Trialkylcyanoborates as Intermediates in a New Conversion of Trialkylboranes into Trialkylcarbinols

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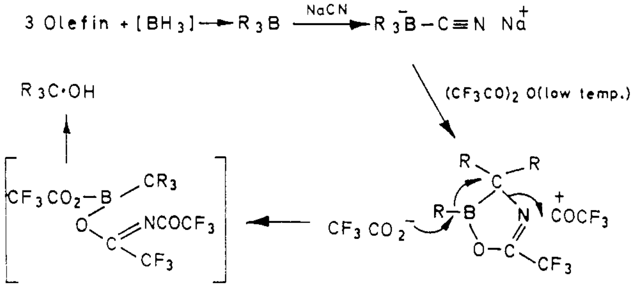
Summary Warming trialkylcyanoborates with an excess of trifluoroacetic anhydride results in three migrations from boron to carbon to give, on oxidation, high yields of trialkylcarbinols.

THE reaction of trialkylboranes with carbon monoxide to yield trialkylcarbinols *i.e.* $R_3B \rightarrow R_3COH$ has been studied by Hillman[1] and particularly by Brown and his colleagues[2] who have vividly summarised the unique potentialities of reactions involving three migrations from boron to carbon.[3] However, fairly drastic conditions are required and very recently the Purdue school has shown that the potassium triethylcarboxide-induced reaction of tri-n-butylborane with chlorodifluoromethane followed by oxidation gives a high yield (g.l.p.c.) of tri-n-butylmethanol. Chloroform was also used and gave a lower but very acceptable yield.[4]



We have previously used sodium cyanide as a one-carbon source and trialkylcyanoborates as intermediates in a high-yield synthesis of ketones,[5] and an extension of this work leads to a new, highly convenient method for trialkylcarbinol preparation, which proceeds in neutral, homogeneous conditions. This merely involves the addition at low temperatures of an excess (>2·0 mol equiv.) of trifluoroacetic anhydride (TFAA) to the trialkylcyanoborate solution, followed by warming at 45° for several hours, and a standard oxidation. The yields given in the Table represent isolated purified products and are calculated on the olefin added at the beginning of the process.

% Yields of carbinols from olefins

Olefin	Product	Yield %
But-1-ene	$(n\text{-Butyl})_3C\cdot OH$	73
Hept-1-ene	$(n\text{-Heptyl})_3C\cdot OH$	79
Oct-1-ene	$(n\text{-Octyl})_3C\cdot OH$	75

The mechanism of the third migration is unknown, but addition of various salts (*e g.* NaI, NaCN) speeds up the reaction. It may be that the overall process proceeds as shown. This would explain the salt effects and points the way ahead for the design of mild reaction conditions suitable for hindered olefins.

A typical procedure is as follows. Octene (2·89 g, 25·8 mmoles) in THF (5 ml) was hydroborated with B_2H_6 (4·3 mmoles) in THF (6·15 ml) in the usual fashion and washed on to a stirred suspension of finely powdered NaCN (11·2 mmoles) in THF. The mixture was stirred for 1 h at 22°, cooled to −78° and TFAA (12·9 mmoles) added. The reaction vessel was allowed to warm to 22° and after 1 h more TFAA (21·5 mmoles) was added and the solution warmed on an oil bath at 45° for 12 h. The excess of anhydride was destroyed with NaOH and oxidation was effected using NaOH (3N, 12 ml) and H_2O_2 (50%, 8 ml) at 25° for 3 h, then at 50° for 15 min. The product was taken into pentane and the crude neutral fraction purified by chromatography on a dry silica gel column. Elution with dichloromethane yielded trioctylmethanol (2·37 g, 75%).

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[1] M. E. D. Hillman, *J. Amer. Chem. Soc.*, 1962, **84**, 4715; 1963, **85**, 982; 1963, **85**, 1626.
[2] H. C. Brown and M. W. Rathke, *J. Amer. Chem. Soc.*, 1967, **89**, 2737.
[3] H. C. Brown, *Accounts Chem. Res.*, 1969, **2**, 65.
[4] H. C. Brown, B. A. Carlson, and R. H. Prager, *J. Amer. Chem. Soc.*, 1971, **93**, 2070.
[5] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1970, 1528.

1,1,2-Trimethylpropyldialkylcyanoborates as Intermediates for the Synthesis of Symmetrical, Unsymmetrical, Functionalised, and Cyclic Ketones

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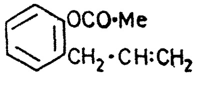
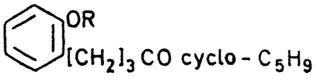
Summary The insertion reaction of cyanide into thexyldialkylcyanoborates, using acylation at low temperatures followed by oxidation, provides the mildest known method for the high-yield production of ketones from olefins *via* organoboranes.

WE have recently reported a new one-carbon insertion reaction into trialkylboranes which uses sodium cyanide as a convenient one-carbon source and trialkylcyanoborates as stable intermediates. Acylation of the cyanoborates followed by oxidation gives ketones in high yields, the migration processes taking place in mild, neutral conditions.[1]

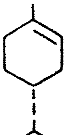
However, although the yields on the overall reaction are high, the practical difficulty remains that one alkyl group is effectively lost. To circumvent this general difficulty, Brown introduced thexylborane (1,1,2-trimethylpropyl



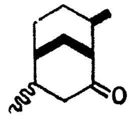
(I)



(II) R = Ac
(III) R = H

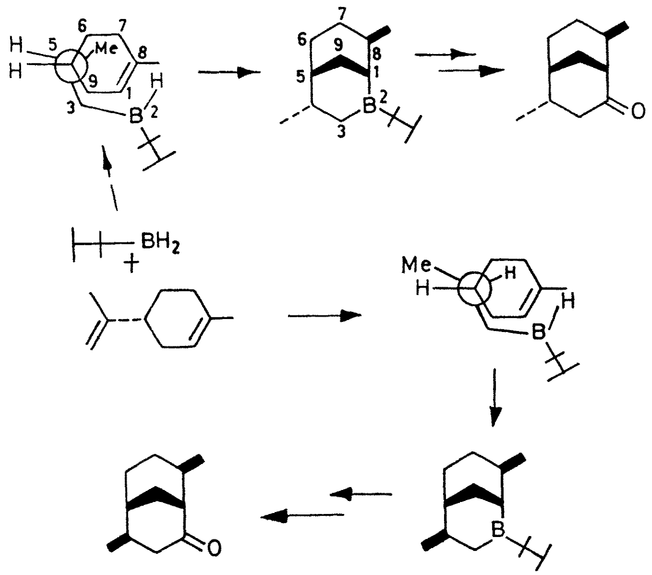


(IV)



(V)

borane) as a substitute for borane itself.[2,3] The bulky organic moeity shows little tendency to migrate and can finally be discarded. However, in the ketone synthesis using carbon monoxide the thexyldialkylboranes react sluggishly and pressures of carbon monoxide of 1000 lb/in^2 at 50° for several hours have normally to be used.[4] Our hope was that the homogeneous conditions of the trialkylcyanoborate reaction (and hence the high effective concentrations of reactants) would remove this barrier to the utilisation of the thexylboranes.



In practice thexyldialkylcyanoborates behaved no differently from the simple salts, the standard migration conditions being addition of trifluoroacetic anhydride (TFAA) to a solution of the salt at −78°. The reaction mixture is allowed to warm to room temperature over 15—30 min, after which time reaction is complete. The whole process, including the oxidation which follows, is carried out in one flask, no special techniques being required, and for mildness and convenience presents a contrast to the carbon monoxide analogue. In no case was there any evidence for the migration of the thexyl group, and by suitable choice of order of addition of the olefins unsymmetrical ketones are readily available. In such cases no dismutation occurred as g.l.c. analysis of the crude products showed only traces of symmetrical ketones. The Table gives yields of representative reactions, the yields being calculated on the olefins added and the isolated purified product, according to:

$$\begin{tikzcd}
\mathrm{Me_2C{:}CMe_2} + [\mathrm{BH_3}] \arrow[r] & \text{Thexyl BH}_2 \arrow[r, "\text{1. Olefin A}", "\text{2. Olefin B}"'] \arrow[dr, dashed] & \text{Thexyl B R}^{\mathrm{A}}\,\mathrm{R}^{\mathrm{B}} \arrow[d, "\text{1. NaCN} \quad \text{2. }(\mathrm{CF_3CO})_2\mathrm{O} \quad \text{3. Oxidation}"] \\
 & & \mathrm{R}^{\mathrm{A}}\,\mathrm{CO}\,\mathrm{R}^{\mathrm{B}}
\end{tikzcd}$$

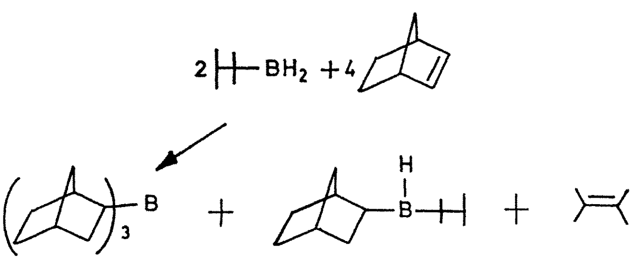
It can be seen that the conditions are sufficiently mild so that even an iodo-ketone may be directly formed. Choice of a peracid as oxidant[5] allows the acetylated ketone to be isolated whereas use of buffered peroxide can cause complete hydrolysis. The final example emphasises the unique possibilities for high yield ring formation. In the case of (+)-limonene the product is a mixture (1 : 1) of two ketones, readily separated by preparative g.l.c. Their formation is due to *cis*-attack by thexylborane on either side of the vinyl group with respect to the ring; the other reactions are necessarily stereospecific.†

% Yields of ketones from olefins and thexylborane

Olefin A	Olefin B	Product	Yield %
Cyclopentene	Cyclopentene	Dicyclopentyl ketone	80
Oct-1-ene	Oct-1-ene	Di-n-octyl ketone	78[a]
Cyclopentene	Oct-1-ene	Cyclopentyl octyl ketone	83[a]
Cyclopentene	8-Chloro-oct-1-ene	8-Chloro-octyl cyclopentyl ketone	76[a]
Cyclopentene	8-Iodo-oct-1-ene	8-Iodo-octyl cyclopentyl ketone	76
Cyclopentene	(I)	(II)	80[b]
Cyclopentene	(I)	(III)	80[c]
(IV)		(V)	95[d]

[a] We thank Mr. G. Cowley and Mr. K. Murty who carried out these experiments as part of undergraduate research projects. [b] Oxidation using *m*-chloroperbenzoic acid at 0°/30 min. [c] Oxidation using $NaHCO_3/H_2O_2$ for 1 h at 20°, then 1 h at 45°. [d] Infusion pump used for hydroboration.

When norbornene alone was used as the olefin the reaction gave only 35% yield of di-*exo*-norbornyl ketone[1] due, we believe, to the well-documented displacement of a thexyl group[3], *i.e.*,



The cyanide insertion reaction into thexyldialkylboranes can now be used synthetically as a gentle process for the stereospecific† production of ketones in high yield. The overall process consists of joining two olefins together directly with a carbonyl group to yield a ketone. In this context the thexylboron portion of the thexyldialkylborane intermediate is equivalent to a carbonyl group.

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† That the migrations proceed as expected with retention will be shown separately.

[1] A. Pelter, M. G. Hutchings and K. Smith, *Chem. Comm.*, **1970**, **1529**.
[2] H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, 1962, **84**, 1478.
[3] G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, 1963, **85**, 2066.
[4] H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, 1967, **89**, 5285.
[5] J. R. Johnson and M. G. van Camden, *J. Amer. Chem. Soc.*, 1938, **60**, **121**.