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Factors affecting reactions of trialkylcyanoborates with imidoyl chlorides/trifluoroacetic anhydride

Dyfyr Heulyn Jones [a], Keith Smith [a,*], Mark C. Elliott [a,*], Gamal A. El-Hiti [b]

[a] School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK
[b] Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University, PO Box 10219, Riyadh 11433, Saudi Arabia

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ABSTRACT

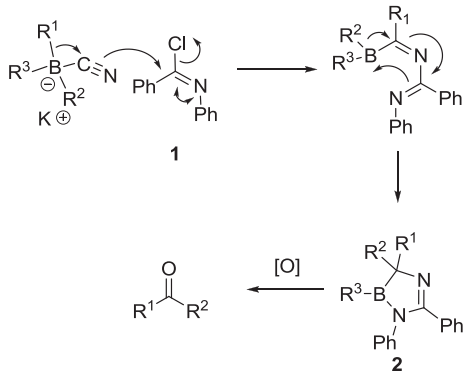
Methods for generating *tert*-alkyl organoboron species are in high demand as they are invaluable intermediates for the synthesis of quaternary carbon centres. Herein we report investigations into generation of *tert*-alkyl organoboron species using imidoyl chlorides as reagents in the organoboron cyanidation reaction. Although alkenyl side-products predominate in particularly hindered cases, *tert*-alkyl organoboron species can be successfully generated for less hindered examples.

1. Introduction

The formation of C–C bonds using boron-to-carbon alkyl group migrations is an invaluable transformation in organic chemistry.[1] Such reactions can involve one, two or three migrations, depending on the number of available leaving groups. There has been considerable interest of late in such migration reactions that give rise to *tert*-alkyl organoboron species, as there are protocols available to use these in the generation of otherwise difficult to synthesise quaternary carbon centres.[2–8]

Several organoboron reactions have been developed that utilize all three alkyl groups of a trialkylborane, giving a *tert*-alcohol as the final product following oxidation of the *tert*-alkyl organoboron intermediate.[9–12] Of these reactions, the cyanidation reaction is particularly useful as it proceeds under mild conditions, is tolerant of sensitive functional groups and the doubly-migrated ketone product is also accessible using the appropriate reaction conditions.[11,13–15]

Although trifluoroacetic anhydride (TFAA) or benzoyl chloride is usually the acylating reagent used in the cyanidation reaction, it has been shown that *N*-phenylbenzimidoyl chloride (**1**) successfully induces two boron–carbon migrations to give the intermediate **2**, which on oxidation gives the ketone product (Scheme 1).[15] Since it is possible to envisage introducing chirality into the imidoyl chloride, it was of interest to us to investigate whether a third migration could be induced in the cyanidation reaction when using an imidoyl chloride as the acylating reagent.



Scheme 1. Imidoyl chloride-induced cyanidation reaction.

It was reasoned that by adding excess trifluoroacetic anhydride (TFAA) to the intermediate of type **2** (Scheme 1), acylation would occur on nitrogen, thereby promoting the migration of the third and final alkyl group, as occurs in the direct reaction of trialkylcyanoborates with excess TFAA.[13] Our results indicate that such a process is indeed possible in cases when the trialkylborane is not extremely hindered.

* Corresponding authors. Tel.: +44 (0)29 20870600 (K.S.); tel.: +44 (0)29 20874686 (M.C.E.); e-mail addresses: smithk13@cardiff.ac.uk (K. Smith), elliottmc@cardiff.ac.uk (M.C. Elliott).

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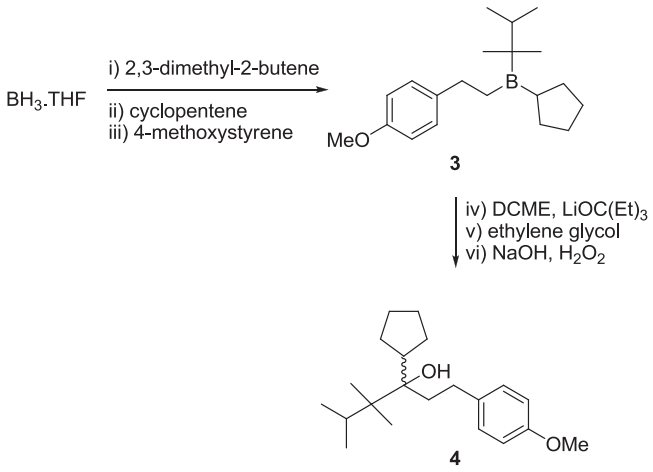
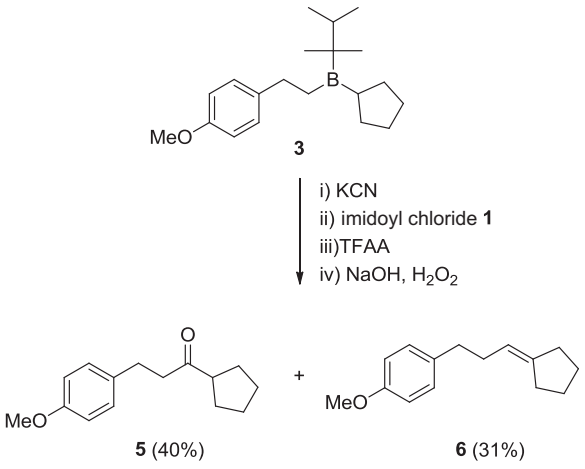
2. Results/discussion

The mixed trialkylborane **3** was chosen as the first substrate to be studied, as a chiral *tert*-alcohol product would allow evaluation of any future cyanidation reactions utilizing chiral imidoyl chlorides. An authentic sample of racemic *tert*-alcohol **4** was prepared by the sequential hydroboration of 2,3-dimethyl-2-butene, cyclopentene and 4-methoxystyrene to give **3**, which was subsequently taken through the dichloromethyl methyl ether (DCME) protocol to give **4** (Scheme 2).[12]



Scheme 2. Formation of a chiral tertiary alcohol by the DCME reaction.

Mixed organoborane **3** was converted into its cyanoborate by stirring under nitrogen with powdered potassium cyanide for 1 h. This was then stirred overnight at room temperature with *N*-phenylbenzimidoyl chloride (**1**), before excess TFAA was added and the reaction mixture heated to 40 °C for 14 h ^{1}H NMR analysis following oxidation and work-up showed the presence of ketone **5** and novel alkene **6** (Scheme 3) in a 62:38 ratio, respectively, with no presence of *tert*-alcohol **4**. After chromatographic separation, compound **5** was isolated in 40% yield and compound **6** in 31% yield.



Scheme 3. Reaction of imidoyl chloride **1** with mixed trialkylborane **3**.

Ketone **5** is almost certainly the product from the oxidation of the intermediate of type **2** following two migrations, whilst alkene **6** may be the product of protodeboronation of intermediate **2**, along with elimination of amine, facilitated by small amounts of acid present in the TFAA. Such alkenyl species have been reported as minor side products in the traditional cyanidation reaction when using particularly hindered trialkylboranes,[11] and also in the DCME reactions of certain borinic esters[16], which, upon heating, give the alkenyl products almost quantitatively.[17]

Many factors (both steric and electronic in nature) affect boron-to-carbon migrations,[1] and so imidoyl chlorides **7**–**9** were chosen to probe whether the electronic and/or steric characteristics of the imidoyl chloride could influence the reaction in such a way as to promote the third alkyl group migration to give, after oxidation, tertiary alcohol **4**. Imidoyl chlorides **7** and **8** (Fig. 1) were chosen to test whether an electron-withdrawing substituent could promote the third migration, while imidoyl chloride **9** was chosen to probe whether the third migration could be promoted by the alleviation of steric hindrance around boron.[1]

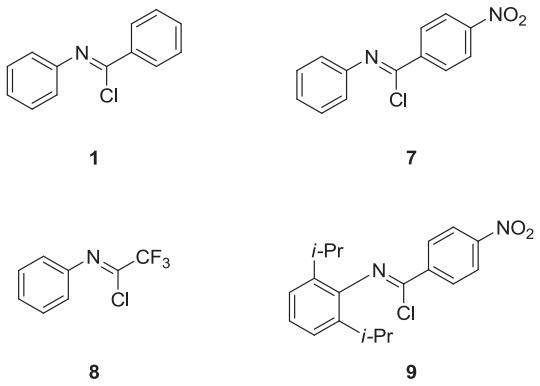


Fig. 1. Imidoyl chlorides chosen for study.

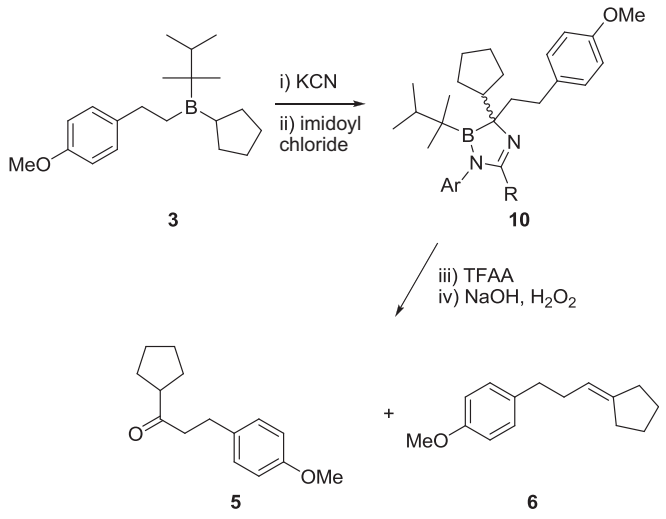
Imidoyl chlorides **7**–**9** were added to the potassium cyanoborate salt of **3** and, following stirring at room temperature overnight, an aliquot was taken, oxidised and worked-up. Ketone **5** was clearly visible as the major product by ^{1}H NMR analysis of the products when using imidoyl chlorides **7** and **9**, indicating that the first two migrations had been successful. When using imidoyl chloride **8**, however, only the alcohols arising from the oxidation of **3** could be seen in the ^{1}H NMR spectrum of the product. An aliquot taken after heating the reaction mixture of **8** overnight at 80 °C contained only trace amounts of **5**, while further heating resulted in darkening of the solution and formation of a black polymeric material. Imidoyl chlorides possessing electron–withdrawing substituents are known to be less prone to attack by nucleophiles,[18] which could explain the apparent lack of reactivity of imidoyl chloride **8** with the potassium cyanoborate salt of **3**.

Excess TFAA was added to the reaction mixtures involving **7** and **9**, and the reaction mixtures were heated to 40 °C overnight (Table 1). ^{1}H NMR analysis following work-up for both reactions showed an identical ratio of **5** and **6**, with no sign of *tert*-alcohol **4** (Table 1). The presence of the bulky isopropyl groups of **9** seemed to have had minimal effect on the course of the reaction, whilst the addition of a nitro group into the 4-position of the aryl ring of **7** increased the production of alkene **6**.

Given that alkene side-products of type **6** are seen in traditional cyanidation reactions (using TFAA alone as the acylating reagent) only when particularly bulky trialkylboranes are used,[11] it was reasoned that boranes lacking the bulky thexyl (2,3-dimethyl-2-butyl) group of intermediate **10** might allow the third migration to give a *tert*-alcohol product. Attempts were therefore made to displace the thexyl group from **10**.

Using **7**, intermediate **10** was heated to 100 °C with excess 1-octene in an attempt to replace the thexyl group with an *n*-octyl group via a displacement reaction (Entry 5, Table 1).[19] ^{1}H NMR analysis following subsequent reaction with TFAA and oxidation showed the presence of **5** (ca. 61% yield) and 1-octene (ca. 79%

Table 1
Initial investigative reactions using trialkylborane **3**



Entry	Imidoyl chloride	Product proportions[a]	
		5 (%)	**6** (%)
1	**1**	62 (40)[b]	38 (31)[b]
2	**7**	22	78
3	**8**	0	Trace
4	**9**	22	78
5	**7** (excess 1-octene)	100	0
6	**7** (acetaldehyde)	100	0

[a] Based on relative integrations by ^{1}H NMR spectroscopy.
[b] Isolated yields in parentheses.

recovered) but no *n*-octanol, indicating that the reaction pathway to give **6** had been suppressed completely, although incorporation of the *n*-octyl group had been unsuccessful.

A similar approach of replacing the thexyl group with an *n*-butyl group was attempted by first displacement with acetaldehyde,[20] followed by addition of *n*-BuLi to displace the ethoxy group generated (Entry 6, Table 1). This again resulted in the complete suppression of the reaction pathway to give **6**, but none of the *tert*-alcohol from migration of the *n*-butyl group was observed by ^{1}H NMR spectroscopy. The only product identified was **5**, the yield of which was in the order of 70%.

A possible explanation for these results is that the methods were successful in displacing 2,3-dimethyl-2-butene (thexene) but not in the subsequent incorporation of an alkyl group.

To ascertain whether the steric bulk of **3**/**10** was responsible for the formation of **6**, a brief study was carried out of substrate scope for the reaction using imidoyl chloride **7**, using trialkylboranes of different steric hindrance (Table 2).

To our delight, the reaction of tri-*n*-octylborane (which would have contained around 17% of the 2-octylbis(1-octyl)borane isomer, as the hydroboration of 1-octene with BH_3 is not entirely regioselective)[21] with **7**, followed by reaction with TFAA and oxidation, gave a mixture of ketone and *tert*-alcohol (Entry 1, Table 2), strongly suggesting that the production of **6** was indeed due to the steric bulk of **3**. In fact, the *tert*-alcohol products arising from three migrations were even accessible with moderately hindered trialkylboranes such as tricyclopentylborane (Entry 2, Table 2) and di-*n*-octylthexylborane (Entry 3, Table 2), along with various amounts of the ketone and alkene products. The latter result shows that migration of a thexyl group is possible for this reaction, and by comparison with the lack of migration of the group in the case of **3** suggests that increasing bulk at the migration terminus is responsible for diversion of the reaction pathway to give alkene products. The migration of the thexyl group was entirely during the final rearrangement step, so that no thexyl-containing ketone was found. This is consistent with previous results for cyanidation reactions,[15] but in contrast with the situation for some other reactions, such as our recently reported reactions with halomethyllithium reagents.[6,22]

3. Conclusion

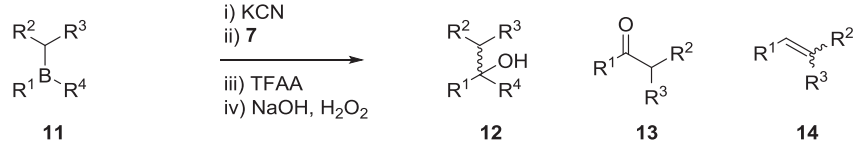
In conclusion, promoting a third boron–carbon migration in organoboron intermediates obtained from reactions of imidoyl chlorides with trialkylcyanoborates is possible for trialkylboranes that are relatively unhindered. Several imidoyl chlorides of different electronic character and steric hindrance were tested in reactions with trialkylborane **3**; all except one of the imidoyl chlorides reacted to give a double-migrated intermediate, which on further reaction with TFAA gave alkene **6**, most likely due to steric compression in the necessary transition state for a third migration due to a combination of hindrance at the migration terminus and a bulky migrating group. For less hindered trialkylboranes, the intermediates from reactions with imidoyl chloride **7** react with TFAA and following oxidation give the *tert*-alcohol products from a third boron–carbon migration. This opens up the exciting possibility of developing an enantioselective synthesis of moderately unhindered *tert*-alcohols through the use of chiral imidoyl chlorides in the cyanidation reactions of unsymmetrical trialkylboranes. Further work is now needed in order to identify suitable trialkylborane-reagent combinations.

4. Experimental section

4.1. General experimental details

Melting point determinations were performed by the open capillary method and are reported uncorrected. ^{1}H and ^{13}C NMR

Table 2
Substrate scope using imidoyl chloride **7**



Entry	Substituents R				Yield (%)		
	R^1	R^2	R^3	R^4	**12**	**13**	**14**
1	*n*-C_8H_{17}	*n*-C_7H_{15}	H	*n*-C_8H_{17}	49[a] (**12a**)	17 (**13a**)	0
2	*c*-Pent	$-(CH_2)_4-$		*c*-Pent	39 (**12b**)	29 (**13b**)	1[b]
3	*n*-C_8H_{17}	*n*-C_7H_{15}	H	Thexyl	15 (**12c**)	18 (**13a/c**)	10[c] (**14c**)
4	4-$MeOC_6H_4(CH_2)_2$	$-(CH_2)_4-$		Thexyl	0	5 (**5**)	55 (**6**)

[a] Based on isolated yields following purification.
[b] a 93:7 mixture of **14** and an isomeric alkene.
[c] 88:12 *E*/*Z* ratio.

chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and coupling constants J are reported to the nearest 0.1 Hz. C, CH, CH_2, or CH_3 ^{13}C signals are assigned from DEPT-90 and 135 spectra. Low and high-resolution mass spectra were recorded on a time-of-fight mass spectrometer using electron impact (EI). High-resolution mass spectra were recorded only for novel compounds. IR spectra were recorded on a FT–IR spectrometer as a thin film (liquid samples) or applied as a solution in chloroform, and the chloroform was allowed to evaporate (solid samples). Column chromatography was carried out using either 60A (35–70 μm) silica or neutral alumina, and thin layer chromatography was conducted on aluminium-backed silica plates. Imidoyl chlorides **1**, and **7**–**9** were prepared using literature procedures.[15,18,23,24]

4.2. Synthesis of an authentic sample of 4

An oven-dried 100 mL round bottomed flask equipped with a magnetic stirrer bar and septum was flushed with N_2 for 10 min. Borane-THF complex solution (1.0 M, 5.0 mL, 5.0 mmol) was added drop-wise and the flask was cooled to −10 °C using an ice-salt bath. 2,3-Dimethyl-2-butene (0.63 g, 7.5 mmol) was added drop-wise with stirring, and the solution left to stir for a further 90 min before being cooled to between −30 and −20 °C (dry ice-acetonitrile). Cyclopentene (0.44 mL, 5.0 mmol) was added slowly with stirring, and the reaction mixture was left to stir for 90 min. 4-Methoxystyrene (0.67 mL, 5.0 mmol) was added drop-wise and the solution left to warm to room temperature (rt) and stirred for an additional 1 h. Dichloromethyl methyl ether (0.50 mL, 5.5 mmol) was added drop-wise at 0 °C, and a freshly prepared solution of lithium 3-ethylpentan-3-olate in THF (prepared by the drop-wise addition of *n*-BuLi to a solution of 3-ethyl-3-pentanol) introduced drop-wise via a cannula with stirring over a 20 min period. Once the addition was complete, the ice bath was removed and the mixture left to stir for a further 1 h. Anhydrous ethylene glycol (0.90 mL, 16.0 mmol) was added and the solution was left to stir for 1 h at rt. The flask was then placed in an ice bath, and a solution of sodium hydroxide (1.20 g in 5 mL of distilled water) added carefully drop-wise. Once the initial reaction subsided, a solution of hydrogen peroxide in water (30% by weight, 4.0 mL) and ethanol (5 mL) were added. The mixture was heated to 45–50 °C for a further 1 h, with additional ethanol added as needed to dissolve any precipitate. The aqueous layer was saturated with potassium carbonate, and extracted with diethyl ether (3×20 mL). The combined organic extracts were then washed with brine and distilled water, and dried ($MgSO_4$), filtered and the solvents evaporated in vacuo to give the crude product (55% yield by GC analysis using tetradecane as an internal standard). A sample was purified by column chromatography on neutral aluminium oxide (hexane, followed by 2:1 hexane: diethyl ether) to give pure racemic **4** as a viscous yellow oil/semi-solid; R_f=0.54 (1:2 diethyl ether/hexane); ν_{max} (neat/cm^{-1}): 3584 (OH), 1612 (C=C); δ_H (400 MHz; $CDCl_3$): 7.05 (2H, d, J=8.6 Hz, CH), 6.75 (2H, d, J=8.6 Hz, CH), 3.70 (3H, s, CH_3), 2.60 (2H, app t, J=8.9 Hz, CH_2), 2.30–0.90 (12H, m, CH, CH_2), 0.85–0.80 (12H, m, CH_3); δ_C (125 MHz; $CDCl_3$): 158.1 (quat C), 135.8 (quat C), 129.5 (CH), 114.3 (CH), 80.7 (quat C), 55.7 (CH_3), 47.7 (quat C), 44.5 (CH), 38.8 (CH_2), 33.7 (CH), 31.8 (CH_2), 25.7 (CH_2), 21.7 (CH_2), 20.7 (CH_3), 20.5 (CH_3); UV–vis λ_{max}: 228 nm; HRMS; EI m/z: calcd for $C_{21}H_{34}O_2$ 318.2559, found 318.2548 (M^+, 100%).

4.3. General procedure 1. Reaction of imidoyl chloride 1 with mixed trialkylborane 3

An oven dried three-necked flask equipped with a magnetic stirrer bar, stopcock, and septum was set up. Dry potassium cyanide (0.342 g, 5.5 mmol) was ground up prior to use with a pestle and mortar, and transferred into a bent side arm closed at one end, and was fitted to the remaining neck of the flask. The flask was flushed with N_2 for 10 min, and cooled to 0 °C. Mixed trialkylborane **3** (5.0 mmol) was prepared as described above. The side arm was rotated to introduce the cyanide, and the mixture left to stir for an additional hour, whereupon the cyanide dissolved. *N*-Phenylbenzimidoyl chloride (**1**) (1.295 g, 5.5 mmol, in 6 mL of dry diglyme) was added drop-wise to the solution of **3**, and the reaction mixture left to stir overnight at rt. Trifluoroacetic anhydride (7 mL, 50.0 mmol, excess) was added drop-wise, and the mixture heated to 40 °C for 14 h. Excess trifluoroacetic anhydride was evaporated under reduced pressure via the stopcock, and the mixture cooled to 0 °C. The mixture was oxidised as in the synthesis of **4**, and ^1H NMR analysis following oxidation and work-up showed the presence of **5** and **6** in a 62:38 ratio, respectively. The compounds were separated by column chromatography (silica, *n*-hexane then an increasingly more polar hexane–diethyl ether mixture) to give **5** (0.46 g, 40%), as a viscous yellow oil;[25] R_f=0.30 (*n*-hexane); ν_{max} (neat/cm^{-1}): 1708 (C=O), 1612 (C=C); δ_H (400 MHz; $CDCl_3$): 7.10 (2H, d, J=8.6 Hz, CH), 6.83 (2H, d, J=8.6 Hz, CH), 3.77 (3H, s, CH_3), 2.88–2.79 (3H, m, CH_2, CH), 2.77–2.70 (2H, m, CH_2), 1.83–1.47 (8H, m, CH_2); δ_C (125 MHz; $CDCl_3$): 212.4 (quat C), 158.0 (quat C), 133.5 (quat C), 129.3 (CH), 113.9 (CH), 55.3 (CH_3), 51.6 (CH), 43.6 (CH_2), 29.0 (CH_2), 28.8 (CH_2), 26.0 (CH_2); LRMS; EI^+ m/z (%): 232 (M^+, 36%), 163 (54), 121 (100); and **6** (0.33 g, 31%), as a colourless oil; R_f=0.45 (*n*-hexane); ν_{max} (neat/cm^{-1}): 3031 (alkene CH), 1612 (C=C); δ_H (400 MHz; $CDCl_3$): 7.11 (2H, d, J=8.6 Hz, CH), 6.83 (2H, d, J=8.6 Hz, CH), 5.43–5.16 (1H, m, CH), 3.79 (3H, s, CH_3), 2.56 (2H, t, J=7.3 Hz, CH_2), 2.32–2.16 (4H, m, CH_2), 2.11 (2H, t, J=6.8 Hz, CH_2), 1.67–1.52 (4H, m, CH_2); δ_C (125 MHz; $CDCl_3$): 157.7 (quat C), 143.8 (quat C), 134.7 (quat C), 129.3 (CH), 119.2 (CH), 113.7 (CH), 55.2 (CH_3), 35.1 (CH_2), 33.6 (CH_2), 31.8 (CH_2), 28.6 (CH_2), 26.4 (CH_2), 26.3 (CH_2); HRMS; EI–MS m/z: calcd for $C_{15}H_{20}O$ 216.1514, found 216.1513 (M^+, 60%).

4.4. Reaction of imidoyl chlorides 7–9 with the cyanoborate from mixed trialkylborane 3

Imidoyl chlorides **7**–**9** were reacted with the cyanoborate from mixed trialkylborane **3** in a similar manner as for imidoyl chloride **1**, giving various amounts of **5** and **6** by ^1H NMR analysis of the crude product following work-up (Table 1).

4.5. Reaction of imidoyl chloride 7 with the cyanoborate from mixed trialkylborane 3 (excess 1-octene)

General procedure 1 was repeated using imidoyl chloride **7**; however, before addition of the TFAA, 1-octene (2.35 mL, 15.0 mmol) was added, and the reaction mixture was heated to 100 °C for 6 h. TFAA was then added as before, and the procedure was identical thereafter. ^1H NMR analysis of the crude product (1.71 g) showed the presence of excess 1-octene and **5** (in a 79:21 ratio, respectively, corresponding to a 61% yield of **5**, by relative integrations in the ^1H NMR spectrum), but no trace of **6**, *tert*-alcohol arising from *n*-octyl group migration, thexanol or 1-octanol was present.

4.6. Reaction of imidoyl chloride 7 with the cyanoborate from mixed trialkylborane 3 (acetaldehyde)

General procedure 1 using imidoyl chloride **7** was repeated to the point until the reaction with imidoyl chloride **7** was complete. Acetaldehyde (0.56 mL, 10.0 mmol) was added drop-wise by syringe, and the solution left to stir at rt for 36 h. Excess acetaldehyde was removed under a fast stream of N_2, and a solution of *n*-BuLi in hexanes (1.45 M, 3.45 mL, 5.0 mmol) was added drop-wise with vigorous stirring at −78 °C. The addition of TFAA and subsequent

steps were then carried out as in general procedure 1. Analysis of the crude product by ^{1}H NMR spectroscopy showed only ketone **5**, with no presence of alkene **6** or *tert*-alcohol arising from migration of the *n*-butyl group.

4.7. Substrate scope reaction (i)

An oven dried three-necked flask equipped with a magnetic stirrer bar, stopcock, and septum was set up. Dry potassium cyanide (0.342 g, 5.5 mmol) was ground up prior to use with a pestle and mortar, and transferred into a bent side arm closed at one end, and was fitted to the remaining neck of the flask. The flask was flushed with N_2 for 10 min, and cooled to 0 °C. Borane-SMe_2 complex (10.0 M, 0.5 mL, 5.0 mmol) was added, followed by the drop-wise addition of 1-octene (2.33 mL, 15.0 mmol). Following completion of addition, the solution was warmed to rt and was left to stir for 3 h. Imidoyl chloride **7** was introduced as a solution in dry diglyme (1.43 g in 6 mL); the procedure thereafter was identical to general procedure 1. The crude product was purified by column chromatography on neutral alumina (hexane, followed by 3:1 hexane: diethyl ether) to give di-*n*-octyl ketone[15] (**13a**, 0.22 g, 17%) as colourless sheets; mp 49–50 °C (lit. 48–48.5 °C[15]); R_f=0.8 (4:1 hexane/diethyl ether); ν_{max} (neat/cm^{-1}): 1706 (C=O); δ_H (400 MHz; $CDCl_3$): 2.37 (4H, t, J=7.5 Hz, CH_2C=O), 1.59–1.48 (4H, m, CH_2), 1.32–1.16 (20H, m, CH_2), 0.87 (6H, t, J=6.8 Hz, CH_3); δ_C (125 MHz; $CDCl_3$): 211.8 (quat C, C=O), 42.8 (CH_2, CH_2C=O), 31.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 23.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3); LR CIMS m/z (%): 296 (M^+ +CH_3CN, 100%); and tri-*n*-octylmethanol (**12a**, 0.90 g, 49%),[11] as a colourless oil; R_f=0.57 (1:1 diethyl ether/hexane); ν_{max} (neat/cm^{-1}): 3390 (OH); δ_H (400 MHz; $CDCl_3$): 5.75 (1H, s, OH), 1.40–1.20 (42H, m, CH_2), 0.80 (9H, t, J=6.0, CH_3); δ_C (125 MHz; $CDCl_3$): 74.4 (quat C, COH), 39.8 (CH_2), 32.8 (CH_2), 31.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 23.9 (CH_2), 23.1 (CH_2), 14.2 (CH_3); LRMS; EI m/z (%): 350 (M^+–OH, 62%), 255 (100), 237 (41), 154 (94), 139 (100), 126 (53), 111 (96), 97 (100), 69 (98).

4.8. Substrate scope reaction (ii)

The procedure for substrate scope reaction (i) was repeated using tricyclopentylcyanoborate (5.0 mmol). Separation of the components by column chromatography on neutral alumina (4:1 hexane: diethyl ether) gave dicyclopentyl ketone[15] (**13b**, 0.249 g, 29%, contaminated with 4% cyclopentylmethylenecyclopentane) as a colourless oil; R_f=0.70 (3:1 hexane/diethyl ether); ν_{max} (neat/cm^{-1}): 1705 (C=O); δ_H (400 MHz; $CDCl_3$): 2.96–2.85 (2H, m, CH), 1.81–1.41 (16H, m, CH_2); δ_C (125 MHz; $CDCl_3$): 216.0 (quat C, C=O), 50.7 (CH), 26.1 (CH_2), 25.2 (CH_2); LRMS; EI$^+$ m/z (%): 166 (M^+, 24%), 97 (98), 69 (100); and tricyclopentylmethanol (**12b**, 0.41 g, 39%),[26] as a light yellow oil; R_f=0.48 (3:1 hexane/diethyl ether); ν_{max} (neat/cm^{-1}): 3522 (OH); δ_H (400 MHz; $CDCl_3$): 2.13–1.97 (3H, m, CH), 1.64–1.25 (24H, m, CH_2); δ_C (125 MHz; $CDCl_3$): 77.6 (quat C, COH), 47.9 (CH), 27.9 (CH_2), 25.2 (CH_2); LR EIMS m/z (%): 218 (M^+–H_2O, 5%), 149 (100), 107 (27), 81 (82), 67 (73)

4.9. Substrate scope reaction (iii)

2,3-Dimethyl-2-butene (0.63 g, 7.5 mmol) was added drop-wise to neat borane-dimethyl sulfide (10.0 M, 5.0 mmol) at 0 °C, and then the reaction mixture was left to stir for 2 h. Dry THF (5 mL) was added, followed by the drop-wise addition of 1-octene (1.57 mL, 10 mmol). The reaction mixture was left to stir for 2 h at 0 °C. The procedure thereafter was the same as substrate scope reaction (i) to give the crude products, which were separated by column chromatography on neutral alumina (hexane, followed by increasingly polar diethyl ether/hexane eluents) to give heptadec-8-ene as a mixture of isomers (*Z*)/(*E*): 88:12 by relative integrations in the ^{1}H NMR spectrum (**14c**, 0.12 g, 10%) as a colourless oil; R_f=0.91 (4:1 hexane/ethyl acetate); ν_{max} (neat/cm^{-1}): 3004 (alkene CH); (NMR spectra were consistent with those reported for (*Z*)-heptadec-8-ene);[27] LRMS; EI$^+$ m/z (%): 238 (M^+, 45%), 119 (100), 111 (21), 97 (44), 84 (100), 71 (100), 57 (100); di-*n*-octyl ketone, (**13a/c**, 0.23 g, 18%), R_f=0.8 (4:1 hexane/diethyl ether); and di-*n*-octylthexylmethanol[11] (**12c**, 0.26 g, 15%) as a yellow oil; R_f=0.63 (4:1 hexane/ethyl acetate); ν_{max} (neat/cm^{-1}): 3533 (OH); δ_H (400 MHz; $CDCl_3$): 1.80 (1H, app sep, J=6.8 Hz, CH), 1.58–1.42 (4H, m, CH_2), 1.30–1.10 (24H, m, CH_2), 0.85 (6H, d, J=6.8 Hz, CH_3), 0.80 (6H, t, J=6.7 Hz, CH_3), 0.75 (6H s, CH_3); δ_C (125 MHz; $CDCl_3$): 79.6 (quat C, COH), 43.7 (quat C), 36.4 (CH_2), 32.8 (CH), 31.9 (CH_2), 30.8 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 25.0 (CH_2), 22.7 (CH_2), 20.3 (CH_3), 20.1 (CH_3), 14.0 (CH_3); HR EI+-MS m/z (%): calculated for $C_{23}H_{47}$ 323.3678, found 323.3663 (M^+–OH, 28%).

4.10. Substrate scope reaction (iv)

The procedure for substrate scope reaction (i) was repeated using mixed trialkylborane **3** (see general procedure 1) to give the crude products, which were separated by column chromatography on silica (hexane) to give **5** (0.058 g, 5% yield) and **6** (0.59 g, 55% yield).

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