Preliminary communication

The facile displacement of 2,3-dimethyl-2-butene in the reaction of bulky olefins with thexylcycloalkylboranes. A convenient synthetic route to certain mixed organoboranes
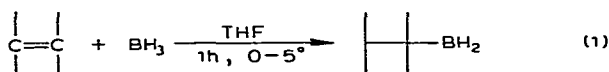
CLINTON F. LANE and HERBERT C. BROWN

Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907 (U.S.A.)
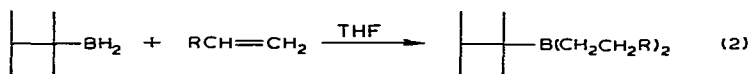
It was previously observed that the highly hindered dialkylborane, diisopino-campheylborane, failed to hydroborate *trans*-olefins and hindered olefins[1]. Instead, α-pinene was displaced, presumably forming the corresponding isopinocampheyldi-alkylboranes. However, at the time there was no interest in such mixed organoboranes, $RR'_2 B$, and no attempt was made to characterize the products.

More recently, the development of the carbonylation reaction[2] and the bromination reaction[3] as routes from organoboranes to carbon structures has provided a major incentive to develop simple synthetic routes to such mixed organoboranes. We now wish to report that the treatment of thexylmonocycloalkylboranes with hindered olefins proceeds with facile displacement of 2,3-dimethyl-2-butene and provides a highly convenient synthesis of certain cycloalkyldialkylboranes.
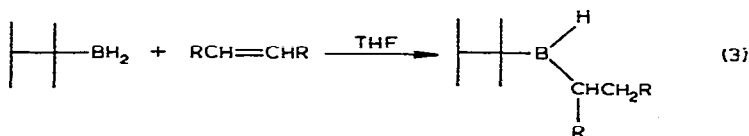
Hydroboration of 2,3-dimethyl-2-butene with borane in THF proceeds cleanly to the monoalkylborane stage[4] (Eqn. 1).

$$\underset{\displaystyle |\quad\,|}{\overset{\displaystyle |\quad\,|}{C=C}} \;+\; BH_3 \xrightarrow[\text{1h, 0–5°}]{\text{THF}} \quad \longmapsto\!\!\!\longmapsto\!\!-BH_2 \qquad (1)$$

Treatment of thexylborane (2,3-dimethyl-2-butylborane) with 1-alkenes provides the corresponding thexyldialkylboranes[4] (Eqn. 2).

$$\longmapsto\!\!\!\longmapsto\!\!-BH_2 \;+\; RCH\!=\!CH_2 \xrightarrow{\text{THF}} \longmapsto\!\!\!\longmapsto\!\!-B(CH_2CH_2R)_2 \qquad (2)$$

However, the corresponding reaction with an internal olefin proceeds rapidly only to the dialkylborane stage (Eqn. 3).

$$\longmapsto\!\!\!\longmapsto\!\!-BH_2 \;+\; RCH\!=\!CHR \xrightarrow{\text{THF}} \longmapsto\!\!\!\longmapsto\!\!-B\!\!\begin{array}{c} {}^H \\ \diagdown \\ \underset{\displaystyle R}{\underset{|}{CHCH_2R}} \end{array} \qquad (3)$$

All attempts to force the reaction to the trialkylborane stage only caused a slow displacement of 2,3-dimethyl-2-butene with the presumed formation of the corresponding tri-sec-alkylborane. However, use of a terminal olefin for the last stage proceeds simply, providing the desired simple "mixed" trialkylboranes, such as thexyl-cycloalkyl-n-alkylborane[5] (Eqn. 4).
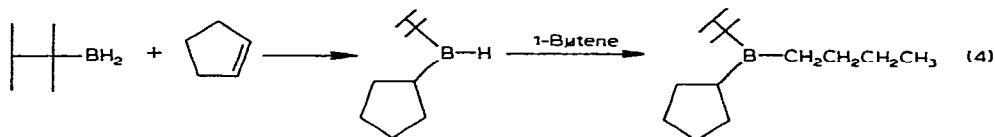

These "mixed" boranes have proved highly valuable for the synthesis of ketones via the reaction with carbon monoxide[5].
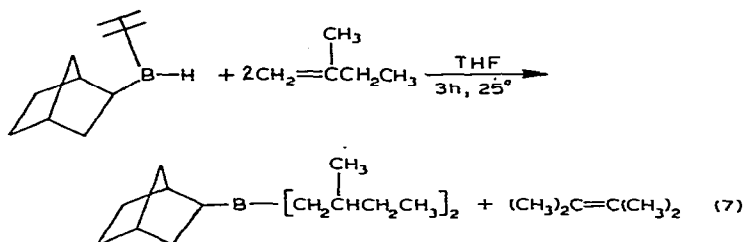
We wished to apply the bromination procedure to such "mixed" boranes. However, in extending the scope of the synthesis to 2-methyl-1-alkenes we observed a marked difference in the behavior of 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene. 2-Methyl-1-butene added in the anticipated manner (Eqn. 5).
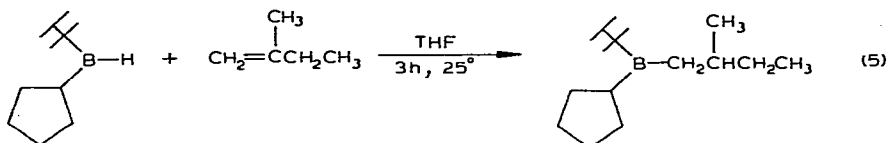
However, the reaction of 2,4,4-trimethyl-1-pentene proceeded almost entirely with displacement (Eqn. 6).
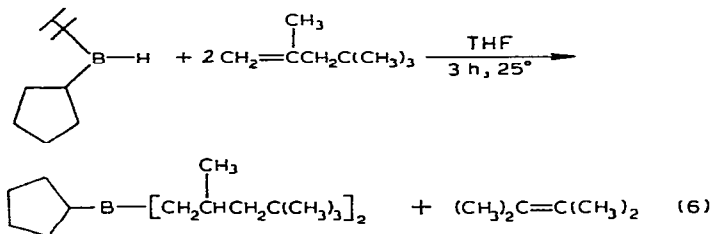
This marked difference in the behavior of 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene was unexpected. We considered that it must be a result of the large difference in the steric requirements of the two olefins. If so, an increase in the steric requirements of the cycloalkyl group should result in the displacement reaction being observed even with 2-methyl-1-butene. Indeed, treatment of thexylcyclohexylborane with 2-methyl-1-butene resulted in 35% displacement. Similarly, treatment of thexyl-exo-norbornylborane with the olefin produced bis(2-methyl-1-butyl)-exo-norbornylborane (Eqn. 7) in a yield of approximately 85%.

$$\text{(thexylnorbornylborane)}\quad B\!-\!H \; + \; 2\,CH_2\!\!=\!\!\underset{CH_3}{\overset{|}{C}}CH_2CH_3 \;\xrightarrow[3h,\;25^\circ]{THF}$$

$$B\!-\!\left[CH_2\underset{CH_3}{\overset{|}{C}}HCH_2CH_3\right]_2 \; + \; (CH_3)_2C\!\!=\!\!C(CH_3)_2 \qquad (7)$$

The experimental results are summarized in Table 1.

TABLE 1

REACTION OF THEXYLCYCLOALKYLBORANES [a] WITH TERMINAL OLEFINS [b]

| Cycloalkyl	Terminal olefin	Products [c]	Yield [d] (mmol)	Displacement (%)
Cyclopentyl	1-Hexene	Thexyl alcohol	9.9	1
		Cyclopentanol	10.0	
		1-Hexanol	10.0	0
Cyclopentyl	2-Methyl-1-butene	Thexyl alcohol	8.2	18 [e]
		Cyclopentanol	9.9	
		2-Methyl-1-butanol	11.0	10
Cyclopentyl	2,4,4-Trimethyl-1-pentene	Thexyl alcohol	2.0	80
		Cyclopentanol	10.0	
		2,4,4-trimethyl-1-pentanol	17.9	79
Cyclohexyl	2-Methyl-1-butene	Thexyl alcohol	6.3	37 [e]
		Cyclohexanol	10.1	
		2-Methyl-1-butanol	13.4	34
exo-Norbornyl	2-Methyl-1-butene	Thexyl alcohol	1.2	88
		Norbornanol	10.0	
		2-Methyl-1-butanol	17.9	79

[a] Prepared by alowing 10 mmol of thexylborane to react with 10 mmol of cycloalkene for 1 h at 0–5°. [b] In all cases the terminal olefin (24 mmol) was allowed to react with the thexylcycloalkyl-borane (10 mmol) for 3 h at 20–25°. [c] Following alkaline hydrogen peroxide oxidation. Structures assigned by comparison with authentic samples. Also present was 2,3-dimethyl-2-butene but the amount was not determined quantitatively. [d] By GLPC analysis. [e] Complete displacement would probably occur if the reaction was allowed to proceed longer or if the reaction temperature was increased.

In order to test our conclusion that the displacement actually proceeds cleanly to the formation of the cycloalkyldialkylboranes, as proposed in Eqns. 6 and 7, the products were subjected to α-bromination in the presence of water[3]. Oxidation of the intermediate gave excellent yields of the 1-alkylcycloalkanols (Eqns. 8, 9), confirming the structures of the mixed boranes.
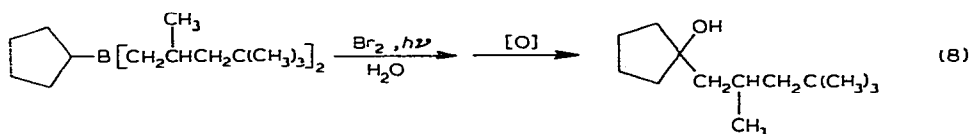
$$88\% \text{ by GLPC}; \ 75\% \text{ isolated} \qquad (8)$$
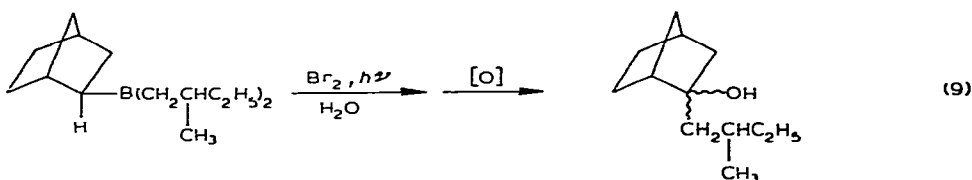
$$78\% \text{ by GLPC}; \ 62\% \text{ isolated} \qquad (9)$$

The following procedure for the preparation of 1-(2,4,4-trimethyl-1-pentyl)-cyclopentanol is representative. A dry 500-ml flask, equipped with a septum inlet, thermometer well, pressure-equalizing dropping funnel, reflux condenser, and magnetic stirrer, was flushed with dry nitrogen and then maintained under a positive nitrogen pressure. The flask was cooled to 0–5° and charged with 200 ml of dry THF and 36 ml of a 2.80 M solution of borane (100 mmol of BH_3) in THF. Thexylborane was then formed by the drop-wise addition of 11.9 ml (100 mmol) of 2,3-dimethyl-2-butene. Stirring was continued for 1 h at 0–5° to ensure completion of the reaction. Cyclo-pentene (8.9 ml, 100 mmol) was then added and allowed to react at 0–5° for 1 h. Then 38 ml (240 mmol) of 2,4,4-trimethyl-1-pentene was added and the reaction was stirred for 3 h at 20–25°. The THF and excess olefins were removed at reduced pressure and replaced with 100 ml of methylene chloride and 50 ml of water. Bromine (6 ml, 117 mmol) was then added at 0–5° and the reaction temperature was maintained at < 25° until the bromine color disappeared (~ 30 min). The reaction was again cooled to 0–5° and sodium hydroxide (70 ml of a 6 N aqueous solution), ethanol (100 ml), and hydrogen peroxide (33 ml of a 30% aqueous solution) were added in the order given while maintaining the temperature below 10°. The reaction mixture was then heated to reflux (~ 42°) and maintained at reflux for 1 h to ensure complete oxidation. After cooling, diethyl ether (100 ml) was added, the aqueous layer was saturated with sodium chloride, and the upper organic layer was separated, washed once with saturated aqueous sodium chloride, and dried over anhydrous potassium carbonate. Vacuum distillation yielded 14.8 g (75%) of 1-(2,4,4-trimethyl-1-pentyl)cyclopentanol, b.p. 63–64° (0.4 mm) n_D^{20} 1.4629.

It is evident that the present development makes available a highly convenient route to certain mixed organoboranes, $RR_2'B$. For many such derivatives this appears to be the simplest synthetic route available. In addition to the importance of this development in synthetic application, a very important result is the implication that the remarkably facile displacement of 2,3-dimethyl-2-butene from thexylborane may be a general characteristic of bulky trialkylboranes, i.e., displacement reactions may be

expected to undergo enormous rate enhancements with increasing steric crowding in the organoborane. Consequently, this unusually facile room temperature displacement reaction may even be capable of accounting for certain previously reported anomalous results; *e.g.*, the apparent rapid isomerization of the product from the hydroboration of 1-methyl-cyclooctene[6], and the formation of t-butyldiisobutylborane in the reaction of t-butyl magnesium halide with boron trifluoride[7].

ACKNOWLEDGEMENT

REFERENCES

1 H.C. Brown, N.R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, 86 (1964) 1071.
2 H.C. Brown, *Accounts Chem. Res.*, 2 (1969) 65, and references cited therein.
3 C.F. Lane and H.C. Brown, *J. Amer. Chem. Soc.*, 93 (1971) 1025.
4 G. Zweifel and H.C. Brown, *J. Amer. Chem. Soc.*, 85 (1963) 2066.
5 H.C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, 89 (1967) 5285
6 H.C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 83 (1961) 2544;
   V.K. Varma, *Ph.D. Thesis, Purdue University*, Lafayette, Indiana, 1967, p. 62.
7 G.F. Hennion, P.A. McCusker and A.J. Rutkowski, *J. Amer. Chem. Soc.*, 80 (1958) 617.