the less hindered position of the double bond, then all results are consistent with Scheme 1.

Scheme 2 encounters much more serious objections. Competition here is between α-transfer and β-elimination. A similar situation is present in the bromination of vinylboranes[22]. The intermediate 1,2-dibromo compound can undergo either α-transfer or β-elimination (eqn. 11). In this case, disiamylborane gives good yields of



vinyl bromides by thermal elimination of R'_2BBr. Dicyclohexylborane does not give any vinyl bromide. Presumably, α-transfer occurs more readily in this case. In other words disiamylborane undergoes β-elimination more readily than dicyclohexylborane. If the products of mercuration of vinylboranes are to arise by a similar competition, we must say that dicyclohexylborane undergoes a β-elimination more readily than disiamylborane. This is inconsistent with the bromination results. Furthermore, the role of steric effects is not readily accommodated by this scheme.

Finally, Scheme 3 readily accommodates all factors. An increase in the steric bulk at either end of the molecule tends to direct the point of attack of the mercuric acetate towards the site of less steric hindrance. Since the mercuration of saturated organoboranes proceeds readily, there appears to be no need to invoke a new mode of reaction, namely an addition–elimination mechanism, to account for the mercuration of vinylboranes.

Conclusion

The mercuration of dicyclohexylvinylboranes offers a highly convenient stereospecific route to vinylmercury salts*. The reaction starts with readily available acetylenes and should readily accommodate functional groups. Consequently, this reaction offers major advantages over the standard organolithium and magnesium procedures. The yields are excellent for the conversion of terminal acetylenes although somewhat lower for internal acetylenes. Vinylmercurials have previously found considerable use in the synthesis of a great number of other vinylmetallics and metalloids[12] and should prove to be quite useful in organic synthesis. We are exploring such possibilities.

EXPERIMENTAL SECTION

Materials

All glassware was dried thoroughly in a drying oven and cooled under a stream of nitrogen. THF was dried over lithium aluminum hydride, distilled and kept under nitrogen. The borane/tetrahydrofuran solution was prepared by the procedure of Brown and Sharp[11c]. Cyclohexene (Matheson, Coleman and Bell) and 2-methyl-2-butene (Phillips, 99%) were used directly as obtained. 1-Pentyne and 3,3-dimethyl-1-butyne from Farchan and cyclohexylethyne, phenylethyne and 3-hexyne from Chem. Samples were used directly as obtained. Mercuric acetate (J. T. Baker) was also used directly.

Preparation of vinylboranes

Tri-*cis*-3-hexenylborane was prepared by adding 12.4 ml of 2.69 *M* borane (33.3 mmoles) in THF to 8.22 g of 3-hexyne (100 mmoles) in 78 ml of THF at 0°. After stirring several hours at 0°, the reaction was stirred overnight at room temperature.

Disiamylborane was prepared by slowly adding 14.16 g of 2-methyl-2-butene (200 mmoles) at 0° to 100 ml of a 1.0 *M* solution of borane in THF and stirring 24 h at that temperature. 100 mmoles of 1-pentyne (6.81 g) were added and the mixture was stirred overnight at room temperature.

The dicyclohexylvinylboranes were prepared in a manner identical to that of *trans*-disiamyl-1-pentenylborane except the appropriate acetylene was added after stirring only 1 h at 0°. The resulting solution was allowed to stir overnight at room temperature.

Mercuration of vinylboranes

The mercuration of the vinylboranes was accomplished by adding 31.9 of powdered mercuric acetate (100 mmoles) at 0° (unless otherwise specified) to the well stirred solution of vinylborane while backflushing with nitrogen. The reactions were

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* We have recently found[23] that the hydroboration–mercuration of acetylenes with 1,3,2-benzodioxaborole provides a convenient alternate route to these same vinylmercurials.

stirred a few minutes at 0° and then filtered free of metallic mercury. The mercury often would not coagulate and had to be collected as a suspension. After washing the mercury with THF, the vinylmercurial solution and washings were poured into 400 ml of ice cold water containing 5.84 g of sodium chloride (100 mmoles). The THF was removed under vacuum and the white solid collected by filtration. After washing the solid with lots of water and three 100-ml portions of 0° pentane (−50° pentane for vinylmercury chlorides derived from internal acetylenes), the product was dried overnight under vacuum. All compounds could be readily recrystallized from 95% ethanol. Melting points, elemental analyses, and NMR and infrared spectra were obtained for all compounds.

Mercury and olefin analyses

If the mercury would coagulate sufficiently, it was collected, washed with water and acetone and weighed. Otherwise, the gray mercury was dissolved in approximately 10–20 ml of 50% nitric acid. An equal volume of water was added and just sufficient 1 *M* potassium permanganate solution to turn the solution pink for a minute. Sufficient aqueous oxalic acid was then added to decolorize the potassium permanganate. Approximately 0.5 ml of saturated ferric ammonium sulfate indicator was added and the resulting solution titrated with 0.20 *M* potassium thiocyanate until the orange color just appeared. If a yellow-orange color appeared immediately upon titration, more nitric acid was added. A white precipitate appears approximately half way through the titration.

$$Hg^{2+} + 2\,SCN^- \rightarrow Hg(SCN)_2\downarrow$$

All olefin analyses were carried out by GLC on a 10 ft 5% SE–30 column using an appropriate internal standard.

Spectra

The NMR spectra were measured on a Varian T-60 NMR spectrometer. The spectra of *trans*-styrylmercury chloride was recorded in DMSO-d_6 while all other spectra were obtained on saturated solutions of the vinylmercury chloride in deuterochloroform. TMS was used in all cases as internal standard. The infrared spectra of all compounds were recorded as solid dispersions in potassium bromide on a Perkin–Elmer Model 700 infrared spectrometer.

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