HOMOLYTIC ALKYLTHIYLDEALKYLATION OF MIXED ALKYLBORANES

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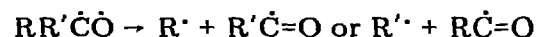
Summary

The relative ease of displacement of different alkyl groups in mixed alkyl-boranes by butylthiyl radicals derived from butanethiol follows the sequence p-R < s-R < t-R.
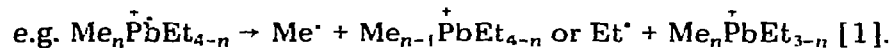

Most of the information which is available about the relative ease of separation of two alkyl radicals $R^{\cdot}$ and $R^{\prime \cdot}$ from a common multivalent centre, X, relates to the unimolecular β-scission of radical species, $RR'XY^{\cdot}$. Typical examples are the fragmentation reactions of alkoxyl radicals

$$R_2R'CO^{\cdot} \rightarrow R_2C{=}O + R'^{\cdot} \text{ or } RR'C{=}O + R^{\cdot}$$

of ketone triplets

$$RR'\dot{C}\dot{O} \rightarrow R^{\cdot} + R'\dot{C}{=}O \text{ or } R'^{\cdot} + R\dot{C}{=}O$$

or of radical cations

e.g. $Me_n\overset{+\cdot}{P}bEt_{4-n} \rightarrow Me^{\cdot} + Me_{n-1}\overset{+}{P}bEt_{4-n}$ or $Et^{\cdot} + Me_n\overset{+}{P}bEt_{3-n}$ [1].

Very little has been reported about the equivalent bimolecular reactions ($Y^{\cdot} + RXR' \rightarrow YXR' + R^{\cdot}$ or $YXR + R'^{\cdot}$), because S_H2 reactions do not usually occur at saturated carbon centres. The recent recognition that S_H2 reactions do occur at multivalent metallic centres [2], however, has provided a new context within which this phenomenon can be studied, and the following relative leaving abilities are in the literature.

ROO· + t-BuB-i-Bu$_2$ t-Bu/i-Bu ca. 4.5   Ref. 3.

RCH$_2$—CH=CH—Ȯ + n-Bu$_{2.82}$ B-s-Bu$_{0.18}$ s-Bu > n-Bu   Ref. 4.

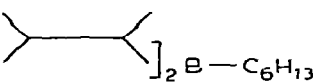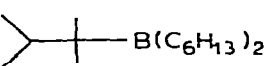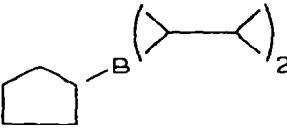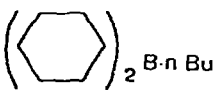(CH$_2$CO)$_2$N· + PhCH$_2$Sn-n-Bu$_3$ PhCH$_2$ ≫ n-Bu   Ref. 5.

A knowledge of the selectivity of displacement is important if the S_H2 reactions of the mixed boranes are to be used in synthetic procedures [6]. Whilst the relative reactivities of two trialkylboranes towards S_H2 dealkylation may be such that $k(R_3B) > k(R_3'B)$, this does not imply that R will be displaced more rapidly than R' in the mixed borane R$_2$BR'; as we show below, the converse often holds.

We have now investigated the reaction of a series of mixed trialkylboranes with n-butanethiol in chlorobenzene at room temperature, initiated by di-t-butyl

$$R_2R'B + BuSH \xrightarrow{k} BuSBR_2 + R'H, \text{ or } BuSBRR' + RH \tag{1}$$

hyponitrite. The hydrocarbons which were formed were analysed by gas—liquid chromatography, and the results are given in Table 1, where the reactivity ratio, r, ex-

TABLE 1

Trialkylborane		n-BuSH (M)	Yield of hydrocarbons[b]	Reactivity ratio[c]
Composition[a]	Conc. (M)		(%)	r
![structure]]$_2$B—C$_6$H$_{13}$	2.0	0.4	90	1.4
![structure] B(C$_6$H$_{13}$)$_2$	2.0	0.4	105	6.9
![structure] B ( )$_2$	2.0	0.4	88	2.7
s-Bu$_2$BC$_6$H$_{13}$	1.4	1.4	97	3.5
( )$_2$B-n Bu	1.2	1.2	105	19.0

[a] C$_6$H$_{13}$ = n-hexyl. [b] Yield with respect to thiol. [c] $r = \dfrac{[s\text{-RH}]}{[p\text{-RH}]}$ or $\dfrac{[t\text{-RH}]}{[p\text{-RH}]}$ or $\dfrac{[cyclo\text{-}C_5H_{10}]}{[iso\text{-}C_5H_{12}]}$, statistically corrected for the number of alkyl groups in the reactant.

presses the statistically corrected relative leaving abilities of the two alkyl groups.
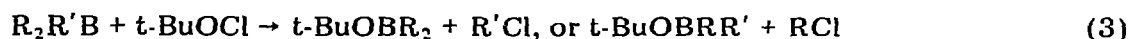
Discussion

The alkylthiyldealkylation reaction (eqn. 2) is exothermic (by ca. 10 kcal

$$BuS^{\cdot} + BR_3 \xrightarrow{k_2} BuSBR_2 + R^{\cdot} \tag{2}$$

mol^{-1}), and for simple trialkylboranes has been shown to be very rapid, with rate constants of about 10^7 l mol^{-1}s^{-1} [7]. Attempts to identify the presence of a 4-coordinate boron intermediate in reactions of this type have been unsuccessful. We assume that the S_H2 reaction proceeds through an elongated trigonal pyramidal transition state which closely resembles the reactants, and the three alkyl groups are only slightly distorted away from their initial coplanar disposition about the boron. The unpaired electron will still be located mainly on the sulphur atom, and only to a small degree on the alkyl group which is to be displaced.

The value of the rate constant (k_2) for the reaction of a tri-n-alkylborane is greater than that for a tri-s-alkylborane (e.g. k(n-Bu$_3$B)/k(s-Bu$_3$B) = 70 at 50°) [7], presumably because of steric compression involving the bulky s-alkyl groups as the thiyl radical approaches the boron to form the transition state. On the other hand, in the reaction of the mixed alkylboranes (see Table 1) n-alkyl groups are displaced less readily than s- or t-alkyl groups, and this order of reactivity is usually ascribed to extra hyperconjugative stabilisation of the s- and t-alkyl radicals. In the present reactions (and in the alkylperoxy- and alkoxy-dealkylation reactions of ref. 3 and 4), the selectivity is low probably because the radical nature of the alkyl group is developed to only a small degree in the transition state.

An attempt was also made to determine the relative ease of displacement of the alkyl groups by t-butoxyl radicals derived from t-butyl hypochlorite [8]:

$$R_2R'B + t\text{-BuOCl} \rightarrow t\text{-BuOBR}_2 + R'Cl, \text{ or } t\text{-BuOBRR'} + RCl \tag{3}$$

The alkylboranes were treated with t-butyl hypochlorite for 2 h at 0° in tri-chlorotrifluoroethane as solvent and a hydrocarbon (cyclopentane or cyclohexane) as to-reactant so that the reactivity of the borane could be determined. Trichloroethylene was added to suppress chain reactions carried out by chlorine atoms. The alkyl chlorides which were formed were analysed by GLC, but the chlorine balance was found to be poor (14-43%), and the system appears to be unsuitable for determining relative reactivities. Presumably, whereas simple alkyl boranes give the alkyl chlorides in good yield [8], highly branched alkyl groups sterically hinder the boron so that attack of the t-butoxyl radical is diverted to the alkyl group.

Experimental

Preparation of materials

Bis(1,2-dimethylpropyl)-n-hexylborane. Diborane, generated from boron

trifluoride etherate (5.7 g, 0.04 mol) in diglyme (15 ml) and sodium borohydride (1.15 g, 0.03 mol) in diglyme (30 ml), was swept by a slow stream of nitrogen into 2-methyl-2-butene (7.0 g) in tetrahydrofuran (50 ml). 1-Hexene (4.2 g, 0.05 mol) was then added at 0', when an exothermic reaction occurred. The tetrahydrofuran and excess of olefin were removed at room temperature under reduced pressure, giving bis(1,2-dimethylpropyl)-n-hexylborane which was carefully distilled at 75-77°/0.1 mm, keeping the temperature of the flask as low as possible to avoid disproportionation of the product: yield 2.1 g (75%). NMR (in CCl₄) CH₃/CH + CH₂: found, 21.0/14.4. Calcd., 21.0/14.0. Oxidation with alkaline hydrogen peroxide gave 1,2-dimethylpropanol and n-hexanol in the ratio of 2/1 (GLC).

(1,1,2-Trimethylpropyl)di-n-hexylborane. The borane was prepared by a similar procedure from sodium borohydride (0.03 mol), boron trifluoride etherate (0.04 mol) 2,3-dimethyl-2-butene (0.05 mol) and 1-hexene (0.1 mol). The product was not distilled. NMR CH₃/CH₂ + CH: found, 18.0/23.5. Calcd., 18.0/21.0.

Bis(1,2-dimethylpropyl)cyclopentylborane. This was prepared in the same way as the corresponding hexyl compound, except that the addition to cyclopentene was allowed to proceed for 4 h, and the product was not distilled to avoid disproportionation. Yield 90%. NMR CH₃/CH + CH₂: found, 18.0/13.7. Calcd., 18.0/13.0.

Di-s-butyl-n-hexylborane. Di-s-butyl-n-butylthioborane (b.p. 95°/1 mm, 4.28 g, 0.02 mol) made in the usual way [6] from tri-s-butylborane, was cooled to −78° and 1-hexene (1.8 g, 0.022 mol) was added followed by THF (10 ml). Lithium aluminium hydride dissolved in THF (1.5 M, 4 ml, 0.005 mol) was added by syringe to the stirred solution, the mixture allowed to warm to room temperature and stirred for 1 h. Solvent and excess 1-hexene were removed at the pump and fractional distillation gave the required borane (3.0 g, 70%) b.p. 58-60°/0.4 mm. GLC of the product at 105° on a 3 ft. silicone gum rubber column showed that it was mainly a single compound, retention time 6 min, but accompanied by a small amount (≈ 5% on peak area) of an unknown, retention time 12 min. Oxidation followed by analysis for hexanol gave a yield of 95% of that expected.

Di(cyclohexyl)-n-butylborane. Cyclohexene (4.1 g, 0.05 mol) was added to diborane dissolved in THF (1.0 M in BH₃, 25 ml) at 0°. A white precipitate of dicyclohexylborane dimer formed, and the reaction was stirred for 1 h. It was allowed to warm to room temperature and 1-butene (1.4 g, 0.025 mol) was added with stirring, after which the precipitate disappeared (this took ca. 5 min) and the reaction was stirred for a further 30 min. The solvent was removed at the pump and the required borane (5.1 g, 87%) came over at 82°/0.5 mm (lit. 106°/3 mm). Oxidation of a sample gave 98% of the required quantity of cyclohexanol (estimated by GLC on a 3 ft. 4% PEGA column, octanol as internal standard). Examination on a 3 ft. silicone gum rubber column at 105° showed the product to be one compound only.

Reaction of organoboranes with butanethiol

The reactions were carried out at 23° in chlorobenzene solution, using di-t-butyl hyponitrite as initiator [7]. After 1 h the hydrocarbons were distilled

at room temperature into a flask cooled in liquid nitrogen, and analysed by GLC. Experiments with synthetic mixtures of the hydrocarbons showed that recovery was complete. The molar ratios of reactants and products are given in the Table 1.

Acknowledgement

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