two are assigned to two unbound carboxylate groups and other two are assigned to bound carboxylate groups. ^{13}C chemical shifts of solid complexes are influenced by the environment of vanadium(V), such as type of cation, hydrogen bonding of water molecule, etc. There are substantial differences between the solid-state and solution ^{13}C spectra of sample. In general, the multiple signals could arise from either an induced nonequivalence in the solid-state where the site symmetry is lower than the molecular symmetry or because the unit cell contains molecules which are magnetically nonequivalent.[14] It may be possible to distinguish these two possibilities from the X-ray structure. But the complexes show two sets of resonances, which correspond to the two magnetically inequivalent (but chemically identical) molecules generated by the 2_1 symmetry operation within the unit cell.[15] The MAS ^{51}V spectra of the vanadium(V) complexes are shown in Figure 2, and the center bands are indicated by asterisk. All of the complexes show similar sideband patterns. The large shielding anisotropy at high magentic field (9.4 T) causes the spectra to be broken up into centerbands and an extensive set of spinning sidebands, which are spaced by integer multiples of the spinning frequency. The isotropic chemical shift frequencies are independent of the spinning speed and can easily be identified by varying the spinning rate. All of the complexes show two discernible ^{51}V patterns, corresponding two magnetically inequivalent sites. The results are also consistent with those of CP/MAS ^{13}C spectra. The isotropic chemical shift values obtained from the solid-state measurements, compared to those in solution, are summarized in Table 3. From the proximity of ^{51}V chemical shifts in solution and solid-state complexes, we guess that the geometries in the solid-state might also be retained in the solution. In conclusion, NMR spectroscopy has been proved to be a powerful tool in the characterization of solution and solid-state vanadium(V) complexes.

Experimental

Preparation of vanadium(V) complexes. The vanadium complexes, $(NH_4)_3[VO_2Y]$, $Na_3[VO_2Y] \cdot 4H_2O$ and $(NH_4)[VO_2H_2Y] \cdot 3H_2O$, were prepared by the method of Przyborowski *et al.*[16]

NMR measurements. ^1H, ^{13}C and ^{15}V spectra of samples in D_2O were recorded on a JEOL GSX-400 NMR spectrometer at 400, 100.5 and 105 MHz, respectively, at 298 K. ^{13}C spectra of solid samples (*ca.* 0.2 g) were recorded on a Bruker MSL-300 spectrometer (75.47 MHz) with CP/MAS technique at room temperature. A spectral width of 29411 Hz and an accumulation of *ca.* 200 transients with an acquisition time of 0.85 s were used. The contact time was 2 ms and the delay between each scan was 5 s. MAS ^{51}V spectra of the vanadium(V) complexes were recorded on a Bruker MSL-400 spectrometer (105 MHz) at room temperature using a spin rate of 10 kHz. The ordinary single pulse sequence was used without ^1H dipolar decoupling. The ^1H and ^{13}C chemical shifts are referenced to external TMS. And ^{51}V shifts are referenced to external $VOCl_3$.

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Isopinocampheylhaloborane-Methyl Sulfide as Regioselective Monohydroboration Reagent. Synthesis of Aldehydes and Ketones from Alkynes in High Isomeric Purity

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Thexylhaloborane-methyl sulfide (ThxBHX·SMe_2, X=Cl, Br, I) appeared to be exceptionally valuable monohydroboration reagents for the selective hydroboration of alkynes of different structural types.[1] These reagents monohydroborate both internal and terminal alkynes cleanly with high regio- and stereospecificity to provide a valuable synthetic route to isomerically pure aldehydes and ketones.

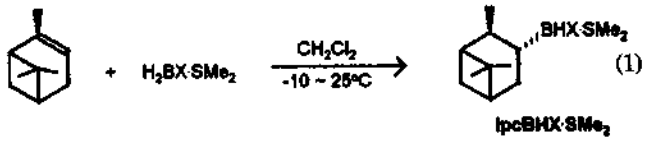
Table 1. Directive Effects in the Monohydroboration of Alkynes with Isopinocampheylhaloborane-Methyl Sulfide in Methylene Chloride at 25℃

Alkyne	Products	Product distribution, %[a,b]		
		IpcBHCl·SMe_2	IpcBHBr·SMe_2	IpcBHI·SMe_2
1-Hexyne	Hexanal	92	96	98
	2-Hexanone	8	4	2
1-Heptyne	Heptanol	95(96)[c]	97(98)	99
	2-Heptanone	5(4)	3(2)	1
2-Hexyne	2-Hexanone	87	90	95
	3-Hexanone	13	10	5
3,3-Dimethyl-1-butyne	3,3-Dimethylbutanol	97	98.5	>99.9
	3,3-Dimethyl-2-butanone	3	1.5	trace
4,4-Dimethyl-2-pentyne	4,4-Dimethyl-2-pentanone	93	96	99
	4,4-Dimethyl-3-pentanone	7	4	1
Phenylethyne	Phenylacetaldehyde	99	99.5	>99.9
	Acetophenone	1	0.5	trace
1-Phenyl-1-propyne	1-Phenyl-2-propanone	99.5	99.5	>99.9
	1-Phenyl-1-propanone	0.5	0.5	trace

[a]The distribution is deduced by GC analysis from the oxygenated products of the intermediate alkenylboranes. [b]Total yields are 90±5%. [c]The figures in parenthesis are yields at 0°

Such exceptional monohydroborating ability seems to arise from the structural fitness of thexyl group in the hydroboration reaction. Accordingly, we extended our work to examine the more readily available isopinocampheyl(Ipc) group for such purpose. The Ipc group is readily derived from α-pinene, the most abundant monoterpene in the world.[2] In this letter, we described the directive effect in the monohydroboration of alkynes with IpcBHX·SMe_2 (X=Cl, Br, I) as a potential route to synthesize isomerically pure aldehydes and ketones from alkynes.

The reagents are readily prepared by the hydroboration of α-pinene with the corresponding $H_2BX·SMe_2$ (X=Cl, Br, I) in methylene chloride (eq. 1). Initially, the rate and stoi-



(1)

chiometry of the reaction of IpcBHX·SMe_2 with representative terminal and internal alkynes were investigated. Stoichiometric amounts of the alkynes and the reagents were employed in CH_2Cl_2 solution at 25°. The results reveal that, in general, the terminal alkynes undergo hydroboration at a rate slightly faster than the internal alkynes. The relative rate of hydroboration with IpcBHX·SMe_2 toward alkynes depends on the steric and electronic nature of the reagents, as anticipated. Thus, the rate is in order of IpcBHCl·SMe_2 >IpcBHBr·SMe_2≫IpcBHI·SMe_2. All the terminal and internal alkynes examined undergo the hydroboration readily with IpcBHX·SMe_2 at 25° in the stoichiometric ratio (1 : 1). Especially noteworthy is the hydroboration of alkynes with excess reagents. All the reagents even in an excess amount undergo a clean monohydroboration with either internal or terminal alkynes at 25°.

The directive effect of various unsymmetrically substituted acetylenes toward IpcBHX·SMe_2 was next examined. The regioselectivity for the addition of BH was determined by oxidation of the intermediate alkenylisopinocampheylhaloboranes with hydrogen peroxide. The distribution of carbonyl isomers was then quantified by GC analysis and the experimental results are summarized in Table 1.

As the Table shows, all the isopinocampheylhaloboranes achieve the clean monohydroboration of both internal and

Table 2. Directive Effects (% Substitution) in 1-Substituted Propynes

$RC^b{=}C^aCH_3$

Hydroborating reagent	R			
	n-Pr		Ph	
	b	*a*	*b*	*a*
B_2H_6[a,b]	40	60	74	26
$THxBH_2$[a,b]	39	61	43	57
$HBBr_2·SMe_2$[c]	25	75	64	36
Catecholborane[d]	40	60	27	73
2,2'-biphenoxyborane[e]	39	61	16	84
9-BBN[f]	22	78	65	35
Mes_2BH[g]	10	90	2	98
$CHex_2BH$[a,b]	33	67	29	71
Sia_2BH[a,b]	39	61	19	81
ThxBHCl·SMe_2[h]	2	98	3	97
ThxBHBr·SMe_2[h]	1.5	98.5	1	99
ThxBHI·SMe_2[h]	1	99	1	99
IpcBHCl·SMe_2	13	87	0.5	99.5
IpcBHBr·SMe_2	10	90	0.5	99.5
IpcBHI·SMe_2	5	95	trace	>99.9

[a]Reference 3; [b]Reference 4; [c]Reference 5; [d]Reference 6; [e]Reference 7; [f]Reference 8; [g]Reference 9; [h]Reference 1.

terminal alkynes with high regioselectivity. Especially, IpcBHI·SMe_2 shows almost perfect regioselectivity in these hydroboration reactions at 25°. Even in the hydroboration of internal alkynes the reagent shows an exceptional regioselectivity.

Results for 2-hexyne and 1-phenyl-1-propyne, representative 1-substituted propyne derivatives, are listed in Table 2 along with directive effects for several other hydroborating reagents for comparision.[1,3-9] The results indicate a prominent directive effect for IpcBHX·SMe_2 placing the boron at the less hindered position. Comparision with other substituted boranes such as $HBBr_2$·SMe_2,[5] $ThxBH_2$,[5] Sia_2BH,[5] and 9-BBN[8] reveals a superior regioselectivity for IpcBHX·SMe_2 apparently due to the steric and electronic nature of the reagents. In comparision with ThxBHX·SMe_2,[1] IpcBHX·SMe_2 shows rather better results for 1-phenyl-1-propyne but dose not approach to the regioselectivity for 2-hexyne. In particular, regioselective hydroboration with the iodo derivative provides a valuable synthetic route to isomerically pure aldehydes and ketones from alkynes.

Experimental Section

All glassware used was dried thoroughly in a drying oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisture-sensitive materials were carried out under a dry nitrogen atmosphere. All chemicals were commercial products of the highest purity, and which were carefully purified by standard methods before use. Monochloroborane-methyl sulfide (H_2BCl·SMe_2) and monobromoborane-methyl sulfide (H_2BBr·SMe_2) were used as received from Aldrich. Monoiodoborane-methyl sulfide (H_2BI·SMe_2) was prepared from iodine and borane-methyl sulfide (Aldrich), as described previously.[10] CH_2Cl_2 was pretreated by stirring over concentrated H_2SO_4 and distilling from P_2O_5. Alkynes used were distilled under nitrogen from a small amount of $NaBH_4$. Yields reported in all cases are of analytically pure compounds. ^{11}B-NMR spectra were recorded on a Bruker WP 80 SY spectrometer. Chemical shifts are with reference to BF_3·OEt_2. GC analyses were carried out on a Varian 3300 FID chromatograph equipped with a Varian 4400 integrator/plotter using Carbowax 20 M capillary column (15 m).

Preparation of Isopinocampheylhaloborane-Methyl Sulfide (IpcBHX·SMe_2) in CH_2Cl_2

The fallowing reaction is typical of the procedure adopted in the preparation of IpcBHX·SMe_2 A 100 m*l* round-bottomed flask equipped with magnetic stirring bar, septum-covered sidearm, and connector tube leading to a mercury bubbler was charged with 16.1 m*l* of 6.2 M neat BH_2I·SMe_2 (100 mmol) and 16.9 m*l* of CH_2Cl_2. Then 14.6 g of α-pinene (105 mmol) was added slowly while stirring at room temperature. The reaction mixture was stirred at room temperature for 48 hrs. The usual analysis for active hydride by hydrolysis showed this solution to be 2.50 M in IpcBHI·SMe_2: ^{11}B-NMR δ −1.7 ppm (d, J_{BH}=123 Hz).

Regioselectivity of Hydroboration of Unsymmetrically Substituted Alkynes with IpcBHX·SMe_2

The regioselectivity of hydroboration was determined by oxidizing the intermediate alkenylboranes to the corresponding carbonyl compounds with hydrogen peroxide, followed by GC analysis.

Analysis for 1-Alkynes. To a 25° solution of 0.58 m*l* of 1-hexyne (0.415 g, 5.05 mmol), 0.85 g of dodecane (5.0 mmol) as an internal standard and 1.7 m*l* of CH_2Cl_2 were added, and finally 2.0 m*l* of a 2.50 M IpcBHI·SMe_2 solution in CH_2Cl_2 was injected into this mixture at 25°. After 12 h, the reaction mixture was cooled to 0°, neutralized with 2 m*l* of 2.5 N NaOH, followed by addition of 5 m*l* of buffer solution (pH 7). Then the mixture was oxidized by adding 1.5 m*l* of 30% H_2O_2 dropwise at 0°. The mixture was stirred for 2 h at 0°. Then the aqueous layer was saturated with K_2CO_3 and the organic layer was separated. Analysis of the organic layer by GC on a Carbowax 20 M capillary column revealed the presence of 98% hexanal and 2% 2-hexanone in a total yield of 92%.

Analysis for 2-Alkynes. To a 25° solution of 0.62 m*l* of 1-phenyl-1-propyne (0.581 g, 5.0 mmol), 0.85 g of dodecane (5.0 mmol) as an internal standard and 1.7 m*l* of CH_2Cl_2 was added 2.0 m*l* of a 2.50 M IpcBHI·SMe_2 solution in CH_2Cl_2. After 12 h at 0°, the reaction mixture was cooled to 0°, quenched with 5 m*l* of 3 N NaOH, and oxidized by adding 2.5 m*l* of 30% H_2O_2. The aqueous layer was saturated with K_2CO_3 and the organic layer was separated. Analysis of the organic layer by GC on a Carbowax 20 M capillary column revealed the presence of more than 99.9% 1-phenyl-2-propanone and only a trace of 1-phenyl-1-propanone in a total yield of 93%.

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