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SPECTRAL PROPERTIES OF ALKENYLBORANES. EVIDENCE FOR CONJUGATIVE INTERACTIONS OF BORON WITH CARBON—CARBON π-SYSTEMS

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Summary

Ultraviolet, proton magnetic resonance and infrared spectral studies of a number of alkenylboranes are reported. Appreciable conjugation of carbon—carbon π-systems with boron is indicated. Comparisons of the UV and PMR spectra of alkenylboranes with those of their corresponding methyllithium ate complexes are especially informative. A marked solvent effect upon the PMR spectra of lithium ate complexes of alkenylboranes has been observed.

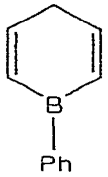
Introduction

The question of the importance of conjugate interactions of vinyl groups with boron in vinylboranes has attracted considerable attention [1]. In a pioneering study, Good and Ritter [2,3] examined the spectral properties of dimethylvinylborane, methyldivinylborane, and trivinylborane. The ^{11}B nuclear magnetic resonance chemical shifts and the ultraviolet absorption maxima of these compounds both correlated well with values calculated using simple Hückel MO theory, and indicated considerable conjugative interactions [2,3].

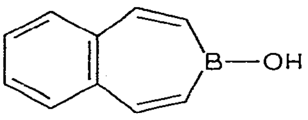
From a study of the photoelectron spectrum of trivinylborane, however, it was concluded that conjugative overlap of the π-orbitals of the vinyl groups with the *p*-orbital of boron is very small [4]. It was suggested that this may be due to twisting of the vinyl groups out of the planar conformation in which overlap is most favorable. A recent electron diffraction study indicated trivinylborane to be planar in the gas phase [5]. These results are to some extent confirmed by Raman and infrared spectra [6,7], although these latter spectra also indicate that non-planar conformations may be important in the gas and liquid phases [7]. Vinyldifluoroborane has been investigated by a variety of physical and spectral methods [8] and found to be planar, although the planarity has been attributed to rotational barriers unrelated to carbon—boron bond conjugation [9].

Recently, nuclear magnetic resonance studies [9—11] have been employed to establish that indeed appreciable conjugation does exist between boron and carbon of vinylboranes. Particularly useful in this regard are ${}^{13}C$ spectra [9,10]; proton spectra are of less value [11]. Theoretical calculations of several types also indicate that conjugative interactions between boron and carbon should be important in vinylboranes [12].

Relatively little data regarding conjugation of boron with carbon—carbon π-systems in divinyl- or 1,3-dienyl-boranes are present in the literature. The interesting cyclic dienylborane I has been prepared, but its UV spectrum was not reported [13]. Conflicting reports concerning the position of the UV absorption maximum of chlorodivinylborane have appeared [2,14].



(I)



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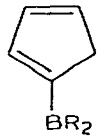


(III)

The similarities of the UV and PMR spectra of borane II and its carbonium ion analog have led to the conclusion that II is aromatic [15]. Finally, cyclopentadienylborane has been found to exist as the non-fluxional, conjugated structure III [16,17].

In the course of our studies on the hydroboration of alkynes [18] and the photocyclization of 1,3-dienylboranes [19], we prepared a number of interesting, highly unsaturated organoboranes. We report here the UV, PMR, and IR spectral properties of some of these. Appreciable conjugation of carbon—carbon π-systems with boron, even in molecules containing very bulky substituents on boron, is indicated.

Experimental

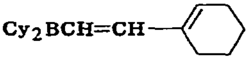
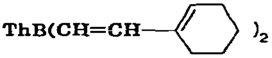
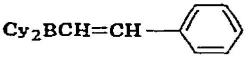
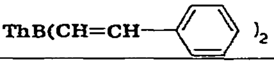
All organoboranes were prepared by established procedures [18] involving hydroboration of the appropriate alkyne or enyne.

Tetrahydrofuran and ether were purified by distillation from lithium aluminum hydride and were stored under nitrogen.

The unsaturated organoboranes are highly susceptible to oxidation. Thus, all transfers and dilutions involving these compounds were carried out with rigorous exclusion of oxygen under a nitrogen atmosphere. Although only a very brief exposure to air was sufficient to markedly alter an absorption spectrum, several hours were required for the absroption maxima to completely disappear. Thus, exposure of a $2.9 \times 10^{-5} M$ THF solution of Vb (Table 1) briefly to air during transfer led to markedly increased absorption below 260 nm (a very broad band). The position and, to a lesser extent, the intensity of the charge transfer band near 270 nm was relatively unaffected. However passage of a slight stream of air through a $2.9 \times 10^{-5} M$ THF solution of Vb for 12 h resulted in the complete disappearance of the 270 nm band with concomitant appearance of an absorption band at 230 nm.

TABLE 1

ULTRAVIOLET SPECTRAL DATA FOR VARIOUS ALKENYL ORGANOBORANES AND ORGANOBORATES

	Organoborane [a]	Solvent [b]	λ_{max} (nm)	10^{-4} ε [c] (M^{-1} cm^{-1})	Ate complex λ_{max} (nm)
IVa	$Cy_2BCH{=}CHC_6H_{13}$	THF	<215		
Va	$ThB(CH{=}CHC_6H_{13})_2$	Et_2O	226	1.9	<215
IVb	$Cy_2BCH{=}CHC(CH_3){=}CH_2$	THF	244	1.8	
		Et_2O	244	2.0	230
		n-Octane	245	1.9	
Vb	$ThB(CH{=}CHC(CH_3){=}CH_2)_2$	Et_2O	268 [d]	3.3	230
		THF	270 [d]		
IVc		Et_2O	244	1.7	232
		THF/Et_2O			229
Vc		THF/Et_2O	278	2.5	236
IVd		Et_2O	264 [e]	2.2	247
Vd		Et_2O	292 [e,f]	3.8	252

[a] Cy_2 = dicyclohexyl; Th = thexyl. [b] THF = tetrahydrofuran; Et_2O = diethyl ether. In all cases the substitution about the double bond is *trans*. [c] The extinction coefficients are based on the yield of alkene or diene obtained on protonolysis. [d] A second band was observed 227 nm region having an intensity approximately half that of the principal band. [e] Other weak bands typical of aromatic systems were also observed. [f] A second band was observed at 217 nm having an intensity approximately half that of the principal band.

The organoboranes were not isolated, but were characterized in solution by their spectral properties and by protonolysis or deuterolysis to the corresponding olefins or deuteroolefins, respectively.

UV spectra were recorded on a Carey Model 14 spectrophotometer employing one cm matched quartz cells with ground stoppers. Extinction coefficient calculations were based on protonolysis product yields. PMR spectra were recorded on a Varian A-60A spectrometer. Chemical shifts were measured in ppm downfield from internal tetramethylsilane. IR spectra were recorded on a Beckmann IR-8 spectrophotometer from solutions in NaCl cells.

Results and discussion

Ultraviolet spectra

The solution UV spectra for all of the alkenylboranes examined, except *trans*-1-octen-1-yldicyclohexylborane (IVa), indicate considerable conjugative interactions of boron with the alkene moieties (Table 1). This is the case despite the fact that all of the organoboranes bear either two large cyclohexyl substituents or the very bulky thexyl(2,3-dimethyl-2-butyl) substituent on boron. Thus, the thexyldialkenylborane Va exhibited a well defined charge transfer band at 226 nm (ε = 1.9 × 10^4 M^{-1} cm^{-1}) in ether * which was shifted to <215 nm upon

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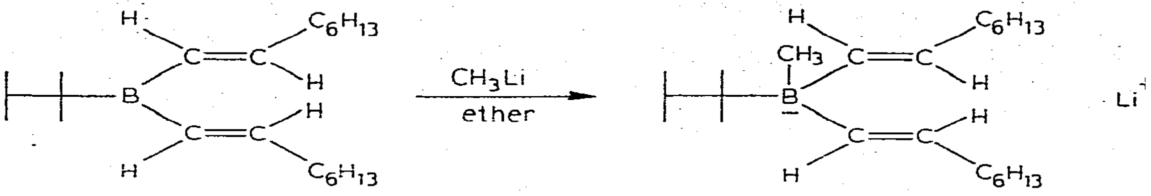
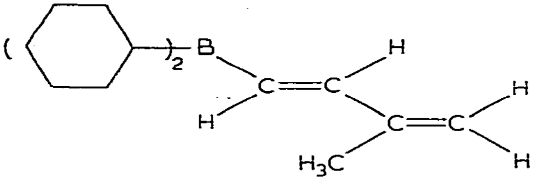
* The relatively intense absorption maxima of vinylboranes have been assigned to charge transfer transitions from the molecular orbital of the alkenyl substituent to boron [1].

treatment of Va with methyllithium. This process forms the corresponding ate complex and results in disruption of the conjugation.

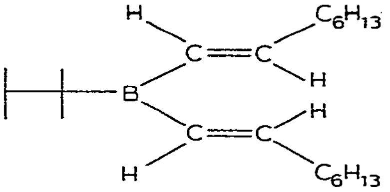


(Va) (λ_{max} 226nm) (λ_{max} <215 nm)

The UV spectra of dienylboranes are of particular interest in connection with the observation that dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane (IVb) undergoes photocyclization [19]. Thus IVb, which contains a five-atom π-system with a terminal boron atom exhibits UV absorption maxima at 242 and 244 nm in THF and ether solvents, respectively. Comparison of the absorption maxima of the two five-atom π-systems IVb and Va indicates that lower energy is required for electronic excitation of a linearly conjugated 1,3-dienylborane than for a "cross-conjugated" 2,4-dienylborane. Treatment of the dienylborane IVb in THF solvent with an equimolar amount of methyllithium in ether produced the corresponding ate complex and resulted in a blue shift of the absorption maximum to 230 nm, close to that reported for isoprene (225 nm).

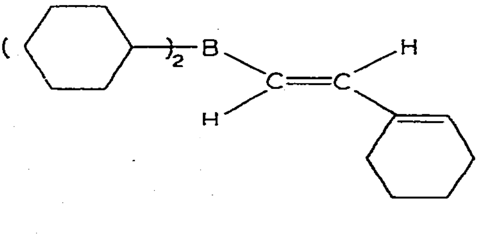


(IVb) (λ_{max} 244 nm)
in ether

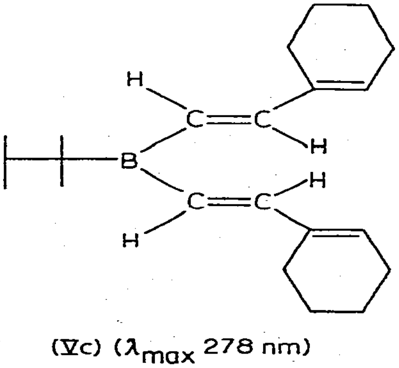


(Va) (λ_{max} 226 nm)
in ether

A marked red shift of the UV absorption maximum ($\Delta\lambda$ = 34 nm) was observed in going from the five-atom π-system containing monodienylborane IVc to the formal nine-atom π-system containing bis-dienylborane Vc. Addition of meth-



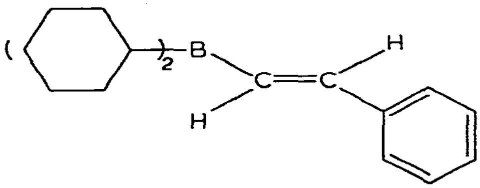
(IVc) (λ_{max} 244 nm)



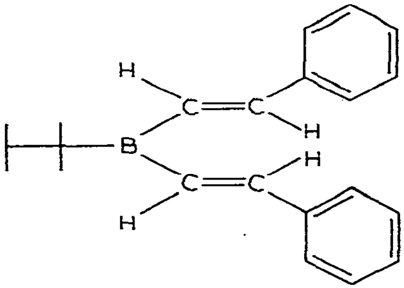
(Vc) (λ_{max} 278 nm)

yllithium should interrupt conjugation of the π-systems with boron in both IVc and Vc, and the resulting ate complexes for both systems would be predicted to have similar UV spectra. In accord with this prediction, the absorption maxima of the methyllithium ate complexes of IVc and Vc were at 232 and 236 nm, respectively, both closely approaching the λ_{max} of 1-vinylcyclohexene (230 nm).

The monostyrylborane IVd exhibited an intense charge-transfer band at 264 nm in ether, which may be compared to the 292 nm, an absorption maximum for the distyrylborane Vd. The absorption maxima for the corresponding lithium methylborates are at similar positions (247 and 252 nm, respectively) to the λ_{max} of styrene (244 nm).



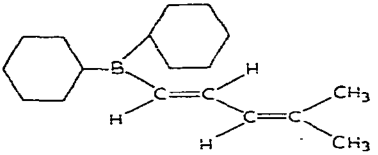
(IVd) (λ_{max} 264 nm)



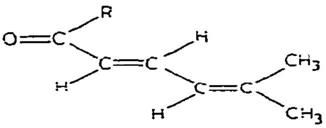
(Vd) (λ_{max} 292 nm)

In conclusion, the UV data which are summarized in Table 1 clearly indicate that the intense absorption maxima of divinyl-, monodienyl and bis-dienylboranes are the result of $\pi \rightarrow \pi^*$ transitions involving some degree of intramolecular charge transfer from molecular orbitals of the alkenyl or alkadienyl substituents to boron. In this connection, however, it should be noted that stabilization by electron delocalization is manifested more in the excited state of a conjugated polyene than in the ground state.

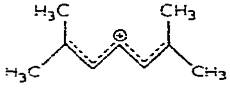
Finally, support for our intuitive feelings regarding electron delocalization in α,β-unsaturated organoboranes was gained by comparing the UV absorption maximum of the dienylborane VI with those of the dienone VII and the dienylcarbonium ion VIII [20]. It is noteworthy that the position of the λ_{max} for the dienylborane VI is much closer to that predicted for the dienone VII than to that observed for the isoelectronic carbocation VIII. This suggests that trivalent boron is electronically similar to carbonyl group carbon, and is in agreement with the observation that many reactions of aldehydes and ketones have counterparts in reactions of organoboranes [21]**. Among the factors which might con-



(VI)
λ_{max} (THF): 251 nm



(VII)
λ_{max}(EtOH): 281 nm*



(VIII)
λ_{max} (96% H_2SO_4): 397 nm

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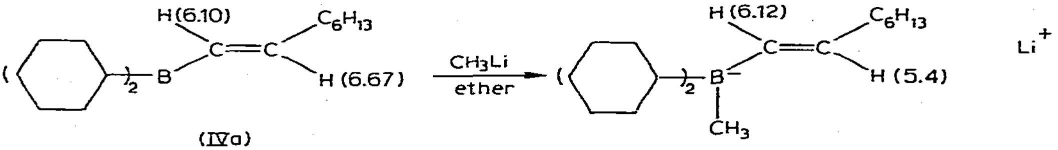
* Calculated using the Woodward constants.

** Ab initio MO theory predicts the boron atom to be a stronger σ donor and weaker π-acceptor than C^+[22].

tribute to the large difference in the λ_{max} values of the dienylborane VI and the carbocation VIII are solvent effects, steric interactions and, most importantly, the fact that the carbonium ion carries a full positive charge.

Proton magnetic resonance spectra

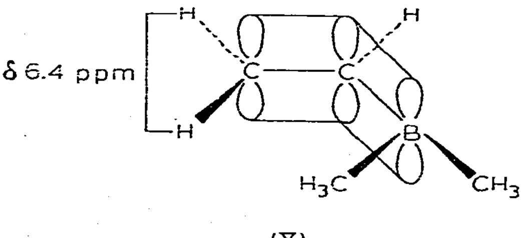
The PMR spectra of conjugated organoboranes, when considered in conjunction with the PMR spectra of their corresponding ate complexes, also provided evidence for conjugative interactions between boron and carbon—carbon π-systems. Thus, the PMR spectrum of *trans*-1-octen-1-yldicyclohexylborane (IVa) in ether exhibited a doublet of triplets at δ 6.67 ppm for the β-proton and a doublet at δ 6.10 ppm for the α-proton. The salient feature of the PMR spectrum is the low-field position of the β-proton, pointing to an electron shift from the double bond into the *p*-orbital of boron. The large (18 Hz) coupling constant observed is typical for *trans*-alkenylboranes [18]. The methyllithium ate complex IX of the vinylborane (IVa) in ether showed a broadened doublet at δ 5.4 ppm for the β-proton and a relatively sharp doublet at δ 6.2 ppm for the α-proton. The B—CH_3 protons under favorable resolution conditions appeared as a quartet at δ —0.61 ppm, possibly indicating coupling of the methyl protons with boron ($I = 3/2$).



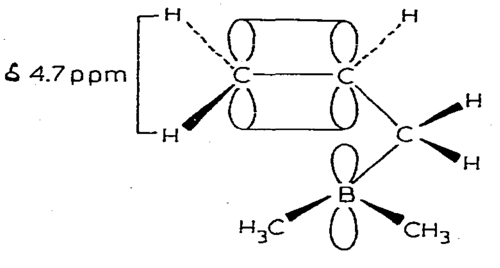
(IVa)

(IX)

In connection with above results it is instructive to compare the magnitudes of the chemical shifts observed for the terminal protons of the vinylborane X [2] with that for the allylborane XI [23]. The deshielding experienced by the terminal vinyl protons of X must result from allylic type π-electron delocalization into the empty *p*-orbital of boron. However, homoallylic type π-electron donation into the *p*-orbital of boron in XI apparently is much less effective. Indeed, the terminal protons in XI, where direct conjugation of the C=C π-bond with boron is precluded, absorb in the same region (δ 4.7 ppm) as do the terminal protons of 1-alkenes (δ 4.9 ppm).

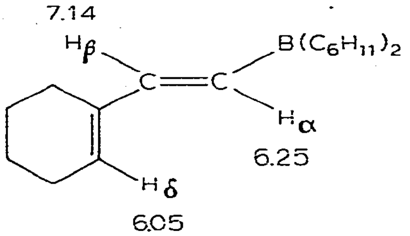


(X)

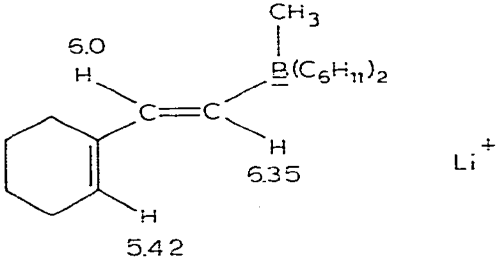


(XI)

Returning to the results of the present study, additional evidence for conjugative interaction between boron and C=C bond systems was derived from a study of the PMR spectra of 1,3-dienylboranes. Thus, the dienylborane IVc in ether solvent exhibits large downfield shifts for the β- and δ-alkenyl protons relative to those of the corresponding ate complex XIII *. These data can be interpreted

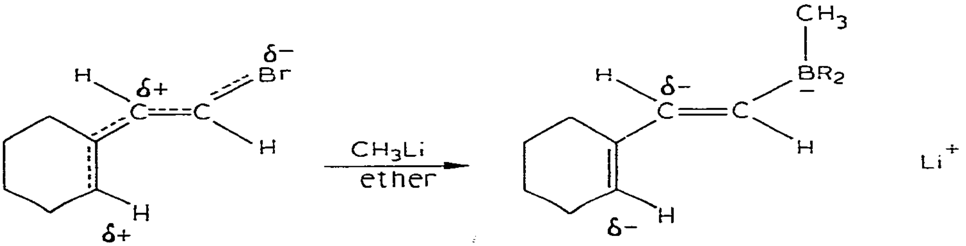


(IVc)



(XIII)

as indicating an appreciable shift of electron density from boron toward the β- and δ-carbon atoms upon ate complex formation. Because the double bond



bearing the boron has a *trans* configuration, any direct interactions of the δ-proton with the boron atom are precluded. Similar results were obtained with other boranes investigated, as shown by the data in Table 2. Data for the reso-

TABLE 2

PMR (60 MHz) DATA FOR *trans* ALKENYL ORGANOBORANES AND ORGANOBORATES IN ETHER

Compound [a]	Alkenyl proton chemical shifts (δ (ppm)) [b,c]					
	Organoborane			Ate complex		
	H_α	H_β	H_δ	H_α	H_β	H_δ
IVa	6.10	6.67		6.12	5.4	
Va	6.4	6.4		6.25	5.4	
IVb	6.24	7.10	5.15	6.47	6.0	4.57 [d]
Vb	6.53	6.87	5.17	6.67	6.2	4.75 [d]
IVc	6.25	7.14	6.05	6.35	6.0	5.42
Vc	6.25	6.75	5.85	6.47	6.0	5.45

[a] For the structures of the compounds see Table 1. [b] Large (18—19 Hz) *trans*-proton coupling constants typical of *trans*-alkenylboranes were observed. [c] The peaks due to the β-protons of the ate complexes are appreciably broadened. The reasons for this broadening have not yet been established. [d] A broadened singlet or unresolved multiplet was observed for the two terminal methylene protons.

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* The proton assignments for IVc and XIII were confirmed by comparison with spectra of the corresponding α-deuteroorganoborane prepared via hydroboration of deuteroethynylcyclohexene with dicyclohexylborane and of its ate complex.

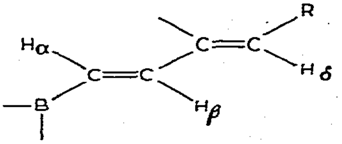
TABLE 3

THE EFFECTS OF SOLVENT CHANGES ON THE PMR SPECTRA OF ALKENYL ORGANOBORANES AND ORGANOBORATES

Compound [a]	Solvent [b]	Alkenyl proton chemical shifts (δ (ppm)) [c]					
		Organoborane			Ate complex		
		H_α	H_β	H_δ	H_α	H_β [d]	H_δ
IVa	Et_2O	6.10	6.67		6.12	5.4	
	THF/Et_2O (3 : 1)	6.10	6.68		5.65	4.8	
	DG/Et_2O (3 : 1)	6.10	6.67		5.62	4.8	
	$TMEDA/Et_2O$ (3 : 1)	6.10	6.67		5.65	4.8	
	$HMPA/Et_2O$ (3 : 1)	5.97	6.45		5.64	4.8	
IVc	Et_2O	6.25	7.14	6.05	6.35	6.0	5.42
	THF/Et_2O (3 : 1)	6.25	7.14	6.05	6.17	5.6	5.02
	$TMEDA/Et_2O$ (3 : 1)	6.25	7.14	6.05	6.22	5.6	5.05

[a] For the structures of the compounds see Table 1. [b] Et_2O = diethyl ether; THF = tetrahydrofuran; DG = diglyme (diethyleneglycol dimethyl ether); TMEDA = tetramethylethylenediamine; HMPA = hexamethylphosphoric triamide.

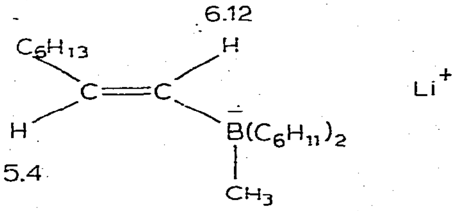
[c]



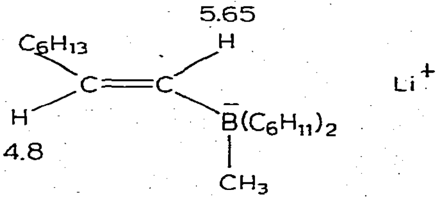
[d] The peaks due to the β-protons of the ate complexes are appreciably broadened in all solvents.

nance signals of the olefinic protons of the styrylboranes IVd and Vd are not reported, however, since they were not sufficiently separated from the aromatic multiplet at δ 7.2—7.7 ppm to allow their identification.

Finally it should be noted that the NMR absorption of the vinyl- and dienylboranes showed little dependence on the type of solvent used. On the other hand, marked solvent effects upon the chemical shifts of the alkenyl protons of the organoborane lithium ate complexes were observed. Thus, the resonance signals of both vinyl protons of the methyllithium ate complex IVa undergo a pronounced upfield shift if an ether solution of the compound is diluted with a more strongly complexing solvent. No such shift is observed upon dilution with ether or hydrocarbon solvents. Surprisingly, however, as shown by the data in Table 3, the chemical shift effects produced by a number of structurally different complexing solvents are the same. Similar, but slightly smaller shifts were ob-



(IVa) in ether

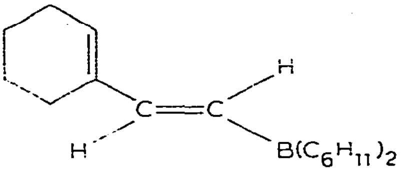


(IVa) in THF/ether

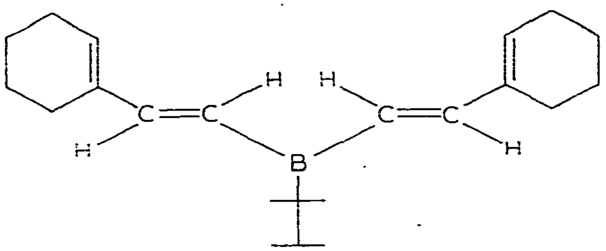
served for all of the olefinic protons of the dienylborane ate complex IVc. It may also be noted that the spectrum of the alkenylborane IVa was unchanged when either ether or THF solutions of the compound were treated with lithium bromide. A possible explanation for the marked effect of the solvents on the spectra of the ate complexes is that the lithium organoborates exist as ion pairs in ether, but as free, dissociated ions or as solvent-separated ion pairs when solvents capable of strongly complexing the cation are present.

Infrared spectra

The infrared spectra of α,β-unsaturated organoboranes exhibit very intense bands in the carbon—carbon double bond stretching vibration region. Interestingly, the position of the C=C stretching vibration is only slightly affected on changing the substituents on boron, as indicated by the data shown in Table 4. For example, the ν(C=C) for IVc, a five-atom π-system and Vc, a nine-atom π-system, are nearly the same. Hence, the absolute position of the ν(C=C) cannot be used to support or discredit the concept of significant conjugative interactions in alkenylboranes. This has been pointed out previously [6].



(IVc) ν(C=C) 1620, 1575 cm^{-1}



(Vc) ν(C=C) 1620, 1570 cm^{-1}

TABLE 4

INFRARED SPECTRAL DATA OF ALKENYL SUBSTITUTED ORGANOBORANES

Organoborane [a]	Solvent	ν(C=C) (cm^{-1})
IVa	THF	1612s
	Octane	1612s
Va	THF	1605s
IVb	THF	1612s 1580s
	Octane	1612s 1580s
Vb	THF	1612m 1575s
IVc	THF	1620m 1575s
Vc	THF	1620m 1570s

[a] For structures of the compounds see Table 1. [b] s, strong; m, medium.

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