Synthesis of 2-Substituted Buta-1,3-dienes from 1,4-Dichlorobut-2-yne *via* Organoboranes[1]

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The reaction of 1,4-dichlorobut-2-yne **1** with a stoichiometric amount of di-*sec*-alkylborane **2**, prepared by the hydroboration of a sterically hindered internal alkene with BH_3 in tetrahydrofuran (THF), gave (*Z*)-(1,4-dichlorobut-2-en-2-yl)di-*sec*-alkylborane **3** stereospecifically. Treatment of compound **3** with methyllithium resulted in migration of an alkyl group from the boron atom to the adjacent carbon atom with elimination of two chlorine atoms to provide 2-*sec*-alkylbuta-1,3-dienes **5a–d**. Similar treatment of (*Z*)-(1,4-dichlorobut-2-en-2-yl)-*tert*-alkyl-primary-alkylborane, prepared by the successive reaction of BH_3 in THF with a tetrasubstituted ethene, relatively hindered terminal alkene, and compound **1**, provided highly pure 2-*tert*-alkylbuta-1,3-dienes **5e** and **5f** whose alkyl group was derived from the tetrasubstituted alkene. On the other hand, similar treatment of compound **3**, derived from a terminal or sterically unhindered internal alkene by a modified hydroboration procedure, provided the corresponding 2-primary-(or 2-*sec*-)alkylbuta-1,3-dienes **5g–m**. 2-(Alk-1-ynyl)buta-1,3-dienes **6a–c** were provided by the successive reaction of dibromoborane–dimethyl sulfide with compound **1**, alk-1-ynyldiethylaluminium and methyllithium, although the yields were less good. Successive treatment of (*Z*)-(1,4-dichlorobut-2-en-2-yl)bis-(1,2-dimethylpropyl)borane **3b** with alkylthiomagnesium bromide and methyllithium afforded exclusively 2-alkylthiobuta-1,3-dienes **8a–f** whose alkylthio group migrated from the boron atom *via* the borate complex.

Alkenylboranes are versatile intermediates and have provided a number of highly regio- and stereo-specific methods for achieving carbon–carbon bond formation.[2] While exploring the chemistry of functionally substituted alkenylboranes[3] having one or more functionalities in the neighbourhood of the alkenyl moiety, we became interested in the hydroboration of 1,4-dichlorobut-2-yne **1**, $ClCH_2C{\equiv}CCH_2Cl$, with dialkylboranes because of the polyfunctional character around the alkenyl moiety of (*Z*)-(1,4-dichlorobut-2-en-2-yl)dialkylborane **3** expected to be formed. Compound **3** has two chlorine atoms: one on the β-carbon atom and the other on the γ-carbon atom. Zweifel *et al.* reported that the reaction of (*Z*)-(1-chloroalk-2-en-2-yl)dialkylborane, whose chlorine atom is on the β-carbon atom, with aq. NaOH resulted in β-elimination of the dialkylboryl group and the chlorine atom to give the corresponding terminal allene,[4] whilst the reaction of (*E*)-(3-chloroalk-1-enyl)dialkylborane, whose chlorine atom is on the γ-carbon atom, with methyllithium resulted in a migration of an alkyl group from the boron atom to the adjacent carbon atom with a concomitant shift of the double bond and elimination of the chlorine atom to give the corresponding allylborane.[5] Pelter *et al.* also reported that (3-halogenoalk-1-enyl)dialkylborane, formed by the reaction of trialkyl alkynyl borate with dihalogenomethane, gave allylborane on elimination of the halogen atom.[6] Accordingly, compound **3** seems to be a potential intermediate. Previously, we communicated briefly that the reaction of compound **3** with a base such as methyllithium resulted in migration of an alkyl group from the boron atom to the adjacent carbon atom with elimination of two chlorine atoms to give 2-alkylbuta-1,3-dienes **5** in good yields.[1]

Since buta-1,3-diene and its derivatives are important in organic synthesis, especially as starting materials in Diels–Alder reactions, the ready and highly selective formation of compounds **5** in our earlier work, led us to report a further detailed study of the synthesis of 2-substituted buta-1,3-dienes from compound **1**.

Results and Discussion

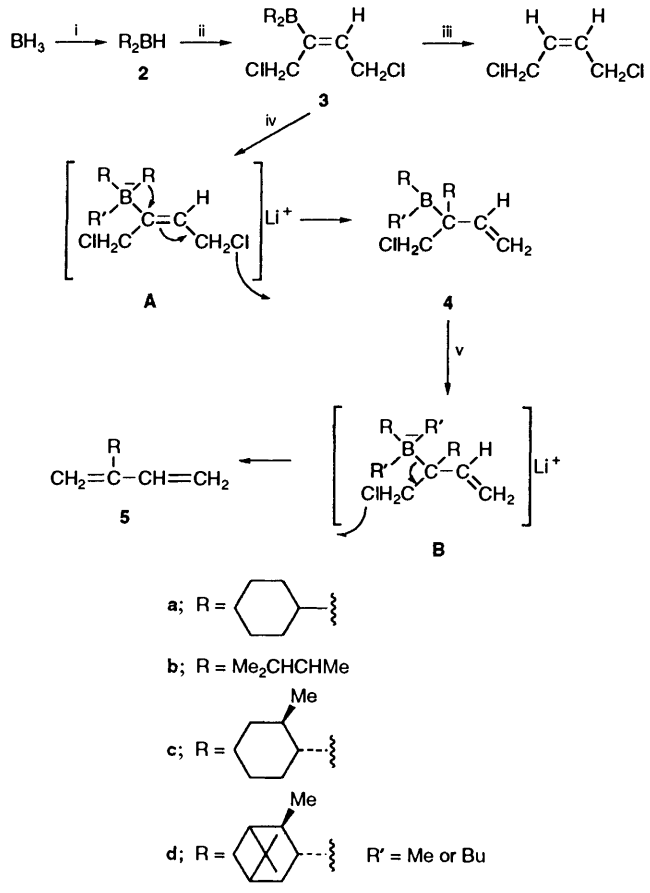
The hydroboration of compound **1** with an equimolar amount of dicyclohexylborane **2a**, prepared by the reaction of BH_3 in THF with 2 mol equiv. of cyclohexene, was carried out at 0 °C. After reaction for 2 h neither the starting alkyne **1** nor the residual hydride of compound **2a** was detected by GLC or by hydrolysis of the reaction mixture, respectively. These facts indicated that the hydroboration proceeds smoothly to the monohydroboration stage.

In order to clarify the stereochemistry of the hydroboration, the hydroboration mixture was treated with acetic acid, which can convert the carbon–boron bond of alkenylborane into a carbon–hydrogen bond with retention of configuration,[7] to give (*Z*)-1,4-dichlorobut-2-ene in quantitative yield and of high stereochemical purity. The *Z* configuration of this product was assigned by comparing its IR and ^1H NMR spectra with those of an authentic sample.

These results showed that the hydroboration provided (*Z*)-(1,4-dichlorobut-2-en-2-yl)dicyclohexylborane **3a** in a stereospecific manner. Similar results were obtained when bis(1,2-dimethylpropyl)borane **2b** was employed as the hydroborating agent (Scheme 1).

On the other hand, oxidation of the hydroboration product **3a** with alkaline hydrogen peroxide at 0 °C gave 2-cyclohexylbuta-1,3-diene **5a** in 42% yield (estimated by GLC) based on the amount of starting material **1**, accompanied by cyclohexanol. This result suggests that the added base, aq. NaOH, caused both migration and elimination to form compound **5a**. To optimize the yield of compound **5a**, the reaction conditions were examined, when it was found that treatment of compound **3a** in THF at −15 °C with 2 mol equiv. of methyllithium in diethyl ether or butyllithium in hexanes gave a near quantitative yield of product (Table 1).

Alkaline hydrogen peroxide oxidation of the reaction mixture, obtained by the reaction with butyllithium, gave nearly 2 mol equiv. of butanol and 1 mol equiv. of cyclohexanol. From these results a reaction mechanism including two borate



Scheme 1 *Reagents:* i, sterically hindered internal alkene; ii, **1**; iii, AcOH; iv, MeLi or BuLi; v, MeLi or BuLi

Table 1 Reaction of (*Z*)-(1,4-dichlorobut-2-en-2-yl)dicyclohexylborane **3a** with bases[a]

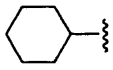
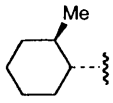
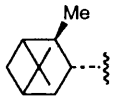
Base	Equiv. (Base/**3a**)	Yield of **5a** (%)[b]
NaOH–H_2O	2	49
	6	49
NaOMe–MeOH	2	74
BuLi–Hexanes	1	49
	2	95
MeLi–Et_2O	1	50
	2	98
	3	98

[a] After the addition of base to compound **3a** in THF at −15 °C, the reaction mixture was stirred for 1 h at 0 °C. [b] Determined by GLC and based on amount of alkyne **1** used.

complexes, **A** and **B**, is proposed as shown in Scheme 1. Reactions similar to the concomitant alkyl group migration and elimination of the chlorine atom on the γ-carbon atom from the borate complex **A**,[5] and to the β-elimination of the trialkylborane and the chlorine atom from the borate complex **B**[4] have appeared in the literature. On the other hand, a similar reaction of compound **3a** with 1 mol equiv. of alkyllithium failed to stop the reaction at the allylborane **4a** stage under the conditions indicated, and gave about 0.5 mol equiv. of compound **5a** (see Table 1).

Similar treatment of compounds **3** derived from 2-methylbut-2-ene, 1-methylcyclohexene, and 2,6,6-trimethylbicyclo[3.1.1]-hept-2-ene (α-pinene), with methyllithium afforded the corresponding 2-*sec*-alkylbuta-1,3-dienes **5b–d** in good yields. However, a similar treatment of (*Z*)-(1,4-dichlorobut-2-en-2-yl)bis(*trans*-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)borane **3d**, derived from a sterically very hindered alkene such as α-pinene, with butyllithium failed to give a satisfactory result, presumably because of steric hindrance. These results are shown in Table 2.

Table 2 Synthesis of 2-alkylbuta-1,3-dienes **5** by successive reaction of the alkyne **1** with the dialkylborane **2**, derived from a sterically hindered internal alkene, and alkyllithium

2	R'Li	Yield of **5** (%)[a]
a; R = 	BuLi	83
	MeLi	85
b; R = $Me_2CHCHMe$	MeLi	73
c; R = 	MeLi	70
d; R = 	BuLi	(12)
	MeLi	68

[a] Isolated yields are based on amount of alkyne **1** used. GLC yield is given in parentheses.

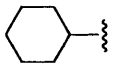
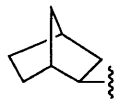
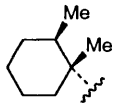
All the products were isolated from the reaction mixtures by column chromatography. Their ^1H and ^{13}C NMR and IR spectra showed that they were isomerically highly pure and supported the expected structures of the products. The configuration of 2-(*trans*-2-methylcyclohexyl)buta-1,3-diene **5c** and 2-(*trans*-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)buta-1,3-diene **5d** was assigned by analogy with a reaction involving transfer of the alkyl group with retention of configuration.[5,8]

Although the present procedure provides a synthetic method for 2-alkylbuta-1,3-diene whose alkyl group is derived from the sterically hindered internal alkene, only one of the two alkyl groups of the dialkylborane was utilized for the formation of compound **5**. To avoid this waste of the alkyl group, 1,1,2-trimethylpropylmonoalkylborane (thexylmonoalkylborane),[9] prepared by successive reaction of BH_3 in THF with 2,3-dimethylbut-2-ene, a tetrasubstituted ethene, and relatively hindered alkene such as cyclohexene, bicyclo[2.2.1]hept-2-ene, or 2-methyl-1-pentene, was employed as the hydroborating agent for compound **1**. In most reactions involving the migration of one alkyl group of alkenyldialkylborane to the α-alkenyl carbon atom, the thexyl group shows less migratory aptitude than another less hindered alkyl group on the same boron atom.[2,9]

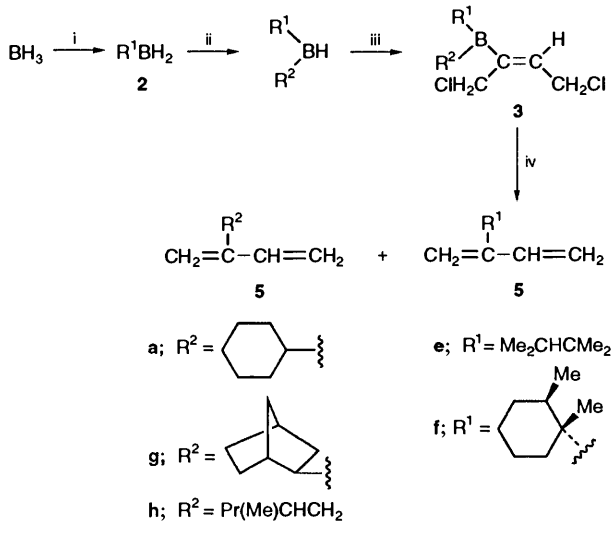
Thus, compound **1** was hydroborated with an equimolar amount of thexylcyclohexylborane **2ae**, and the reaction mixture was treated with 2 mol equiv. of methyllithium under conditions similar to those described above. GLC analysis of the reaction mixture revealed that compound **5a** and 2-(1,1,2-trimethylpropyl)buta-1,3-diene **5e** were obtained in 30 and 48% yield, respectively, based on the amount of starting material **1**. This result indicates that the thexyl group is more susceptible to migration than the cyclohexyl group. A similar result was obtained in the case where bicyclo[2.2.1]hept-2-ene was employed in place of cyclohexene providing 2-(*exo*-bicyclo-[2.2.1]heptan-2-yl)buta-1,3-diene **5g** (23%) and compound **5e** (67%), respectively.

A complete preferential migration of the thexyl group was demonstrated in a similar reaction where thexyl-2-methylpentylborane **2eh**, prepared by the method described above, was

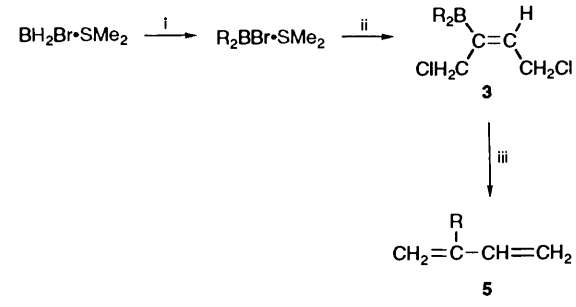
Table 3 Reaction of (*Z*)-(1,4-dichlorobut-2-en-2-yl)-tertiary-alkyl-secondary(or primary)-alkylborane with methyllithium

2		Yield of products (%)[a] $CH_2=C(R^1)-CH=CH_2$ **5**	Yield of products (%)[a] $CH_2=C(R^2)-CH=CH_2$ **5**
e; $R^1 = Me_2CHCMe_2$	**a**; R^2 = 	48	30
e; $R^1 = Me_2CHCMe_2$	**g**; R^2 = 	67	23
e; $R^1 = Me_2CHCMe_2$	**h**; $R^2 = Pr(Me)CHCH_2$	72(65)	0
f; R^1 = 	**h**; $R^2 = Pr(Me)CHCH_2$	75(70)	Trace

[a] GLC yields are based on amount of alkyne **1** used. In parentheses isolated yields are given.



Scheme 2 *Reagents:* i, 2,3-dimethylbut-2-ene or 1,2-dimethylcyclohex-1-ene; ii, cyclohexene, bicyclo[2.2.1]hept-2-ene or 2-methylpent-1-ene; iii, **1**; iv, MeLi



Scheme 3 *Reagents:* i, sterically unhindered alkene; ii, **1**, DIBAH; iii, MeLi

employed as the hydroborating agent providing compound **5e** in 72% yield (estimated by GLC) unaccompanied by 2-(2-methylpentyl)buta-1,3-diene **5h**. A similar preferential migration of the tertiary alkyl group was also observed in the reaction where 1,2-dimethylcyclohexene was employed as the tetrasubstituted ethene providing 2-(*trans,trans*-1,2-dimethylcyclohexyl)buta-1,3-diene **5f** (75%). These results are shown in Table 3. Participation of the tertiary alkyl group in preference to the other alkyl group is one of very few examples in organoborane chemistry.[10]

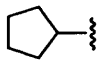
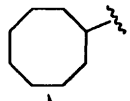
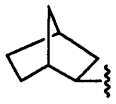
Compounds **5e** and **5f** were isolated from the reaction mixtures by column chromatography. Their ^1H and ^{13}C NMR and IR spectra showed that they were isomerically pure and supported the expected structures of the products. No isomerization of the tertiary alkyl groups was observed. Thus, the present reaction provides a convenient method for the preparation of 2-alkylbuta-1,3-dienes **5** having a very bulky tertiary alkyl group, derived from a sterically hindered internal alkene which can form monoalkylborane on hydroboration with BH_3 in THF, though it sacrifices the relatively hindered alk-1-ene.

On the other hand, an attempt to introduce a tertiary alkyl group not from the dialkylborane but from the *tert*-alkyllithium, added as the base, failed to give the desired product, presumably because the bulky tertiary alkyl anion was unable to attach to the boron atom having relatively bulky alkyl groups.

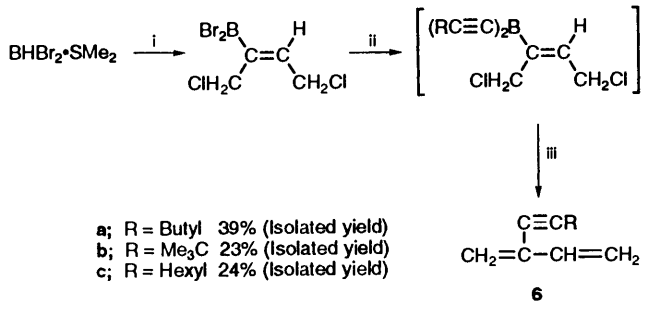
As demonstrated above, in the present method the alkyl group applied to the migration is limited to sterically hindered alkenes whose hydroboration with BH_3 can be stopped at the dialkylborane or monoalkylborane stage.

To apply the present reaction to a terminal alkene and a sterically unhindered internal alkene, whose hydroboration cannot be stopped at the dialkylborane stage by the customary hydroboration with BH_3, a modified procedure was used.[11] Thus, the desired dialkylborane was prepared by reduction of dialkylbromoborane[12] with diisobutylaluminium hydride (DIBAH) as shown in Scheme 3. *In situ* reaction of compound **1** with bis(2-methylpentyl)borane **2h**, obtained from 2-methyl pent-1-ene, followed by the reaction of 4 mol equiv. of methyllithium provided 2-(2-methylpentyl)buta-1,3-diene **5h** in 70% yield (isolated by column chromatography) based on the amount of starting material **1**. Similarly, when bis(*exo*-bicyclo-[2.2.1]heptan-2-yl)borane **2g**, derived from bicyclo[2.2.1]hept-2-ene, was employed as the hydroborating agent, 2-(*exo*-bicyclo[2.2.1]heptan-2-yl)buta-1,3-diene **5g** was obtained in 68% yield. The results, similarly obtained by using several types of sterically unhindered alkenes, are shown in Table 4. These demonstrate that the present reaction is also applicable to the introduction of the sterically unhindered alkyl group as well as the hindered one.

Table 4 Synthesis of 2-alkylbuta-1,3-dienes **5** by successive reaction of the alkyne **1** with the dialkylborane **2**, derived from sterically unhindered alkene, and methyllithium

2	Yield of 5 (%)[a]
h; R = Pr(Me)CHCH$_2$	70
i; R = Hexyl	46
j; R = Ph(Me)CHCH$_2$	62
k; R = Me$_3$Si(CH$_2$)$_3$	54
l; R = 	82
m; R = 	51
g; R = 	68

[a] Isolated yields are based on amount of alkyne **1** used.



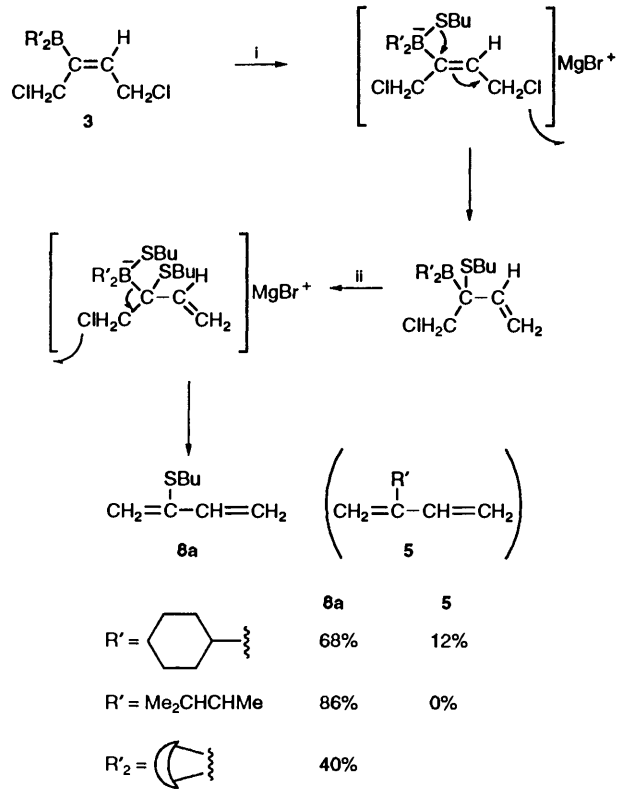
Scheme 4 *Reagents:* i, **1**, BBr_3; ii, $Et_2AlC{\equiv}CR$; iii, MeLi

It has been reported that the alk-1-ynyl group on the boron atom in a borate complex migrates in preference to cyclohexyl or 1,2-dimethylpropyl group on the same boron atom.[3b,13] Accordingly, it seemed probable that the present reaction could provide a method for the synthesis of 2-(alk-1-ynyl)buta-1,3-diene **6**.

A first attempt where 2 mol equiv. of alk-1-ynyllithium was allowed to react directly with compound **2a** gave an unexpected result, causing preferential migration of the cyclohexyl group to the alk-1-ynyl group. However, compound **6** could be synthesized by using a modified procedure including hydroboration of compound **1** with dibromoborane–dimethyl sulfide complex ($BHBr_2$•SMe_2)[14] and conversion of alk-1-ynyllithium into alk-1-ynyldiethylaluminium[15] (Scheme 4). Thus, compound **6**, substituted by a hex-1-ynyl, 3,3-dimethylbut-1-ynyl or oct-1-ynyl group, was isolated from the reaction mixture by column chromatography.

As indicated in Scheme 4, the yields of compounds **6** were so poor that the reaction procedure needs to be appropriately modified to be of use as a synthetic method.

Previously, we found that an alkylthio[3c] or an alkylseleno[3d] group migrated to the adjacent alkynyl carbon atom in preference to a secondary alkyl group when attached to the same boron atom in a borate complex. If the present reaction proceeds through the borate complexes as shown in Scheme 1, the use of alkylthio-* or alkylseleno-† magnesium halide instead of methyllithium is expected to provide the corresponding 2-alkylthio- or 2-alkylseleno-buta-1,3-diene.



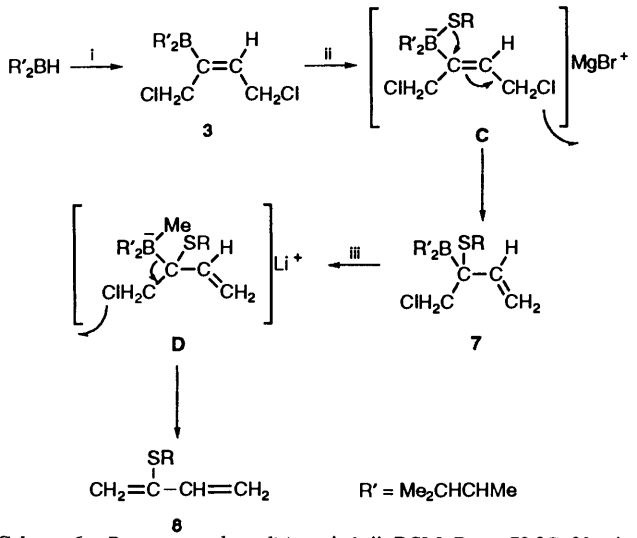
Scheme 5 *Reagents and conditions:* i, BuSMgBr, 0 °C; ii, BuSMgBr, 0 °C

As expected, successive treatment of compound **1** with 1 mol equiv. of compound **2a** and 2 mol equiv. of butylthiomagnesium bromide in THF at 0 °C provided 2-butylthiobuta-1,3-diene **8a** in 68% yield (estimated by GLC) based on the amount of starting material **1** together with a small amount of compound **5a**; this indicated that the alkylthio group migrated preferentially from the boron atom (Scheme 5). To avoid contamination by the by-product, 9-borabicyclo[3.3.1]nonane (9-BBN)[16] was examined as the hydroborating agent, but the yield of compound **8a** was poor. On the other hand, the use of compound **2b**, instead of compound **2a**, as the hydroborating agent increased the yield of compound **8a** (86%, estimated by GLC) and decreased the contamination by compound **5b** markedly. In this case, however, an appreciable amount of dibutyl disulfide, which was probably formed by coupling of the unchanged butylthio group during formation of compound **8a**, was present during the work-up process and this made the isolation of compound **8a** by column chromatography or by distillation difficult.

If compound **8a** is formed by a similar mechanism (see Scheme 1), the butylthio group on the boron atom in the second borate complex of Scheme 5 does not directly participate in the formation of compound **8a**. Accordingly, the use of methyllithium instead of the second butylthiomagnesium bromide was expected to avoid the formation of dibutyl disulfide. Thus, (*Z*)-(1,4-dichlorobut-2-en-2-yl)bis-(1,2-dimethylpropyl)borane **3b** was treated successively with butylthiomagnesium bromide and methyllithium in a molar ratio of 1:1:1 at −78 °C (Scheme 6). As expected, compound **8a** was obtained almost free of dibutyl disulfide, although the yield was a little decreased (78%, estimated by GLC). This result suggests that the reaction proceeds *via* two borate complexes, **C** and **D** (see Scheme 6), the intermediate **7** being relatively stable in contrast to the intermediate **4** proposed in Scheme 1.

* Alkylthiomagnesium bromide was prepared by the reaction of equimolar amounts of alkanethiol and ethylmagnesium bromide.

† Alkylselenomagnesium halide was prepared by the reaction of equimolar amounts of alkylmagnesium halide and selenium powder.



Scheme 6 *Reagents and conditions:* i, **1**; ii, RSMgBr, −78 °C, 30 min; iii, MeLi, −78 °C, 30 min

The reaction of compound **3** with a number of alkylthiomagnesium bromides was examined in a manner similar to that described above. In all cases examined, highly pure 2-alkylthiobuta-1,3-dienes **8a–f** were isolated from reaction mixtures after work-up and column chromatography (see Table 5). The results obtained showed that this reaction provides a synthetic method for compound **8**.

Although the synthesis of 2-alkylselenobuta-1,3-dienes by a similar reaction procedure was also examined, these compounds seem to be unstable and have yet to be isolated.

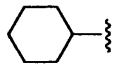
In conclusion, the reaction of (*Z*)-(1,4-dichlorobut-2-en-2-yl)dialkylboranes **3**, prepared by the hydroboration of 1,4-dichlorobut-2-yne **1** with dialkylboranes **2**, with methyllithium proceeded readily and stereo- and/or regio-specifically to give 2-*tert*-, 2-*sec*-, and 2-primary-alkylbuta-1,3-dienes **5** whose alkyl group was derived from the corresponding alkene *via* hydroboration. In addition, the above reaction was also applicable to the syntheses of 2-(alk-1-ynyl)buta-1,3-dienes **6** and 2-alkylthiobuta-1,3-dienes **8** whose alk-1-ynyl and alkylthio groups were not available *via* hydroboration.

Experimental

IR spectra were recorded for liquid films inserted between NaCl plates in an Hitachi 285 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-200 (200 MHz) FT NMR spectrometer for $CDCl_3$ solutions. Chemical shifts are reported in δ values with Me_4Si as internal reference, unless otherwise stated. *J*-Values are given in Hz. ^{13}C NMR spectral processing was performed using the INEPT pulse sequence technique. Mass spectra were recorded with an Hitachi M-52 mass spectrometer operating at 20 eV, unless otherwise stated. GLC analyses using the internal standard method were performed with an Hitachi 163 gas chromatograph equipped with a glass column (10% PEG-20M on Diasolid M, 2 m or 5% FFAP on Diasolid M, 1 m), a flame ionization detector, and a Shimadzu C-R3A Chromatopac digital integrator-recorder.

All reactions were carried out under argon. Alkenes, alkynes and solvents employed in the reactions were used after purification by methods generally employed in similar organoborane chemistry.[17] 1,4-Dichlorobut-2-yne (Aldrich) was dried over $CaCl_2$, purified by distillation, and stored in a refrigerator. Alkanethiols were used after distillation. A 1.4 mol dm^{-3} solution of methyllithium in diethyl ether, a 1.6 mol dm^{-3} solution of butyllithium in hexanes, a 1.0 mol dm^{-3} solution of $BH_2Br{\cdot}SMe_2$ in dichloromethane, a 1.0 mol dm^{-3} solution of $BHBr_2{\cdot}SMe_2$ in dichloromethane, a 1.0 mol dm^{-3} solution of BBr_3 in dichloromethane, a 1.0 mol dm^{-3} solution of DIBAH in hexanes, and 1.0 mol dm^{-3} solution of Et_2AlCl in hexanes were obtained from Aldrich Chemicals. A solution of BH_3 in THF[18] and 3,3-dimethylbut-1-yne[19] were prepared by the literature methods. Aluminium oxide for chromatography was Merck 1076 (Aluminium oxide 90 active basic). Silica gel for chromatography was Wakogel Q-50 (60–200 mesh).

Table 5 Synthesis of 2-alkylthiobuta-1,3-dienes **8** by successive treatment of (*Z*)-(1,4-dichlorobut-2-en-2-yl)bis-(1,2-dimethylpropyl)-borane **3b** with alkylthiomagnesium bromide and methyllithium

RSMgBr	Yield of **8** (%)[a]
a; R = Butyl	68 (78)
b; R = $MeCH_2CHMe$	79
c; R = Me_3C	35
d; R = Hexyl	77
e; R = 	51
f; R = $PhCH_2$	68

[a] Isolated yields are based on amount of alkyne **1** used. GLC yield is given in parentheses.

Procedure for the Synthesis of 2-sec-*Alkylbuta*-1,3-*dienes* **5a–d**.—A dry 100 cm^3 round-bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap, and a magnetic stirring bar, was flushed with argon. In the flask, a dialkylborane **2** (20 mmol) was prepared by the hydroboration of a sterically hindered internal alkene (40 mmol) with BH_3 (20 mmol) in THF under conditions described in the literature.[2,17,18]

1,4-Dichlorobut-2-yne **1** (2.46 g, 20 mmol) was added to the dialkylborane at −15 °C, and the reaction mixture was stirred for 2 h at 0 °C [except in the case of bis(*trans*-2-methylcyclohexyl)borane **2c** for which the reaction was carried out at room temperature for 4 h]. To the reaction mixture at −15 °C was added a solution of methyllithium (28.57 cm^3, 40 mmol) in diethyl ether, and the mixture was stirred for 1 h at 0 °C. The reaction mixture was then treated with ice-cooled water (20 cm^3) at 0 °C, and extracted three times with diethyl ether. The combined extracts were washed with cold brine (in the analytical reaction GLC analyses were carried out at this point), and dried (K_2CO_3) in a refrigerator. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was put on a basic aluminium oxide column cooled by a jacket through which cold ethanol (−20 ~ −15 °C) was circulated. Elution with pentane gave the corresponding 2-alkylbuta-1,3-diene **5a–d**.

2-*Cyclohexylbuta*-1,3-*diene* **5a** (2.32 g, 85%) (Found: C, 88.0; H, 12.0. $C_{10}H_{16}$ requires C, 88.2; H, 11.8%); ν_{max}(film)/cm^{-1} 3080, 2920, 2845, 1780, 1735, 1630, 1590, 1445, 1390, 1285, 1270, 1120, 1070, 1035, 990, 945, 895, 885, 860 and 740; δ_H 1.05–2.00 (10 H, m, ring 2-, 3-, 4-, 5- and 6-H_2), 2.10–2.20 (1 H, m, ring 1-H), 4.94 (1 H, d, *J* 1.0, C*H*H=C), 4.99 (1 H, d, *J* 1.0, CH*H*=C), 5.02 (1 H, d, *J* 10.2, CH=C*H*H), 5.26 (1 H, d, *J* 17.1, CH=CH*H*) and 6.32 (1 H, dd, *J* 17.1 and 10.2, C*H*=CH_2); δ_C 26.53 (CH_2), 26.92 (2 × CH_2), 32.93 (2 × CH_2), 39.23 (CH), 112.35 (=CH_2), 112.74 (=CH_2), 138.87 (=CH) and 152.15 (=C); *m*/*z* 136 (M$^+$, 42%), 121 (88), 108 (28), 107 (65), 95 (42), 94 (67), 93 (58), 82 (30), 81 (77), 80 (42), 79 (88), 68 (51), 67 (100), 55 (32) and 54 (33).

2-(1,2-*Dimethylpropyl*)*buta*-1,3-*diene* **5b** (1.81 g, 73%) (Found: C, 86.6; H, 13.4. C_9H_{16} requires C, 87.0; H, 13.0%); ν_{max}(film)/cm^{-1} 3075, 2955, 2920, 2860, 1780, 1735, 1625, 1590, 1455, 1380, 1370, 1280, 1270, 1120, 1070, 990, 890 and 740; δ_H

0.84 (3 H, d, *J* 6.8, CH*Me*), 0.88 (3 H, d, *J* 6.8, CH*Me*), 1.02 (3 H, d, *J* 7.3, CH*Me*), 1.60–1.80 (1 H, m, C*H*Me$_2$), 2.15–2.35 (1 H, m, C*H*Me), 4.91 (1 H, s, C*H*H=C), 5.01 (1 H, d, *J* 10.7, CH=C*H*H), 5.07 (1 H, s, CH*H*=C), 5.27 (1 H, d, *J* 17.6, CH=CH*H*) and 6.32 (1 H, dd, *J* 17.6 and 10.2, C*H*=CH$_2$); δ_C 16.05 (Me), 18.80 (Me), 21.47 (Me), 31.47 (CH), 41.01 (CH), 112.64 (=CH$_2$), 113.64 (=CH$_2$), 139.11 (=CH) and 151.39 (=C); *m/z* 124 (M^+, 19%), 109 (30), 95 (38), 82 (80), 81 (44), 79 (22), 70 (23), 68 (23), 67 (100), 55 (18), 53 (18), 45 (22), 43 (53) and 41 (28).

2-(trans-2-*Methylcyclohexyl*)*buta*-1,3-*diene* **5c** (2.10 g, 70%) (Found: C, 87.6; H, 12.4. $C_{11}H_{18}$ requires C, 87.9; H, 12.1%); ν_{max}(film)/cm^{-1} 3080, 2920, 2845, 1780, 1735, 1625, 1590, 1440, 1390, 1370, 1285, 1270, 1120, 1070, 1035, 990, 965, 890, 865, 830 and 740; δ_H 0.78 (3 H, d, *J* 6.3, ring 2-Me), 1.10–2.15 (10 H, m, ring 1- and 6-H, and 2-, 3-, 4- and 5-H$_2$), 4.92 (1 H, s, C*H*H=C), 5.00 (1 H, d, *J* 10.7, CH=C*H*H), 5.06 (1 H, s, CH*H*=C), 5.31 (1 H, d, *J* 17.6, CH=CH*H*) and 6.35 (1 H, dd, *J* 17.6 and 10.7, C*H*=CH$_2$); δ_C 20.35 (Me), 26.68 (CH$_2$), 26.95 (CH$_2$), 34.32 (CH$_2$), 35.80 (CH$_2$), 36.46 (CH), 46.94 (CH), 112.47 (=CH$_2$), 113.35 (=CH$_2$), 139.16 (=CH) and 151.20 (=C); *m/z* 150 (M^+, 40%), 135 (63), 122 (18), 121 (63), 109 (19), 108 (46), 107 (54), 96 (27), 95 (67), 94 (51), 93 (86), 82 (34), 81 (99), 80 (34), 79 (100), 68 (40), 67 (71) and 55 (43).

2-(trans-2,6,6-*Trimethylbicyclo*[3.3.1]*heptan*-3-*yl*)*buta*-1,3-*diene* **5d** (2.59 g, 68%) (Found: C, 88.0; H, 12.0. $C_{14}H_{22}$ requires C, 88.35; H, 11.65%); ν_{max}(film)/cm^{-1} 3080, 2900, 1780, 1735, 1625, 1590, 1465, 1450, 1385, 1370, 1270, 1215, 1140, 1120, 1070, 1010, 990, 910, 890, 850 and 740; δ_H 0.97 (3 H, d, *J* 7.3, ring 2-Me), 1.10 (3 H, s, ring 6-Me), 1.23 (3 H, s, ring 6-Me), 1.50–2.45 (7 H, m, ring 2-, 3- and 5-H, and 4- and 7-H$_2$), 2.63–2.83 (1 H, m, ring 1-H), 5.00 (1 H, s, C*H*H=C), 5.07 (1 H, d, *J* 10.3, CH=C*H*H), 5.10 (1 H, s, CH*H*=C), 5.38 (1 H, dd, *J* 17.6 and 1.0, CH=CH*H*) and 6.42 (1 H, dd, *J* 17.6 and 10.3, C*H*=CH$_2$); δ_C 21.33 (Me), 22.98 (Me), 28.41 (Me), 34.24 (CH$_2$), 35.41 (CH$_2$), 39.04 (C), 40.20 (CH), 41.47 (CH), 41.93 (CH), 48.04 (CH), 112.28 (=CH$_2$), 113.59 (=CH$_2$), 138.70 (=CH) and 152.93 (=C); *m/z* 190 (M^+, 4%), 175 (9), 161 (7), 147 (45), 135 (66), 119 (28), 107 (35), 105 (39), 95 (37), 93 (62), 91 (53), 83 (100), 79 (37), 69 (51) and 55 (52).

Procedure for the Synthesis of 2-tert-*Alkylbuta*-1,3-*dienes* **5e** *and* **5h**.—The experimental set-up was the same as that described in the synthesis of compounds **5a–d**. The flask was cooled to −15 °C and charged with a solution of BH_3 (20 mmol) in THF. To the stirred solution was added a tetrasubstituted alkene (20 mmol), and the reaction mixture was stirred for 2 h at 0 °C. 2-Methylpent-1-ene (1.68 g, 20 mmol) was added to the resulting monoalkylborane at −20 °C, and the reaction mixture was stirred for 1 h at the same temperature. Then 1,4-dichlorobut-2-yne **1** (2.46 g, 20 mmol) was added to the mixed dialkylborane at −20 °C. The reaction mixture was allowed to warm to 0 °C and then stirred for 2 h at the same temperature to complete the hydroboration. A solution of methyllithium (28.57 cm^3, 40 mmol) in diethyl ether was added to the reaction mixture at −15 °C, and the mixture was stirred for 1 h at 0 °C. By procedures similar to those described in the synthesis of compounds **5a–d**, compounds **5e** and **5h** were isolated from the reaction mixtures.

2-(1,1,2-*Trimethylpropyl*)*buta*-1,3-*diene* **5e** (1.80 g, 65%) (Found: C, 86.5; H, 13.5. $C_{10}H_{18}$ requires C, 86.9; H, 13.1%); ν_{max}(film)/cm^{-1} 3075, 2950, 2920, 2850, 1790, 1625, 1605, 1465, 1415, 1375, 1135, 1070, 985, 915 and 900; δ_H 0.78 (6 H, d, *J* 6.8, CH*Me*$_2$), 0.98 (6 H, s, CMe$_2$), 1.60–1.80 (1 H, m, C*H*Me$_2$), 4.75 (1 H, d, *J* 1.5, C*H*H=C), 4.98 (1 H, dd, *J* 10.7 and 2.0, CH=C*H*H), 5.11 (1 H, s, CH*H*=C), 5.37 (1 H, dd, *J* 17.1 and 2.4, CH=CH*H*) and 6.40 (1 H, dd, *J* 17.1 and 10.7, C*H*=CH$_2$); δ_C 17.41 (2 × Me), 23.01 (2 × Me), 33.95 (CH), 40.79 (C), 108.58 (=CH$_2$), 114.64 (=CH$_2$), 137.31 (=CH) and 156.33 (=C); *m/z* 138 (M^+, 11%), 123 (17), 109 (7), 96 (25), 95 (100), 82 (17), 81 (36), 79 (22), 67 (61), 55 (29), 43 (22) and 41 (14).

2-(trans,trans-1,2-*Dimethylcyclohexyl*)*buta*-1,3-*diene* **5h** (2.30 g, 70%) [Found: M^+, 164.2901 (JEOL TMS-D 300). $C_{12}H_{20}$ requires *M*, 164.2908]; ν_{max}(film)/cm^{-1} 3075, 2920, 2850, 1790, 1625, 1600, 1460, 1440, 1415, 1375, 1145, 1110, 1060, 1005, 990, 910, 900, 850 and 740; δ_H 0.66 (3 H, d, *J* 6.8, ring 2-Me), 0.98 (3 H, s, ring 1-Me), 1.15–1.80 (9 H, m, ring 2-H, and ring 3-, 4-, 5- and 6-H$_2$), 4.80 (1 H, d, *J* 1.5, C*H*H=C), 4.99 (1 H, dd, *J* 10.7 and 2.4, CH=C*H*H), 5.14 (1 H, s, CH*H*=C), 5.36 (1 H, dd, *J* 16.6 and 2.4, CH=CH*H*) and 6.49 (1 H, dd, *J* 16.6 and 10.7, C*H*=CH$_2$); δ_C 15.95 (Me), 16.37 (Me), 22.06 (CH$_2$), 26.41 (CH$_2$), 30.21 (CH$_2$), 36.07 (CH), 38.14 (CH$_2$), 41.59 (C), 109.41 (=CH$_2$), 114.78 (=CH$_2$), 137.31 (=CH) and 156.72 (=C).

Procedure for the Synthesis of 2-primary- *or* 2-sec-*Alkylbuta*-1,3-*dienes* **5g–m**.—A dry 200 cm^3 round-bottomed flask equipped as described in the synthesis of compounds **5a–d** was flushed with argon. The flask was cooled to 0 °C and charged with a solution of $BH_2Br{\cdot}SMe_2$ (10 cm^3, 10 mmol) in dichloromethane. To the stirred solution was added an unhindered alkene (20 mmol), and the reaction mixture was stirred for 2 h at 25 °C (except in the case of cyclooctene in which the reaction was carried out at room temperature for 24 h) to complete the hydroboration. After removal of dichloromethane and dimethyl sulfide under reduced pressure with a water aspirator, dry diethyl ether (40 cm^3) and dry dimethyl sulfide (2 cm^3) were added to the resulting dialkylbromoborane at 0 °C, and the solution was stirred for 30 min at the same temperature. 1,4-Dichlorobut-2-yne **1** (1.23 g, 10 mmol) was added to the cooled solution (−78 °C), followed by the slow addition of a solution of DIBAH (10 cm^3, 10 mmol) in hexanes. The reaction mixture was brought to 0 °C, stirred for 3 h at the same temperature and for an additional 2 h at room temperature to complete the hydroboration. A solution of methyllithium (28.57 cm^3, 40 mmol) in diethyl ether was added to the reaction mixture at −15 °C, and the mixture was stirred for 1 h at 0 °C. By procedures similar to those described in the synthesis of compounds **5a–d**, compounds **5g–m** were isolated from the reaction mixtures.

2-(exo-*Bicyclo*[2.2.1]*heptan*-2-*yl*)*buta*-1,3-*diene* **5g** (1.01 g, 68%) (Found: C, 88.7; H, 11.3. $C_{11}H_{16}$ requires C, 89.1; H, 10.9%); ν_{max}(film)/cm^{-1} 3080, 2950, 2860, 1785, 1625, 1590, 1450, 1385, 1310, 1295, 1240, 1210, 1135, 1055, 990, 890, 845 and 760; δ_H 1.08–1.68 (8 H, m), 2.20–2.40 (3 H, m), 4.96 (2 H, s, CH$_2$=C), 5.03 (1 H, dd, *J* 10.7 and 1.0, CH=C*H*H), 5.23 (1 H, d, *J* 17.6, CH=CH*H*) and 6.34 (1 H, dd, *J* 17.6 and 10.7, C*H*=CH$_2$); δ_C 29.06 (CH$_2$), 30.11 (CH$_2$), 36.14 (CH$_2$), 36.56 (CH), 37.77 (CH$_2$), 40.57 (CH), 42.32 (CH), 112.81 (=CH$_2$), 113.11 (=CH$_2$), 139.64 (=CH) and 150.74 (=C); *m/z* 148 (M^+, 13%), 133 (12), 119 (22), 107 (12), 106 (22), 105 (23), 94 (11), 93 (16), 92 (29), 91 (37), 82 (20), 81 (29), 80 (74), 79 (93), 67 (100), 66 (19) and 41 (14).

2-(2-*Methylpentyl*)*buta*-1,3-*diene* **5h** (0.97 g, 70%) (Found: C, 86.6; H, 13.4. $C_{10}H_{18}$ requires C, 86.9; H, 13.1%); ν_{max}(film)/cm^{-1} 3080, 2960, 2925, 2870, 1790, 1590, 1460, 1375, 1150, 990, 895 and 735; δ_H 0.84 (3 H, d, *J* 6.8, CH*Me*), 0.89 (3 H, t, *J* 6.8, CH$_2$*Me*), 1.20–1.75 (5 H, m, 2-H, and 3- and 4-H$_2$), 1.87–2.02 (1 H, m, C*H*H–CH), 2.18–2.33 (1 H, m, CH*H*–CH), 4.94 (1 H, s, C*H*H=C), 5.04 (1 H, d, *J* 10.3, CH=C*H*H), 5.04 (1 H, d, *J* 1.5, CH*H*=C), 5.11 (1 H, d, *J* 17.6, CH=CH*H*) and 6.35 (1 H, dd, *J* 17.6 and 10.3, C*H*=CH$_2$); δ_C 14.35 (Me), 19.67 (Me), 20.21 (CH$_2$), 31.11 (CH), 39.52 (CH$_2$), 39.64 (CH$_2$), 113.28 (=CH$_2$), 116.83 (=CH$_2$), 139.11 (=CH) and 145.34 (=C); *m/z* 138 (M^+, 8%), 123 (7), 108 (26), 94 (15), 81 (9), 80 (12), 70 (8), 69 (22), 68 (34), 67 (100), 66 (24), 55 (23), 43 (73) and 41 (17).

2-*Hexylbuta*-1,3-*diene* **5i** (0.64 g, 46%) (Found: C, 86.7; H, 13.3. $C_{10}H_{18}$ requires C, 86.9; H, 13.1%); ν_{max}(film)/cm^{-1} 3080, 2960, 2930, 2860, 1790, 1590, 1465, 1375, 990, 895 and 725; δ_H

0.89 (3 H, t, *J* 6.4, Me), 1.15–1.60 [8 H, m, $(CH_2)_4$], 2.20 (2 H, t, *J* 6.8, CH_2), 4.99 (2 H, s, CH_2=C), 5.04 (1 H, dd, *J* 10.7 and 1.0, CH=C*H*H), 5.22 (1 H, d, *J* 17.6, CH=CH*H*) and 6.37 (1 H, dd, *J* 17.6 and 10.7, C*H*=CH_2); δ_C 14.10 (Me), 22.64 (CH_2), 28.14 (CH_2), 29.31 (CH_2), 31.35 (CH_2), 31.76 (CH_2), 113.01 (=CH_2), 115.42 (=CH_2), 139.04 (=CH) and 146.63 (=C); *m*/*z* 138 (M^+, 2%), 123 (1), 109 (2), 108 (6), 95 (8), 94 (1), 81 (5), 80 (14), 78 (4), 68 (12), 67 (100), 66 (34), 55 (9), 53 (9), 43 (9) and 41 (13).

2-(2-*Phenylpropyl*)*buta*-1,3-*diene* **5j** (1.07 g, 62%) (Found: C, 90.4; H, 9.6. $C_{13}H_{16}$ requires C, 90.6; H, 9.4%); ν_{max}(film)/cm^{-1} 3080, 3020, 2960, 2920, 2850, 1940, 1790, 1590, 1490, 1450, 1370, 1025, 1010, 990, 895, 750 and 700; δ_H 1.24 (3 H, d, *J* 6.8, Me), 2.30–2.65 (2 H, m, C*H*$_2$CH), 2.85–3.10 (1 H, m, C*H*Me), 4.86 (1 H, s, C*H*H=C), 5.00 (1 H, d, *J* 1.5, CH*H*=C), 5.08 (1 H, d, *J* 11.2, CH=C*H*H), 5.26 (1 H, d, *J* 17.6, CH=CH*H*), 6.34 (1 H, dd, *J* 17.6 and 11.2, C*H*=CH_2) and 7.15–7.35 (5 H, m, Ph); δ_C 21.67 (Me), 38.09 (CH), 40.69 (CH_2), 113.42 (=CH_2), 117.56 (=CH_2), 125.92 (=CH), 126.87 (2 × =CH), 128.28 (2 × =CH), 138.77 (=CH), 144.51 (=C) and 147.45 (=C); *m*/*z* 172 (M^+, 12%), 157 (5), 143 (6), 130 (6), 105 (10), 104 (100) and 78 (11).

2-[3-(*Trimethylsilyl*)*propyl*]*buta*-1,3-*diene* **5k** (0.71 g, 54%) (Found: C, 63.1; H, 15.7. $C_7H_{20}Si$ requires C, 63.5; H, 15.2%); ν_{max}(film)/cm^{-1} 3080, 2950, 1780, 1590, 1455, 1410, 1290, 1245, 1170, 1030, 990, 905, 890, 860, 835, 755 and 690; δ_H($CDCl_3$; $CHCl_3$ δ_H 7.25) −0.02 (9 H, s, Me_3Si), 0.45–0.60 (2 H, m, C*H*$_2$$SiMe_3$), 1.40–1.60 (2 H, m, C*H*$_2$$CH_2SiMe_3$), 2.15–2.30 (2 H, m, C*H*$_2$$CH_2CH_2SiMe_3$), 4.97 (1 H, s, CH*H*=C), 5.00 (1 H, d, *J* 1.0, C*H*H=C), 5.03 (1 H, d, *J* 10.7, CH=C*H*H), 5.21 (1 H, d, *J* 17.6, CH=CH*H*) and 6.36 (1 H, dd, *J* 17.6 and 10.7, C*H*=CH_2); δ_C($CDCl_3$; $CHCl_3$ δ_C 77.5) −1.38 (3 × Me), 17.02 (CH_2), 22.98 (CH_2), 35.61 (CH_2), 113.35 (=CH_2), 115.90 (=CH_2), 139.28 (=CH) and 146.75 (=C); *m*/*z* 168 (M^+, 3%), 143 (10), 125 (26), 101 (29), 99 (20), 97 (19), 94 (32), 85 (9), 75 (17), 74 (43), 73 (100), 68 (34), 59 (44) and 45 (7).

2-*Cyclopentylbuta*-1,3-*diene* **5l** (1.00 g, 82%) (Found: C, 88.15; H, 11.85. C_9H_{14} requires C, 88.45; H, 11.55%); ν_{max}(film)/cm^{-1} 3080, 2950, 2860, 1780, 1625, 1590, 1450, 1385, 1285, 1240, 1070, 1030, 990 and 890; δ_H 1.30–2.00 (8 H, m, ring 2-, 3-, 4- and 5-H_2), 2.62–2.82 (1 H, m, ring 1-H), 4.98 (2 H, s, CH_2=C), 5.05 (1 H, dd, *J* 10.7 and 1.0, CH=C*H*H), 5.28 (1 H, d, *J* 17.6, CH=CH*H*) and 6.38 (1 H, dd, *J* 17.6 and 10.7, C*H*=CH_2); δ_C 25.07 (2 × CH_2), 31.96 (2 × CH_2), 40.81 (CH), 112.38 (=CH_2), 113.18 (=CH_2), 139.52 (=CH) and 150.40 (=C); *m*/*z* 122 (M^+, 31%), 107 (29), 93 (41), 81 (100), 79 (68) and 67 (39).

2-*Cyclooctylbuta*-1,3-*diene* **5m** (0.84 g, 51%) (Found: C, 87.2; H, 12.8. $C_{12}H_{20}$ requires C, 87.7; 12.3%); ν_{max}(film)/cm^{-1} 3080, 2920, 2850, 1780, 1625, 1590, 1460, 1440, 1390, 1350, 1035, 990, 890 and 815; δ_H 1.30–1.87 (14 H, m, ring 2-, 3-, 4-, 5-, 6-, 7- and 8-H_2), 2.40–2.60 (1 H, m, ring 1-H), 4.95 (1 H, s, CH*H*=C), 4.97 (1 H, s, C*H*H=C), 5.02 (1 H, d, *J* 10.7, CH=C*H*H), 5.26 (1 H, d, *J* 17.6, CH=CH*H*) and 6.30 (1 H, dd, *J* 17.6 and 10.7, C*H*=CH_2); δ_C 25.93 (2 × CH_2), 26.46 (CH_2), 26.90 (2 × CH_2), 32.23 (2 × CH_2), 38.55 (CH), 112.42 (=CH_2), 113.13 (=CH_2), 139.08 (=CH) and 153.68 (=C); *m*/*z* 164 (M^+, 11%), 149 (16), 134 (35), 120 (31), 108 (29), 107 (29), 106 (38), 95 (31), 94 (51), 93 (37), 92 (63), 81 (48), 80 (98), 79 (44), 78 (75), 68 (31), 67 (100), 66 (99), 54 (56), 53 (27), 43 (12) and 41 (27).

Procedure for the Synthesis of 2-(*Alk*-1-*ynyl*)*buta*-1,3-*dienes* **6a–c**.—The experimental set-up was the same as that described in the synthesis of compounds **5g–m**. The flask was cooled to 0 °C and charged with a solution of $BHBr_2$·SMe_2 (10 cm^3, 10 mmol) in dichloromethane. 1,4-Dichlorobut-2-yne **1** (1.23 g, 10 mmol) was added to the stirred solution, followed by the addition of a solution of BBr_3 (5 cm^3, 5 mmol) in dichloromethane;[20] the reaction mixture was then stirred for 24 h at 0 °C. After removal of dichloromethane under reduced pressure, dry THF (25 cm^3) was added to the reaction flask.

In another argon-flushed 200 cm^3 round-bottomed flask equipped as described above were placed alk-1-yne (35 mmol) and dry THF (35 cm^3), and then the flask was cooled to −70 °C. To the stirred solution was added dropwise a solution of butyllithium (21.88 cm^3, 35 mmol) in hexanes, and the mixture was stirred for 30 min at the same temperature. The flask was cooled to −78 °C, and a solution of Et_2AlCl (35 cm^3, 35 mmol) in hexanes was added dropwise to the resulting alk-1-ynyllithium. After being stirred for 30 min at −78 °C, the reaction mixture was warmed to 0 °C. The resulting alk-1-ynyldiethylaluminium was transferred slowly to the first flask (−78 °C) using a double-ended needle. The reaction mixture was stirred for 30 min at −78 °C, and allowed to warm to room temperature. A solution of methyllithium (50 cm^3, 70 mmol) in diethyl ether was added to the reaction mixture at −15 °C, and the mixture was stirred for 1 h at 0 °C. By procedures similar to those described in the synthesis of compounds **5a–d**, compounds **6a–c** were isolated from the reaction mixtures.

2-(*Hex*-1-*ynyl*)*buta*-1,3-*diene* **6a** (0.52 g, 39%) (Found: C, 89.3; H, 10.7. $C_{10}H_{14}$ requires C, 89.5; H, 10.5%); ν_{max}(film)/cm^{-1} 3090, 2960, 2930, 2860, 2230, 1780, 1570, 1460, 1375, 1330, 1105, 985, 915, 890 and 745; δ_H 0.93 (3 H, t, *J* 6.8, Me), 1.15–1.70 [4 H, m, $(CH_2)_2$Me], 2.37 (2 H, t, *J* 6.8, C≡CCH_2), 5.22 (1 H, d, *J* 10.2, CH=C*H*H), 5.34 (1 H, s, CH*H*=C), 5.43 (1 H, s, C*H*H=C), 5.62 (1 H, dd, *J* 17.1 and 1.5, CH=CH*H*) and 6.35 (1 H, dd, *J* 17.1 and 10.2, C*H*=CH_2); δ_C 13.62 (Me), 18.99 (CH_2), 22.01 (CH_2), 30.84 (CH_2), 77.23 (≡C), 92.89 (≡C), 117.36 (=CH_2), 122.64 (=CH_2), 130.47 (=C) and 136.68 (=CH); *m*/*z* 134 (M^+, 55%), 119 (14), 105 (30), 92 (28), 91 (100), 79 (32), 78 (23), 77 (20), 65 (21) and 41 (21).

2-(3,3-*Dimethylbut*-1-*ynyl*)*buta*-1,3-*diene* **6b** (0.31 g, 23%) (Found: C, 89.0; H, 11.0. $C_{10}H_{14}$ requires C, 89.5; H, 10.5%); ν_{max}(film)/cm^{-1} 3080, 2960, 2925, 2860, 2210, 1780, 1565, 1450, 1375, 1360, 1310, 1250, 1205, 1110, 985, 915 and 890; δ_H 1.29 (9 H, s, CMe_3), 5.22 (1 H, d, *J* 10.2, CH=C*H*H), 5.33 (1 H, d, *J* 2.0, H*H*C=C), 5.42 (1 H, s, *H*HC=C), 5.61 (1 H, dd, *J* 17.1 and 1.5, CH=CH*H*) and 6.36 (1 H, dd, *J* 17.1 and 10.2, C*H*=CH_2); δ_C 30.60 (C), 31.01 (3 × Me), 77.18 (≡C), 101.16 (≡C), 117.27 (=CH_2), 122.42 (=CH_2), 130.33 (=C) and 136.68 (=CH); *m*/*z* 134 (M^+, 46%), 119 (100), 91 (67) and 41 (34).

2-(*Oct*-1-*ynyl*)*buta*-1,3-*diene* **6c** (0.39 g, 24%) (Found: C, 88.15; H, 11.85. $C_{12}H_{18}$ requires C, 88.0; H, 11.2%); ν_{max}(film)/cm^{-1} 3080, 2950, 2925, 2855, 2225, 1780, 1565, 1455, 1375, 1325, 985, 915, 890 and 725; δ_H 0.89 (3 H, m, Me), 1.10–1.65 [8 H, m, $(CH_2)_4$], 2.37 (2 H, t, *J* 6.8, ≡CCH_2), 5.22 (1 H, d, *J* 10.2, CH=C*H*H), 5.34 (1 H, s, H*H*C=C), 5.43 (1 H, s, *H*HC=C), 5.63 (1 H, dd, *J* 17.1 and 1.0, CH=CH*H*) and 6.36 (1 H, dd, *J* 17.1 and 10.2, C*H*=CH_2); δ_C 14.05 (Me), 19.31 (CH_2), 22.57 (CH_2), 28.60 (CH_2), 28.72 (CH_2), 31.35 (CH_2), 77.25 (≡C), 92.94 (≡C), 117.34 (=CH_2), 122.62 (=CH_2), 130.47 (=C) and 136.68 (=CH); *m*/*z* 162 (M^+, 14%), 147 (8), 133 (17), 119 (18), 105 (58), 94 (14), 93 (15), 92 (23), 91 (100), 79 (39), 78 (17), 77 (13), 55 (13), 43 (22) and 41 (28).

Procedure for the Synthesis of 2-*Alkylthiobuta*-1,3-*dienes* **8a–f**.—The experimental set-up was the same as that described in the synthesis of compounds **5a–d**. In the flask, bis(1,2-dimethylpropyl)borane (10 mmol) was prepared by the hydroboration of 2-methylbut-2-ene (1.40 g, 20 mmol) with BH_3 (10 mmol) in THF at 0 °C for 2 h. 1,4-Dichlorobut-2-yne **1** (1.23 g, 10 mmol) was added to the dialkylborane at −15 °C, and the reaction mixture was stirred for 2 h at 0 °C to complete the hydroboration.

In another argon-flushed 100 cm^3 round-bottomed flask, with a reflux condenser and equipped as described in the above experimental set-up, a solution of ethylmagnesium bromide (10 mmol) in THF (30 cm^3) was prepared by reaction of magnesium turnings (0.25 g, 10 mmol) with ethyl bromide (1.09 g, 10 mmol).

To the vigorously stirred solution was added dropwise the alkanethiol (10 mmol) at room temperature. Ethane was evolved during the period of the addition. After being stirred for 1 h at room temperature, the resulting alkylthiomagnesium bromide in THF was transferred slowly to the first flask (−78 °C) using a double-ended needle. The reaction mixture was stirred at −78 °C for 30 min, after which a solution of methyllithium (7.14 cm^3, 10 mmol) in diethyl ether was added slowly to it at −78 °C. The mixture was stirred for 30 min at the same temperature and then warmed slowly to 0 °C; it was then stirred for 1 h at the same temperature. After treatment of the reaction mixture as described in the synthesis of compounds **5a–d**, compounds **8a–f** were isolated by column chromatography on silica gel with pentane–dichloromethane (95:5) as eluent.

2-*Butylthiobuta*-1,3-*diene* **8a** (0.97 g, 68%) (Found: C, 67.3; H, 10.15. $C_8H_{14}S$ requires C, 67.5; H, 9.9%); ν_{max}(film)/cm^{-1} 3080, 2960, 2925, 2860, 1820, 1620, 1565, 1460, 1375, 1290, 1270, 1230, 1145, 1100, 1030, 980, 910, 845 and 735; δ_H 0.93 (3 H, t, *J* 7.3, Me), 1.35–1.75 [4 H, m, $(CH_2)_2$Me], 2.74 (2 H, t, *J* 7.3, SCH_2), 5.04 (1 H, d, *J* 1.0, H*H*C=C), 5.17 (1 H, d, *J* 10.7, CH=C*H*H), 5.31 (1 H, s, *H*HC=C), 5.54 (1 H, d, *J* 17.1, CH=CH*H*) and 6.44 (1 H, dd, *J* 17.1 and 10.7, C*H*=CH_2); δ_C 13.67 (Me), 22.18 (CH_2), 30.55 (CH_2), 30.84 (CH_2), 112.33 (=CH_2), 115.66 (=CH_2), 136.87 (=CH) and 142.54 (=C); *m*/*z* 142 (M^+, 25%), 127 (10), 113 (9), 109 (11), 87 (14), 86 (100), 85 (24), 71 (34), 53 (18) and 41 (15).

2-(1-*Methylpropylthio*)*buta*-1,3-*diene* **8b** (1.12 g, 79%) (Found: C, 67.1; H, 10.1. $C_8H_{14}S$ requires C, 67.5; H, 9.9%); ν_{max}(film)/cm^{-1} 3080, 2970, 2920, 2870, 1820, 1615, 1565, 1450, 1375, 1280, 1220, 1150, 1055, 1025, 980, 910, 845 and 780; δ_H 0.99 (3 H, t, *J* 7.3, CH_2*Me*), 1.28 (3 H, d, *J* 6.8, CH*Me*), 1.60–1.80 (2 H, m, CH_2Me), 2.97–3.17 (1 H, m, C*H*Me), 5.17 (1 H, d, *J* 10.7, CH=C*H*H), 5.20 (1 H, s, H*H*C=C), 5.41 (1 H, s, *H*HC=C), 5.59 (1 H, d, *J* 17.1, CH=CH*H*) and 6.43 (1 H, dd, *J* 17.1 and 10.7, C*H*=CH_2); δ_C 11.45 (Me), 20.16 (Me), 29.38 (CH_2), 41.59 (CH), 116.15 (=CH_2), 116.19 (=CH_2), 137.19 (=CH) and 141.64 (=C); *m*/*z* 142 (M^+, 35%), 127 (12), 113 (8), 87 (22), 86 (100), 85 (17), 71 (47), 53 (43), 45 (17) and 41 (33).

2-(1,1-*Dimethylethylthio*)*buta*-1,3-*diene* **8c** (0.50 g, 35%) (Found: C, 67.3; H, 10.0. $C_8H_{14}S$ requires C, 67.5; H, 9.9%); ν_{max}(film)/cm^{-1} 3080, 2960, 2910, 2850, 1820, 1610, 1560, 1465, 1450, 1360, 1220, 1160, 1020, 980 and 910; δ_H 1.31 (9 H, s, CMe_3), 5.21 (1 H, d, *J* 10.2, CH=C*H*H), 5.59 (1 H, d, *J* 1.5, CH*H*=C), 5.76 (1 H, s, C*H*H=C), 5.77 (1 H, dd, *J* 16.6 and 1.5, CH=CH*H*) and 6.51 (1 H, dd, *J* 16.6 and 10.2, C*H*=CH_2); δ_C 31.40 (3 × Me), 45.75 (C), 118.09 (=CH_2), 128.02 (=CH_2), 138.96 (=CH) and 140.18 (=C); *m*/*z* 142 (M^+, 66%), 127 (10), 109 (21), 87 (12), 86 (100), 85 (16), 71 (55), 58 (15), 57 (98), 53 (20), 45 (13) and 41 (90).

2-*Hexylthiobuta*-1,3-*diene* **8d** (1.31 g, 77%) (Found: C, 70.2; H, 10.8. $C_{10}H_{18}S$ requires C, 70.5; H, 10.65%); ν_{max}(film)/cm^{-1} 3080, 3000, 2950, 2920, 2850, 1810, 1700, 1615, 1565, 1460, 1375, 1285, 1255, 1230, 1210, 1140, 1030, 980, 910, 845 and 725; δ_H 0.89 (3 H, m, Me), 1.20–1.75 [8 H, m, $(CH_2)_4$Me], 2.74 (2 H, t, *J* 7.3, SCH_2), 5.03 (1 H, d, *J* 1.0, H*H*C=C), 5.17 (1 H, d, *J* 10.7, CH=C*H*H), 5.31 (1 H, s, *H*HC=C), 5.54 (1 H, d, *J* 17.1, CH=CH*H*) and 6.44 (1 H, dd, *J* 17.1 and 10.7, C*H*=CH_2); δ_C 14.01 (Me), 22.54 (CH_2), 28.43 (CH_2), 28.75 (CH_2), 31.13 (CH_2), 31.40 (CH_2), 112.25 (=CH_2), 115.64 (=CH_2), 136.87 (=CH) and 142.51 (=C); *m*/*z* 170 (M^+, 22%), 115 (17), 91 (13), 87 (28), 86 (100), 85 (22), 71 (24), 55 (15), 53 (14), 43 (24) and 41 (13).

2-*Cyclohexylthiobuta*-1,3-*diene* **8e** (0.86 g, 51%) (Found: C, 71.05; H, 9.9. $C_{10}H_{16}$ requires C, 71.4; H, 9.6%); ν_{max}(film)/cm^{-1} 3080, 3000, 2920, 2840, 1810, 1615, 1565, 1445, 1335, 1265, 1230, 1200, 1025, 995, 980, 910, 885, 845, 815, 785 and 735; δ_H 1.15–2.10 (10 H, m, ring 2-, 3-, 4-, 5- and 6-H_2), 2.90–3.10 (1 H, m, ring 1-H), 5.17 (1 H, d, *J* 9.8, CH=C*H*H), 5.21 (1 H, s, H*H*C=C), 5.40 (1 H, s, *H*HC=C), 5.59 (1 H, d, *J* 17.6, CH=CH*H*) and 6.43 (1 H, dd, *J* 17.1 and 9.8, C*H*=CH_2); δ_C 25.83 (CH_2), 26.02 (2 × CH_2), 33.08 (2 × CH_2), 43.46 (CH), 116.22 (2 × =CH_2), 137.21 (=CH) and 141.13 (=C); *m*/*z* 168 (M^+, 35%), 87 (71), 86 (100), 83 (32), 81 (24), 71 (23), 67 (22), 55 (79) and 41 (31).

2-*Benzylthiobuta*-1,3-*diene* **8f** (1.20 g, 68%) (Found: C, 74.7; H, 7.0. $C_{11}H_{12}S$ requires C, 74.95; H, 6.85%); ν_{max}(film)/cm^{-1} 3080, 3020, 2920, 2840, 1615, 1590, 1565, 1495, 1450, 1225, 1070, 1030, 980, 915, 850, 720 and 695; δ_H 3.96 (2 H, s, SCH_2), 5.08 (1 H, s, H*H*C=C), 5.19 (1 H, d, *J* 11.2, CH=C*H*H), 5.32 (1 H, s, *H*HC=C), 5.56 (1 H, d, *J* 17.1, CH=CH*H*), 6.43 (1 H, dd, *J* 17.1 and 11.2, C*H*=CH_2) and 7.20–7.40 (5 H, m, Ph); *m*/*z* 176 (M^+, 23%), 143 (18), 92 (10), 91 (100), 85 (9), 65 (8) and 45 (9).

References

1 Preliminary communications of this work have appeared: A. Arase and M. Hoshi, *J. Chem. Soc., Chem. Commun.*, 1987, 531; M. Hoshi, Y. Masuda and A. Arase, *J. Chem. Soc., Chem. Commun.*, 1987, 1629.

2 For example: A. Pelter and K. Smith, *Comprehensive Organic Chemistry*, eds. D. H. R. Barton and W. D. Ollis, Pergamon, Oxford, 1979, vol. 3, p. 791; H. C. Brown, *Organic Synthesis Today and Tomorrow*, eds. B. M. Trost and C. R. Hutchinson, Pergamon, Oxford, 1982, p. 121; D. S. Matteson, *The Chemistry of the Metal–Carbon Bond*, ed. F. R. Hartley, Wiley, Chichester, 1987, vol. 4, ch. 3; A. Pelter, K. Smith and H. C. Brown, *Borane Reagents*, Academic, London, 1988.

3 (*a*) A. Arase, M. Hoshi and Y. Masuda, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 209; (*b*) M. Hoshi, Y. Masuda and A. Arase, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1683; (*c*) M. Hoshi, Y. Masuda and A. Arase, *J. Chem. Soc., Chem. Commun.*, 1985, 714 and 1068; (*d*) M. Hoshi, Y. Masuda and A. Arase, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3764.

4 G. Zweifel, A. Horng and J. T. Snow, *J. Am. Chem. Soc.*, 1970, **92**, 1427.

5 G. Zweifel and A. Horng, *Synthesis*, 1973, 672.

6 A. Pelter and C. R. Harrison, *J. Chem. Soc., Chem. Commun.*, 1974, 828.

7 H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, 1961, **83**, 3834.

8 G. Zweifel, R. P. Fisher, J. T. Snow and C. C. Whitney, *J. Am. Chem. Soc.*, 1971, **93**, 6309.

9 E. Negishi and H. C. Brown, *Synthesis*, 1974, 77.

10 H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, 1971, **93**, 3777; A. Arase and Y. Masuda, *Chem. Lett.*, 1976, 1115.

11 M. Hoshi, Y. Masuda and A. Arase, *J. Chem. Soc., Perkin Trans. 1*, 1990, 3237; *Bull. Chem. Soc. Jpn.*, 1992, **65**, 685; Y. Masuda, M. Hoshi and A. Arase, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 3294; M. Hoshi, Y. Masuda and A. Arase, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 914.

12 H. C. Brown, N. Ravindran and S. U. Kulkarni, *J. Org. Chem.*, 1979, **44**, 2417.

13 A. Pelter, K. Smith and N. Tabata, *J. Chem. Soc., Chem. Commun.*, 1975, 857.

14 H. C. Brown and J. B. Campbell, Jr., *J. Org. Chem.*, 1980, **45**, 389.

15 J. Fried, C.-H. Lin and S. H. Ford, *Tetrahedron Lett.*, 1969, 1379.

16 H. C. Brown, C. G. Scouten and R. Liotta, *J. Am. Chem. Soc.*, 1979, **101**, 96.

17 H. C. Brown, G. W. Kramer, A. B. Levy and M. M. Midland, *Organic Syntheses via Boranes*, Wiley, New York, 1975.

18 G. Zweifel and H. C. Brown, *Org. React.*, 1963, **13**, 1.

19 W. L. Collier and R. S. Macomber, *J. Org. Chem.*, 1973, **38**, 1367.

20 H. C. Brown and J. Chandrasekharan, *Organometallics*, 1983, **2**, 1261; *J. Org. Chem.*, 1988, **53**, 4811.

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