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Toward an understanding of the factors responsible for the 1,2-migration of alkyl groups in borate complexes*

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Abstract: The anionotropic 1,2-migration of an organic substituent from a tetrasubstituted borate ion, often referred to as an "ate" complex, to an acceptor atom is at the basis of the most useful application of organoboranes in organic synthesis. We recently showed that chiral sulfur ylides react with boranes to give homologated products with high enantiomeric excess. In considering reactions with mixed boranes, the issue of which group would migrate arises. Although we are primarily interested in sulfur ylide reactions with boranes, in this review we have summarized the most important factors that are responsible for which group migrates from a broad spectrum of reactions involving borate complexes. We also discuss the use of blocking/nonmigrating groups and highlight when they are effective and not effective. Consideration of the most important factors that affect the outcome of which group migrates and understanding how and why blocking groups work, provides a strategy for designing boranes with nonmigrating groups for use in new reactions of these useful synthetic intermediates.

Keywords: anionotropic; 1,2-migration; borate complexes; organoboranes; chiral sulfur ylides; migratory aptitude; ylides.

INTRODUCTION

Organoboranes are versatile synthetic intermediates as they can be converted into a broad range of functional groups [1]. Such transformations, which usually occur with retention of configuration, proceed via a tetrasubstituted borate ion, and subsequent 1,2-shift of one of the substituents on boron with concomitant expulsion of the leaving group. We recently showed that sulfur ylides react with organoboranes to give homologated boranes, which can be subsequently converted into alcohols or amines with very high enantioselectivity [2] (Fig. 1).

Considering the possibility of broadening the scope of this process and in particular to applying it in synthesis, we became interested in the use of nonsymmetrical boranes. However, in such situations one has to attend which of the three groups on boron will migrate. There are, of course, thousands of papers describing related rearrangements of borate complexes, but there are no general rules governing migratory aptitude of a boron substituent [3]. To highlight the complexity of the issues, methyl and

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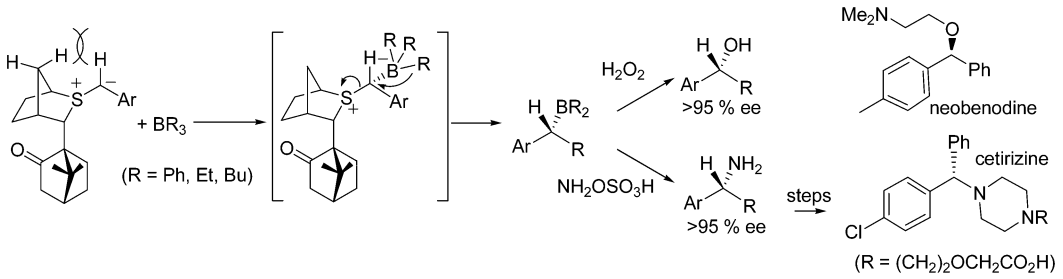


Fig. 1 Homologation of organoboranes with chiral sulfur ylides.

thexyl groups, which clearly are at the opposite extremes of steric demand, are both often nonmigrating groups.

In this review, we summarize the most important factors that control which group migrates in the 1,2-rearrangement of organoborate complexes and highlight examples from the literature which are controlled by essentially a single factor. We also discuss the use of blocking groups, again highlighting reactions in which they work effectively and reactions where they do not.

In the rearrangement of borate complexes there is a primary stereoelectronic requirement for the migrating group to align antiperiplanar to the leaving group (Fig. 2). The factors that affect which group migrates include the nature of the migrating group, the nature of the groups left behind, the nature of the leaving group Y, the nature of the migrating terminus X, the degree of charge development on X, and the ability of the migrating group to carry charge.

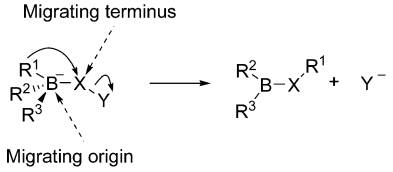


Fig. 2 1,2-Rearrangement of borate complexes.

The most important steric factors consist of:

1. Steric hindrance around boron (back strain) [4]. This factor should favor the migration of the bulkiest group, thus producing a relief of the steric strain in a highly hindered borate complex. The migratory order for alkyl groups should be 3° > 2° > 1°.
2. Steric hindrance around the migrating terminus [4]. This factor will favor the migration of the least hindered group. The migratory order should be 1° > 2° > 3°.
3. Compression of the bond angles in the migrating group at the transition state for migration [4]. This effect should be especially important for a highly substituted migrating carbon and will disfavor the migration of hindered groups. The migratory order should be 1° > 2° > 3°.
4. Nonbonded interactions of the substituents at the migrating terminus with the substituents attached to boron [5,6]. A careful examination of the different conformers at the ate complex should indicate which group prefers to migrate when *factor 4* prevails. For example, if the leaving group is sterically hindered, the preferred conformation of the ate complex will place the bulkiest boron substituent anti to it, and so in this case the migratory order will be 3° > 2° > 1°.

Electronic factor:

5. Because the migrating group carries partial negative charge, some publications [3,4] suggests that the migratory aptitude should follow the stability of these species and decrease in the order 1° > 2° > 3°.

It is clear that the migratory aptitude of alkyl groups is affected by an array of different factors, and the final result will depend on which factor(s) prevail. In the following discussion, we present reactions which are predominantly controlled by one of the above factors.

1,2-MIGRATIONS DOMINATED BY STERIC FACTORS: *FACTOR 4*

The reaction of organoboranes with 1 equiv of trimethylamine *N*-oxide (TMANO) [6–8] results in oxidation of one of the three groups on boron. In the case of the nonsymmetrical borane **1**, it was found that the bulkier groups were preferentially oxidized [6] (Fig. 3). The selectivity observed in the oxidation with TMANO (the migratory aptitude decreases in the order 3° > 2° > 1°) can be accounted for the preferred conformation of the ate complex in which the bulkiest group on boron occupies the position anti to the bulky Me_3N group.

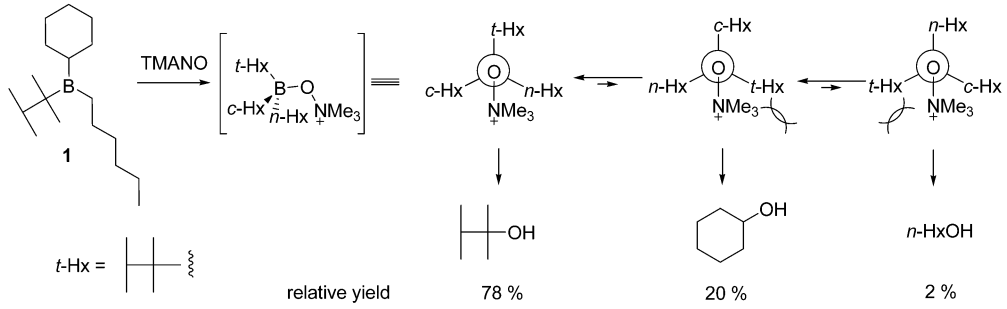


Fig. 3 Oxidation of trialkylborane with TMANO.

In reactions of 9-borabicyclo[3.3.1]nonane (9-BBN) derivatives (Fig. 4) with TMANO, the bicyclooctyl group rather than the R group migrates [6], again because of the preferred conformation of the ate complex.

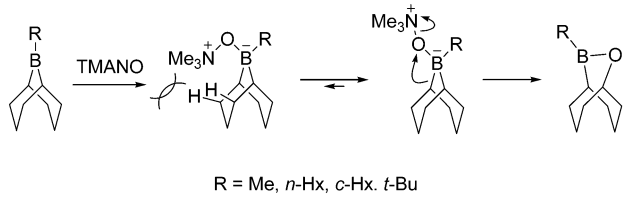


Fig. 4 Oxidation of 9-BBN-*B*-alkylboranes with TMANO.

1,2-MIGRATIONS DOMINATED BY ELECTRONIC FACTOR: *FACTOR 5*

Carbonylation of organoboranes

Carbonylation of organoboranes can be effected in two ways: (i) direct treatment with carbon monoxide [9] or (ii) treatment with CN^- followed by trifluoracetic anhydride (TFAA) [10,11]. The mecha-

nisms of these reactions are shown in Fig. 5, and both processes occur via similar intermediates **2** and **3** for the first migration step.

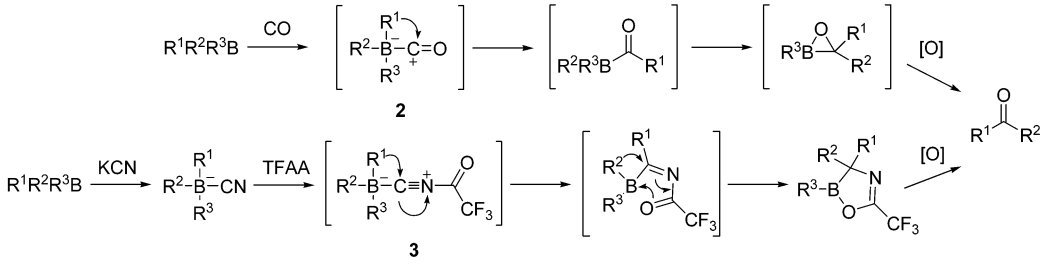


Fig. 5 Carbonylation of organoboranes.

In reactions with boranes **4** [12] and **5** [13] (carbonylation process) and boranes **6** [10] and **7** [11] (cyanidation process) no ketones bearing the most hindered group were isolated (Fig. 6). These results show that the order in the migration step for these reactions is 1° >2° > 3°, suggesting that the 1,2-migration is dominated by electronic factors relating to the ability of the migrating group to carry negative charge (*factor 5*).

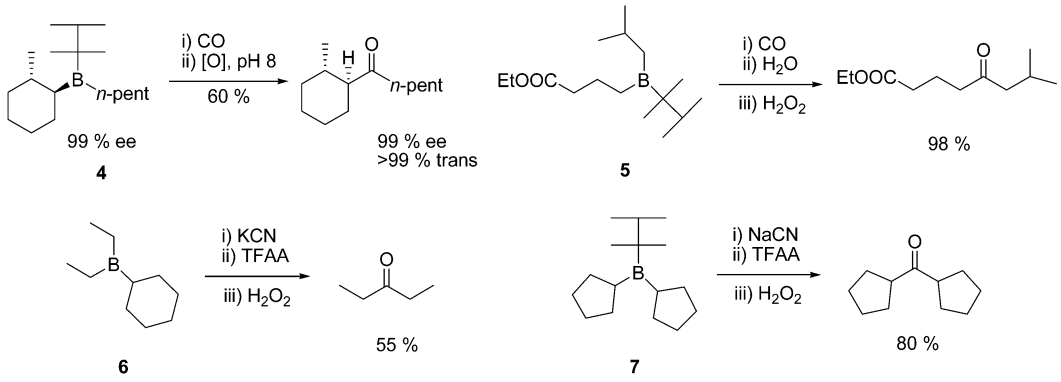


Fig. 6 Carbonylation of different boranes.

Since the migrating terminus is completely unhindered, steric *factors 2* and *4* are completely irrelevant. Steric hindrance around the boron atom could potentially have played a role, but this would have favored migration of the bulkiest group. Since the opposite order is found, electronic factors clearly dominate this process.

Electrophilically activated triple bonds

The iodine-induced rearrangement of ethynyltrialkylborates [14] followed by spontaneous deiodoboration produces the corresponding alkyl-substituted alkyne (Fig. 7).

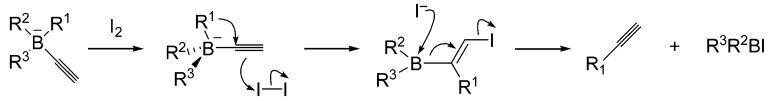


Fig. 7 Iodine-induced rearrangement of ethynyltrialkylborates.

Slayden investigated a number of reactions where competition for migration could be quantified and then critically examined [4]. In this study, one group (thexyl) was completely inert to migration, and there was a preference for the migration of 1° alkyl over 2° alkyl groups.

The iodine-induced rearrangement of *B*-alkynyl-*B*-alkyl-9-borabicyclo[3.3.1]nonanes preferentially produced the cyclooctyl-substituted alkynes as the major migratory products (Fig. 8).

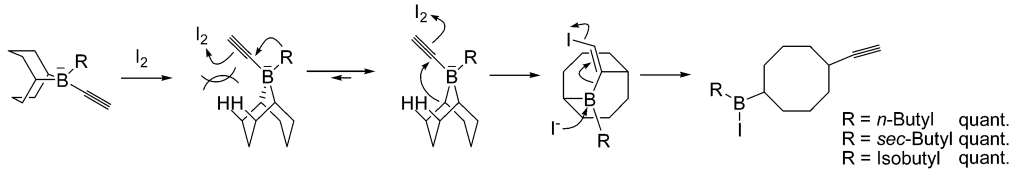


Fig. 8 Iodine-induced rearrangement of *B*-alkynyl-*B*-alkyl-9-borabicyclo[3.3.1]nonanes.

The order of migratory aptitude is bicyclooctyl > *n*-butyl > cyclohexyl, *iso*-butyl, *sec*-butyl > thexyl. Except for the 9-BBN group, the order is generally 1° > 2° > 3°, results that implicate electronic factors as dominating (*factor 5*). The migrating terminus is unhindered, and as was the case for carbonylation, it seems that steric factors are less important here as well. However, the differences of migratory aptitude between various secondary groups and the preferential migration of 9-BBN (see later) suggests that there are other competing effects in operation.

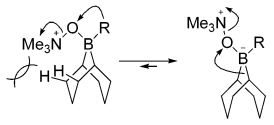
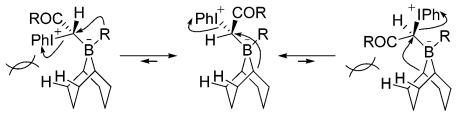
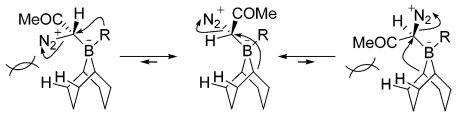
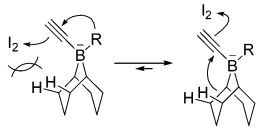
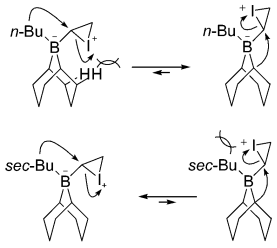
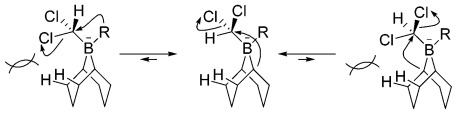
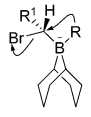
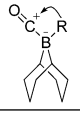
Blocking groups: Scope and limitations

Because of the subtle interplay of the different factors, it is very difficult to predict which group will migrate in nonsymmetrical borate complexes. To reduce this complexity and improve predictability, nonmigrating groups on boron have been introduced. However, as is illustrated in the following examples, nonmigrating groups do not always remain attached to boron and in fact sometimes dominate the migration. Factors that contribute to such changes in behavior are discussed below.

9-Borabicyclo[3.3.1]nonane

9-BBN was introduced by H. C. Brown as a nonmigrating group [15]. Although we have not been able to find the exact reasoning behind this, we believe it is due to the increased torsional strain in converting the [3.3.1] into a [3.3.2] bicyclic structure [16]. However, as can be seen in Table 1, *there are only a few instances where it acts as a nonmigrating group*, usually the bicyclooctyl group preferentially migrates [17]!

Table 1 Selected examples of the rearrangement of 9-BBN derivatives.

Entry	Reaction (ate complex)	9-BBN migration	Factor	Ref.
1		Migrates exclusively	Conformation of the ate complex dominates outcome (*factor 4*)	[6]
2		Migrates exclusively	Conformation of the ate complex dominates outcome (*factor 4*)	[18]
3		Migrates *n*-hexyl (0 %) 9-BBN (80 %)	Conformation of the ate complex dominates outcome (*factor 4*)	[19]
4		Migrates 94–100 % of migration	Nonbonded interactions between the incoming electrophile and the groups attached to the boron	[4]
5		Migrates A *n*-Bu (31 %) 9-BBN (69 %) B *sec*-Bu (61 %) 9-BBN (39 %) (relative yield)	Conformation of the ate complex dominates outcome (*factor 4*)	[5]
6		Migrates 1° group (2 %) 9-BBN (85 %)	Conformation of the ate complex dominates outcome (*factor 4*)	[20]
7	 R^1 = COR^2, CO_2R^3, CN	Nonmigrating group	Torsional strain in expansion from [3.3.1] to [3.3.2]	[21]
8		Nonmigrating group	Torsional strain in expansion from [3.3.1] to [3.3.2]	[22]

Examples where the bicyclooctyl group migrates preferentially seem to be controlled by the preferred conformation of the ate complex. If one particular conformation dominates as in entry 1 [6], where the leaving group cannot easily align antiperiplanar to the B–R bond, then the bicyclooctyl group migrates. This may also apply to entries 2 [18] and 3 [19] in Table 1. Entry 4 [4] is also affected by similar considerations, but this time it is the accessible space available to the electrophile (opposite the bicyclooctyl group) that controls the outcome of the reaction. Entry 5 [5] is also controlled by conformation, but is now more finely balanced. The preferred conformation of the iodonium ion is influenced by the size of the substituent on boron, which in turn affects which group migrates.

There is a major difference in outcome of reactions in entries 2, 3, and 7 [21], where the only difference in structure is the nature of the leaving group. In entries 2 and 3, very good leaving groups are present and the bicyclooctyl group migrates preferentially, whereas in entry 7 the leaving group is smaller and less good and the boron substituent R migrates instead. It is possible that in the case of the smaller and less good leaving group (entry 7), the increased conformational flexibility of the ate complex coupled with a later transition state, allows the inherently stable bicycle structure to remain intact and the R group to migrate. It is difficult to rationalize why the borabicycle migrates in entry 6 [20] when it bears greater similarity to entry 7 than entries 2 and 3.

Carbonylation (entry 8) [22] is not affected by conformation of the ate complex and so, because of the inherent stability of the bicycle structure, the R group migrates preferentially.

What is clear from this analysis is that the conformation of the ate complex (*factor 4*) plays a major role in controlling the outcome of the reactions and that the rigid and hindered 9-BBN structure usually forces the leaving group to be anti to the ring B–C bond rather than the boron substituent resulting in ring migration.

Thexyl group

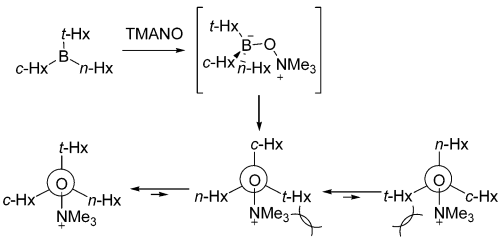
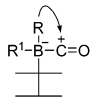
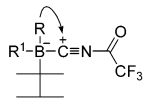
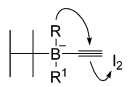
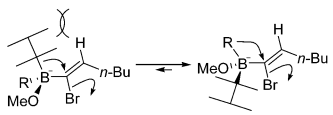
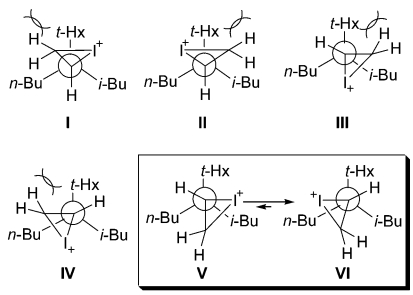
The thexyl group [23] has been used as a nonmigrating group. It is highly hindered and, because of compression of bond angles during migration will suffer increased strain if it migrates (*factor 3*). Steric hindrance at the migrating terminus (*factor 2*) and electronic effects (*factor 5*) will also disfavor migration of the thexyl group.

In rearrangement reactions involving highly hindered leaving groups, the thexyl group migrates because of the strongly preferred conformation of the ate complex in which the two largest groups are anti [6] (Table 2, entry 1).

At the other extreme involving rearrangement reactions of completely unhindered migrating terminus {carbonylation [12,13,24] (entry 2)/cyanidation [10,25] (entry 3)} the thexyl group does not migrate presumably because the least sterically hindered groups are best able to carry negative charge during the migration (*factor 5*).

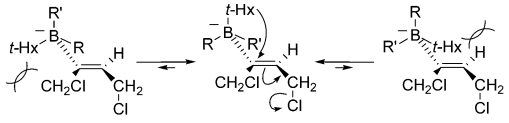
The large thexyl group influences the conformation of the ate complex in other examples. For the reaction shown in entry 5 [26], the thexyl group cannot occupy a position antiperiplanar to the leaving group as this would result in severe $A^{1,3}$ strain, so it does not migrate.

Table 2 Selected examples of the thexyl group behavior in the rearrangement of organoborates.

Entry	Reaction (ate complex)	Thexyl group migration	Factor	Ref.
1		Migrates *n*-Hx (2 %) *c*-Hx (20 %) *t*-Hx (78 %) (relative yield)	Conformation of the ate complex dominates outcome (*factor 4*)	[6]
2		Nonmigrating group	Controlled by the ability of R group to carry negative charge (*factor 5*)	[12] [13] [24]
3		Nonmigrating group	Controlled by the ability of R group to carry negative charge (*factor 5*)	[10] [25]
4		Nonmigrating group	Controlled by ability of R group to carry negative charge (*factor 5*)	[4]
5		Nonmigrating group	$A^{1,3}$ strain disfavors the migration of thexyl group (*factor 4*)	[26]
6		Nonmigrating group *i*-Bu (69 %) *n*-Bu (31 %) (relative yield)	Conformation of the ate complex dominates outcome (*factor 4*)	[5]

(*continues on next page*)

Table 2 (*Continued*).

Entry	Reaction (ate complex)	Thexyl group migration	Factor	Ref.
7		Migrates A 1° group (0 %) *t*-Hx (72 %) B 2° group (30 %) *t*-Hx (48 %)	$A^{1,2}$ and $A^{1,3}$ strain favors the migration of thexyl group (*factor 4*)	[27]

In the iodination of ethenyltrialkylborates [5] (Fig. 9), the thexyl group is nonmigrating (Table 2, entry 6). Again, this can be rationalized by the preferred conformation of the iodonium ion, which places the larger CH_2 group away from the bulky thexyl group. Of the two preferred conformations, **VI** should be favored over **V**, and this correlates with the outcome of the reaction: the ratio of *n*-Bu:*i*-Bu migration was 31:69.

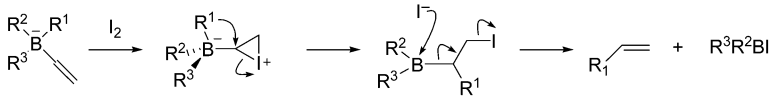


Fig. 9 Iodination of ethenyltrialkylborates.

Conformation of the ate complex also seems to play a dominant role in the rearrangement of the vinyl chloride [27] (Table 2, entry 7). In this case, the preferred conformation has the bulkiest group perpendicular to the alkene to minimize $A^{1,2}$ and $A^{1,3}$ strain. This position is, therefore, occupied by the thexyl group which migrates because it is properly aligned with the orbitals of the leaving group.

The bulk of the thexyl group has a major impact on the conformation of the ate complex, and from analysis of the preferred conformation one can predict whether it will migrate or not.

Methyl group

The methyl group is at the opposite end of the spectrum in terms of steric hindrance relative to the thexyl group. Just as the thexyl group had a big impact on the conformation of the ate complex because of its large size, so too will the methyl group because of its small size relative to other groups. This, together with other factors, has rendered methyl an effective nonmigrating group in many instances.

The reaction of MeLi with borane **8** furnishes an ate complex which undergoes 1,2-rearrangement to ultimately give diene **9** (Fig. 10). In this example, the methyl group never migrates (Table 3, entry 1), and there is some preference for 3° over 2° [27] (Table 4). These results show that the order of migration is 3º > 2° > 1°. As indicated previously, the preferred conformation of the ate complex that minimizes $A^{1,2}$ and $A^{1,3}$ strain positions the bulkiest group perpendicular to the π system, and it is the group occupying this position which migrates. Methyl, being the smallest group, would not occupy this position and so does not migrate.

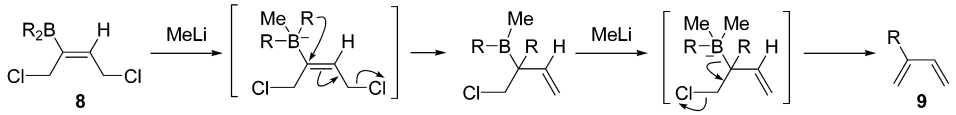


Fig. 10 Methyllithium-induced rearrangement in (*Z*)-(1,4-dichlorobut-2-en-2-yl)dialkylboranes.

Table 3 Selected examples of the methyl behavior in the rearrangement of organoborates.

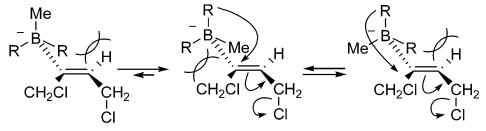
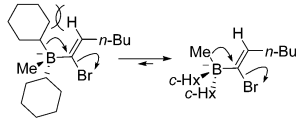
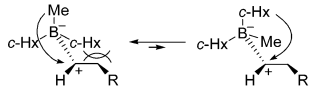
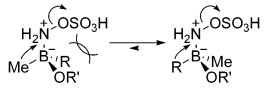
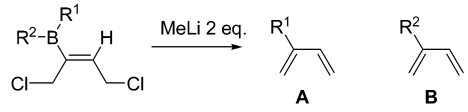
Entry	Reaction (ate complex)	Methyl group migration	Factor	Ref.
1		Nonmigrating group	Conformation of the ate complex or relief of steric strain dominates outcome (*factors 1 and 4*)	[27,28]
2		Migrates Me (74 %) *c*-Hx (23 %)	Conformation of the ate complex dominates outcome (*factor 4*)	[29]
3		Nonmigrating group Less than 5 % of Me migration	Conformation of the ate complex or relief of steric strain dominates outcome (*factors 1 and 4*)	[30]
4		Nonmigrating group	Conformation of the ate complex or relief of steric strain dominates outcome (*factors 1 and 4*)	[31]

Table 4 Methyllithium-induced rearrangement in (*Z*)-(1,4-dichlorobut-2-en-2-yl)dialkylboranes.



Entry	R^1	R^2	A (yield %)	B (yield %)
1	Me_2CHCMe_2 (thexyl)	cyclohexyl	48	30
2	Me_2CHCMe_2 (thexyl)	$Pr(Me)CHCH_2$	72	0
3	cyclohexyl	cyclohexyl	85	
4	$Me_2CHCHMe$	$Me_2CHCHMe$	73	

A related ate complex is generated in the reaction of *trans*-1-hexenyldicyclohexylmethylborate [30] with hydrogen chloride, but in this case, small amounts of methyl migration are observed (Table 3, entry 3). As before, the preferred conformation of the ate complex is the one with the largest group parallel with the empty π orbital of the carbocation, and this is the group that migrates (Fig. 11).

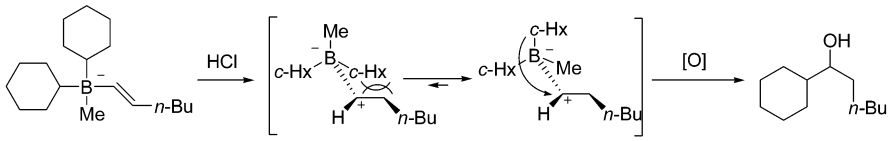


Fig. 11 Proton-induced migration in vinylboranes.

The reaction of trialkylboranes with hydroxylamine-*O*-sulfonic acid (HSA) [32] is limited to transfer of only two of the three alkyl groups. Methyl has also been used to increase the yield of the reaction, and this suggests that steric factors may play an important role in this kind of reaction.

Using 2 equiv of HSA, two different boron species can be formed after the first migration, and the factors that control the second migration can change, so it is difficult to predict the migration aptitude depending on the final distribution of the final products. However, a 94 % yield of norbornylamine [32c] indicates that 2 × methyl migration did not occur (Fig 12).

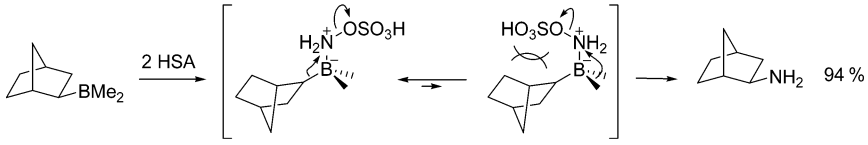


Fig. 12 Amination of trialkylboranes with HSA.

In the reaction of borinic esters with HSA [31] in THF, only one of the two alkyl groups is transferred, and so from product distribution it is clear which group migrated (Table 3, entry 4). The formation of cyclohexyl amine **10** shows that 2° > 1° (Fig. 13).

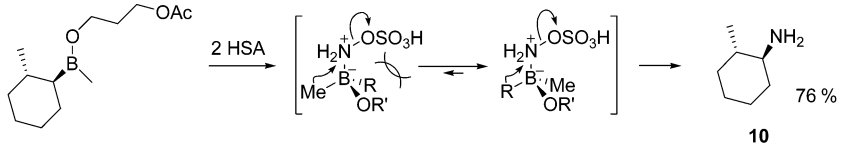


Fig. 13 Amination of borinic esters with HSA.

It is possible that the reaction is controlled by the conformation of the ate complex, and in this case, the preferred conformation places the largest boron substituent anti to the large leaving group (*factor 4*). Migration of bulky groups also relieves steric hindrance around boron, which may be another contributing factor (*factor 1*).

Entry 2 in Table 3 [29] provides one example where methyl group migrates preferentially. In this case, the reaction is very similar to the process previously discussed (Table 2, entry 5) and highlights the importance of considering factors (importance of conformation) rather than following rules (e.g., group X is a nonmigrating group). As before, the preferred conformation of the ate complex places methyl antiperiplanar to the Br atom to minimize $A^{1,3}$ strain.

9-Oxa-10-borabicyclo[3.3.2]decane

Treatment of *B*-substituted-9-oxa-10-borabicyclo[3.3.2]decane (9-OBBD) **11** (Soderquist borinate) [6] with nucleophiles bearing a leaving group at the α position results in exclusive migration of the *B*-alkyl substituents on the boron atom (Fig. 14).

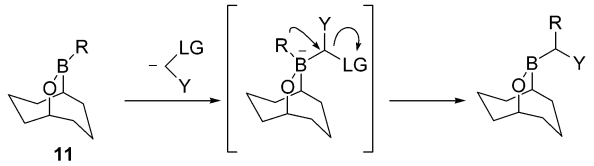
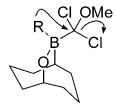
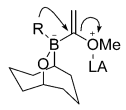
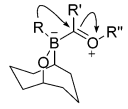


Fig. 14 9-OBBD as a nonmigrating group.

Reaction of lithiated α,α-dichloromethyl methyl ether (DCME) [33] with borinate **11** (Table 5, entry 1) resulted in exclusive migration of the boron substituent R whether it was 1°, 2°, or 3° [34]. This inertness to migrating of the framework in the Soderquist borinate was also observed in the reaction with lithiated 1-methoxyethene [35] (Table 5, entry 2) and glycosylidene carbenes [36] (Table 5, entry 3).

Table 5 Examples of the behavior of 9-OBBD in the rearrangement of organoborates.

Entry	Reaction (ate complex)	9-OBBD migration	Factor	Ref.
1		Nonmigrating group	Torsional strain in expansion from [3.3.2] to [3.3.3]	[34]
2		Nonmigrating group	Torsional strain in expansion from [3.3.2] to [3.3.3]	[35]
3		Nonmigrating group	Torsional strain in expansion from [3.3.2] to [3.3.3]	[36]

The reluctance of the side chain to migrate can be accounted for by the increased strain generated in converting a [3.3.2] bicycle into a [3.3.3] bicycle, which would contain two bridged 8-membered rings.

REARRANGEMENTS OF SULFONIUM SALTS AS LEAVING GROUPS

Returning to sulfur ylides, there is one example where the intermediate ate complex was generated by a different route. The reaction of trialkylboranes with thiomethoxymethyllithium, followed by the treatment of the resultant α-thioorganoborate complexes with methyl iodide, produces the one carbon homologated organoboranes in high yield [37] (Fig. 15). Table 6 shows some examples employing mixed trialkylboranes.

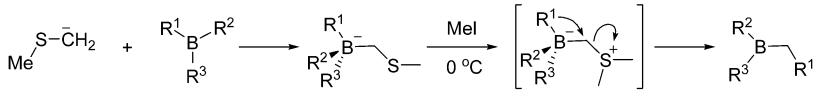
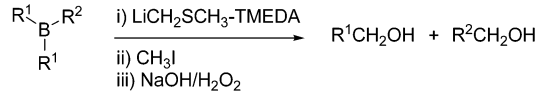


Fig. 15 Homologation of organoboranes via α-thioorganoborate anions.

Table 6 Homologation of organoboranes via α-thioorganoborate anions.



Entry	R^1	R^2	R^1CH_2OH (yield %)	R^2CH_2OH (yield %)
1	9-BBN	Ph	11	73
2	siamyl	*Trans*-1-hexenyl	28	72
3	siamyl	*n*-pentyl	67	21
4	*n*-pentyl	thexyl	88	trace

Ph and hexenyl groups are inherently better migrating groups because they can use their π system to aid migration (entries 1 and 2). The preferred migration of pentyl over thexyl (1° > 3°) and then siamyl over pentyl (2° > 1°) is more difficult to rationalize and shows that the outcome of the rearrangement reaction is a result of a delicate balance between opposing factors. In entry 3, conformation of the ate complex may dictate which group migrates (Fig. 16), and in entry 4, this factor must be outweighed by electronic factors which inhibit the migration of groups that cannot stabilize negative charge, thus leading to the outcome observed.

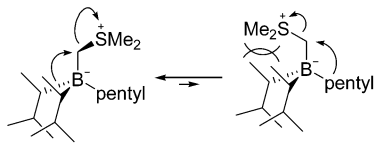


Fig. 16 Favored migration of siamyl group.

CONCLUSIONS

This review highlights the factors that are responsible for influencing the outcome of 1,2-rearrangements of borate complexes. In only a few types of reactions is there a clear-cut single factor responsible that results in a particular order of migrating aptitude, and these involve highly hindered leaving groups (reaction with TMANO) in which the reaction is dominated by conformation, and an unhindered migrating terminus (carbonylation), which are dominated by electronic factors. In analyzing traditional nonmigrating groups, only the Soderquist borinate bicycle works in all cases. In the cases of 9-BBN, thexyl, and methyl, they all occasionally migrate, but in the case of 9-BBN, this is the norm rather than the exception! In any of the cases involving these groups, it seems that the conformation of the ate complex plays a dominant role in determining which group migrates. The problem we face in trying to predict the outcome of rearrangement reactions is *the extent* to which the conformation of the ate complex contributes to the final outcome and whether, for that particular reaction, other factors have equal or even greater importance. Nevertheless, for many reactions, a consideration of the conformation required for migration (migrating group antiperiplanar to LG) of the ate complex goes a long way in helping to think about which group will migrate preferentially.

REFERENCES AND NOTES

1. (a) H. C. Brown. *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, New York (1972); (b) H. C. Brown. *Organic Synthesis via Boranes*, Wiley-Interscience, New York (1975); (c) J. Weill-Raynal. *Synthesis* 633 (1976); (d) H. C. Brown and B. Singaram. *Pure Appl. Chem.* **59**, 879 (1987); (e) A. Pelter, K. Smith, H. C. Brown. *Borane Reagents*, Academic Press, New York (1988); (f) D. S. Matteson. *Chem. Rev*. **89**, 1535 (1989); (g) D. S. Matteson. *Tetrahedron* **45**, 1859 (1989); (h) *Science of Synthesis: Vol. 6 Boron Compounds*, D. E. Kaufmann and D. S. Matteson (Eds.), Georg Thieme Verlag, Stuttgart-New York (2004).
2. V. K. Aggarwal, G. Y. Fang, A. T. Schmidt. *J. Am. Chem. Soc*. **127**, 1642 (2005).
3. An excellent discussion of the outcome of 1,2 migrations involving different borate complexes coupled with computational analysis is provided in: A. Bottoni, M. Lombardo, A. Neri, C. Trombini. *J. Org. Chem*. **68***,* 3397 (2003).
4. S. W. Slayden. *J. Org. Chem.* **46**, 2311 (1981).
5. S. W. Slayden. *J. Org. Chem.* **47**, 2753 (1982).
6. J. A. Soderquist and M. R. Najafi. *J. Org. Chem.* **51**, 1330 (1986).
7. J. A. Soderquist and C. L. Anderson. *Tetrahedron Lett.* **27**, 3961 (1986).
8. G. W. Kabalka and S. W. Slayden. *J. Organomet. Chem*. **125**, 273 (1977).
9. H. C. Brown. *Acc. Chem. Res*. **2**, 65 (1969).
10. A. Pelter, M. G. Hutchings, K. Smith, D. J. Williams. *J. Chem. Soc., Perkin Trans. 1* 145 (1975).
11. A. Pelter, K. Smith, M. G. Hutchings, K. Rowe. *J. Chem. Soc., Perkin Trans. 1* 129 (1975).
12. H. C. Brown, R. K. Bakshi, B. Singaram. *J. Am. Chem. Soc*. **110**, 1529 (1988).
13. H. C. Brown and E. Negishi. *J. Am. Chem. Soc.* **89**, 5285 (1967).
14. (a) A. Suzuki, M. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, M. M. Midland. *J. Am. Chem. Soc.* **95**, 3080 (1973); (b) M. M. Midland, J. A. Sinclair, H. C. Brown. *J. Org. Chem.* **39**, 731 (1974); (c) A. Pelter, K. Smith, M. Tabata. *J. Chem. Soc., Chem. Commun*. 857 (1975).
15. (a) E. F. Knights and H. C. Brown. *J. Am. Chem. Soc*. **90**, 5280 (1968); (b) E. F. Knights and H. C. Brown. *J. Am. Chem. Soc*. **90**, 5281 (1968); (c) E. F. Knights and H. C. Brown. *J. Am. Chem. Soc*. **90**, 5283 (1968).
16. Slayden [4] believes that the migration of 9-BBN results in relief of strain, thus favoring ring expansion. It is not clear which of the two bridged bicycles [3.3.1] or [3.3.2] is the more strained.
17. In addition to the selected examples discussed there are other reactions where 9-BBN fails as a nonmigrating group: (a) H. C. Brown, M. M. Midland, A. B. Levy. *J. Am. Chem. Soc.* **94**, 2114 (1972); (b) M. Naruse, K. Utimoto, H. Nozaki. *Tetrahedron Lett.* 1847 (1973); (c) J. B. Campbell Jr. and G. A. Molander. *J. Organomet. Chem.* **156**, 71 (1978); (d) J. A. Soderquist and I. Rivera. *Tetrahedron Lett*. **30**, 3919 (1989).
18. M. Ochiai, Y. Tuchimoto, N. Higashiura. *Org. Lett*. **6**, 1505 (2004).
19. J. Hooz and D. M. Gunn. *Tetrahedron Lett*. 3455 (1969).
20. H. C. Brown, R. G. Nalk, B. Singaram, C. Pyun. *Organometallics* **4***,* 1925 (1985).
21. (a) H. C. Brown, H. Nambu, M. M. Rogic. *J. Am. Chem. Soc*. **91**, 6852 (1969); (b) H. C. Brown, H. Nambu, M. M. Rogic. *J. Am. Chem. Soc.* **91**, 6854 (1969); (c) H. C. Brown, H. Nambu, M. M. Rogic. *J. Am. Chem. Soc.* **91**, 6855 (1969).
22. (a) H. C. Brown, J. L. Hubbard, K. Smith. *Synthesis* 701 (1979); (b) H. C. Brown, T. M. Ford, J. L. Hubbard. *J. Org. Chem.* **45**, 4067 (1980).
23. G. Zweifel and H. C. Brown. *J. Am. Chem. Soc.* **85**, 2066 (1963).
24. (a) H. C. Brown, U. S. Racherla, S. M. Singh. *Synthesis* 922 (1984); (b) H. C. Brown, D. Basavaiah, U. S. Racherla. *Synthesis* 886 (1983).
25. S. U. Kulkarni, H. D. Lee, H. C. Brown. *J. Org. Chem*. **45**, 4542 (1980).
26. H. C. Brown, D. Basavaiah, S. U. Kulkarni, H. D. Lee, E. Negishi, J.-J. Katz. *J. Org. Chem*. **51**, 5270 (1986).

27. M. Hoshi and A. Arase. *J. Chem. Soc., Perkin Trans 1* 2693 (1993).
28. A. Arase and M. Hoshi. *J. Chem. Soc., Chem. Commun*. 531 (1987).
29. A. Arase, M. Hoshi, Y. Masuda. *Bull. Chem. Soc. Jpn.* **57**, 209 (1984).
30. G. Zweifel and R. P. Fisher. *Synthesis* 339 (1974).
31. H. C. Brown, K.-W. Kim, T. E. Cole, B. Singaram. *J. Am. Chem. Soc.* **108**, 6761 (1986).
32. (a) H. C. Brown, W. R. Heydkamp, E. Breuer, W. S. Murphy. *J. Am. Chem. Soc.* **86**, 3565 (1964); (b) M. W. Rathke, N. Inoue, K. R. Varma, H. C. Brown. *J. Am. Chem. Soc.* **88**, 2870 (1966); (c) H. C. Brown, K. Kim, M. Srebnik, B. Singaram. *Tetrahedron* **43**, 4071 (1987).
33. (a) H. C. Brown, B. A. Carlson, R. H. Prager. *J. Am. Chem. Soc.* **93**, 2070 (1971); (b) B. A. Carlson and H. C. Brown. *J. Am. Chem. Soc.* **95**, 6876 (1973); (c) H. C. Brown and B. A. Carlson. *J. Org. Chem.* **38**, 2422 (1973).
34. J. A. Soderquist, J. Martinez, Y. Oyola, I. Kock. *Tetrahedron Lett*. **45**, 5541 (2004).
35. J. A. Soderquist, J. Ramos, K. Matos. *Tetrahedron Lett*. **38**, 6639 (1997).
36. (a) A. Vasella, W. Wenger, T. Rajamannar. *Chem. Commun*. 2215 (1999); (b) W. Wenger and A. Vasella. *Helv. Chim. Acta* **83**, 1542 (2000).
37. E. Negishi, T. Yoshida, A. Silveira Jr., B. L. Chiou. *J. Org. Chem*. **40**, 814 (1975).