Scope of the Reaction of Organoboranes with Organolithiums as a Method of Preparation of Lithium Organoborates. Stability of Lithium Organoborates

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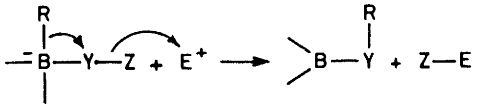
The scope and limitations of the reaction of organoboranes with a representative series of organolithiums as a method for the preparation of lithium organoborates have been examined by spectroscopic means (*i.r.*, ^1H *and* ^{13}C n.m.r.). The results indicate that, although the complexation reaction is highly general, the following limitations exist. In addition to the known limitation that hindered alkyl-lithiums with β-hydrogen atoms tend to give triorganoborohydrides in their reaction with triorganoboranes, charge-delocalized organolithiums derived from carbon acids whose pK_a are lower than *ca.* 20, such as cyclopentadienyl-lithium, indenyl-lithium, and α-lithioacetophenone, do not form lithium organoborates to any detectable extent under the conditions used. Equilibration of an organoborate with an appropriate organoborane or organolithium followed by treatment with iodine and g.l.c. analysis of the organic products provides a generally applicable and highly sensitive method for determining the stability of the organoborate with respect to dissociation which is often difficult to examine by spectroscopic methods. This method has been applied to examination of the stability of several representative lithium organoborates.

IT has recently been demonstrated that organoborates are unique nucleophiles capable of reacting with various electrophilic reagents (E^+) *via* either intermolecular transfer [equation (1)] or intramolecular transfer [equation (2)] of one or more boron-bound organic groups.[1] The required organoborates have been most commonly prepared by the reaction of organoboranes with basic organometallic compounds (MR^1) [2] [equation (3)]. Despite the fact that a number of organoborates have been synthesized as both well-characterized products and unidentified intermediates by this complexation reaction, its scope and limitations have not been well delineated.[1-4] Little is known about the thermodynamic stability of the organoborate products.


(1)


(2)

$$MR^1 + BR^2_3 \rightleftharpoons MBR^1R^2_3 \qquad (3)$$

R = organic group, Y–Z = suitably functionalized substituted.

During the course of our investigation of various reactions of organoborates, it often became essential to be able to synthesize the required organoborates as discrete species stable to dissociation into the corresponding organoboranes and the basic organometallic reagents. Since the basic organometallic reagents are, in general, intrinsically far more reactive toward electrophilic reagents than the corresponding organoborates they can favourably compete with the organoborates for electrophilic reagents, even if they are present in small quantities. These considerations led us to undertake a systematic study of the reaction of organoboranes with organometallic compounds with emphasis on (a) delineation of its scope and limitations as a method of preparation of organoborates and (b) determination of the stability of the organoborate products with respect to dissociation.

Previous Results and Methods of Analysis.—In a limited number of cases, the formation of organoborates has been established by isolation and *X*-ray analysis of crystalline organoborates.[5] Besides being time consuming, this method is limited to examination of the precise structure of thermally stable crystalline organoborates. However, the available *X*-ray data have provided certain useful information not readily obtainable by other means. Thus, they have revealed that, while some organoborates, such as $LiB(CH_3)_4$, exist as polymeric compounds,[5a] the monomeric ion pair formulation is an accurate representation in other cases.[5b] A recent ^7Li n.m.r. study [6] also supports the simple ion pair model [equation (4)] as a representation of organoborates in solution.

In the present study, our attention is mainly focused on the nature of the B–C bonds in organoborates rather than the three-dimensional structures. We therefore

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[1] For reviews, see E. Negishi, (*a*) *J. Organometallic Chem.*, 1976, **108**, 281; (*b*) J. Organometallic Chem. Library, 1976, **1**, 93.

[2] For a few earlier syntheses of organoborates by this reaction, see (*a*) J. R. Johnson, H. R. Snyder, and M. G. Van Campen, jun., *J. Amer. Chem. Soc.*, 1938, **60**, 115; (*b*) H. I. Schlesinger and H. C. Brown, *ibid.*, 1940, **62**, 3429. Frankland found that trimethylborane reacted with ammonia and potassium hydroxide, E. Frankland and B. F. Duppa, *Proc. Roy. Soc.*, 1859, **10**, 568.

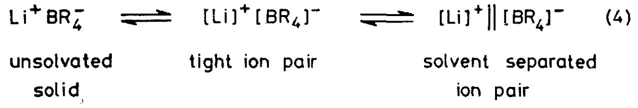
[3] (*a*) G. E. Coates, M. L. H. Green, and K. Wade, ' Organometallic Compounds,' Methuen, London, 1969, 3rd edn., vol. 1; (*b*) A. N. Nesmeyanov and R. A. Sokolik, ' The Organic Compounds of Boron, Aluminium, Gallium, Indium and Thallium,' The World Publishing Company, Ohio, 1967.

[4] For reviews on ' ate ' complexes, see (*a*) W. Tochtermann, *Angew. Chem. Internat. Edn.*, 1966, **5**, 351; (*b*) G. Wittig, *Quart. Rev.*, 1966, **20**, 191.

[5] (*a*) D. Grove, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, 1971, **93**, 1553; (*b*) J. Hooz, S. Skiyama, F. J. Cedar, M. J. Bennett, and R. M. Tuggle, *ibid.*, 1974, **96**, 274.

[6] R. J. Hogan, P. A. Scherr, A. T. Weibel, and J. P. Oliver, *J. Organometallic Chem.*, 1975, **85**, 265.

tentatively adopt the ion pair model as the gross structure of a stable organoborate in solution.

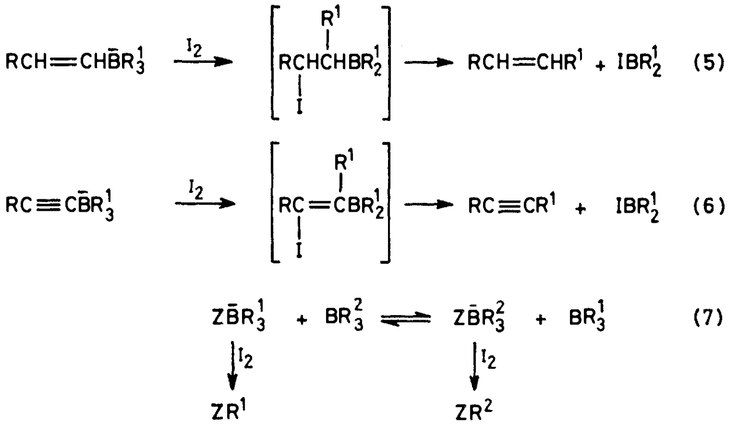


$$Li^+BR_4^- \rightleftharpoons [Li]^+[BR_4]^- \rightleftharpoons [Li]^+\|[BR_4]^- \quad (4)$$

unsolvated solid — tight ion pair — solvent separated ion pair

Damico[7] found that the i.r. spectra of alkylborates containing the α-C–H bond exhibited a strong characteristic band at 2 760—2 800 cm^{-1} attributable to the α-C–H stretching. The range 2 760—2 800 cm^{-1} is shifted by 100—150 cm^{-1} from that for the normal aliphatic C–H stretching, indicating that the α-hydrogen possesses appreciable hydride character as originally suggested by Wittig.[8] However, it is difficult to gain any quantitative information on alkylborates based on i.r. data. The same author[7] also found that the ^{1}H n.m.r. spectra of alkylborates exhibited a characteristic broad multiplet at δ −0.4 ± 0.1 attributable to the α-methylene protons. ^{11}B N.m.r. can also provide a quantitative method for analysis of organoborates.[9] At present, however, the accessibility of ^{11}B n.m.r. facilities is somewhat limited. On the other hand, ^{13}C n.m.r. has become a routine tool over the past several years. Despite its inherent limitations due to variable nuclear Overhauser effect (NOE) and variable relaxation times (T_1), it is, in principle, more generally applicable to examination of the nature of the C–B bond than ^{1}H n.m.r., since it does not require the presence of α-protons. A few tetra-alkylborates, such as lithium tetra-n-butylborate and lithium 9-di-n-butylborabicyclo[3.3.1]-nonane, have recently been examined by ^{13}C n.m.r.[10] However, its applicability as a quantitative or semi-quantitative tool for examination of organoborates has not been demonstrated.

As detailed in the following section, the results of our preliminary study have revealed that, while the spectroscopic methods provide useful information on the complexation reaction between organolithiums and organoboranes and on the approximate stability of the resultant organoborates, the accuracy of these methods is often too low to permit detection of a minor but potentially significant dissociation of an organoborate. Consequently, we have considered various chemical methods as potentially useful analytical tools for this purpose, and have recognized that the known reaction of organoborates with iodine could serve as a quantitative tool in many cases. Several groups of workers including ourselves have studied the organoborate–iodine reaction. The results indicate that alkenyl- and alkynyl-borates generally react with iodine by an intramolecular transfer mechanism,[11] which involves a 1,2-migration of a boron-bound group from the boron to the adjacent electrophilic carbon as shown in equations (5) and (6). In many cases, the reaction proceeds rapidly even at low temperatures and the indicated products are formed cleanly in excellent yields. In the absence of any strong base, such as sodium hydroxide, organoboranes do not generally react with iodine at any appreciable rates.[12] It is then evident that this iodination would be highly suited for probing a possible exchange reaction [equation (7)] between these αβ-unsaturated organoborates ($Z\bar{B}R^1{}_3$) and organoboranes ($BR^2{}_3$), provided that the iodination process is sufficiently faster than the exchange process.



$$RCH{=}CH\bar{B}R^1_3 \xrightarrow{I_2} \left[RCH(I)CH(R^1)BR^1_2\right] \longrightarrow RCH{=}CHR^1 + IBR^1_2 \quad (5)$$

$$RC{\equiv}C\bar{B}R^1_3 \xrightarrow{I_2} \left[RC(I){=}C(R^1)BR^1_2\right] \longrightarrow RC{\equiv}CR^1 + IBR^1_2 \quad (6)$$

$$\begin{array}{ccccccc} Z\bar{B}R^1_3 & + & BR^2_3 & \rightleftharpoons & Z\bar{B}R^2_3 & + & BR^1_3 \\ \downarrow I_2 & & & & \downarrow I_2 & & \\ ZR^1 & & & & ZR^2 & & \end{array} \quad (7)$$

RESULTS AND DISCUSSION

The scope of the present study is limited to the reaction of triorganoboranes with organolithiums. Tri-n-butyl- and tri-n-hexyl-borane were chosen as simple trialkylboranes. As discussed later in detail, the ^{1}H n.m.r. signals for the alkenyl hydrogens of alk-1-enylboranes provide valuable structural information. Therefore, dicyclohexyl-(*E*)-hex-1-enylborane (2) was also chosen as an additional organoborane. As a representative

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[7] R. Damico, *J. Org. Chem.*, 1964, **29**, 1971.

[8] G. Wittig *Angew. Chem.*, 1958, **70**, 65.

[9] H. C. Brown and G. W. Kramer, personal communication.

[10] (*a*) D. J. Hart and W. T. Ford, *J. Org. Chem.*, 1974, **39**, 363; (*b*) Y. Yamamoto, H. Toi, A. Sonoda, and S. Murahashi, *Chem. Letters*, 1975, 1199.

[11] (*a*) For a review on the iodination reaction of organoboranes and organoborates, see G. Zweifel, *Intra-sci. Chem. Report*, 1973, **7**, 181; (*b*) A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, *J. Amer. Chem. Soc.*, 1973, **95**, 3080.

[12] H. C. Brown, M. W. Rathke, and M. M. Rogic, *J. Amer. Chem. Soc.*, 1968, **90**, 5038.

series of organolithiums, n-butyl- (pK_a >50),[13a] phenyl- (pK_a 43),[13a] (*E*)-hex-1-enyl- (pK_a 37—43),[13b] benzyl- (pK_a 41),[13a] methylthiomethyl-,[13d] methylsulphinylmethyl- (pK_a 35),[13e] phenylsulphonylmethyl- (pK_a 27),[13f] hex-1-ynyl-lithium (pK_a *ca.* 25),[13g] α-lithioacetophenone (pK_a 22),[13f] indenyl- (pK_a 20), [13h] and cyclopentadienyl-lithium (pK_a 16) [13i] were selected.

The organolithium reagents and organoboranes were first mixed in a 1 : 1 ratio in solvent systems consisting mainly of tetrahydrofuran (THF) and hexane at room temperature. After appropriate times the mixtures were examined by i.r. and ^1H n.m.r. In cases where formation of stable organoborates were indicated, equimolar mixtures of the organoborate and an organoborane were prepared. ^1H N.m.r. spectra were taken in order to determine whether or not any exchange which was fast on the n.m.r. time scale had taken place between the organoborate and the added organoborane. In the absence of such a fast exchange, we may safely conclude that the spectral data observed with the reaction mixtures derived from equimolar amounts of organolithiums and organoboranes are those of the organoborates formed. In this connection, it is worth mentioning here that recent ^{11}B n.m.r. studies [14] of certain trialkylborohydride–trialkylborane systems indicate a rapid hydride exchange between the two reactants at ambient temperature. If no fast exchange was observed, the 1 : 1 mixtures of organoborates and organoboranes were subjected to the iodination reaction, and the organic products were examined by g.l.c. Additional experiments were performed as needed.

TABLE 1

I.r. absorption data for the reaction of tri-n-butylborane with organolithium reagents

Organolithium	α-Methylene C–H stretching band (cm^{-1}) [a]
$LiBu^n$	2 770 [b,c]
LiPh	2 800 [b,c]
(*E*)-$Li(CH{=}CHBu^n)$	2 745
$LiCH_2Ph$	2 790
$LiCH_2SCH_3$	2 740
$LiCH_2SOCH_3$	2 740
$LiCH_2SO_2Ph$	2 770
$LiC{\equiv}CBu^n$	2 750
$LiCH_2COPh$	2 900
Cyclopentadienyl-lithium	2 940

[a] Solvent THF unless otherwise noted. [b] In CH_3CN. [c] Ref. 7.

Spectroscopic Investigation.—(a) *Preliminary examinations by i.r. and* ^1H *n.m.r.* The i.r. and ^1H n.m.r. spectral data observed with the 1 : 1 reaction mixtures are summarized in Tables 1 and 2, respectively. The results indicate the following. (i) n-Butyl-, phenyl-, (*E*)-hex-1-enyl-, benzyl-, methylsulphinylmethyl-, phenylsulphonylmethyl-, and hex-1-ynyl-lithium react with tri-n-butylborane to form the corresponding organoborates, as judged by (a) the characteristic i.r. stretching bands [7] at 2 740—2 800 cm^{-1} and (b) the broad ^1H n.m.r. peaks [7] centred at δ 0.0 ± 0.3, the areas of which corresponded to roughly six (eight in the case of $LiBBu^n{}_4$) hydrogen atoms. (ii) α-Lithioacetophenone and indenyl-, and cyclopentadienyl-lithium, on the other hand, show no tendency to form the corresponding organoborates. Thus, the characteristic i.r. and ^1H n.m.r. absorptions were absent in the regions specified above. The ^1H n.m.r. singlet for the ring protons of cyclopentadienyl-lithium at δ 5.84 remained unchanged upon addition of tri-n-butylborane.

TABLE 2

^1H N.m.r. data for the reaction of tri-n-butylborane with organolithium reagents

Organolithium	α-Methylene protons [a,b] δ [c,d]	Other protons [b] Assignment	δ [c]
Bu^n	−0.3 (8 H)		
LiPh	+0.2 [e]		
(*E*)-$Li(CH{=}CHBu^n)$	−0.1 (6 H)	*f*	
$LiCH_2Ph$	0.0 (6 H)	Ring [g]	7.20 (s)
$LiCH_2SCH_3$	−0.15 (6 H)		
$LiCH_2SOCH_3$	−0.1 (6 H)		
$LiCH_2SO_2Ph$	+0.1 (6 H)		
$LiC{\equiv}CBu^n$	−0.1 (6 H)		
$LiCH_2COPh$	*h*		
Indenyl-lithium	*h*	Aromatic ring [i]	6.8 (m)
Cyclopentadienyl-lithium	*h*	Ring [j]	5.85 (s)

[a] For the n-butyl groups of tri-n-butylborane. [b] All spectra were run in solvent systems consisting mainly of THF. [c] Chemical shifts are given in p.p.m. relative to Me_4Si. [d] The chemical shift for the α-methylene protons of tri-n-butylborane is δ +0.9, while the shift for the α-methylene protons of n-butyllithium is δ −0.85. [e] Unable to integrate due to partial overlap of the broad band with other peaks. [f] See Table 3. [g] Ring protons, δ 5.9 (m). [h] No signal between δ +0.9 and −1.0. [i] Aromatic ring protons of indenyl-lithium δ 6.8 (m). [j] Ring protons of cyclopentadienyl-lithium δ 5.84 (s).

(b) ^1H *N.m.r. examination of lithium* (E)-*hex*-1-*enylborates*. The spectroscopic results presented above not only confirm the findings of Damico [7] but demonstrate the general applicability of i.r. and ^1H n.m.r., in particular the latter, as tools for examining organoborates. Unfortunately, however, the ^1H n.m.r. α-methylene peak is a broad multiplet (half-width *ca.* 20 Hz) which tends to overlap with other signals in the same region. As a result, the accuracy of the area measurement is at best ±10%. It is therefore difficult to distinguish a pure sample of an organoborate from a 90 : 10 mixture of the same organoborate and its dissociation products based solely on the α-methylene peak measurement of the

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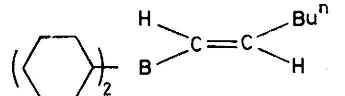
[13] The pK_a values are those of the conjugate carbon acids. (*a*) A. Streitwieser, jun., and C. H. Heathcock, ' Introduction to Organic Chemistry,' Macmillan, New York, 1976; (*b*) estimated from the pK_a values for related compounds reported in refs. 5*a* and *c*; (*c*) D. J. Cram, ' Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965; (*d*) we have been unable to find a pK_a value for this compound in the literature; (*e*) H. O. House, ' Modern Synthetic Reactions,' Benjamin, San Francisco, 1972, 2nd edn., p. 494; (*f*) F. G. Bordwell and W. S. Matthews, *J. Amer. Chem. Soc.*, 1974, **96**, 1214; (*g*) estimated from the reported pK_a values for related compounds, A. Streitwieser, jun., and D. M. E. Reuben, *ibid.*, 1971, **93**, 1794; (*h*) A. Streitwieser, jun., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *ibid.*, 1967, **89**, 59; (*i*) A. Streitwieser, jun., and L. L. Nebenzahl, *ibid.*, 1976, **98**, 2188.

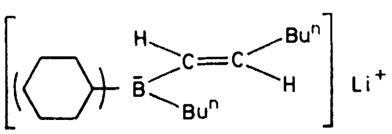
[14] C. A. Brown, 172nd National Meeting of the American Chemical Society, San Francisco, 1976, Abstract ORGN 153. See also H. Nöth and B. Wrackmeyer, *Chem. Ber.*, 1974, **107**, 3070; B. Wrackmeyer, *J. Organometallic Chem.*, 1976, **117**, 313.

organoborate. The α-methylene signals of tri-n-butylborane severely overlap with that of the methyl protons and are not amenable to quantitative examination.

Fortunately, we have noted that both α- and β-alkenyl proton peaks of dicyclohexyl-(*E*)-hex-1-enylborane (2) as well as of lithium n-butyldicyclohexyl-(*E*)-hex-1-enylborate (3) appear as well defined multiplets.[15,*] *Significantly*, the chemical shift of the β-alkenyl proton peaks of (3) is clearly distinguishable from that of the parent organoborane (2). Moreover, the relative positions of the α- and β-proton peaks are reversed in going from the borane (δ 6.40 and 6.90, respectively) to the borate (δ 6.18 and 5.38, respectively). The peak assignments are based on (a) the peak multiplicity and (b) the observation that the α-proton peak is broadened due to the $^{11}B-^{1}H$ coupling and ^{11}B quadruple moment. Finally, mixtures of (2) and (3) exhibit β-proton signals of the individual components at the same positions as those of pure samples, indicating that no fast exchange between (2) and (3) takes place. Even 5 mol % of one in the other can readily be detected. Thus, ^{1}H n.m.r. examination of alkenylborates in conjunction with that of the parent alkenylboranes provides reliable information on the organoborane–organolithium reaction, especially on the stability or dissociation of the organoborate products. The dramatic change in the chemical shift for the β-proton peaks in going from alkenylboranes to alkenylborates may be accounted for in terms of $p_{\pi}-p_{\pi}$ interaction present in the alkenylboranes.[16]



(2)



(3)

We have therefore treated dicyclohexyl-(*E*)-hex-1-enylborane with several representative organolithiums and have examined the products by ^{1}H n.m.r. To minimize interferences exerted by THF and other solvents, if any, the solvents used for the reaction were replaced with [$^{2}H_6$]benzene. The spectral results are summarized in Table 3.

The products derived from n-butyl-, phenyl-, benzyl-, methylthiomethyl-, methylsulphinylmethyl-, and hex-1-ynyl-lithium all exhibit the characteristic β-alkenyl proton peaks in the δ 5.3—5.7 region without showing any peak for the β-proton of dicyclohexyl-(*E*)-hex-1-enylborane (2) in the δ 6.7—6.9 region. On the other hand, the product obtained by mixing α-lithioacetophenone with (2) shows the same β-proton multiplet as that of (2), indicating that there is essentially no reaction between the two species. Due to interference with THF sidebands, the β-proton multiplet was not detected for the mixture of phenylsulphonylmethyl-lithium and (2). However, the formation of the corresponding organoborate was indicated by (a) the absence of any peak in the δ 6.7—6.9 region and (b) the reversal in the tilting pattern of the α-proton doublet. On removal of the solvents, the characteristic borate pattern of the α- and β-proton was lost with no detection of the α- and β-proton absorption for (2). These results indicate that the expected phenylsulphonylmethylborate was initially formed but decomposed on removal of the solvents. No attempts to identify any decomposition products were made.

TABLE 3

^{1}H N.m.r. chemical shifts for the olefinic protons of lithium (*E*)-hex-1-enylborates $LiB(C_6H_{11})_2(CH=CHBu^n)R$

R	α-Proton	β-Proton
b	6.40	6.90
b	6.12 [c]	6.73 [c]
Bu^n	6.18	5.38 [d]
Ph	6.36	5.66 [d]
CH_2Ph	6.00	5.26 [d]
CH_2SCH_3	6.50	5.60 [d]
CH_2SOCH_3	5.93	5.39 [d]
CH_2SO_2Ph	5.76 [c]	*e* [c,d]
$C\equiv CBu^n$	6.20	5.73 [d]
CH_2COPh	6.16 [c]	6.73 [c]

[a] Spectra run in [$^{2}H_6$]benzene unless otherwise noted. Shifts are relative to Me_4Si. [b] Values for dicyclohexyl-(*E*)-hex-1-enylborane. [c] Solvent THF. [d] No absorption was in the region δ 6.73—6.90. [e] No absorption due to overlap with THF sidebands.

The results presented above indicate that, in cases where formation of organoborates is observed, these lithium tetraorganoborates do not generally undergo a fast ligand exchange with organoboranes and that the organoborate formation observed with n-butyl-, phenyl-, benzyl-, and hex-1-ynyl-lithium is essentially complete, no dissociation being detected.

(c) ^{13}C *N.m.r.* It has so far been assumed that the reaction of an organolithium reagent (LiR^1) with a trialkylborane (BR^2_3) would yield $LiBR^2_3R^1$, if at all. However, the product can, in principle, disproportionate to form a mixture of two or more of the five possible organoborates $LiBR^2_nR'_{4-n}$ ($n = 0—4$) under the reaction conditions. All the results presented so far are consistent with any such mixtures, the overall $R^2 : R^1$ ratio of which is 3. In fact, the reaction of n-butyl-lithium with borane in THF (BH_3,THF), for example, has been shown to produce even at low temperatures a mixture of all five possible borates [17] [equation (8)].

The high sensitivity of ^{13}C n.m.r. to even minor environmental differences prompted us to apply this spectroscopic tool to the establishment of the precise composition of the product obtained by the LiR^1–BR^2_3 reaction. As a test system, we chose the following set of

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[*] During the course of our study, similar ^{1}H n.m.r. results have been reported by Zweifel *et al.*[16]

[15] K. W. Chiu, Ph.D. Dissertation, Syracuse University, 1976.

[16] G. Zweifel, G. M. Clark, T. Leung, and C. C. Whitney, *J. Organometallic Chem.*, 1976, **117**, 303.

[17] H. C. Brown and E. Negishi, unpublished results.

lithium arylborates: $LiBPh_nBu^n{}_{4-n}$ (n = 1—4). Reactions (9)—(12) were carried out for the preparation of these arylborates. After evaporation of the solvents at room temperature under reduced pressure, the residues were dissolved in [$^2H_6$]acetone and their ^{13}C n.m.r. spectra were recorded. The results are summarized in Table 4, along with the chemical shifts for BPh_3. The assignment of the *ipso*- and *meta*-carbon signals are primarily based on the reported ^{11}B–^{13}C coupling constants of a few tetraphenylborates,[18] which are known to be by far the largest for $^1J_{^{11}B-^{13}C}$ due to the *ipso*-carbon atom, followed by $^3J_{^{11}B-^{13}C}$ due to the *meta*-carbon atoms. Distinction between the signal for the *ortho*-carbon atoms and that for the *para*-carbon atom is based on the relative integration which was *ca.* 2 : 1.

$$LiBu^n + BH_3 \xrightarrow{THF} LiBH_4 + LiBH_3Bu^n + LiBH_2Bu^n{}_2 + LiBHBu^n{}_3 + LiBBu^n{}_4 \qquad (8)$$

$$LiPh + BPh_3 \longrightarrow LiBPh_4 \qquad (9)$$

$$LiBu^n + BPh_3 \longrightarrow LiBPh_3Bu^n \qquad (10)$$

$$LiPh + BBu^n{}_3 \longrightarrow LiBPhBu^n{}_3 \qquad (11)$$

$$LiBPhBu^n{}_3 \xrightarrow{I_2} BPhBu^n{}_2 \xrightarrow{LiPh} LiBPh_2Bu^n{}_2 \qquad (12)$$

TABLE 4

^{13}C N.m.r. data for lithium phenylborates $LiBPh_nBu^n{}_{4-n}$

	Chemical shift of aromatic carbons [a] (δ)		
n	*ortho*	*meta*	*para*
1	133.5	125.2	120.2
2	134.0	125.2	120.7
3	135.6	125.6	121.4
4	136.7	125.6	121.9

[a] Spectra were run in [$^2H_6$]acetone. Chemical shifts are in p.p.m. relative to Me_4Si. Peak assignments are based on ^{11}B–^{13}C coupling constants and peak integrations. With the exception of lithium tetraphenylborate, no resonance signal could be seen for the *ipso*-carbon. ^{13}C N.m.r. data for the aromatic carbons of triphenylborane are as follows: *ortho*, δ 127.8, *meta*, δ 138.8, *para*, δ 131.6 p.p.m.

TABLE 5

Reaction of lithium organoborates $LiBR^1{}_2(R^2)(Z)$ with iodine in the presence of organoboranes $BR^3{}_2R^4$

						Product (%) [a]	
Z	R^1	R^2	R^3	R^4	*t*/h [b]	(I) [c]	(II) [d]
Bu^n	Bu^n	Bu^n	n-C_6H_{13}	n-C_6H_{13}	24	Bu^n (100)	n-$C_6H_{13}I$ [e]
Ph	Bu^n	Bu^n	n-C_6H_{13}	n-C_6H_{13}	24	Bu^n (98)	n-$C_6H_{13}I$ [e]
(*E*)-(CH=$CHBu^n$)	Bu^n	Bu^n	n-C_6H_{13}	n-C_6H_{13}	24	$Bu^nCH=CHBu^n$ [f,g]	n-$C_6H_{13}CH=CHBu^n$
$PhCH_2$	C_6H_{11}	(*E*)-(CH=CHC_5H_{11})	C_6H_{11}	(*E*)-(CH=CHC_6H_{13})	24	$C_6H_{11}CH=CHC_5H_{11}$ [g,h]	$C_6H_{11}CH=CHC_6H_{13\text{-}n}$ [e,g]

[a] By g.l.c. [b] Time of mixing lithium organoborate with the organoborane. [c] Product derived from the iodination of the original borate. [d] Product derived from the iodination of the borate formed by the reaction of LiZ with $BR^3{}_2R^4$. [e] Trace. [f] Yields based on the amount of iodine consumed. [g] The stereochemistry has not been determined for the product. [h] In addition, 15% of benzyl iodide was formed.

Significantly, each of the four arylborates exhibits a distinct set of signals for the *ortho*- and *para*-carbon atoms, although the peaks for the *meta*-carbon atoms in all cases appear essentially at the same position (δ 125.4 ± 0.2 p.p.m.). The *ortho*- and *para*-carbon signals observed with a mixture of any two of the four arylborates are essentially base-line separated (*ca.* 10 Hz). The signals for the *ipso*-carbon atoms were either ill defined or unobservable, except with $LiBPh_4$. These results have clearly established the following. First, in each of the reactions (9)—(12) the indicated arylborate is formed as an essentially single product, which does not readily undergo disproportionation under the reaction conditions. Secondly, ^{13}C n.m.r. clearly distinguishes all four arylborates. Although we have not yet applied this technique to other cases, it shows considerable promise as a tool for examining the compositions of organoborates, for which there has been no dependable method.

Stability of Lithium Tetraorganoborates.—The scope and limitations of the reaction of organolithium reagents with trialkylboranes as a method for the preparation of lithium tetraorganoborates are now reasonably well delineated. However, the sensitivity of the spectroscopic methods is generally too low to detect a minor but potentially significant dissociation of an organoborate. As detailed in the Introduction, we therefore explored the applicability of the iodination reaction of organoborates as a tool for probing the stability of organoborates with respect to dissociation.

Those stable organoborates which are obtained by the reaction of tri-n-butylborane with n-butyl-, phenyl-, (*E*)-hex-1-enyl-, benzyl-, and hex-1-ynyl-lithium were chosen for this investigation. Each of these lithium tetraorganoborates was mixed with an equimolar amount of tri-n-hexylborane at room temperature in a mixture of THF and hexane. Portions were withdrawn at appropriate times, treated with iodine, and analysed by g.l.c., after oxidation with alkaline hydrogen peroxide. Care was taken not to add iodine in any excess so as not to produce iodinated products from organoboranes.

The results of the g.l.c. analyses summarized in Table 5 indicate the following. First, in the cases of lithium tetra-n-butylborate and lithium phenyltri-n-butylborate (4), n-butyl iodide was formed in a nearly quantitative yield (1 mole per mole of organoborate). No more than a trace (<2%) of n-hexyl iodide was present even after 24 h at room temperature, and there was no indication that the amount of n-hexyl iodide was increasing with time. Since the reaction of lithium n-butyltri-n-hexylborate with an equivalent of iodine produced a

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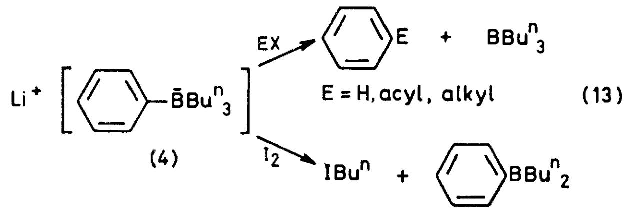
[18] (*a*) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 4940; (*b*) J. D. Odom, L. W. Hall, and P. D. Ellis, *Org. Magnetic Resonance*, 1974, **6**, 360.

roughly 3 : 1 mixture of n-hexyl and n-butyl iodides in an essentially quantitative combined yield, the reactivities of these two groups are roughly comparable. These results clearly indicate that neither of these organoborates undergoes dissociation or exchange with tri-n-hexylborane under the conditions used.

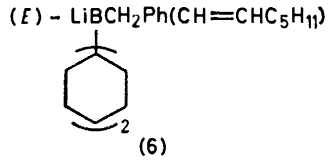


The exclusive formation of n-butyl iodide in the case of lithium phenyltri-n-butylborate (4) is quite unexpected, since the reaction of alkenylborates, a related class of αβ-unsaturated organoborates, with iodine is known to proceed by the intramolecular transfer mechanism to form the corresponding alkenes [11] [equation (5)], and since the reaction of (4) with methanesulphonic acid,[19] acyl halides,[20] and certain alkyl halides [19] have yielded either exclusively or predominantly benzene, phenyl ketones, and phenylated alkanes, respectively, along with tri-n-butylborane [equation (13)].

A 1 : 1 mixture of lithium (*E*)-hex-1-enyltri-n-butylborate (5) and tri-n-hexylborane reacted with one equivalent of iodine to produce only dec-5-ene.* No detectable amount of dodec-5-ene was formed. We conclude that (5) does not dissociate under these conditions.

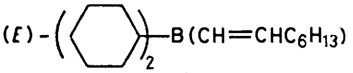
(*E*)-$LiB(CH{=}CHBu^n)Bu^n_3$

(5)



(*E*)-$LiBCH_2Ph(CH{=}CHC_5H_{11})(C_6H_{11})_2$

(6)



(*E*)-$(C_6H_{11})_2B(CH{=}CHC_6H_{13})$

(7)

$LiB(C{\equiv}CBu^n)Bu^n_3$

(8)

$LiB(C{\equiv}CBu^n)(C_6H_{13})_3$

(9)

The reaction of lithium benzyltri-n-hexylborate with one molar equivalent of iodine produced a mixture of benzyl iodide and n-hexyl iodide in 44 and 25% yield, respectively. In search for a cleaner reaction than that mentioned above, lithium benzyldicyclohexyl-(*E*)-oct-1-enylborate was treated with one molar equivalent of iodine. Somewhat unexpectedly, 1-cyclohexyloct-1-ene [21] was obtained (58%) as essentially the only intramolecular transfer product along with benzyl iodide (35%). Thus, the benzyl group did not migrate from boron to the adjacent carbon in competition with the cyclohexyl group. On the other hand, the same benzyl group was transferred exclusively in the intermolecular transfer process. Although we have not been successful in observing formation of a single product in the iodination of benzylborates, either of the above reactions can be used to probe the stability of benzylborates. We therefore mixed lithium benzyldicyclohexyl-(*E*)-hept-1-enylborate (6) with an equimolar amount of dicyclohexyl-(*E*)-oct-1-enylborane (7) and subjected the resultant mixture to the iodination–oxidation–g.l.c. sequence. Even after 24 h, no detectable amount of 1-cyclohexyloct-1-ene [21] was formed, the only observable iodination products being 1-cyclohexylhept-1-ene [21] (58%), 1-phenyloct-2-ene [21] (trace), and benzyl iodide (15%). We conclude that (6) does not dissociate under the reaction conditions.

An important conclusion to be drawn here is that the iodination of these organoborates does not involve the predissociation of the organoborates. The organoborates themselves must be the actual reactive species.

*Lithium Alk-*1*-ynyltrialkylborates*.—A 1 : 1 mixture of lithium hex-1-ynyltri-n-butylborate (8) and tri-n-hexylborane was subjected to the iodination–oxidation–g.l.c. sequence. The results summarized in Table 6 indicate that a ready exchange takes place between the two reactants, producing roughly equimolar amounts of dec-5-yne and dodec-5-yne after 6 h at room temperature. Roughly the same result was obtained from a 1 : 1 mixture of lithium hex-1-ynyltri-n-hexylborate (9) and tri-n-butylborane.

Such an exchange reaction can take place either associatively or dissociatively. To distinguish these two processes, (8) was mixed with one equivalent of hept-1-ynyl-lithium, and the mixture subjected to the same analytical sequence. In this case, however, two

TABLE 6

Reaction of lithium hex-1-ynyltri-n-butylborate with iodine in the presence of tri-n-hexylborane

	Yield (%) [a]	
t/h [b]	Dec-5-yne	Dodec-5-yne
0	50 (100)	0 (0)
1.5	56 (81)	13 (19)
3	34 (64)	19 (36)
6	32 (51)	31 (49)
24	25 (52)	23 (48)

[a] By g.l.c. The numbers in parentheses are normalized. [b] Time of mixing lithium hex-1-ynyltri-n-butylborate with tri-n-hexylborane.

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* Although the stereochemistry has not been established, a recent paper on a related reaction indicates that the alkene products are largely *trans*. [21]

[19] E. Negishi and R. E. Merrill, unpublished results.

[20] E. Negishi, K. W. Chiu, and T. Yoshida, *J. Org. Chem.*, 1975, **40**, 1676.

[21] A. B. Levy and N. J. LaLima, *J. Org. Chem.*, 1978, **43**, 1279.

equivalents of iodine were used, as alkynyl-lithiums also react with iodine. An almost equally ready equilibration, which was complete between 6 and 24 h, was observed. Due to the stable nature of hept-1-ynyl-lithium in the solvents used, no undesirable side reactions which have precluded the use of more reactive organolithiums, such as n-butyl-lithium, were observed in this case. Since it is highly unlikely that the alkynylborate (8) and hept-1-ynyl-lithium, both of which are basic, react with each other by an associative process, we conclude that the reaction proceeds dissociatively.

EXPERIMENTAL

General.—All operations involving organoboron compounds were performed under nitrogen. I.r. spectra were recorded using a Perkin-Elmer 137 or Perkin-Elmer 621 spectrometer. ^1H N.m.r. spectra were obtained using a Varian T-60A or Perkin-Elmer R-20A spectrometer at ambient temperature with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were obtained using a Varian CFT-20 (20 MHz) spectrometer at ambient temperature with tetramethylsilane as standard. G.l.c. analyses were performed on a Perkin-Elmer 3920 or Hewlitt–Packard 5750 gas chromatograph using a 6 ft × 0.125 in column of 10% SE-30 on Chromosorb W.

Materials.—Tri-n-butylborane was obtained from Callery Chemical Company and distilled before use. Triphenylborane, n-butyl-lithium, and s-butyl-lithium were obtained from Alfa Products. Tri-n-hexyl-,[22] tri-s-butyl-,[22] dicyclohexyl-(*E*)-hex-1-enyl-,[22] dicyclohexyl-(*E*)-hept-1-enyl-[22] and dicyclohexyl-(*E*)-oct-1-enyl-borane,[22] phenyl-,[23] (*E*)-hex-1-enyl-,[24] benzyl-,[25] allyl-,[26] methylthiomethyl-,[27] methylsulphinylmethyl-,[28] indenyl-,[29] and cyclopentadienyl-lithium[30] were prepared according to reported methods. Phenylsulphonylmethyl-lithium was prepared by the reaction of methyl phenyl sulphone with one equivalent of n-butyl-lithium at 0 °C in THF. Hex-1-ynyl- and hept-1-ynyl-lithium were prepared by treatment of the corresponding alk-1-yne with one equivalent of n-butyl-lithium at 0 °C in THF. α-Lithioacetophenone was prepared by the treatment of acetophenone with one equivalent of lithium di-isopropylamide at −30 °C in THF. Benzene, diethyl ether, THF, and toluene were distilled from lithium aluminium hydride and stored over molecular sieves.

Sample Preparation.—^1H *N.m.r. Procedure* A. No attempts were made to separate the organoborate from the solvents and by-products. Benzene (1/6 equiv.) was usually added to the organoborate solution as an internal standard. In the cases where benzene could not be used due to peak overlap, either tetramethylsilane or cyclohexene was used as internal standard. A portion was transferred into a 5 mm (o.d.) n.m.r. sample tube fitted with a septum cap and flushed with nitrogen.

Procedure B. Solvents were removed under reduced pressure from a solution of an organoborate. The resulting material was dissolved in [$^2H_6$]benzene (*ca.* 1.0M). A portion was transferred into a 5 mm (o.d.) n.m.r. sample tube fitted with a septum cap and flushed with nitrogen.

^{13}C *N.m.r.* The solvents were removed under reduced pressure and the residue was dissolved in [$^2H_6$]acetone (*ca.* 1.0M). A portion was transferred into an 8 mm (o.d.) n.m.r. sample tube fitted with a septum cap and flushed with nitrogen.

I.r. No attempts were made to separate the organoborate from the solvents and by-products. A portion was transferred into a sealed liquid i.r. sample cell fitted with septum caps and flushed with nitrogen.

Preparation of Lithium Organoborates.—General procedure. A dry flask with a septum inlet, a magnetic stirring bar, a reflux condenser and an outlet connected to a mercury bubbler was flushed with nitrogen. Either THF or diethyl ether was added followed by addition of the organoborane. The stirred mixture was cooled to 0 °C and the organolithium was slowly added. The mixture was stirred at 0 °C for 0.5 h, then allowed to warm to room temperature. Alternatively, the organoborane was slowly added to a cooled (−78 to 0 °C where appropriate) solution of the organolithium in the preparative solvent. The mixture was stirred for 0.5 h at the addition temperature, then allowed to warm slowly to room temperature.

Di-n-butylphenylborane. To lithium phenyltri-n-butylborate [prepared by the reaction of bromobenzene (0.79 g, 0.53 ml, 5 mmol) in ether (10 ml) with n-butyl-lithium (2.00 ml of a 2.5M hexane solution, 5 mmol) followed by the addition of tri-n-butylborane (0.91 g, 1.22 ml, 5 mmol)] was added at room temperature iodine (1.27 g, 5 mmol) dissolved in THF (10 ml). The mixture was stirred for 0.5 h. The resultant solution of di-n-butylphenylborane was used in subsequent reactions without removal of solvent or by-products. For characterization, the solvent was removed under reduced pressure from a portion of di-n-butylphenylborane to give a clear oil, $\delta_H[(CD_3)_2CO]$ 0.9 (6 H, m), 1.5 (12 H, m), and 7.6 (5 H, m); $\delta_C[(CD_3)_2CO]$ 14.3 (CH_3), 26.8, 28.1 (β- and α-CH_2), 128.4 (*o*-C), 132.2 (*p*-C), and 134.5 p.p.m. (*m*-C).

Reaction of s-Butyl-lithium with Trialkylboranes.—The following reaction with n-butyldi-s-butylborane is representative. To a solution of n-butyl-di-s-butylborane (4.55 g, 25 mmol) in THF (43 ml) was added s-butyl-lithium (31 ml of a 0.8N-hexane solution, 25 mmol) at 0 °C. After stirring for 1 h at 0 °C, the mixture was examined by i.r. (2 020 cm^{-1}). A portion was treated with 3N-HCl, and the amount of hydrogen evolved was measured (20 mmol of H_2 evolved). The hydrolysed mixture was neutralized with aqueous $NaHCO_3$ and analysed by g.l.c. n-Butyldi-s-butylborane was recovered in 91%.

Reaction of Lithium Organoborates with Iodine in the Presence of an Organoborane.—General procedure. To a stirred solution of a lithium organoborate in the solvent used for preparation was added an equimolar amount of an organoborane. To this solution was added a hydrocarbon as an internal standard. The resultant mixture was stirred at room temperature, and portions were removed at appropriate times, cooled to either −78 or 0 °C and quenched with a THF solution of iodine (0.5M) until the colour of

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iodine persisted. After stirring for an additional 0.5 h, the mixture was allowed to reach 0 °C followed by the addition of aqueous sodium hydroxide and hydrogen peroxide solutions. The stirred mixture was heated at 50 °C for 1 h. Upon cooling, the aqueous phase was saturated with potassium carbonate and the organic phase analysed directly by g.l.c.

Reaction of Lithium Hex-1-*ynyltri-n-butylborate with Iodine in the Presence of Hept*-1-*ynyl-lithium.*—Lithium hex-1-ynyltri-n-butylborate–hept-1-ynyl-lithium (1 : 1) was treated according to the general procedure. Two equivalents of iodine were used in the iodination step. The product distribution was dec-5-ene (28%), dodec-5-ene (28%).

Reaction of Lithium n-Butyltri-n-hexylborate with Iodine.—To lithium n-butyltri-n-hexylborate prepared by the reaction of n-butyl-lithium (0.83 ml of a 2.4M hexane solution, 2 mmol) with tri-n-hexylborane (10.0 ml of a 0.2M THF solution, 2 mmol) was added n-dodecane (0.34 g, 0.45 ml, 2 mmol). The solution was cooled to 0 °C and quenched with iodine (0.5M THF solution) until the colour of iodine began to persist. After stirring for 0.5 h, sodium hydroxide (3 ml of a 3M aqueous solution, 9 mmol) and hydrogen peroxide (3 ml of a 30% aqueous solution, 29 mmol) were added to the mixture. The stirred solution was heated to 50 °C for 1 h. Upon cooling, the aqueous phase was saturated with potassium carbonate and the organic phase analysed directly by g.l.c. The product distribution was n-butyl iodide (28%), n-hexyl iodide (73%).

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