The Chemistry of Organoborates. Part I. New, High Yield Ketone Syntheses by Reaction of Trialkylcyanoborates with Acylating Agents or *N*-Phenylbenzimidoyl Chloride [1-3]

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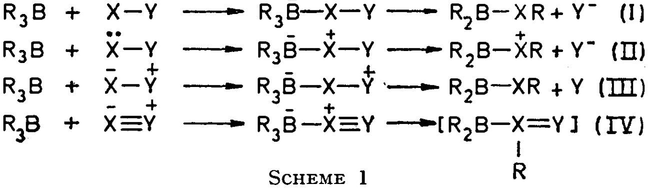
From general considerations of the chemistry of organoborates it is clear that the reactions of organocyanoborates with electrophilic reagents have outstanding synthetic potential. The acylation reactions have been studied and it is shown that trialkylcyanoborates react with trifluoroacetic anhydride at low temperatures, with *N*-phenylbenzimidoyl chloride at room temperature, and with benzoyl chloride on warming to give cyclic intermediates which on oxidation give ketones in excellent yields. In contrast to the carbonylation of organoboranes this one-pot synthesis can be applied to 1,1,2-trimethylpropyl (thexyl) derivatives without the need for special conditions. Examples of the synthesis of fused and bridged polycyclic ketones and of functionalised and unsymmetrical ketones indicate the scope of the reaction.

1,2-MIGRATIONS of an organic group from boron to an acceptor atom are most important in organic synthesis [4] as well as being of fundamental interest. For ionic † reactions migration is normally initiated by nucleophilic attack of an electron-rich species upon the electron-deficient borane, the charge-separated complex so formed stabilising itself by intramolecular migration.[5,6] We have termed the overall process the NACM reaction (nucleophilic attack, carbanionotropic migration) and it is the presumed basis for a large number of reactions of organoboranes. However, mechanistic studies are needed to confirm the generalisations made. Reactions such as those of alkaline hydrogen peroxide [7] [Scheme 1, equation (I)] or chloramine [8] [Scheme 1, equation (II)] with organoboranes may reasonably be represented as 1,2-NACM reactions. Simple ylides such as trimethylamine oxide,[9] Wittig reagents,[10] sulphonium ylides,[6] and diazocarbonyl compounds [11] behave similarly, though in these cases migration is accompanied by expulsion of a neutral molecule [Scheme 1, equation (III)] rather than an anion. Multiply bonded species with ylidic character such as carbon monoxide [4,12] and isonitriles [13] also fit within the scheme



$$\begin{array}{llll}
R_3B + \bar{X}{-}Y & \longrightarrow R_3\bar{B}{-}X{-}Y & \longrightarrow R_2B{-}XR + Y^- & \text{(I)} \\
R_3B + \ddot{X}{-}Y & \longrightarrow R_3\bar{B}{-}\overset{+}{X}{-}Y & \longrightarrow R_2B{-}\overset{+}{X}R + Y^- & \text{(II)} \\
R_3B + \overset{-}{X}{-}\overset{+}{Y} & \longrightarrow R_3\bar{B}{-}X{-}\overset{+}{Y} & \longrightarrow R_2B{-}XR + Y & \text{(III)} \\
R_3B + \overset{-}{X}{\equiv}\overset{+}{Y} & \longrightarrow R_3\bar{B}{-}\overset{+}{X}{\equiv}Y & \longrightarrow [R_2B{-}\underset{\displaystyle R}{\underset{|}{X}}{=}Y] & \text{(IV)}
\end{array}$$

SCHEME 1

but migration is not accompanied by expulsion of either a neutral molecule or an ion [Scheme 1, equation (IV)]. The latter two reactions (III) and (IV) are of particular interest since new carbon–carbon bonds are produced, and extensive investigations of the carbonylation process have served to introduce new and powerful reactions into synthetic organic chemistry.[4]

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† The term ' ionic ' is used to cover all those reactions which are not free radical in nature.

[1] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1970, 1529.

[2] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1971, 1048.

[3] A. Pelter, *Intra-science Chem. Report*, 1973, **7** (1), 133.

[4] H. C. Brown, ' Boranes in Organic Chemistry,' Cornell University Press, Ithaca, 1972.

[5] K. Smith, Ph.D. Thesis, University of Manchester, 1971.

[6] J. J. Tufariello and L. T. C. Lee, *J. Amer. Chem. Soc.*, 1966, **88**, 4757.

[7] H. C. Brown, C. Snyder, B. C. Subba Rao, and G. Zweifel, paper in preparation referred to in ref. 4, p. 322; *cf.* H. C. Brown and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1956, **78**, 5694; *J. Org. Chem.*, 1957, **22**, 1136.

[8] H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *J. Amer. Chem. Soc.*, 1964, **86**, 3565.

[9] R. Köster and Y. Morita, *Angew. Chem. Internat. Edn.*, 1966, **5**, 580; *Annalen*, 1967, **704**, 70.

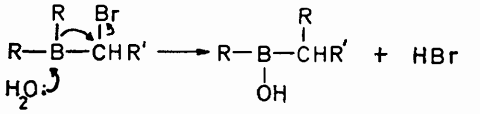
[10] R. Köster and B. Rickborn, *J. Amer. Chem. Soc.*, 1967, **89**, 2782.

[11] J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, 1968, **90**, 5936.

[12] M. E. D. Hillman, *J. Amer. Chem. Soc.*, 1962, **84**, 4715; 1963, **85**, 982, 1626.

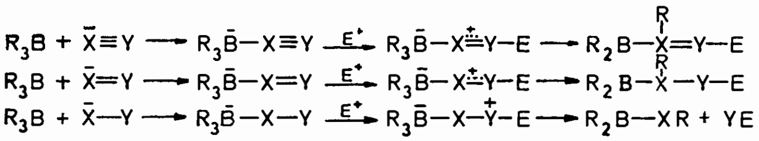
[13] G. Hesse and H. Witte, *Angew. Chem. Internat. Edn.*, 1963, **2**, 617.

In reactions (I)—(IV) (Scheme 1) the acceptor atom for the migrating group is part of the nucleophilic reagent. However, other conditions for migration exist as illustrated in reaction (V)[14] where the acceptor atom forms part of the organoborane and migration is induced by attack of a nucleophile (water) on the boron atom.


(V)

Consideration of possible methods for producing migration made it clear that a particularly useful approach might be the attack of a suitable electrophile on a stable borate salt, *i.e.* the NACM reaction would be broken down into two discrete and controllable steps (Scheme 2).

Attack on the borates need not lead to migration and other possibilities are shown in Scheme 3: examples of such reactions have been encountered in our studies. However, since the desired reactions (Scheme 2) would open up routes of great synthetic potential and theoretical interest, a systematic study was initiated. It was also borne in mind that a great variety of organoboranes [*i.e.* Ar_3B, $(RCH{=}CH)_3B$, R_2BX, $R^1R^2R^3B$, *etc.*] were readily available and each series had its own specific possibilities.

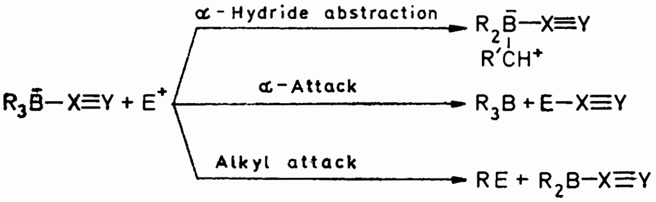


$$R_3B + \bar{X}{\equiv}Y \longrightarrow R_3\bar{B}{-}X{\equiv}Y \xrightarrow{E^+} R_3\bar{B}{-}X\overset{+}{=}Y{-}E \longrightarrow R_2B{-}\overset{R}{X}{=}Y{-}E \qquad (VI)$$

$$R_3B + \bar{X}{=}Y \longrightarrow R_3\bar{B}{-}X{=}Y \xrightarrow{E^+} R_3\bar{B}{-}X\overset{+}{-}Y{-}E \longrightarrow R_2B{-}\overset{R}{X}{-}Y{-}E \qquad (VII)$$

$$R_3B + \bar{X}{-}Y \longrightarrow R_3\bar{B}{-}X{-}Y \xrightarrow{E^+} R_3\bar{B}{-}X{-}\overset{+}{Y}{-}E \longrightarrow R_2B{-}XR + YE \qquad (VIII)$$

SCHEME 2



SCHEME 3

We first investigated reaction (VI) and this paper reports the results of some studies in which X≡Y is C≡N and $E^{(+)}$ is $RCO^{(+)}$ or its equivalent. The salts involved are cyanoborates and the various rearrangements proceeding from them are known collectively as the cyanoborate process.

RESULTS AND DISCUSSION

Acylation of Trialkylcyanoborate Salts.—We studied trialkylcyanoborate salts since the cyanide anion might provide a useful alternative to carbon monoxide as a one-carbon insertion unit into organoboranes. The advantages of the cyanide anion are listed below. (i) A preliminary study showed that the required salts are readily made by mixing a trialkylborane and an alkali metal cyanide in an ether solvent at room temperature. The reaction may be followed visually by the dissolution of the metal cyanide or by the appearance of a band at *ca.* 2125 cm^{-1} in the i.r. spectrum of the solution. The solutions are stable in these conditions and indeed even aqueous solutions can be prepared.[15] (ii) The solubility of the salts in organic solvents means that, in contrast to the carbonylation procedures, problems arising from the heterogeneity of the reaction mixtures are absent. (iii) A wide range of electrophilic reagents to induce migration is available (*i.e.* H^+, R^+, RCO^+, Hal^+, *etc.*) and a suitable choice might allow further reactions of the primary intermediate such that one, two, or three migrations might be achieved. (iv) The nitrogen of the cyanide anion could be retained throughout and lead to compounds unattainable by carbonylation.

Reaction with acetyl chloride. Sodium cyanotri-n-octylborate reacted readily at room temperature with acetyl chloride but oxidation of the intermediate always gave di-n-octyl ketone in less than 50% yield. This was attributed to the abstraction of a proton from acetyl chloride by a basic intermediate leading in turn to the abstraction of cyanide anion from unchanged cyanotri-n-octylborate. A similar proposal was made by Hesse[16] whose study of the reaction of cyanotriethylborate gave essentially the same results. The reaction was promising, as the desired β-attack [Scheme 2, equation (VI)] had occurred and therefore attention was focused on acylating reagents lacking an α-proton. It is of interest that acetic anhydride gave only poor yields of migrated products even under relatively harsh conditions.

Reactions using benzoyl chloride. Trialkylcyanoborates reacted on warming with benzoyl chloride in ether solvents. Oxidation of the reaction products with alkaline hydrogen peroxide gave dialkyl ketone and alkanol, which were separated by dry column chromatography on silica. The yields of isolated ketone were synthetically significant (65—87%) (Table 1).

The pathway proposed is illustrated in Scheme 4 (R′ = Ph) and up to the production of intermediate (1) it is a simple example of reaction (VI). However, (1) could not be isolated nor could oxidation products derived from it be characterised. Instead intra-

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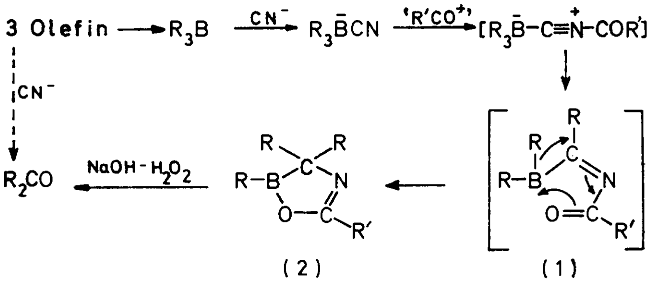
[14] C. F. Lane and H. C. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 1025.

[15] H. Witte, E. Brehm, and G. Hesse, *Z. Naturforsch.*, 1967, **22*b***, 1083.

[16] E. Brehm, A. Haag, G. Hesse, and H. Witte, *Annalen*, 1970, **737**, 70.

molecular nucleophilic attack on the boron atom occurs, accompanied by further migration to give (2). This Scheme is in line with one proposed for the reaction of pivaloyl chloride with trialkylcyanoborates.[16]



Scheme 4

Table 1

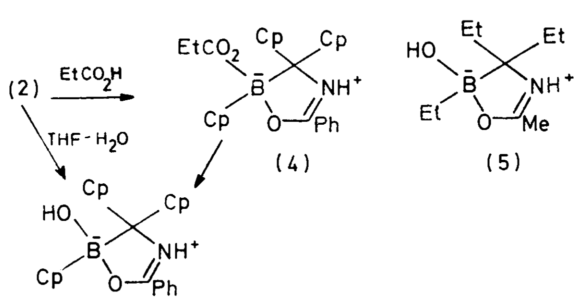
Yield (%) * of ketones from olefins *via* the cyanoborate process

R in R_3B	Electrophilic reagent PhCO·Cl	 $(CF_3CO)_2O$
n-Octyl	82	95
n-Butyl	74	94
Cyclopentyl	87	84
Cyclohexyl	65	100
Norbornyl	85	99

* Yields in this and all following Tables of preparative reactions are based on isolated, purified product.

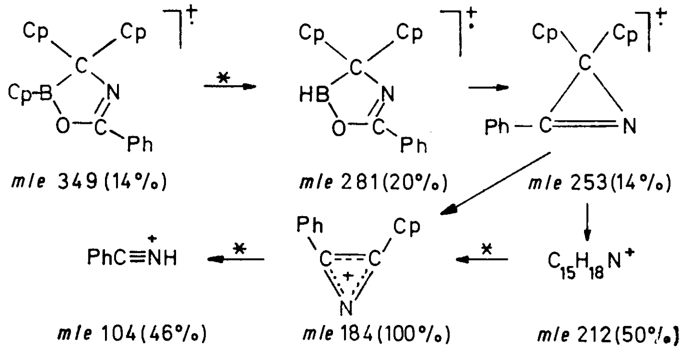
The reaction of cyanotricyclopentylborate with benzoyl chloride was investigated further. Isolation of the intermediate (2; R = Cp, R' = Ph) (Cp = cyclopentyl) by removal of tetrahydrofuran (THF) gave a viscous, air-labile oil which gave variable analyses. There was an intense band at 1650 cm^{-1} in the i.r. spectrum but no band due to C≡N stretching. The n.m.r. spectrum had signals at τ 1·98 (2H, m), 2·66 (3H, m), 7·73br (2H, m), and 8·0—9·3 (intense). The signals were in accord with structure (2) and the mass spectrum was identical with that of the hydrate (3).

The hydrate was produced by addition of water to a solution of (2; R = Cp, R' = Ph) in THF, precipitation by addition of petroleum, and recrystallisation from methanol–water. Addition of propionic acid gave a similar adduct (4) which was converted into (3) on recrystallisation from methanol–water. The i.r. spectrum of (3) shows bands at 3210—3050 [absent in (2)], 1630 and 1610 (doublet), 1590 (intense), and 1515 cm^{-1}. This spectrum is analogous to that reported for (5).[16] The ^1H n.m.r. spectrum of (3) is similar to that of (2) but contains an additional band at τ 7·33 (2H) which exchanges with D_2O.



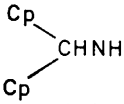
Cp = cyclopentyl throughout

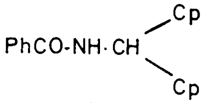
The mass spectra of (2) and (3) were identical, indicating that no skeletal change had occurred in the transformation of (2) into (3), and that (3) was converted back into (2) thermally before volatilisation in the mass spectrometer inlet. The main breakdown patterns are indicated in Scheme 5, each peak having been accurately mass measured. This Scheme differs significantly from that reported for (5) but is in good agreement with structure (2).



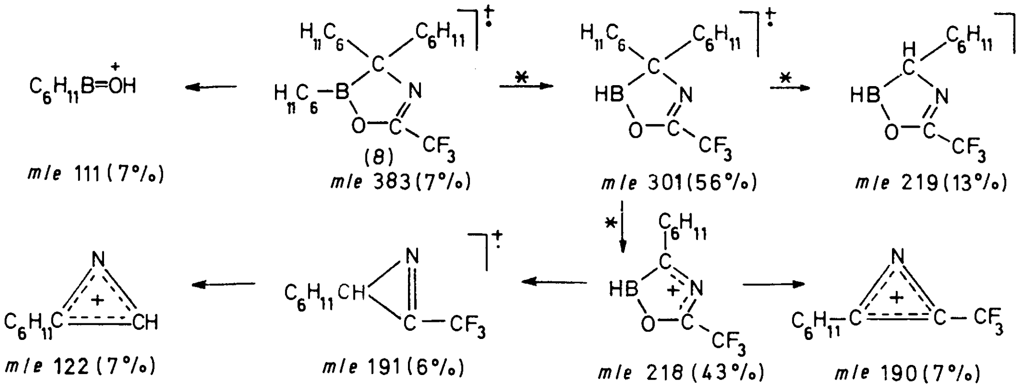
Scheme 5 Asterisks indicate the observation of a metastable peak for the transformation. No attempt has been made to determine the actual structures of the ions nor the specific sites of fragment losses

The hydrate (3) is insoluble in light petroleum and carbon tetrachloride but quite soluble in methanol, ether, and acetone. It is very stable to both acids and alkalies but prolonged hydrolysis with concentrated alkali at 100° gave (dicyclopentylmethyl)amine (6) and *N*-dicyclopentylmethylbenzamide (7) in an overall yield of 71%. This reaction, which constitutes a novel amide and amine synthesis, was the first to fulfil our hopes that the nitrogen atom of the cyanide anion could be retained in useful organic products. The amide (7) is of particular interest as it contains all the separate carbon units of the reaction (olefin, cyanide, and benzoyl group) joined together in a fashion consistent with the structure proposed for intermediate (2).


(6)

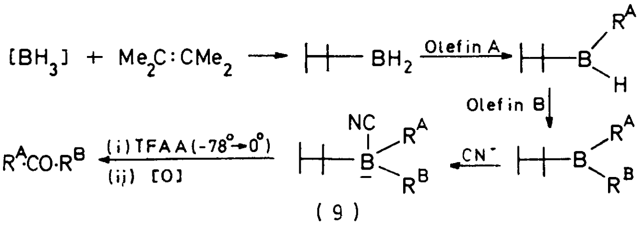

(7)

Reactions with trifluoroacetic anhydride.—Trifluoroacetic anhydride (TFAA) was a most potent and efficient migration agent. Reaction was effected by adding the reagent to a solution of the cyanoborate held at −78° and allowing the mixture to warm to room temperature. When reactant proportions and solvent were correctly controlled (see below), subsequent oxidation gave high yields of ketone (Table 1). The whole process is carried out in one flask and is a simple and mild new method for the production of ketones. The tricyclohexyl intermediate (8) (Scheme 6) was isolated by syringing the solution from precipitated potassium trifluoroacetate. The THF was removed and an i.r. and mass spectral analysis made. The i.r. spectrum (CCl_4 solution) showed the expected bands at 1680 and 1640 cm^{-1} plus an unusual one at 1740 cm^{-1}, possibly showing the large influence of the CF_3 group on the $>C=N-$ unit. The mass spectral breakdown is shown in Scheme 6, all peaks having been accurately mass measured to establish the elemental composition. Reaction with water dissolved in THF gave the hydrate which precipitated from aqueous methanol as crystals, m.p. 144—145°.*



SCHEME 6 Base peak is C_6H_{11} (100%) and other hydrocarbon peaks are C_5H_7 (29%) and C_7H_{11} (16%)

Use of dialkylcyanothexylborates for ketone synthesis.—It was most important to study the reactions of dialkylcyanothexylborates[12] since symmetrical or unsymmetrical ketones might be produced from these compounds without the loss of potentially valuable alkyl groups (Scheme 7).



SCHEME 7

In contrast to the conditions for carbonylation of dialkylthexylboranes, the derivatives (9) proved as amenable to the same mild conditions as the simple trialkylcyanoborates and in all cases (Table 2) the thexyl groups migrated more slowly than any other group. The use of a thexyl group necessarily involves some lowering of yield[17] but oxidation still gave ketones in very acceptable overall yields based on olefins A and B in Scheme 7. Labile substituents such as iodide and acetoxyphenyl may be carried through the process successfully.

Compound (11b) was produced when the oxidation was carried out by using *m*-chloroperbenzoic acid at 0°,[18] whilst (11a) was the product from the use of mildly alkaline hydrogen peroxide.[4] From (+)-limonene the two ketones (13a and b) result, this being an extremely effective method for producing a bridged ring system. The two isomers (13a and b) are produced owing to the lack of discrimination, in the initial hydroboration, between the two sides of the aliphatic olefin group with respect to the unsaturation in the ring.[2,19] The further intramolecular hydroboration is stereospecific in that the bridging methylene group and the 8-methyl group are *cis*.

TABLE 2

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]
	8-Chloro-oct-1-ene	8-Chloro-octyl cyclopentyl ketone	76[a]
	8-Iodo-oct-1-ene	8-Iodo-octyl cyclopentyl ketone	76
	(10)	(11a)	80
	(10)	(11b)	80
(+)-Limonene (12)		(13a) + (13b)	85 [b]
(14)		(15)	80 [c]

[a] We thank Mr. G. Cowley and Mr. K. Murti who carried out these experiments as part of undergraduate projects. [b] This yield does not allow for 11% recovered limonene. Our previous report[2] gave an absolute yield of 95% based on the limonene converted. [c] Allowing for recovered olefin this corresponds to an absolute yield of 87%.

The mass spectrum of the mixture of thioacetals derived from (13a and b) was in complete accord with the assigned structures.[19] The ketones themselves were readily separated by preparative g.l.c. and gave almost identical mass spectra which agreed with the assigned structures.

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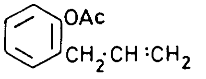
* *X*-Ray studies on this substance and (3) are being carried out by Dr. D. N. J. White, University of Glasgow.

[17] E. Negishi and H. C. Brown, *Synthesis*, 1974, 77.

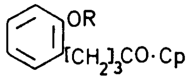
[18] J. R. Johnson and M. G. van Campen, jun., *J. Amer. Chem. Soc.*, 1938, **60**, 121.

[19] M. G. Hutchings, Ph.D. Thesis, University of Manchester, 1972.

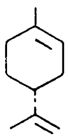
The stereochemistry at C-8 was assigned on the basis of the solvent induced shifts of the methyl groups in the ^{1}H n.m.r. spectrum.[20] One epimer gave shifts of +18·3 and +12·1 Hz (60 MHz spectrum) between carbon tetrachloride and benzene whilst the other shifted by +18·5 and +14·9 Hz. The corresponding 8-*endo*-methyl and 8,8-dimethyl ketones lacking the 4-methyl group have been prepared[21] and it was shown that the 8-*endo*- and 8-*exo*-methyl groups gave shifts of 0 and +14·5 Hz respectively. It is therefore certain that the 8-methyl group in both (13a and b) is *exo*, and hence the two compounds are epimeric at C-4. Models show that the signal of the 4-methyl group in both epimers would be expected to shift upfield.[20]



(10)



(11) a R = H
b R = Ac



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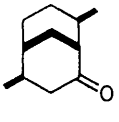
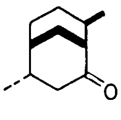
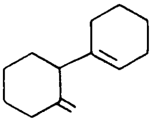


(13a)



(13b)



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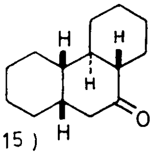

(15)

The isolation of one crystalline compound (15) (80%) from (14) was most striking from the view of production of fused ring systems.* The assignment of structure is based on a comparison of the major (90%) hydrocarbon derived by Clemmensen reduction of (15) with an authentic sample.[22,†] An independent confirmation of structure by the use of lanthanide induced shifts in the ^{1}H n.m.r. spectrum will be reported separately.

Effect of solvent variation and proportions of reactants. Benzoylation reactions gave no trace of trialkylmethanol (from migrations of three alkyl groups from boron to carbon) and hence were not studied in detail.

The use of 1 equiv. of TFAA with tri-s-alkylcyanoborates in diglyme gave rise to the products of only two migrations, and even with an excess of TFAA the reaction could be stopped at this stage. The best yields of ketones were produced by use of the proportions of reactants R_3B : NaCN : TFAA 1·0 : 1·1 : 1·2. On using THF as solvent, some product of a triple migration is observed, but not enough to be troublesome.

With tri-n-alkylcyanoborates the third migration is considerably easier in all the solvents tried and trialkylmethanol is present on oxidation even when a limited amount of TFAA is used. The effect of change of solvent was studied in a series of reactions of potassium cyanotri-n-hexylborate with TFAA in which the proportions of reactants $(n\text{-}C_6H_{13})_3\bar{B}{\cdot}CN$: TFAA were normally 1·0 : 1·1 and each reaction was on a 5 mmolar scale in 25 ml of solvent. Only when bis-(2-methoxyethyl) ether (diglyme) was solvent, when the reaction was also used for preparative purposes, was the proportion changed to 1·0 : 1·05. The TFAA was added at −78°, the cooling bath removed, and the reaction mixture allowed to stand for 1 h before oxidation. The yields of the products obtained as determined by g.l.c. using internal standards are shown in Table 3.

TABLE 3

Variation of reaction product with solvent

Solvent	Ketone (A) (%)	Trialkyl-methanol (B) (%)	A + 2B
Petroleum	13	49	111
Et_2O	20	46	112
CH_2Cl_2	26	39	104
Diglyme	94	5	104 *
THF	31	36	103

* 1·05 mol. equiv. of TFAA used.

As 2 mol. equiv. of TFAA are required to produce the trialkylmethanol and only 1·1 mol. equiv. are present, the total A + 2B should be 110 if all the TFAA is used for producing ketone and trialkylmethanol (for the diglyme experiment A + 2B should be 105). Table 3 indicates that there are no significant side reactions. In diglyme the yield of trialkylmethanol is equivalent to the excess of FAA present so that use of this solvent gives excellent yields of ketone. Of course the same ketones may be obtained through dialkylcyanothexylborates in any solvent tried but the fact that the third migration may be observed at all in such mild conditions was of the utmost interest and laid the foundation for the study of this reaction reported in the following paper.[23]

Reactions using N-*phenylbenzimidoyl chloride as electrophile.* It seemed likely that imidoyl chlorides would behave similarly to acylating agents to yield compounds such as (16) (Scheme 8). For convenience *N*-phenylbenzimidoyl chloride was used. It reacted with cyanoborates rather more readily than did benzoyl chloride, reaction being essentially complete in 3 h at 23°, though good yields may be obtained after only 1 h (Table 4). In general, use of diglyme gave rather

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* We thank Mr. D. J. Williams (University College of Swansea) for allowing us to use this result.

† We thank Professor Y. Mazur, Rehovot, for supplying us with this compound.

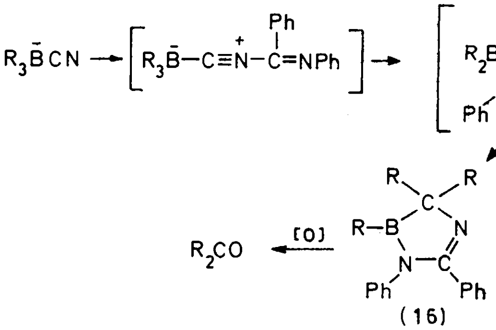
[20] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1969.

[21] F. Leyendecker, G. Mandville, and J. M. Conia, *Bull. Soc. chim. France*, 1970, 556.

[22] D. Kogan and Y. Mazur, *Tetrahedron Letters*, 1971, 2401.

[23] A. Pelter, M. G. Hutchings, K. Rowe, and K. Smith, following paper.

better results than use of THF, though the differences are not major.



SCHEME 8

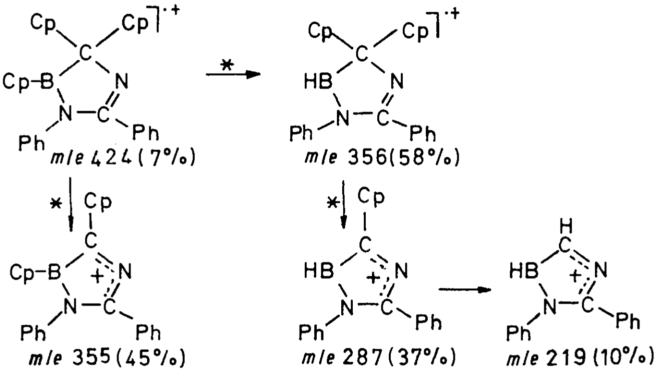
Compound (16; R = cyclopentyl) was chosen for further study and was isolated as usual. The mass spectral fragmentation is shown in Scheme 9, all ions having been mass measured.

The ring system of compounds (16) was even more resistant to hydrolysis than that of compounds (2). Anhydrous propionic acid at 120° for 90 h, 5—32N-sulphuric acid for 24—90 h at 80°, and 5N-sodium hydroxide solution in various solvents over a range of times and temperatures all failed to yield amine or amide.

TABLE 4

Reactions of organocyanoborates, $R_3\bar{B}CN$, with *N*-phenylbenzimidoyl chloride at 23°

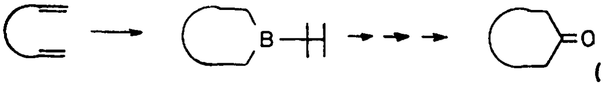
Alkene	Solvent	Time (h)	Yield of ketone (%)
Oct-1-ene	Diglyme	3	86
	THF	3	68
Hex-1-ene	Diglyme	1	72
	Diglyme	3	80
But-1-ene	Diglyme	1	77
	Diglyme	3	86
Cyclopentene	THF	1	76
	THF	3	79
	Diglyme	3	88
Cyclohexene	Diglyme	3	80



SCHEME 9 Other peaks: PhC≡NPh, *m/e* 180 (100%); $PhNH_2^{\cdot+}$ *m/e* 93 (20%); PhC≡$\overset{+}{N}$H, *m/e* 104 (10%); Ph^+, *m/e* 77 (30%)

In summary, the overall conversion depicted in Scheme 10 (A) may be conveniently carried out in a stereospecific fashion[24] in excellent yields by the use of organocyanoborate salts. Various electrophilic reagents induce migration in such salts, the most efficient being TFAA which may be used at low temperatures even on dialkylcyanothexylborates. The use of the latter salts allows the production of symmetrical, unsymmetrical, functionalised, bridged, and fused ring ketones [Scheme 10 (A) and (B)], all in excellent yield. The thexylboron group in the cyanoborate reaction is thus equivalent to a carbonyl group. The one-pot reactions require no special apparatus and are of synthetic value.

$$\text{Olefin A} + \text{Olefin B} + CN^- \longrightarrow\!\!\longrightarrow R^A{\cdot}CO{\cdot}R^B \qquad \text{(A)}$$


(B)

SCHEME 10

EXPERIMENTAL

Ether solvents were distilled from calcium hydride or lithium aluminium hydride under nitrogen prior to use. Other solvents and liquid reagents were purified by standard procedures.[25] *N*-Phenylbenzimidoyl chloride was distilled under reduced pressure, stored under nitrogen, and transferred in a dry box. Diborane was kept as a BF_3-free solution in THF[26] and was standardised prior to use. Sodium and potassium cyanides were oven-dried and powdered prior to use. But-1-ene was prepared and used as a standard solution in THF. I.r. spectra were recorded on a Perkin-Elmer 257, n.m.r. spectra on a Varian HA 100, and mass spectra on A.E.I. MS9 and MS12 spectrometers. All manipulations prior to work-up were carried out in dry glassware under nitrogen. Dry syringes were used to transfer liquids. Hydroborations were carried out according to published procedures.[4,26] Where high-dilution conditions were required, for example in cyclic hydroboration of dienes using thexylborane, slow addition of the reagents was controlled by a Braun-Melsungen continuous infusion apparatus.

The standard reaction vessel was a 100 ml three-necked flask equipped with a magnetic stirrer. One outlet was connected *via* a three-way tap to a vacuum pump or to a cylinder of oxygen-free nitrogen (with pressure-release bubbler). The second was sealed with a tap capped by a silicone rubber septum which was used for introduction of reagents or for sampling. The third, non-vertical neck was fitted with a sealed tube bent to an angle of *ca.* 100°. Prior to the start of any reaction this tube was charged beyond the bend with the required amount of cyanide and fitted so that the outer extremity pointed downwards. At the appropriate time, the tube was rotated through 180°, thus allowing the cyanide to fall cleanly into the reaction vessel.

Whenever possible, products were compared directly with authentic samples. In all cases the mass spectra of the ketones were taken and were as expected.

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[24] A. Pelter, M. G. Hutchings, and K. Smith, *J.C.S. Chem. Comm.*, 1973, 186.

[25] D. D. Perrin, W. L. F. Armarego, and D. W. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, London, 1966.

[26] H. C. Brown, 'Hydroboration,' Benjamin, New York, 1962.

Preparation of Ketones by Reaction of Sodium Trialkylcyanoborates with Benzoyl Chloride.—The apparatus described above, assembled hot and then allowed to cool under nitrogen, was charged with sodium cyanide (0·53 g, 11 mmol) in the side-arm. The whole apparatus was deoxygenated by repeated evacuation followed by filling with nitrogen. The trialkylborane was then prepared by addition of diglyme (15 ml), olefin (30 mmol), and BH_3–THF (10 mmol; 6·7 ml of 1·5M solution in THF) according to published conditions.* When hydroboration was complete the side-arm was rotated to introduce the cyanide, and the mixture was stirred vigorously for 1 h at 25°, by which time all but the excess of NaCN had dissolved.

Benzoyl chloride (1·69 g, 12 mmol) was added whilst the temperature was kept below *ca.* 40° (detected by hand). The flask was then placed in an oil-bath at 45° and warmed for 7 h whilst stirring was maintained. The flask was cooled to 0° and sodium hydroxide (3N; 12 ml) and then hydrogen peroxide (50%; 8 ml; *slow, careful* addition) were added. When the initial vigorous reaction subsided, the cooling bath was removed. The oxidation was completed by stirring for 3 h at 25° and 15 min at 50°, after which the mixture was extracted into pentane (150 ml). The extract was washed with 2N-NaOH (2 × 25 ml), 2N-HCl (2 × 25 ml), and water (8 × 25 ml), dried ($MgSO_4$), filtered, and evaporated [for dibutyl ketone the aqueous washes were saturated with a salt, NaCl (alkali or neutral) or NH_4Cl (acid)].

This crude, neutral extract was transferred with the aid of a little pentane to the top of a column packed with dry silica (*ca.* 100 g), which was then eluted with pentane (250 ml) to remove hydrocarbons. The ketone was then eluted in substantially pure form with either benzene or dichloromethane. Alcohols were finally removed from the column with diethyl ether.

No attempt was made to maximise yields of individual ketones, but all were subjected to the standard procedure described above. The following ketones were prepared in this way. (Other experiments sometimes gave higher yields.)

Di-n-octyl ketone (2·08 g, 82%) was eluted by benzene and apart from a little 7-methylhexadecan-8-one, formed by migration of the secondary group formed as impurity during hydroboration, the product was essentially pure (g.l.c.). Recrystallisation from methanol gave product, m.p. 48—48·5° (lit.,[27] 53°, but *cf.* ref. 28, where product was also contaminated by secondary isomer, m.p. 49·5—50·5°).

Di-n-butyl ketone (1·05 g, 74%) was eluted by dichloromethane, and apart from some contamination with the secondary isomer, 3-methyloctan-4-one, it was essentially pure (g.l.c.). Distillation, b.p. 185° at 760 mmHg (lit.,[27] 188° at 760 mmHg), gave product, n_D^{19} 1·4233 (lit.,[28] n_D^{20} 1·4201).

Dicyclopentyl ketone (1·44 g, 87%) was eluted by dichloromethane, and was essentially pure (g.l.c.). It was distilled (b.p. 92—93° at 5 mmHg) to give product, n_D^{22} 1·4785 (lit.,[28] n_D^{20} 1·4796); dinitrophenylhydrazone, m.p. 94° (lit.,[28] 93—94°).

Dicyclohexyl ketone (1·26 g, 65%) was eluted by dichloromethane and was essentially pure (g.l.c.). Distillation gave product, n_D^{19} 1·4849 (lit.,[28] n_D^{20} 1·4847).

Di-2-*exo*-norbornyl ketone (1·85 g, 85%) was eluted by benzene and was essentially pure (g.l.c.). Recrystallisation from methanol gave product, m.p. 52—54° (lit.,[28] 53—54°).

Preparation of 4,4,5-*Tricyclopentyl*-2-*phenyl*-1-*oxa*-3-*azonia*-5-*boratacyclopent*-2-*en*-5-*ol* (3).—The reaction of sodium cyanotricyclopentylborate [from tricyclopentylborane (10 mmol) and NaCN (10 mmol)] with benzoyl chloride (10·5 mmol) was performed as for the standard preparation of ketones, except that only THF was used as solvent. After 7 h at 45° deoxygenated water (*ca.* 3 ml) was added and the mixture was stirred at 25° overnight. The whole was then extracted into pentane (100 ml) and washed with water (25 ml). The organic layer was evaporated, and the residue dissolved in pentane (100 ml) and washed with more water. As the remaining THF was washed out, crystals of (3) separated. Recrystallisation from methanol–water gave a white crystalline *solid*, m.p. 167—168° (Found: C, 75·3; H, 9·2; N, 4·0. $C_{23}H_{34}BNO_2$ requires C, 75·2; H, 9·2; N, 3·8%). The substance is soluble in acetone, ether, and methanol, and insoluble in pentane, carbon tetrachloride, and water; $\lambda_{max.}$ (EtOH) 236 nm (ε 16,700), $\lambda_{max.}$ (+NaOH) 221 (ε 68,000), and 236 nm (16,700); for detailed i.r., n.m.r., and mass spectral data, see the Discussion section.

Solvent Effects in Reactions of Potassium Cyanotri-n-hexylborate with Trifluoroacetic Anhydride (*TFAA*).—A standard solution of potassium cyanotri-n-hexylborate (1M) in THF was prepared by adding potassium cyanide (3·58 g, 55 mmol) to a solution of tri-n-hexylborane (50 mmol) in THF, and stirring vigorously for 1 h in the usual apparatus. The solution of tri-n-hexylborane was prepared in the flask from hex-1-ene (12·6 g, 150 mmol) and BH_3–THF (33·3 ml; 1·5M). [Because of the higher than usual concentration the addition of hex-1-ene was slower (5—10 min), the flask was cooled in an ice–salt–water-bath during the addition, and the stirring rate was increased.] After dissolution of the cyanide the total volume of the solution was 50 ± 1 ml. The excess of cyanide was allowed to settle out and 5 ml aliquot portions were withdrawn from the supernatant solution.

Each aliquot portion was transferred to a 25 ml flask previously filled with nitrogen by repeated evacuation–readmission of nitrogen and equipped with a magnetic stirrer. The solution was evaporated (finally at 50° and 0·5 mmHg) to remove as much THF as possible. The solvent under investigation (10 ml) was then added, and the whole was stirred until homogeneous. The mixture was cooled to −78° and TFAA (1·15 g, 5·5 mmol) was added. The cooling bath was removed and the mixture was allowed to come to room temperature over 1 h, after which time the flask was cooled to 0° and 3N-NaOH (10 ml) followed by hydrogen peroxide (6 ml; 50%) were added. Oxidation and extraction were carried out as usual to give a crude neutral extract to which hexadecane (0·60 g) as g.l.c. standard was added. Integration of the g.l.c. trace (1 m column, 4% PEGA on Chromosorb W, temperature programme from 50 to 190°) gave the yields of ketone and trialkylmethanol formed in the reaction (see Table2).

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* Ref. 4 cites the original references where the hydroboration conditions are described. For the simple trialkylboranes, 1 h at 25° is generally suitable. Tricyclohexylborane may require 3 h.

[27] 'Handbook of Chemistry and Physics,' 53rd edn., The Chemical Rubber Company, Cleveland, 1973.

[28] M. W. Rathke and H. C. Brown, *J. Amer. Chem. Soc.*, 1967, **89**, 2738.

Preparation of Ketones via *Reaction of Symmetrical Trialkylcyanoborates with TFAA*.—Sodium trialkylcyanoborates, $R_3BCN\ Na^+$ (R = n-octyl, n-butyl, cyclopentyl, cyclohexyl, 2-norbornyl) were prepared from the trialkylborane (10 mmol) and sodium cyanide (11 mmol) in THF–diglyme in the same manner as described above. The THF was removed under reduced pressure and nitrogen was readmitted to the apparatus. The mixture was cooled to −78° and TFAA (for quantity see specific examples) was added. The cooling bath was removed and the mixture was allowed to come to room temperature (*ca.* 15 min). The mixture was then oxidised, the products were extracted, and the ketones (identical with authentic samples) were separated and purified as described under their preparation using benzoyl chloride: di-n-octyl ketone, TFAA 1·20 g (10·5 mmol) used, yield 2·42 g (95%); di-n-butyl ketone, TFAA 2·20 g (10·5 mmol) used, yield 1·33 g (94%); dicyclopentyl ketone, TFAA 2·53 g (12 mmol) used, yield 1·39 g (84%); dicyclohexyl ketone, TFAA 2·53 g (12 mmol) used, yield 1·94 g (100%); di-exo-2-nornornyl ketone, TFAA 2·53 g (12 mmol) used, yield 2·16 g (99%).

Application of the Cyanoborate Process using Dialkylcyanothexylborates to the Synthesis of Ketones.—The standard apparatus was set up and sodium cyanide (0·53 g, 11 mmol) was put in the side-arm. The apparatus was then deoxygenated by repeated evacuation–readmission of nitrogen. The particular dialkylthexylborane was prepared by successive addition of THF (15 ml), BH_3–THF (1·5M; 6·7 ml, 10 mmol), 2,3-dimethylbut-2-ene (0·84 g, 10 mmol), olefin A (10 mmol), and olefin B (10 mmol),[4,17] whilst stirring was maintained. Unless otherwise stated, standard conditions [4,17] were used to prepare the dialkylthexylboranes. The cyanide was then admitted and vigorous stirring was maintained for 1 h at 25°. The flask was cooled to −78° and TFAA (2·53 g, 12 mmol) was added with stirring. The cooling bath was removed and the mixture was allowed to come to room temperature over 1 h. The mixture was cooled to 0° and 3N-NaOH (12 ml), then 50% hydrogen peroxide (8 ml; slow addition) were added. After the initial vigorous reaction subsided the cooling bath was removed and oxidation was completed over 3 h at 25° and 15 min at 50°. The mixture was extracted into pentane (150 ml) and worked up as before. Most of the 2,3-dimethylbutan-2-ol was removed during the evaporation. The ketones were separated by chromatography as described above, elution being with benzene (dichloromethane for dicyclopentyl ketone). The yield at this stage was of essentially pure product (g.l.c.). Analytical samples were distilled (dioctyl ketone was recrystallised).

Di-n-octyl ketone. Oct-1-ene (2·24 g, 20 mmol) gave the ketone (1·97 g, 78%).

Dicyclopentyl ketone. Cyclopentene (1·36 g, 20 mmol) gave the ketone (1·33 g, 80%).

Cyclopentyl n-octyl ketone. Cyclopentene (0·68 g, 10 mmol) and oct-1-ene (1·12 g, 10 mmol) gave the *ketone* (1·74 g, 83%), $\nu_{max.}$ (film) 1705 cm^{-1}; n_D^{24} 1·4496, b.p. 68° at 0·45 mmHg (Found: C, 80·25; H, 12·15%; M^+, 210·1983. $C_{14}H_{26}O$ requires C, 80·0; H, 12·3%; *M*, 210·1983).

8-*Chloro-octyl cyclopentyl ketone*. Cyclopentene (0·68 g, 10 mmol) and 8-chloro-oct-1-ene (1·47 g, 10 mmol) gave the *ketone* (1·86 g, 76%), $\nu_{max.}$ (film) 1705 cm^{-1}; n_D^{19} 1·4740, b.p. 115° at 0·45 mmHg (Found: C, 68·6; H, 10·2%; M^+, 244·1592. $C_{14}H_{25}ClO$ requires C, 68·7; H, 10·2%. $C_{14}H_{25}{}^{35}ClO$ requires *M*, 244·1594).

Cyclopentyl 8-*iodo-octyl ketone*. Cyclopentene (0·68 g, 10 mmol) and 8-iodo-oct-1-ene (2·38 g, 10 mmol) gave the *ketone* (2·55 g, 76%), $\nu_{max.}$ (film) 1702 cm^{-1}; n_D^{19} 1·5150, b.p. 130° at 0·5 mmHg (Found: C, 50·0; H, 7·6%; M^+, 336·0959. $C_{14}H_{25}IO$ requires C, 50·0; H, 7·4%; *M*, 336·0952). The compound was identical with a sample obtained by treating 8-chloro-octyl cyclopentyl ketone with NaI in acetone.

Preparation of 3-o-*Hydroxy- and* 3-o-*Acetoxy-phenylpropyl Cyclopentyl Ketone*.—Cyclopentylthexylborane (10 mmol) in THF was prepared as in the previous experiments, and to this at 0° was added 3-*o*-acetoxyphenylpropene (1·76 g, 10 mmol), and the mixture was stirred for 3 h at 25°. Sodium cyanide (0·54 g, 11 mmol) was introduced from the side-arm and vigorous stirring was maintained for 1 h at 25°. The mixture was cooled to −78° and TFAA (2·53 g, 12 mmol) was added. The temperature was allowed to rise to 25° over 1 h and the mixture was then cooled for oxidation as in (*a*) or (*b*).

(*a*) The flask was cooled to 0° and saturated aqueous sodium hydrogen carbonate solution (15 ml) was added. When effervescence (due to hydrolysis of excess of TFAA and reaction with trifluoroacetic acid) ceased, hydrogen peroxide (8 ml; 50%) was carefully added and the mixture was stirred for 1 h at 25° followed by 1 h at 40°. Extraction into pentane (150 ml) followed by successive washing with sodium carbonate (2 × 25 ml; 2N) and very dilute acid (25 ml; 0·01N HCl), drying ($MgSO_4$), and evaporation gave a crude extract which was separated as described above (elution with dichloromethane). Continuous pumping of the eluate removed any remaining 2,3-dimethylbutan-2-ol to give essentially pure *cyclopentyl* 3-o-*hydroxyphenylpropyl ketone* (1·86 g, 80%), m.p. 22—23°, $\nu_{max.}$ (mull) 1695 and 3300 cm^{-1}; n_D^{24} 1·5230 (Found: C, 79·5; H, 10·7%; M^+, 232·1462. $C_{15}H_{20}O_2$ requires C, 79·5; H, 10·9%; *M*, 232·1463).

(*b*) The reaction mixture was cooled to 10° and *m*-chloroperbenzoic acid (3·9 g, 22·5 mmol; enough to cleave 2 B–C bonds) in CH_2Cl_2 (15 ml) was added. After 30 min the products were extracted into pentane (150 ml) and successively washed with aqueous solutions of Na_2CO_3 (25 ml; 2N), $Na_2S_2O_3$ (25 ml; 2N), Na_2CO_3 (25 ml; 2N), and very dilute acid (25 ml; 0·01N-HCl), dried ($MgSO_4$), and evaporated. The crude extract was separated as above (elution with dichloromethane). The product was slightly impure (i.r., g.l.c.) so a portion was further purified by preparative t.l.c. (silica developed by 20% EtOAc in pentane). This pure *sample* was used to obtain response data (cyclopentyl 8-iodo-octyl ketone as g.l.c. standard) so that a g.l.c. estimate of the amount of product in the bulk eluate could be made. This showed an 80% yield, $\nu_{max.}$ 1703 and 1760 cm^{-1}, $\lambda_{max.}$ (EtOH) 225, 262, and 269 nm, b.p. 105° at 5 mmHg; n_D^{21} 1·5113 (Found: C, 74·4; H, 7·9%; M^+, 274·1564. $C_{17}H_{22}O_3$ requires C, 74·4; H, 8·0%; *M*, 274·1569). The product was identical with that obtained by treatment of cyclopentyl 3-*o*-hydroxyphenylpropyl ketone with acetic anhydride in pyridine.

Preparation of 4,8-*Dimethylbicyclo*[3.3.1]*nonan*-2-*one*.—The standard apparatus was charged with sodium cyanide (0·38 g, 7·6 mmol) in the side-arm and deoxygenated. Thexylborane was prepared in the reaction flask by mixing THF (9·6 ml), BH_3–THF (4·6 ml; 1·5M; 6·9 mmol), and 2,3-dimethylbut-2-ene (0·8 ml, 0·58 g, 6·9 mmol) at 0°.

After 1 h at 0° this solution was withdrawn into a 25 ml syringe. In an identical syringe was placed (+)-limonene (1·13 ml, 0·94 g, 6·9 mmol) in THF (13·9 ml). THF (10 ml) was placed in the reaction vessel under N_2 and was stirred at 0°. The two syringes were fitted to an automatic infusion apparatus set to administer 15 ml h^{-1} (each syringe). After 1 h the cooling bath was removed and the mixture was stirred for 1 h at 20°. The cyanide was admitted and the whole was vigorously stirred for 1 h at 20°, followed by cooling to −78°. TFAA (1·2 ml, 1·9 g, 8·3 mmol) was added and the temperature was allowed to rise to 20° over 1 h. The contents were oxidised as usual with 3N-NaOH (10 ml) and 50% H_2O_2 (7 ml) and then extracted into diethyl ether (150 ml), washed (2N-NaOH, 2 × 25 ml; H_2O, 4 × 25 ml), dried ($MgSO_4$), and evaporated. The crude extract was chromatographed as before. Elution with pentane gave limonene (0·1 g, 11%) and then dichloromethane eluted the ketone (0·98 g, 85% yield, 95% conversion). G.l.c. analysis (1 m column, 8% PEGA on 60—80 Chromosorb A, 140°) indicated two ketones in approximately equal amounts and no significant impurities. The two ketones (13a and b) were separated by preparative g.l.c. the faster running epimer had $[\alpha]_D^{25}$ −66·0 ± 0·6° ($CHCl_3$); $\nu_{max.}$ (film) 1701 cm^{-1}, and the slower running epimer $[\alpha]_D^{25}$ +72·6 ± 0·7° ($CHCl_3$); $\nu_{max.}$ (film) 1701 cm^{-1}. For the mixture of epimers, $n_D^{21.5}$ 1·4825 (Found: C, 79·5; H, 10·7. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%).

1-(2-*Methylenecyclohexyl*)*cyclohexene*.*—A solution of n-butyl-lithium (1·46M; 90 ml, 0·13 mol) in petroleum was added to dry ether (200 ml) in a three-necked, round-bottom flask equipped with a pressure-equalised addition funnel, reflux condenser, and mechanical stirrer. To the stirred solution methyltriphenylphosphonium bromide (47·5 g, 0·13 mol) was added cautiously over 5 min, and the mixture was stirred for 4 h at 23°. 2-(Cyclohex-1-enyl)-cyclohexanone [29] (26 g, 0·143 mol) was added dropwise to the red solution, which caused decolourisation and the separation of a precipitate. The mixture was heated under reflux for 15 h, cooled, and filtered. The filtrate was washed with water (5 × 20 ml) and dried ($MgSO_4$). At this stage examination by g.l.c. (1 m, 4% PEGA at 120°) showed the required olefin (t_R 2 min) together with some starting material (t_R 12 min). The g.l.c. yield was 80%. The ether was removed, and the crude product put on a column of dry, neutralised silica (500 g). (It is important that the silica be neutralised or isomerisation of the product results.) Elution with pentane gave an olefinic hydrocarbon (17·3 g, 75%). Run on a 1 m, 4% PEGA column at 70°, 94% of the product came off at 8 min and 1% at 5·5 min. The latter peak was shown by comparison to be due to a trace of the conjugated isomer. The product (Found: C, 88·6; H, 11·4%; M^+, 176·1564. $C_{13}H_{20}$ requires C, 88·6; H, 11·4%; M, 176·1565), had n_D^{20} 1·5011, τ ($CDCl_3$) 5·5 (1H, q, J ca. 1·5 Hz), 5·4 (1H, q, J ca. 1·5 Hz), and 4·6 (1H, sextet, J ca. 1·5 Hz).

cis,*anti*,trans-*Perhydrophenanthren*-9-*one* (15).—Using the standard apparatus, thexylborane (10 mmol) in THF (30 ml) and 1-(2-methylenecyclohexyl)cyclohexene (1·76 g, 10 mmol) in THF (30 ml) were added simultaneously by means of an infusion apparatus to stirred THF (10 ml) at 0° over 3 h. The flask was then kept at 25° for 1 h. Potassium cyanide (0·7 g; *ca.* 8% excess) was added at 0° to the reaction and the mixture stirred at 23° for 1 h after which almost all the solid had disappeared. The solution was cooled to −78° and TFAA (1·68 ml, 12 mmol) added. After addition was complete the cooling bath was removed and the mixture stirred for 1 h, after which it was oxidised in the normal way for 12 h with NaOH (5N; 10 ml) and 50% H_2O_2 (10 ml). Work-up gave crude product which was chromatographed as usual. Elution with pentane gave starting olefin (0·135 g, 0·077 mmol), and elution with dichloromethane gave cis,*anti*,trans-*perhydrophenanthren*-9-*one* (1·52 g, 80% yield, 87% conversion), m.p. 60—62° (corrected), $\nu_{max.}$ 1705 cm^{-1}, single g.l.c. peak (1 m, 2% PEGA on Chromosorb W column at 150°; N_2 16 lb in^{-2}). Recrystallisation from light petroleum did not raise the m.p.† (Found: C, 81·4; H, 10·8%; M^+, 206·1671. $C_{14}H_{22}O$ requires C, 81·5; H, 10·7%; *M*, 206·1671).

Preparation of 4,4,5-*Tricyclohexyl*-2-*trifluoromethyl*-1-*oxa*-3-*aza*-5-*boracyclopent*-2-*ene* (8) *and its Water Adduct*.—Potassium cyanotricyclohexylborate (10 mmol) was prepared in THF (20 ml) from tricyclohexyl borane (10 mmol) and KCN (0·68 g, 10·5 mmol) as previously described for the sodium salt. The mixture was cooled to −78° and TFAA (2·21 g, 10·5 mmol) was added. The cooling bath was removed and the mixture was allowed to come to room temperature (*ca.* 30 min). The supernatant liquid was withdrawn and evaporated. Pentane was added to precipitate remaining potassium trifluoroacetate and the supernatant was again withdrawn and evaporated to give (8) as a viscous, air-sensitive oil, $\nu_{max.}$ (CCl_4) 1740, 1684, 1650, 1208, and 1159 cm^{-1} (Found: M^+, 383·2607. $C_{21}H_{33}{}^{11}BF_3NO$ requires *M*, 383·2607).

The product was dissolved in THF (10 ml), deoxygenated water (3 ml) was added, and the mixture stirred overnight. THF was removed at the pump, and pentane (100 ml) was added. Further washing with water precipitated a white, crystalline solid. Recrystallisation from aqueous methanol gave the *hydrate* as needles, m.p. 144—145° (Found: C, 62·3; H, 9·2; N, 3·4%; M^+, 401·2713. $C_{21}H_{35}{}^{11}BF_3NO_2$ requires C, 62·8; H, 8·7; N, 3·5%; *M*, 401·2713), $\nu_{max.}$ (mull) 3370, 3340 (NH, OH), 1715 [$CF_3C(:N)O$], 1545 (δ NH), 1215, and 1185 cm^{-1} (CF_3); τ 3·28 (1H, slowly exch. with D_2O) and 7·77 (2H, t).

Reaction of Sodium Cyanotri-n-octylborate with Acetyl Chloride.—Sodium cyanotrioctylborate (8·6 mmol) in diglyme (20 ml) was prepared as previously described [oct-1-ene (2·89 g, 25·8 mmol); BH_3–THF (5·73 ml; 1·5M); NaCN (0·46 g, 9·4 mmol)]. The solution was cooled to −78° and acetyl chloride (0·74 g, 9·5 mmol) was added. The mixture was allowed to come to room temperature and stirred for 15 h before oxidation [3N-NaOH (12 ml); 50% H_2O_2 (8 ml)], extraction, and separation in the way described for the preparation of ketones using benzoyl chloride. Dioctyl ketone (0·85 g, 40%) was isolated. Repetition under more forcing conditions never gave yields >46%.

Preparation of Ketones via *Reaction of Potassium Trialkylcyanoborates with* N-*Phenylbenzimidoyl Chloride*.—Potassium trialkylcyanoborates (10 mmol) were prepared in either THF or diglyme (12 ml) as described above for

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* We thank Mr. D. J. Williams for the details of this experiment.

† For full details of the establishment of stereochemistry of this ketone, see D. J. Williams, Ph.D. thesis, University of Wales, 1974.

[29] K. K. Kelly and J. J. Matthews, *J. Chem. Eng.*, 1969, **14**, 277.

the corresponding sodium salts (products derived from hex-1-ene were treated in identical manner to those from oct-1-ene at all stages). *N*-Phenylbenzimidoyl chloride (2·59 g, 12 mmol) in the same solvent (8 ml) was added at room temperature and the mixture was stirred at 23° for 3 h. Oxidation was effected with 3N-NaOH (12 ml) and 50% hydrogen peroxide (8 ml) as described for the benzoylation reactions. The products were then extracted into diethyl ether (150 ml) and washed with 2N-NaOH (2 × 25 ml), 2N-HCl (2 × 25 ml), and water (10 × 25 ml). Hexane (100 ml) was added and ether was removed under reduced pressure, whereupon benzanilide precipitated from the hexane solution. This was removed by filtration and the filtrate was treated in an identical manner to the crude, neutral extracts obtained in the benzoylation experiments. The following ketones were prepared in this way: di-n-octyl ketone; in diglyme, yield 2·18 g (86%); in THF, yield 1·73 g (68%); di-n-butyl ketone; in diglyme, yield 1·22 g (86%); di-n-hexyl ketone; in diglyme, yield 1·57 g (80%), m.p. 32° (lit.,[27] 33°); dicyclopentyl ketone, in diglyme, yield 1·46 g (88%); in THF, yield 1·31 g (79%); dicyclohexyl ketone; in diglyme, yield 1·55 g (80%).

Preparation of 4,5,5-*Tricyclopentyl*-2,3-*diphenyl*-1,3-*diaza*-4-*boracyclopent*-1-*ene* (16; R = *cyclopentyl*), *and its Water Adduct*.—The reaction of potassium cyanotricyclopentylborate (10 mmol) with *N*-phenylbenzimidoyl chloride (10 mmol) was carried out as above in THF, but the reaction mixture was not oxidised. Instead, pentane (50 ml) was added and the supernatant liquid was syringed from precipitated KCl. Evaporation of solvent gave a viscous oil with mass spectral characteristics consistent with (16; R = cyclopentyl), although impure (see text) (Found: M^+, 424·3050. Calc. for $C_{29}H_{37}{}^{11}BN_2$: *M*, 424·3050).

The oil was taken into toluene (20 ml) and stirred with deoxygenated water (5 ml) for 60 h at 25°. Excess of water was removed, the solution was concentrated to 10 ml, and pentane (50 ml) was added. A pale yellow solid separated and was collected after 15 h. After recrystallisation first from benzene, then from aqueous methanol, the *hydrate* was obtained as crystals, m.p. 148—150° (Found: C, 78·8; H, 8·9; N, 6·5%; $M^+ - H_2O$, 424·3049. $C_{29}H_{39}{}^{11}BN_2O$ requires C, 78·7; H, 8·8; N, 6·3%. $C_{29}H_{37}{}^{11}BN_2$ requires *m/e*, 424·3050), mass spectrum identical with that of the oil except for the disappearance of peaks presumably due to impurities, $\nu_{max.}$ (mull) 3300, 3210 (NH, OH), 1595 (aromatic rings), and 1545 cm^{-1} (δ N–H), τ ($CDCl_3$) 2·75—3·0 (10H, m), 3·84 (1H, slowly exch. with D_2O, $\overset{+}{N}$H?), 6·62 (1H, very slowly exch. with D_2O, OH?), 7·60br (2H), and 7·8—9·3 (aliphatic).

K. S., M. G. H., and K. R. thank the S.R.C. for maintenance grants.

[4/1230 *Received*, 24*th June*, 1974]