Relative Migratory Aptitudes of Alkyl Groups in the Iodination of Lithium Ethynyltrialkylborates

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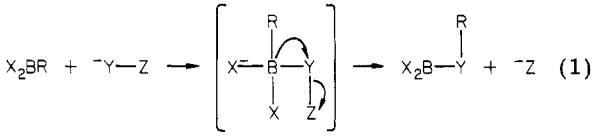
Relative migratory aptitudes of various alkyl groups have been determined in the iodine-induced rearrangement of lithium ethynyltrialkylborates. Trialkylboranes of types $R_{3-n}BR'_n$ and thexyl-BRR' were complexed with lithium acetylide–ethylenediamine. Iodination, followed by deiodoboration of the rearranged intermediates, produced 1-alkynes in amounts which depend, after statistical correction, on the relative rates of alkyl group migration in an intramolecular competition. In some cases, the migratory aptitude was found to depend on the alkyl substitution pattern in the organoborate. The overall migratory aptitude order is bicyclooctyl > *n*-butyl > cyclohexyl, isobutyl, *sec*-butyl > thexyl. When the secondary and primary migrating carbon series are considered separately, the order is consistently bicyclooctyl > cyclohexyl > *sec*-butyl, and *n*-butyl > isobutyl.

The wealth of synthetic methods accruing in organoborane chemistry proceeds from the facility with which trialkylboranes react with nucleophiles to form a wide variety of organoborate complexes.[1,2] In suitably substituted boranes, a 1,2-intramolecular migration can be induced by the presence or generation of an electron-deficient center α to the boron in the organoborate intermediate. These anionotropic rearrangements are conveniently classified[2] according to whether the reaction is spontaneous (eq 1) or electrophilically activated (eq 2–3).



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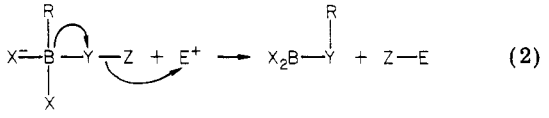

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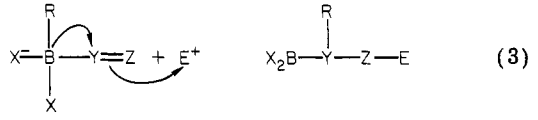

(3)

The stoichiometric limitation of only one alkyl group migration can be especially serious when scarce or expensive alkenes are hydroborated to form the trialkylboranes. Using the common mono- or dialkylboranes, thexyl or 9-BBN, as hydroborating agents provides not only for greater regioselectivity of addition to the alkene but also, in favorable cases, for nontransferable alkyl groups.[3] There are enough exceptions,[4] though, that it would be expedient to be able to accurately predict which group will migrate.

Coupled with the synthetic problem of prediction is the intriguing problem of theoretical interpretation of relative migratory aptitudes. Experimental data suggest that for organoboranes, relative migratory orders can be changed with variation in atomic terminus, leaving group, and degree of charge development adjacent to boron. It is generally conceded, though, that there may be no such thing as "intrinsic migratory aptitude", and thus any observed order developed for a series of compounds is dependent on the reaction mechanism and conditions.[5,6] Nevertheless, organoborate rearrangements offer an excellent opportunity to study several influences on relative migratory aptitudes. The rearrangements are irreversible and thus not affected by the complicated equilibria[6] found in the Wagner–Meerwein and pinacolic rearrangements. The migration origin can supply a variety of migrating groups in an intramolecular competition, and the electron-deficient migration terminus may be generated in several ways.

The present study is the first attempt to discover the conditions which influence intramolecular competitive alkyl group migratory aptitudes in electrophilically induced organoborate rearrangements. Although some previous work has been concerned with competitive migrations,[7] no single work has incorporated, in a simple systematic way, the features presented here.

Analysis and Results

The iodine-induced rearrangement of (1-alkynyl)triorganoborates, followed by deiodoboration, produces the corresponding alkyl-substituted alkynes (eq 4 and 5). The products, yields, and general synthetic utility of the procedure have been established, and the reaction is known to be applicable to a wide variety of organoboranes and acetylides.[7,8]

$$R_3B + LiC{\equiv}CR' \xrightarrow{THF} Li[R_3BC{\equiv}CR'] \quad (4)$$

$$Li[R_3BC{\equiv}CR'] \xrightarrow{I_2,\ -78\ ^\circ C} RC{\equiv}CR' + R_2BI + LiI \quad (5)$$

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(2) E. I. Negishi, *J. Organometal. Chem.*, **108**, 281 (1976).
(3) (a) A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Commun.*, 1048 (1971); (b) H. C. Brown, E. F. Knights, and R. A. Coleman, *J. Am. Chem. Soc.*, **91**, 2144 (1969); (c) N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, *Tetrahedron Lett.*, 2961 (1974).
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Table I. Percent Alkyl Group Migration in the Iodination of Lithium Ethynyltrialkylborates

compd	trialkylborane[a] R	R′	% of alkyne products[b] RC≡CH	R′C≡CH	% migration[c]
		For $RR_2'B$			
1	thexyl	*n*-butyl	0	100	95
2	thexyl	*sec*-butyl	0	100	76
3	thexyl	isobutyl	0	100	83
4	*n*-butyl	cyclohexyl	37	63	75
5	*sec*-butyl	cyclohexyl	25	75	72
6	isobutyl	cyclohexyl	14	86	68
7	cyclohexyl	*n*-butyl	15	85	59
8	cyclohexyl	*sec*-butyl	41	59	55
9	cyclohexyl	isobutyl	32	68	64
10	*n*-butyl	9-BBN	0	(100)[d]	
11	*sec*-butyl	9-BBN	0	(100)[d]	
12	isobutyl	9-BBN	0	(100)[d]	
13	cyclohexyl	9-BBN	6[e]	(94)[d]	
		For $CH(CH_3)_2C(CH_3)_2BRR'$			
14	cyclohexyl	*n*-butyl	27	73	76
15	cyclohexyl	*sec*-butyl	58	42	52
16	cyclohexyl	isobutyl	48	52	69
17	isobutyl	*n*-butyl	23	77	66
18	*sec*-butyl	*n*-butyl	25	75	82

[a] R_3B in the corresponding lithium ethynyltrialkylborate. [b] Determined by GC analysis utilizing an internal standard. Percentages are reported as the average of at least two experiments and deviate by ±3%. [c] Based on the number of millimoles of R_3B. [d] Yield not determined; however, see text and ref 4b and 14. [e] Yield based on the number of millimoles of R-*B*-9-BBN.

For this initial study, the simplest migration terminus, ethynyl (R′ = H), was chosen and introduced as the commercially available lithium acetylide–ethylenediamine complex.[8b,9] Because the migratory aptitudes may depend on the constitution of the trialkylborate, rather than on any inherent reactivity of the individual alkyl–boron bond, organoboranes of types $R'R_2B$ and R'_2RB were included in the study, as were the totally mixed thexyldialkylboranes [$CH(CH_3)_2C(CH_3)_2BRR'$].

Since only one alkyl group is transferred during the reaction, iodination of unsymmetrical trialkylborates produces a mixture of alkylacetylenes in amounts which depend, after correction for the statistical factor, on the relative rates of alkyl group migration in the intramolecular competition. The experimental results are reported in Tables I and II.

The alkyne percentages presented in Table I are obtained from the trialkylborane shown, although some of these trialkylboranes are not produced quantitatively on the basis of the stoichiometry of the starting reagents, BH_3 and alkenes. Before the lithium acetylide–ethylenediamine was added, an aliquot of the trialkylborane solution was oxidized with alkaline hydrogen peroxide. GC analysis of the alcohol products provided information on the composition of the trialkylborane mixture.

Hydroborations of 2-butene and isobutylene with 9-BBN, thexyl-, dicyclohexyl-, or cyclohexylborane, followed by oxidation, produced, respectively, the *sec*-butyl and isobutyl derivatives as the only detectable alcohol isomers.

Table II. Relative Alkyl Group Migratory Aptitudes (*M*) in the Iodination of Lithium Ethynyltrialkyborates

compd	trialkylborane[a] R	R′	*M* (R/R′)[b]
	For $R_{3-n}BR'_n$		
4	dicyclohexyl	*n*-butyl	0.85
5	dicyclohexyl	*sec*-butyl	1.5
6	dicyclohexyl	isobutyl	3.1
7	cyclohexyl	di-*n*-butyl	0.35
8	cyclohexyl	di-*sec*-butyl	1.4
9	cyclohexyl	diisobutyl	0.94
	For $CH(CH_3)_2C(CH_3)_2BRR'$		
14	cyclohexyl	*n*-butyl	0.37
15	cyclohexyl	*sec*-butyl	1.4
16	cyclohexyl	isobutyl	0.92
17	isobutyl	*n*-butyl	0.30
18	*sec*-butyl	*n*-butyl	0.33

[a] R_3B in the corresponding lithium ethynyltrialkylborate. [b] Ratio after statistical correction of product percentages in Table I (see text).

Although hydroboration/oxidation of 1-butene with thexylborane produced a 94:6 mixture of the 1- and 2-butanols, neither the thexyl nor the *sec*-butyl group migrated during the iodination, and thus the exclusive alkyne product was 1-hexyne. The isomeric 1- and 2-butanols were formed in a 97:3 ratio when 1-butene was hydroborated with cyclohexylborane–triethylamine and then oxidized. Again, no alkyne product from *sec*-butyl migration was observed. The hydroborating agents 9-BBN and dicyclohexylborane produced ≤1% of the 2-butyl isomer when added to 1-butene.

There is some uncertainty as to the actual composition of the trialkylborane mixture in the synthesis of the mixed thexyldialkylboranes.[10] In many cases, the dehydroboration of the thexyl group is a serious side reaction. However, hydroboration of the small butenes caused very little problem, and the three alcohols were produced after oxidation in 90–100% yields.

The synthesis of cyclohexylborane requires that it be complexed with triethylamine.[11] For a valid comparison between the dicyclohexylalkylborane and the cyclohexyldialkylborane systems, a control experiment was performed to determine whether the presence of the amine affected the alkyl groups' relative migratory aptitudes. Dicyclohexylborane was synthesized, and 1 equiv of triethylamine was added to it before hydroboration of 1-butene. The usual rearrangement reaction was then carried out. Subsequent analysis showed that the alkyne product ratio was not changed; however, the combined alkyne yield was reduced by approximately 10%. Another experiment revealed that 4 equiv of added triethylamine had effectively suppressed the rearrangement. The case was assumed to hold also for dicyclohexylborane–triethylamine reactions with 2-butene and isobutylene.

It was also of interest to determine if alkylboron hydrides would undergo the rearrangement reaction. To this end, cyclohexylborane–triethylamine, dicyclohexylborane, and thexylcyclohexylborane were subjected to the usual reaction sequence. Only in the case of dicyclohexylborane did any alkyl group migration occur (11%).

The thexyl group did not migrate in any of its combinations with other alkyl groups. Alkaline peroxide oxidation of the iodinated reaction solution resulted in a

(9) Iodination of the ethynyl terminus generated from acetylene and *n*-butyllithium gives a low yield of rearranged product.[8b] Here, when lithium (1-hexynyl)dicyclohexyl-*sec*-butylborate was iodinated both in the absence and presence of ethylendediamine, the alkyl group migratory aptitude ratio was not affected. In ref 8a, phenyl migrates to the 1-alkynyl termini in the absence of ethylenediamine, but in ref 8b, phenyl fails to migrate to the ethynyl terminus in the presence of ethylenediamine.

(10) H. C. Brown, J.-J. Katz, C. F. Lane, and E. I. Negishi, *J. Am. Chem. Soc.*, **97**, 2799 (1975).

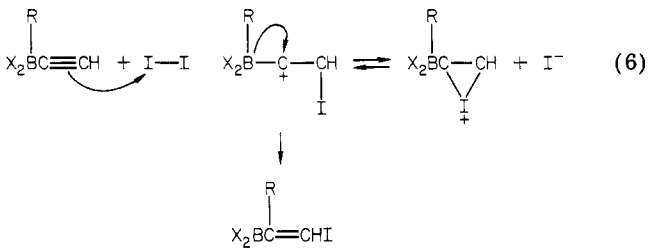
(11) H. C. Brown, E. I. Negishi, and J.-J. Katz, *J. Am. Chem. Soc.*, **97**, 2791 (1975).

nearly quantitative yield of thexyl alcohol. For the isomeric *B*-Bu-9-BBN's, no product of butyl group migration was observed.[12] No attempt was made to identify the product of bicyclic carbon migration, although this compound has been characterized in a study of methanesulfinyl chloride induced rearrangements of alkynyltrialkylborates.[13] In that work and others,[4b,14] the cyclooctyl derivative has been shown to be a major migratory product. It is noteworthy that the cyclohexyl group is transferred, although to a small extent, in competition with the bicyclooctyl group.

The relative migratory aptitudes (*M*) for the different competing groups, presented in Table II, were determined from the percentages of alkyne products from each trialkylborate rearrangement. Since the thexyl group does not migrate in the totally mixed trialkylborates [$CH(CH_3)_2C(CH_3)_2BRR'$], the values are obtained directly from the relationship $M(R/R') = \%R/\%R'$. The statistical correction factor applied to the equation for the cyclohexylbutylborates ($R_{3-n}BR'_n$) is $M(R/R') = (n/3 - n)(\%R/\%R')$.

Discussion

A two-step rearrangement pathway may be postulated as shown in eq 6, although there is no evidence requiring



(6)

the iodonium intermediate.[8a] Almost certainly, there is no addition of I_2 to the triple bond under these conditions.[15,16] Even in this structurally simple 1,2-anionotropic rearrangement, several competing factors may influence the rates of migration of alkyl groups.

Steric factors to be considered are (1) steric strain (back strain) at the migration origin, (2) increased crowding at the migration terminus, (3) compression of the bond angles in the migrating group at the transition state for migration, and (4) nonbonded interactions of the incoming electrophile with the groups attached to boron. If relief of back strain were a controlling factor, then almost certainly there should be a contribution of bulky thexyl group migration in the alkyne products. The structurally simple migration terminus in these compounds probably mitigates any serious consideration of factor 2 as an important effect. The potential angle strain around the migrating carbon in the transition state may increase the energy such that there is no competition in the migration. This effect may be important for the tertiary thexyl group; however, thexyl migration has been observed under similar conditions.[13a] Nonbonded interactions could be especially important if the electrophilic attack and alkyl migration were concerted and occurring in a trans manner. This explanation is advanced to account for predominate bicyclooctyl migration in the methanesulfinyl chloride induced rearrangement.[13a] Here, it may well suffice for the *B*-alkyl-9-BBN case, where the iodine attacks nearer the small alkyl group and trans to the interfering hydrogens on the migrating bicyclooctyl group. However, this is not in accord with the other results in this study wherein the smallest group, *n*-butyl, is most prone to migrate.

Electronic effects on the course of migration are probably most important for the migrating group. Unlike many other carbonium ion rearrangements, there is no new positive charge generated at the former migration origin where stabilization of the incipient cation by the nonmigrating groups may be required. In rearrangements where both the migration origin and terminus have partial positive character in the transition state, the migratory aptitude is often greater for electron-releasing groups,[6] which may reflect an increasing electron demand on the migrating group. However, in the organoborate rearrangements, boron is formally neutral after the migration, and if the transition state occurs early due to concerted electrophilic attack and migration, then the migrating group may acquire some partial negative character.[7a] The migratory order would then be expected to follow carbanion stability order,[16] primary > secondary > tertiary.

Inspection of Table II shows that in certain cases the relative migratory aptitude does depend on the substitution pattern in the ethynyltrialkylborate. No coherent order is easily discernible either between the two sets of cyclohexylbutylborates (**4–6** and **7–9**) or among one set of cyclohexylbutyl isomers. Between the two sets there is only one instance of correspondence of relative migratory aptitude after statistical correction, that of the cyclohexyl-*sec*-butylborates. Among the dicyclohexylbutylborates there is an approximate twofold increase in the cyclohexyl/butyl migration ratio in the series *n*-butyl < *sec*-butyl < isobutyl. However, no such regularity is observed for the cyclohexyldibutylborates. The greater migratory aptitude of cyclohexyl upon changing from the cyclohexyldibutylborates to the dicyclohexylbutylborates seems to be roughly consistent with steric acceleration due to B strain.

Most interesting is the correspondence between the sets of cyclohexyldibutylborates and thexylcyclohexylbutylborates (**7–9** and **14–16**). The cyclohexyl/butyl ratio is approximately the same whether the third alkyl group is another butyl group or a nonmigrating thexyl. If relief of B strain were important in the thexylcyclohexylbutylborates, then an increase in cyclohexyl (or thexyl) migration should be observed. Noteworthy also among the mixed thexyldialkylborates is the similarity of the ratios for the *n*-butyl group and any of the groups cyclohexyl, isobutyl, or *sec*-butyl (**14**, **17**, **18**). This also may indicate a lack of steric sensitivity at the migration origin.

When the data are considered overall, a partial relative migratory aptitude order can be developed: bicyclooctyl > *n*-butyl > cyclohexyl, isobutyl, *sec*-butyl > thexyl. Except for the anomalous position of the bicyclo group, the order is generally primary > secondary > tertiary, a ranking which is compatible with both carbanion character and a favorable steric factor in the migrating group. The greater migratory aptitudes of alkenyl[8f] and alkynyl[7b,e] compared to secondary groups support this interpretation.[17] That there are competing effects is also shown by the migratory aptitude dependence on substitution pattern

(12) Iodination of 1-hexynyl-*B*-*n*-butyl-9-BBN produced a 22% yield of 5-decyne. M. Mark Midland, private communication.

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(15) R. A. Hollins and M. P. A. Campos, *J. Org. Chem.*, **44**, 3931 (1979).

(16) V. L. Heasley, D. F. Shellhamer, L. E. Heasley, D. B. Yaeger, and G. E. Heasley, *J. Org. Chem.*, **45**, 4649 (1980).

(17) J. March, "Advanced Organic Chemistry; Reactions, Mechanisms, and Structure", McGraw-Hill, New York, 1977.

and by the inexact ordering of the cyclohexyl, isobutyl, and *sec*-butyl groups.[18] Furthermore, the secondary bicyclic bond has a greater ease of transferability than would be assumed only on the basis of electronic factors.

However, among the three secondary groups the pattern is clearly bicyclic > cyclic > aliphatic. In the tightly constrained 9-BBN system, migration may provide some strain relief to the bicyclic system, thus accounting for its large migratory aptitude. The cyclohexyl migratory increase, observed only in the dicyclohexylborates, and the large bicyclic migratory aptitude may be related through the structural similarity of the bicyclooctyl- and dicyclohexylborates. The relationship of this rate enhancement to structure and the point of dissimilarity between these two systems and the others are not easily discernible. The primary group order, *n*-butyl > isobutyl, may reflect the electronic and steric differences in the substituents, *n*-propyl and isopropyl, respectively, attached to the migrating primary carbon.

The relative migratory aptitudes of alkyl groups will be best understood when other migrations are studied over a wide range of structure. It should be stressed that although the results presented here provide some insight into the mechanism of organoborate rearrangements, they also can be recognized as only the first step in logically defining the effect of change in substrate on the course of the reaction. Future work will concentrate on other electrophile-induced rearrangements in structurally simple organoborates. Eventually, elaboration of each reaction, in terms of solvent and temperature effects, inductive effects at the migration origin, and steric and inductive effects at the migration terminus, may be studied.

Experimental Section

General Methods. All manipulations were performed in an atmosphere of prepurified nitrogen. Glassware, syringes, and needles were oven dried and then cooled while being flushed with nitrogen. GC analyses were performed on a Bendix 2300 gas chromatograph. Peak integration was carried out by using a Hewlett-Packard 3380S integrator.

Materials. Tetrahydrofuran (Mallincrodt) and cyclohexene (Eastman) were dried with lithium aluminum hydride and distilled under nitrogen. 2,3-Dimethyl-2-butene (Aldrich), lithium acetylide–ethylenediamine (Aldrich), isobutylene (Matheson), 1-butene (Matheson), and *cis*-2-butene (Linde) were used as received. Borane–tetrahydrofuran (Aldrich) and 9-BBN–THF (Aldrich) were titrated according to a standard procedure[1] to determine hyride molarity.

Synthesis of Trialkylboranes. The standard procedures for synthesis of the trialkylboranes are stated below.

A dry, 50-mL, round-bottomed flask equipped with a septum-covered side arm, a magnetic stirring bar, and a gas inlet adaptor connected to an oil bubbler was assembled hot and cooled under a stream of nitrogen. The flask was cooled to 0 °C and charged with 5 mL of THF, 0.3 mL of *n*-decane (GC internal standard), and 5 mL of BH_3–THF (1.0 M, 5 mmol).

The gaseous alkenes were condensed at −10 °C in a septum-capped, nitrogen-flushed, graduated test tube and were delivered, at the indicated time, via a double-tipped needle to the hydroborating solution by gradually warming the test tube.

(A) Thexyldialkylboranes. Thexylborane (5 mmol) was synthesized at 0 °C according to a standard procedure.[19] The appropriate alkene (15 mmol, 50% excess) was added, and the solution was stirred at 0 °C for 2 h.

(B) Dicyclohexylalkylboranes. Dicyclohexylborane (5 mmol) was synthesized at 0 °C according to a standard procedure.[1] The appropriate alkene (7.5 mmol, 50% excess) was added, and the solution was stirred at 0 °C for 1 h and then at room temperature for 0.5 h.

(C) Cyclohexyldialkylboranes.[11] To 5 mmol of thexylborane prepared as described above was added 5 mmol of cyclohexene at −25 °C (dry ice/CCl_4), and the solution was stirred for 1 h. Dehydroboration of the thexyl group was achieved by adding triethylamine (20 mmol) at −25 °C and then allowing the solution to stir for 1 h at room temperature. The solvent and excess triethylamine were removed under reduced pressure. THF (10 mL) was added to the cyclohexylborane–triethylamine, the solution was then cooled to 0 °C, and the appropriate alkene (15 mmol, 50% excess) was added. The solution was stirred at room temperature for 24 h.

(D) Unsymmetrical Thexyldialkylboranes.[10] Thexylborane (5 mmol) was synthesized as described above, after which the solution was cooled to −25 °C (dry ice/CCl_4). The appropriate olefin (corresponding to R in Table I, 5 mmol) was added, and the solution was stirred for 1 h at −25 °C. After addition of the second olefin (corresponding to R′ in Table I), the solution was gradually warmed to room temperature and then stirred for 1 h.

(E) *B*-Alkyl-9-BBN. 9-BBN–THF (0.5 M, 10 mL, 5 mmol) was injected into a glassware assembly identical with that described above. (For the hydroboration of cyclohexene, a reflux condenser was inserted between the flask and the gas-inlet adapter.) The flask was cooled to 0 °C, and the appropriate alkene (7.5 mmol, 50% excess) was added. The solution was brought to room temperature and stirred for the time indicated: 1-butene (2 h, room temperature), 2-butene (24 h, room temperature), isobutylene (2 h, room temperature), cyclohexene (1 h, reflux).

Reaction of Trialkylboranes with Lithium Acetylide–Ethylenediamine and Iodine.[8b] Lithium acetylide–ethylenediamine (0.51 g, 5.5 mmol) was added to the flask containing the trialkylborane (5 mmol), and the solution was then stirred for 2 h at room temperature. After the lithium ethynyltrialkylborate solution was cooled to −78 °C, iodine in THF (5.0 mL, 1 M) was added slowly to the vigorously stirred solution. After 1.5 h at −78 °C, the solution was warmed to room temperature and then treated with 5 mL of 40% potassium hydroxide. The organic phase was analyzed by GC (10% DC 710, Chromosorb W, 6 ft × $^1/_4$ in.) for the 1-alkyne products.

Oxidation of Trialkylboranes. A 2-mL aliquot of the trialkylborane solution (0.5 M) was delivered via syringe to a glassware assembly identical with that described above. The solution was cooled to 0 °C, and 1 mL of 3 N NaOH was then added, followed by the slow addition of 1 mL of 30% H_2O_2. The mixture was stirred either at 50 °C for 1 h or at room temperature overnight. After the mixture was salted out with NaCl, the organic phase was separated and dried over anhydrous $MgSO_4$.

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Registry No. 1, 77123-72-9; 2, 77123-73-0; 3, 77123-74-1; 4, 77123-75-2; 5, 77123-76-3; 6, 77123-77-4; 7, 77123-78-5; 8, 77123-79-6; 9, 77123-80-9; 10, 77123-81-0; 11, 77123-82-1; 12, 77123-83-2; 13, 77123-84-3; 14, 77123-85-4; 15, 77136-30-2; 16, 77123-86-5; 17, 77123-87-6; 18, 77123-88-7; RR'_2B (R = thexyl; R′ = Bu), 42928-38-1; RR'_2B (R = thexyl; R′ = *sec*-Bu), 77123-46-7; RR'_2B (R = thexyl; R′ = *i*-Bu), 42928-40-5; RR'_2B (R = Bu; R′ = cyclohexyl), 6917-84-6; RR'_2B (R = *sec*-Bu; R′ = cyclohexyl), 77123-47-8; RR'_2B (R = *i*-Bu; R′ = cyclohexyl), 6917-83-5; RR'_2B (R = cyclohexyl; R′ = Bu), 38103-70-7; RR'_2B (R = cyclohexyl; R′ = *sec*-Bu), 77123-48-9; RR'_2B (R = cyclohexyl; R′ = *i*-Bu), 77123-49-0; RR'_2B (R = Bu; R′ = 9-BBN), 23532-74-3; RR'_2B (R = *sec*-Bu; R′ = 9-BBN), 53317-06-9; RR'_2B (R = *i*-Bu; R′ = 9-BBN), 63942-77-8; RR'_2B (R = cyclohexyl; R′ = 9-BBN), 53535-83-4; thexylBRR′ (R = cyclohexyl; R′ = Bu), 77123-50-3; thexylBRR′ (R = cyclohexyl; R′ = *sec*-Bu), 77123-51-4; thexylBRR′ (R = cyclohexyl; R′ = *i*-Bu), 77136-27-7; thexylBRR′ (R = *i*-Bu; R′ = Bu), 77136-28-8; thexylBRR′ (R = *sec*-Bu-R′ = Bu), 77136-29-9; lithium acetylide–ethylenediamine complex, 50475-76-8.

(18) The isomeric alkyne products from the iodination of thexyl-*sec*-butylisobutylborate were not sufficiently separable by GC to calculate a relative migratory aptitude.

(19) E. I. Negishi and H. C. Brown, *Synthesis*, 77 (1974).