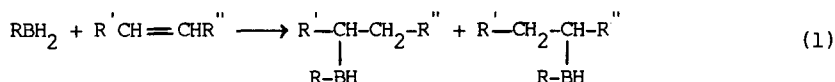A CONVENIENT PREPARATION OF MIXED THEXYLDIALKYLORGANOBORANES

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Abstract: Thexylborane can be treated consecutively with different halomagnesium dialkylcup-
           rates or lithium dialkyl cuprates to afford the corresponding totally mixed thexyl-
           dialkyl organoborane.

There is considerable wealth of synthetic methods[1] in organoboranes and an important need
for the production of mixed organoboranes of the type $R R' R'' B$. Though such organoboranes
may be prepared from the sequential hydroboration of alkenes certain complications may arise.
These include a lack of regiospecificity during the hydroboration of unsymmetrical alkenes gen-
erally affording a mixture of isomers (eq. 1).

$$RBH_2 + R'CH = CHR'' \longrightarrow R'-CH-CH_2-R'' + R'-CH_2-CH-R'' \qquad (1)$$
$$\qquad\qquad\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$\qquad\qquad\qquad\qquad\qquad R-BH\qquad\qquad R-BH$$

Also in several cases the hydroboration proceeds beyond the intermediate organoborane despite
the addition of a calculated quantity of alkene.   Furthermore for the preparation of B-methyl,
B-aryl, B-(1-ethynyl), B-neopentyl and B-benzylorganoboranes hydroboration is not possible and
alternative methods are available.[2]   Previously[3] we reported a novel procedure for the pre-
paration of B-alkyl (or aryl) 9-borabicyclo [3,3,1] nonane using either lithium or halomagnesium
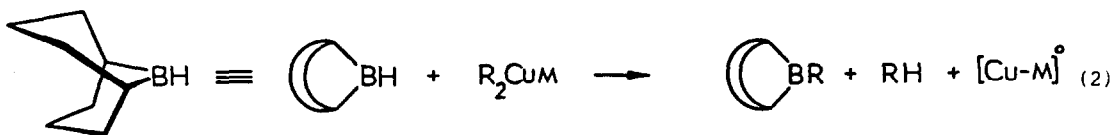
$$M = Li \text{ or } MgBr$$

dialkylcuprates.   This method circumvented the introduction of protic reagents and the problem
of regiospecificity.   We now report the consecutive alkylation of thexylborane with different
halomagnesium dialkylcuprates or lithium dialkylcuprates to afford mixed thexyldialkylorgano-
boranes in high yield.   This procedure not only overcomes the disadvantages outlined above but
allows for a one-pot synthesis of disubstituted thexylorganoboranes (eq.3).
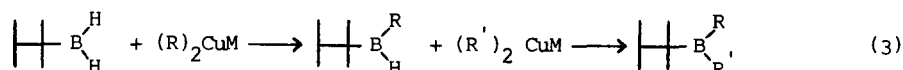
We found that when an ethereal solution of lithium dialkylcuprate was treated with thexylborane
at -20° the reaction mixture immediately darkened.   After a few hours at room temperature a

black precipitate, presumably colloidal copper, resulted while the supernatant remained clear and colourless.

This clear solution was carefully decanted through a double ended needle on to a second dia-lkylcuprate in a second flask at -20° and again the solution rapidly blackened to a heterogeneous mixture. The solution became clear and the appearance of a second black precipitate occurred after several hours at room temperature.[4] Though no advantage could be realised with halomagnesium dialkylcuprates over lithium dialkylcuprates as far as yield was concerned (Table 1) the former reactions were not as clean as the lithium series. Indeed heterogeneous mixtures remained even after 18h at room temperature.

The organoboranes were not isolated but were oxidised to the corresponding alcohol mixtures using alkaline hydrogen peroxide.[5] Continuous extraction of the resulting suspension afforded the alcohols in reasonable yields.[6]

TABLE 1   Reactions of $(R)_2CuM$ and $(R')_2CuM'$ with thexylorganoborane.

ENTRY	R	R'	M	M'	OXIDATION PRODUCTS	(YIELDS%)[7]
1	CH_3	Ph	Li	MgBr	Methanol (68)	Phenol (50)
2	CH_3	nC_3H_7	Li	MgCl	Methanol (72)	Propan.1.ol (62)
3	nC_3H_7	Ph	MgCl	MgBr	Propan.1.ol (60)	Phenol (55)
4	nC_4H_9	Ph	Li	MgBr	Butan.1.ol (68)	Phenol (57)
5	Ph	Ph	MgBr	MgBr	Phenol (68)	

A typical procedure is as follows: A mixture of copper(I) iodide (1,9g; 10.0 m mol) and dry ether (30 mls) was cooled to -25°C and n butyl lithium (1,9M; 10,5 mls; 20,0 m mol) was added slowly. The solution was stirred at this temperature for 30 mins then treated with thexylborane (10,0 m mol)[8] and the whole allowed to reach room temperature (18h). The black colloidal suspension was decanted through a double ended needle on to a stirred ethereal solution of diphenyl bromomagnesium cuprate[9] in a flask at 0°C. The solution immediately blackened and the whole was stirred at room temperature (20°C; 18h). The solvents were stripped under reduced pressure and aqueous sodiumhydroxide (5M. 20 mls) and hydrogen peroxide (30%, 20 mls) added simultaneously at 0°C; the temperature was then raised to 50°C for 2h. The brown suspension was continuously extracted into ether and g.l.c. estimation of the extract revealed the presence of n-butyl-alcohol (68%) and 2,3-dimethyl but. 2.ol (63%)[6]. Acidification of aqueous layer and re-extraction with ether indicated phenol (57%).

In order to establish the synthetic value of this preparation as well as to prove unequivoc-ally the formation of the totally mixed organoborane (RR'B) and that no dismutation of intermedi-ate dialkylboranes had occurred our product (prior to oxidation) was subjected to the cyanoborate process.[10]

It was anticipated that due to the low migratory power of the thexyl group this reaction should produce the corresponding ketone (eq. 4). Our results are shown (Table 2).

Initial problems were realised with the formation of the cyanoborate (1). All magnesium, copper and lithium salts had to be removed before (1) could be prepared. Filtering the eth-ereal solution of the totally mixed organoborane through celite or anhydrous sodium sulphate

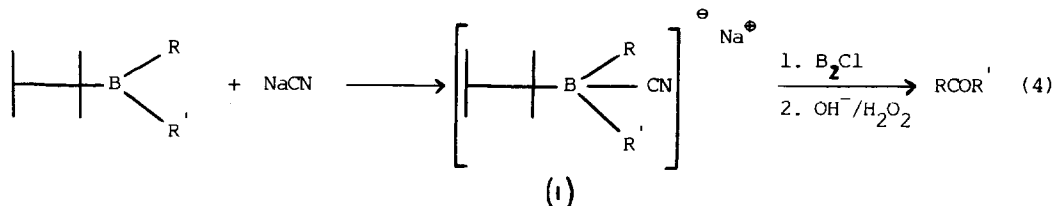under nitrogen failed to remove these salts completely.   Instead

$$(4)$$

TABLE 2: Preparation of ketones from the cyanoborate process on thexylorganoboranes

ENTRY	R	R'	RCOR'	YIELD[11]
1	CH_3	Ph	CH_3COPh	8
2	CH_3	nC_3H_7	$CH_3COC_3H_7$	64
3	Ph	nC_3H_7	$PhCOC_3H_7$	11
4	Ph	Ph	$PhCOPh$	0
5	CH_3	nC_4H_9	$CH_3COC_4H_9$	55

the solution was evaporated, dissolved in dry hexane and then passed through a short column of silica gel.   The hexane solution was then concentrated, the residue dissolved in dry tetrahydrofuran and the product treated successively with NaCN, benzoyl chloride and basic hydrogen peroxide.

It appears from the results (Table 2) that only aliphatic ketones can be prepared in this way.   This may be explained by first considering a possible mechanism.   We believe that there is first an inital oxidative addition of the organocuprate to the electron deficient boron atom of the thexylborane forming a copper III intermediate[12].   This copper species collapses through reductive elimination, producing a B-alkylsubstituted thexylborane hydride and the corresponding alkyl copper (Scheme 1)

SCHEME 1
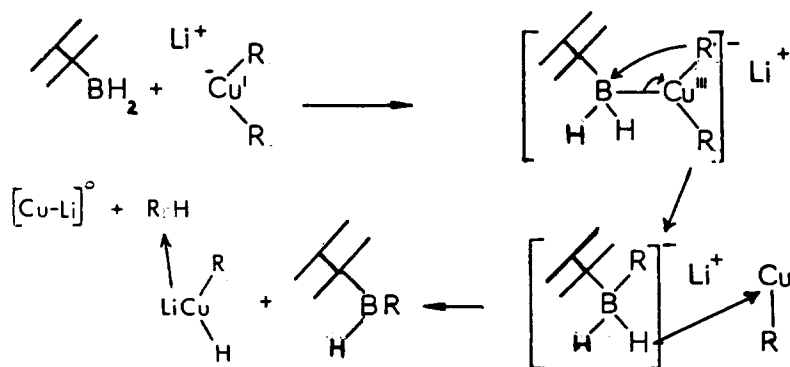
Borohydrides of this nature are well known as reducing agents and a powerful source of hydride ions[13] and it is believed that the H⁻ reduces the alkyl copper to produce an alkylhydrido-cuprate. This thermally decomposes to yield an alkane and a black copper-lithium amalgam. The fact that a second black suspension occurred after the addition of the second dialkylcuprate must indicate a second reduction via hydride and the formation of the totally mixed thexylorgano-borane.

When R and/or R' is aliphatic there appears no difficulty in the hydride effecting a reduction of the alkyl copper. However with the cases where phenyl copper is produced very little of the corresponding aromatic ketone is formed. Instead a considerable amount of biphenyl is produced. Furthermore there was evidence for this biproduct being present before the reaction mixture was subjected to the cyanoborate process. We argue that it must have formed by a thermal decomposition of phenyl copper - a process far more rapid than the nucleophilic attack of the hydride (Scheme 1)[14]. The decomposition of RCu (R=alkyl) at -40°C is slow and does not interfere with the overall reaction. If arylcopper species do thermally collapse before hydride reduction then the lithium thexylhydridoorganoborate $(HEX^t. Ph. RBH)^- Li^+$ would be left in solution. The cyanoborate reaction on these would fail and no corresponding ketone can be produced. Oxidation of such organoborate species would, however, produce the required alcohols satisfying the results obtained in Table[15].

References and Notes:

1. A. Pelter and K. Smith, 'Organic Boron Compounds' in Comprehensive Organic Chemistry, Pergamon Press, 1979 3 p 689.

2. (a) J.L. Hubbard and G.W. Kramer, J. Organomet. Chem., 156, 81, (1978);
   (b) J.A. Sinclair, G.A. Molander and H.C. Brown, J. Amer. Chem. Soc.. 99, 954, (1977);
   (c) H.C. Brown, D. Basavaiah and N.G. Bhat, Organometallics, 2, 1468, (1983).

3. (a) C.G. Whiteley, J. Chem. Soc. Chem. Commun.. 5, (1981); and
   (b) Idem, S. Afr. J. Chem., 35, 9, (1982).

4. The time for the appearance of the black precipitate was dependent on whether lithium or halomagnesium cuprates were used and on the alkyl group transferred.

5. H.C. Brown, 'Boranes in Organic Chemistry', Cornell Univ. Press, Ithaca, New York, (1973).

6. Alcohols were analysed by gas chromatography (flame ionisation) on a Perkin Elmer 900 using a 6' x ⅛" 15% HIEFF 4BP on chromosorb Q.

7. 2,3-dimethylbut.2.ol (thexylalcohol) was produced.

8. Prepared at -10°C from $BH_3(CH_3)_2S$ and 2,3-dimethylbutene. cf Ref. 5 pg. 31.

9. Prepared from the addition of phenyl magnesium bromide (6 mls; 3,4M; 20 m mol) to copper(I) iodide (1,9g; 10.0 m mol) in ether (30 mls) at 0°C.

10. A Pelter, K. Smith, M.G. Hutchings and K. Rowe, J. Chem. Soc., Perkins I, 129, (1975).

11. - Based on GC analysis.

12. For studies on the mechanism for the alkylation of electrophilic species by organo-cuprates see : H.O. House, Acc. Chem. Res., 9, 59, (1976)

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