Homolytic Reactions of Ligated Boranes. Part 9.[1] Overall Addition of Alkanes to Electron-deficient Alkenes by a Radical Chain Mechanism

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Methyl bromoacetate and ethyl 2-bromopropanoate are reduced by $Bu^n_3P{\rightarrow}BH_3$ or $Bu^n_3P{\rightarrow}BH_2Ph$ to methyl acetate and ethyl propanoate, respectively, in chlorobenzene at 80—110 °C in the presence of dibenzoyl peroxide or t-butyl perbenzoate. Amine complexes of borane or phenylborane are much less effective reducing agents. The reductions may also be initiated photochemically and are inhibited by a phenolic radical scavenger. A homolytic chain mechanism is proposed in which the phosphine–boryl radical abstracts halogen from the bromo ester and is subsequently regenerated by reaction of an α-(alkoxycarbonyl)alkyl radical with the phosphine–borane. The latter propagation step, together with halogen abstraction from RI and addition of the derived alkyl radical to the C=C bond, is also involved in the chain reaction between $Bu^n_3P{\rightarrow}BH_2Ph$, an alkyl iodide, and ethyl acrylate according to equation (A); $Bu^n_3P{\rightarrow}BH_3$ reacts similarly but gives lower yields of ester. Reaction (A) proceeds smoothly at 110 °C

$$Bu^n_3P{\rightarrow}BH_2Ph + RI + CH_2{=}CHCO_2Et \longrightarrow RCH_2CH_2CO_2Et + Bu^n_3P{\rightarrow}BHIPh \qquad (A)$$

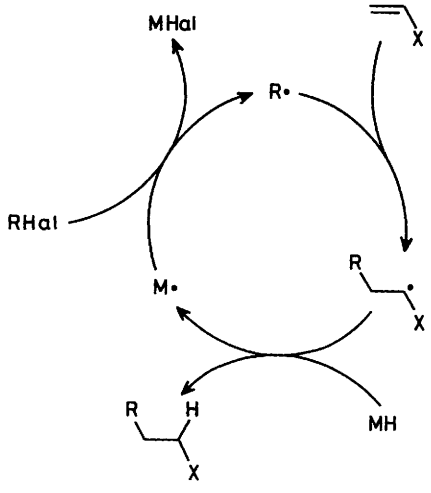
when initiated by t-butyl perbenzoate and moderate yields of isolated esters were obtained from n-butyl iodide, cyclohexyl iodide, and 3β-iodocholest-5-ene. This last iodide gives an epimeric mixture of 3α- and 3β-esters in total isolated yield of *ca.* 50%. Similar addition reactions take place between $Bu^n_3P{\rightarrow}BH_2Ph$, Bu^nI, and diethyl vinylphosphonate or phenyl vinyl sulphone. It is concluded that $Bu^n_3P{\rightarrow}BH_3$ and particularly $Bu^n_3P{\rightarrow}BH_2Ph$ offer promise as alternatives to tin, mercury, and germanium hydrides in radical chain reactions of synthetic value.

In recent years considerable success has been achieved in the design of synthetic pathways which involve free radical chain reactions, and such methods often offer significant advantages over more conventional heterolytic routes.[2] We have previously investigated the structures and elementary reactions of a variety of ligated boryl radicals $L{\rightarrow}\dot{B}H_2$ in fluid solution, using e.s.r. spectroscopy as the principal experimental tool.[3–9] As a development of this work, we are now attempting to devise synthetically useful procedures which incorporate these elementary homolytic reactions as key steps.

One transformation which offers considerable promise for C–C bond formation [2] is the overall addition of an alkane across a suitably activated C=C bond *via* the radical chain sequence shown in Scheme 1, in which the hydrogen atom donor MH is usually a trialkylstannane.[10–14] Giese and his co-workers have developed a closely related synthetic pathway (see Scheme 2) in which an alkylmercury hydride, generated *in situ* from $NaBH_4$ and RHgHal, provides both the source of alkyl radicals R• and the hydrogen atom donor.[10] However, one limitation of these methods can be that R• is trapped by the metal hydride to give alkane rather than undergoing addition to the alkene. Some attempts have been made to find suitable substitutes for R_3SnH in Scheme 1 which are less effective hydrogen donors to R• but which still provide a radical M• capable of propagating the chain by reaction with an alkyl halide. Following initial kinetic studies,[15] trialkylgermanes have found some application as tin hydride replacements [16,17] and very recently a similar role has been suggested for pentamethyldisilane.[18] However, these latter reagents are relatively expensive and more readily available alternatives to tin hydrides are desirable.

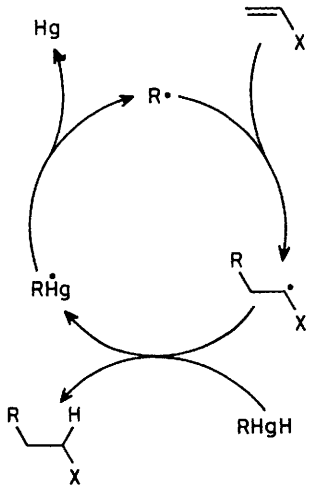
Using e.s.r. spectroscopy, we have shown that the ligated boryl radicals $L{\rightarrow}\dot{B}H_2$ (L = H^-, CN^-, R_3N, R_3P, or R_2S) rapidly abstract halogen from simple alkyl bromides [equation (1; X = Br)]; alkyl chlorides react less rapidly whilst iodides

$$L{\rightarrow}\dot{B}H_2 + R{-}X \longrightarrow L{\rightarrow}BH_2X + R^{\bullet} \qquad (1)$$



Scheme 1.

appear to be most reactive.[3–9] However, hydrogen atom abstraction from $L{\rightarrow}BH_3$ by simple alkyl radicals is very slow, in part because the B–H bond is strong [1,3] but also because polar effects act to disfavour abstraction of electron-rich hydrogen by a nucleophilic radical. An electrophilic carbon radical (such as would be formed by addition of an alkyl radical to an electron-deficient alkene) would be expected to react more rapidly, especially with a sulphide– or phosphine–borane in which the B–H bond appears to be significantly weaker than that in an amine–borane.[3] The aim of the present work was, therefore, to establish the viability of radical chain reactions based on Scheme 1 when MH is a ligated borane. Borane complexes with a wide variety of Lewis bases are readily



Scheme 2.

accessible compounds,[19] many of which are commercially available.

Results and Discussion

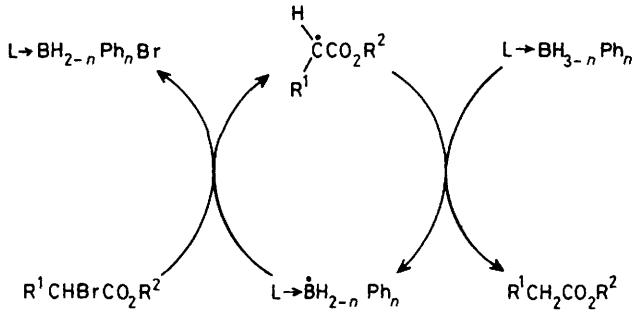
At the outset it was recognised that the major obstacle to maintaining a chain reaction of reasonable length based on Scheme 1 would be the need to discover a ligated borane $L{\rightarrow}BH_3$ of sufficient reactivity towards hydrogen atom abstraction. Ligated phenylboranes $L{\rightarrow}BH_2Ph$ and $L{\rightarrow}BHPh_2$ were also investigated since, by analogy with the stabilising effect of a phenyl substituent when attached to a carbon radical centre, we considered that hydrogen abstraction from these complexes would be more favourable thermodynamically than from $L{\rightarrow}BH_3$. Abstraction should take place most readily when the substituent X [equation (2)] is inductively electron-

$$RCH_2\dot{C}HX + L{\rightarrow}BH_{3-n}Ph_n \longrightarrow RCH_2CH_2X + L{\rightarrow}\dot{B}H_{2-n}Ph_n \quad (2)$$

withdrawing (making $RCH_2\dot{C}HX$ electrophilic), provided that X is not radical-stabilising to the extent of making reaction (2) thermodynamically unfavourable. Electron-deficient alkenes $CH_2{=}CHX$ in which X is *e.g.* $C(O)OR$, $S(O_2)R$, $P(O)(OR)_2$, or $^+PR_3$ would thus be suitable candidates and we chose ethyl acrylate* as the alkene for most of these pilot investigations. Alkyl radicals add rapidly to such electron-deficient alkenes and the ultimate products are worthwhile synthetic targets.

In order to screen a variety of ligated boranes as potential hydrogen atom donors towards α-(alkoxycarbonyl)alkyl radicals, ^{1}H n.m.r. spectroscopy was used to follow a series of small-scale reductions of α-bromo esters. As expected, these reactions proceeded by a radical chain mechanism, presumably that shown in Scheme 3.

Equimolar quantities of methyl bromoacetate and ligated borane (each finally *ca.* 1.2M) were caused to react in chlorobenzene at 80 °C in the presence of dibenzoyl peroxide (2 mol %) as initiator; the samples also contained 1,3,5-tri-t-butylbenzene or methyl phenyl sulphone as an internal stan-



Scheme 3.

dard to enable product yields to be estimated by integration of spectra. With $Me_3N{\rightarrow}BH_3$, $Me_3N{\rightarrow}BH_2Ph$, or pyridine→BH_2Ph, reduction to methyl acetate had taken place only to a very small extent after 1 h, whereas with $Bu^n{}_3P{\rightarrow}BH_3$ conversion of bromoacetate into acetate was *ca.* 35% complete after the same reaction time. With $Bu^n{}_3P{\rightarrow}BH_3$ in the absence of initiator, no reaction was detectable under the same conditions. At 90 °C reduction was complete after 20 min in the presence of dibenzoyl peroxide, whereas no reaction occurred in its absence. When the reaction was initiated photochemically at 85 °C in the presence of di-t-butyl peroxide (10 mol %), by irradiation through quartz with unfiltered light from a 250 W high-pressure mercury discharge lamp, reduction to methyl acetate was complete after 20 min.

Analogous reduction of ethyl 2-bromopropanoate will proceed *via* $MeCHCO_2Et$, which is a more appropriate model for the radical RCH_2CHCO_2Et involved in the acrylate addition reactions (Scheme 1). As expected if hydrogen abstraction from the ligated borane is rate-limiting, ethyl 2-bromopropanoate was reduced more slowly than the bromoacetate. Reactions were carried out in chlorobenzene at 110 °C under nitrogen using t-butyl perbenzoate (10 mol % based on bromo ester) and two mol equiv. of the phosphine–borane. Yields of ethyl propanoate were determined by g.l.c. analysis using *p*-dichlorobenzene as internal standard; most experiments were run in duplicate and the results are gathered in Table 1.

On the basis of these trials, it was concluded that the tributylphosphine complexes of borane and phenylborane offered most promise as reducing agents; the amine–boranes are less effective presumably because of the greater strength of the B–H bonds in these complexes.[1,3] The phosphine complex of diphenylborane is appreciably less effective than $Bu^n{}_3P{\rightarrow}BH_2Ph$, even though the B–H bond is probably weaker in the former compound. There is only one abstractable hydrogen atom in $Bu^n{}_3P{\rightarrow}BHPh_2$ and this is more sterically shielded than the two hydrogen atoms available in $Bu^n{}_3P{\rightarrow}BH_2Ph$; a switch to rate-determining bromine atom abstraction for reduction by the former is also feasible.

Next a series of reactions of an alkyl halide with ethyl acrylate and a ligated borane in chlorobenzene were carried out and yields of ester products [equation (3)] were estimated by g.l.c.

$$RHal + L{\rightarrow}BH_{3-n}Ph_n + CH_2{=}CHCO_2Et \longrightarrow RCH_2CH_2CO_2Et + L{\rightarrow}BH_{2-n}Ph_nHal \quad (3)$$
(1)

analysis. Although reaction conditions were not exhaustively optimised, the following general procedure was eventually adopted. Under an atmosphere of nitrogen or argon, ethyl acrylate in chlorobenzene was added dropwise during *ca.* 15 min to a heated, stirred solution of the alkyl halide (usually the iodide), ligated borane, initiator, and internal standard (1,2,4-trichlorobenzene) in the same solvent. The molar proportions of acrylate, halide, ligated borane, and initiator were usually

* The radical-stabilising effect of an alkoxycarbonyl group is not known with certainty. E.s.r. studies show that substantial barriers (*ca.* 40 kJ mol^{-1}) exist to internal rotation about the $^•C$–C(O) bond in α-(alkoxycarbonyl)alkyl radicals, similar in magnitude to those for the corresponding rotation in α-(alkylcarbonyl)alkyl radicals.[20] However, thermochemical results suggest that the values of $DH°$(C–H) for acetone and for ethane are very similar.[21]

Table 1. Reduction of ethyl 2-bromopropanoate to ethyl propanoate by phosphine–boranes in chlorobenzene at 110 °C[a]

Phosphine–borane	Reagents present (mmol)			Yield of ethyl propanoate (% based on bromo ester)
	Phosphine–borane	Bromo ester	t-Butyl perbenzoate	
$Bu^n_3P\rightarrow BH_3$	5.78	2.89	0.29	90
$Bu^n_3P\rightarrow BH_2Ph$	5.78	2.89	0.29	63
$Bu^n_3P\rightarrow BHPh_2$	5.83	2.91	0.29	12
$Bu^n_3P\rightarrow BH_3$	5.78	2.89	*b*	<0.05[c]

[a] All reactions were carried out in chlorobenzene (2.0 cm^3); after being heated under nitrogen for 1 h the mixtures were analysed by g.l.c. using *p*-dichlorobenzene (*ca.* 1.4 mmol) as internal standard. [b] Reaction mixture contained 0.05 mmol of 4,4′-methylenebis-(2,6-di-t-butylphenol) as inhibitor in place of the initiator. [c] Undetectable by g.l.c.

Table 2. Reactions of ethyl acrylate with alkyl halide and ligated borane in the presence of t-butyl perbenzoate in chlorobenzene at 110 °C[a]

Entry	Alkyl halide	Ligated borane	Ester produced	Ester yield (%)
1	Bu^nI	$Bu^n_3P\rightarrow BH_3$	Ethyl heptanoate	27
2		$Bu^n_3P\rightarrow BH_2Ph$		59
3		$Bu^n_3P\rightarrow BH_2Ph$		50[b]
4		$Bu^n_3P\rightarrow BH_2Ph$		40[c]
5		$Bu^n_3P\rightarrow BH_2Ph$		29[d]
6		$Bu^n_3P\rightarrow BH_2Ph$		<0.05[e,f]
7		$Bu^n_3P\rightarrow BHPh_2$		5
8		$Me_3N\rightarrow BH_2Ph$		0.1
9		$Pyr\rightarrow BH_2Ph$		0.1
10		$Me_3N\rightarrow BH_3$		<0.05[f]
11		$Pyr\rightarrow BH_3$		<0.05[f]
12	Bu^nBr	$Bu^n_3P\rightarrow BH_2Ph$		<0.05[f]
13	cyclo-$C_6H_{11}I$	$Bu^n_3P\rightarrow BH_3$	Ethyl 3-cyclohexyl-propanoate	25[g]
14		$Bu^n_3P\rightarrow BH_2Ph$		44[g]
15		$Bu^n_3P\rightarrow BH_2Ph$		34[c,g]
16	$PhCH_2I$	$Bu^n_3P\rightarrow BH_2Ph$	Ethyl 4-phenyl-butanoate	10
17	$PhCH_2Br$	$Bu^n_3P\rightarrow BH_2Ph$		4

[a] Unless otherwise noted, ethyl acrylate (6.88 mmol) in chlorobenzene (1.0 cm^3) was added to the alkyl halide (0.87 mmol), ligated borane (6.88 mmol), t-butyl perbenzoate (0.17 mmol, 20 mol %), and 1,2,4-trichlorobenzene (*ca.* 0.8 mmol) in chlorobenzene (1.7 cm^3) during 15 min. The reaction mixture was heated for a further 1 h before analysis by g.l.c. Most yields are averages from at least two experiments. [b] t-Butyl perbenzoate (10 mol %) initiator. [c] t-Butyl peracetate (20 mol %) initiator. [d] t-Butyl peracetate (10 mol %) initiator. [e] No initiator present: 4,4′-methylenebis-(2,6-di-t-butylphenol) (2 mol % based on alkyl halide) present as inhibitor. [f] Ethyl heptanoate was undetectable. [g] Reaction mixture heated for 2 h after addition of the acrylate.

8:1:8:0.2, respectively, although in later experiments it was found that use of 4 mol equiv. of acrylate resulted in no decrease in ester yield (based on alkyl halide).* After being stirred for a further 1—2 h at the reaction temperature (generally 110 °C), the mixture was subjected to g.l.c. analysis; the detector response was calibrated using authentic ester products and the results are presented in Table 2. In experiments with $Bu^n_3P\rightarrow BH_2Ph$, all the n-butyl iodide had been consumed after heating for 1 h and all the cyclohexyl iodide had reacted after 2 h. The alkyl iodides were consumed slowly in the absence of acrylate under otherwise identical conditions. For example, *ca.* 65% of the n-butyl iodide present originally remained after heating for 1 h at 110 °C with $Bu^n_3P\rightarrow BH_2Ph$ and t-butyl perbenzoate in chlorobenzene.

Although yields of the esters (**1**) are not as high as those obtained[10–12] when a trialkylstannane is used as hydrogen atom donor, the present method appears to be of value for the synthesis of (**1**) from ethyl acrylate, $Bu^n_3P\rightarrow BH_2Ph$, and a primary or secondary alkyl iodide. The reactions are radical chain processes which may be initiated by thermal decomposition of t-butyl perbenzoate or t-butyl peracetate;† reaction is totally inhibited in the presence of 4,4′-methylenebis-(2,6-di-t-butylphenol) (entry 6). Increasing the reaction temperature to 120 °C resulted in a slight decrease in yields. No ethyl heptanoate is formed when n-butyl iodide is replaced by the bromide (entry 12), presumably because halogen abstraction by $Bu^n_3P\rightarrow\dot{B}HPh$ is now too slow to propagate the chain effectively. The system is obviously finely balanced, since the yield of ethyl heptanoate increases in the order $Bu^n_3P\rightarrow BHPh_2 < Bu^n_3P\rightarrow BH_3 < Bu^n_3P\rightarrow BH_2Ph$ (entries 1, 2, and 7) probably in parallel with the molar rate coefficients for hydrogen atom transfer from the phosphine–boranes to the α-(ethoxycarbonyl)alkyl radical.

The proposed chain mechanism for the reaction between an alkyl iodide, ethyl acrylate, and tributylphosphine–phenylborane is shown in Scheme 4 (X = CO_2Et). Phenyl or methyl

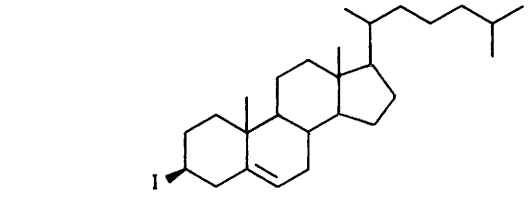
$$Bu^tOCO_2Ph \xrightarrow{heat} Bu^tO^\bullet + CO_2 + Ph^\bullet$$
$$Bu^tO^\bullet + Bu^n_3P\rightarrow BH_2Ph \longrightarrow Bu^tOH + Bu^n_3P\rightarrow\dot{B}HPh$$
} initiation

$$Bu^n_3P\rightarrow\dot{B}HPh + RI \longrightarrow Bu^n_3P\rightarrow BHIPh + R^\bullet$$
$$R^\bullet + CH_2{=}CHX \longrightarrow RCH_2\text{-}\dot{C}HX$$
$$RCH_2\text{-}\dot{C}HX + Bu^n_3P\rightarrow BH_2Ph \longrightarrow RCH_2\text{-}CH_2X + Bu^n_3P\rightarrow\dot{B}HPh$$
} propagation

Scheme 4.

* With 2 mol equiv. of acrylate the ester yield was substantially reduced (to *ca.* 35%).

† Approximate half-lives at 110 °C of t-butyl perbenzoate and t-butyl peracetate are 5.4 and 4.1 h, respectively.[22]



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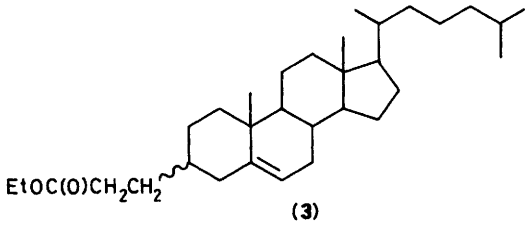

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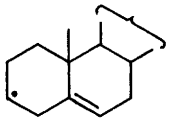

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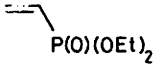

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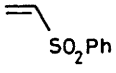

(6)

radicals from the decomposition of t-butyl perbenzoate or peracetate, respectively, will also initiate the chain sequence by reaction with one or more of the starting materials. Various termination steps involving radical–radical reactions are feasible, but without more detailed kinetic studies it is not possible to choose unequivocally amongst them.

Product Isolation.—The esters (**1**) were separated by spinning-plate chromatography on silica using light petroleum–dichloromethane as eluant. Preparative runs were carried out under the optimum conditions of entries 2 and 14 in Table 2 with butyl and cyclohexyl iodides, respectively; the internal standard was omitted from these reaction mixtures. Isolated yields of ethyl heptanoate and ethyl 3-cyclohexylpropanoate were typically *ca.* 40 and *ca.* 30%, respectively, from reactions carried out with 1—2 mmol of alkyl halide. The products showed ^{1}H n.m.r. spectra essentially indistinguishable from those of the authentic esters; analytically pure products could be obtained by h.p.l.c. using dichloromethane as eluant.

Although optimum conversions of alkyl halide into ester were obtained with a relatively large excess of $Bu^n_3P{\rightarrow}BH_2Ph$, the phosphine–borane could be recovered in a pure state and used in subsequent reactions.

In order to establish further the synthetic utility of reaction (3) we have applied it to 3β-iodocholest-5-ene (**2**) on the 1 mmol scale, under the conditions used for cyclohexyl iodide (Table 2, entry 14). The ester product (**3**) was isolated by spinning-plate chromatography on silica as a mixture of the 3α- and 3β-epimers, which could be separated by h.p.l.c. to yield analytically pure esters. The epimers were tentatively identified from their ^{1}H n.m.r. spectra on the following empirical basis. In $CDCl_3$ as solvent the vinylic proton 6-H appears at the same chemical shift (δ 5.43)* for both 3α- and 3β-hydroxycholest-5-ene.[23] However, when the unsaturated benzoyloxy group is present at C-3, although δ(6-H) for the β-epimer remains very similar (5.41), that for the α-epimer (in which the unsaturated group is in the axial position and thus could influence 6-H) is reduced to 5.26.[23] For (**3**) the less abundant epimer showed δ(6-H) 5.29, whilst in the major product the 6-H signal was shifted upfield to 5.25.† We therefore propose that the 3α-ester is the major product from our reaction; on this basis, integration of the vinylic resonances gave the 3α:3β ratio as 1.73:1.

Formation of an epimeric mixture is consistent with the proposed mechanism, since the cholest-5-en-3-yl radical (**4**) could undergo either axial or equatorial attack by ethyl acrylate at C-3 to give the α- or β-epimer, respectively. Predominant axial attack would be in accord with the results of Jensen *et al.*,[24] who found that the 4-t-butylcyclohexyl radical reacts with sulphuryl chloride to give a 2.3:1 mixture of *cis*- and *trans*-1-chloro-4-t-butylcyclohexane by preferential chlorine atom entry into the axial site. Similarly, reaction of a peroxycarboxylic acid with the 4-t-butylcyclohexyl radical results in introduction of an OH group predominantly into an axial site (*cis*:*trans* ratio 4:1).[25]

Other Acceptor Alkenes.—We have also briefly examined the radical chain reactions of n-butyl iodide with $Bu^n_3P{\rightarrow}BH_2Ph$ and diethyl vinylphosphonate (**5**) or phenyl vinyl sulphone (**6**); both (**5**) and (**6**) are known to undergo alkyl radical addition rapidly on account of the electron-withdrawing substituents attached to the double bonds.[26,27] The stabilisation imparted to an alkyl radical by attachment of an α-phosphonyl group is evidently quite small[28] and for an α-sulphonyl group it is probably even smaller,[29] whilst these substituents will render the adduct radicals strongly electrophilic and thus facilitate hydrogen atom abstraction from the phosphine–borane.

Diethyl vinylphosphonate (*ca.* 4 mmol) in chlorobenzene was added to a solution containing butyl iodide, $Bu^n_3P{\rightarrow}BH_2Ph$, and t-butyl perbenzoate (final molar proportions 4:1:8:0.2) in the same solvent at 110 °C. After a further 1 h at 110 °C, g.l.c. analysis of the mixture showed the absence of n-butyl iodide and the presence of diethyl n-hexylphosphonate (*ca.* 25% yield based on butyl iodide) which was isolated in *ca.* 20% yield by spinning-plate chromatography followed by final purification using h.p.l.c. From analogous reactions in which the vinylphosphonate was replaced by phenyl vinyl sulphone, a *ca.* 40% yield of n-hexyl phenyl sulphone was isolated in a similar manner.

Attempted Autoxidation of Ligated Boranes.—In view of the potential use of ligated boranes in synthesis, we briefly investigated the stability of these compounds towards molecular oxygen. A likely mode of reaction would be to give, at least as an initial product, the corresponding hydroperoxide *via* a radical chain pathway as shown in equations (4) and (5).

$$L{\rightarrow}\dot{B}H_{2-n}Ph_n + O_2 \longrightarrow L{\rightarrow}BH_{2-n}Ph_nOO^{\bullet} \quad (4)$$

$$L{\rightarrow}BH_{2-n}Ph_nOO^{\bullet} + L{\rightarrow}BH_{3-n}Ph_n \longrightarrow L{\rightarrow}BH_{2-n}Ph_nOOH + L{\rightarrow}\dot{B}H_{2-n}Ph_n \quad (5)$$

However, when solutions in chlorobenzene containing $Me_3N{\rightarrow}BH_3$, $Bu^n_3P{\rightarrow}BH_3$, or $Bu^n_3P{\rightarrow}BH_2Ph$ (each *ca.* 1M) and di-t-butyl hyponitrite[30] initiator (2 mol %) were stirred at 45 °C under an atmosphere of pure oxygen, no gas absorption was noted during 1.5 h. Similarly no oxygen was absorbed when an equimolar amount of t-butyl bromide was present along with the ligated borane, under which conditions Bu^tOOH and

* We found δ 5.36 for the 3β-epimer.

† Differences in the n.m.r. spectra of the two epimers were accentuated in C_6D_6 as solvent; δ(6-H) was 5.27 and 5.35 for the major and minor components, respectively.

$L \rightarrow BH_{2-n}Ph_nBr$ might be formed by a radical chain process propagated by $Bu^tO^{\bullet}$, $Bu^{t\bullet}$, and the ligated boryl radical, in the event that the latter were to react faster with the alkyl bromide than with O_2. We conclude that peroxyl radicals must abstract hydrogen from the ligated boranes very slowly at 45 °C.

We have calculated the B–H bond strengths in $H_3N \rightarrow BH_3$ and $H_3P \rightarrow BH_3$ to be 416 and 374 kJ mol^{-1}, respectively,[3] although our more recent estimates based on the isodesmic reactions of ethyl radicals with these ligated boranes give values which are 15 kJ mol^{-1} larger.[1] Phenyl substitution at boron should reduce $DH°$(B–H) appreciably (the methyl C–H bond in toluene is *ca.* 43 kJ mol^{-1} weaker than that in ethane[31]). Since $DH°$(ROO–H) is *ca.* 370 kJ mol^{-1},[32] it appears that hydrogen atom abstraction from $Me_3N \rightarrow BH_3$ by a peroxyl radical will be strongly endothermic, accounting for its slowness. However, abstraction from $Bu^n{}_3P \rightarrow BH_2Ph$ could well be exothermic and it is somewhat surprising that this compound does not undergo autoxidation at 45 °C.

Conclusion.—On the basis of the foregoing results, it is evident that $Bu^n{}_3P \rightarrow BH_2Ph$ offers a viable alternative to the trialkylstannanes for effecting overall addition of alkanes to electron-deficient alkenes according to Scheme 4. Tri-n-butylphosphine–borane and –phenylborane transfer hydrogen only very slowly to simple alkyl radicals, but react more rapidly when an electron-withdrawing substituent is attached to the radical centre. This discrimination, which arises because of polar effects, is not shown to the same extent by trialkylstannanes, which transfer hydrogen more rapidly and less selectively.

In general, it seems likely that ligated boranes, which are readily available and easily handled, will find increasing applications in homolytic organic reactions of synthetic importance.

Experimental

N.m.r. spectra were recorded with Varian XL-200 or VXR-400 instruments operating (for ^1H) at 200 or 400 MHz, respectively; chemical shifts are quoted relative to tetramethylsilane internal standard (^1H) or aqueous 85% H_3PO_4 (^{31}P) or $Et_2O \rightarrow BF_3$ (^{11}B) external standards. I.r. spectra were recorded with a Perkin-Elmer 983 instrument and mass spectra were obtained at 70 eV with a VG 7070H spectrometer interfaced to a Finnigan MAT INCOS data system.

G.l.c. analyses were carried out with a Pye-Unicam 304 chromatograph equipped with a flame ionisation detector and a S.C.O.T. capillary column (55 m × 0.5 mm i.d.) containing methylsilicone oil (SP2100) as stationary phase; the carrier gas was nitrogen. For preparative separations by h.p.l.c. a 120 cm × 12.7 mm i.d. column packed with silica gel (Merck 9385) was employed. Spinning-plate chromatography was carried out with a model 7924 Chromatotron (Harrison Research, Palo Alto, California); the stationary phase was a 4 mm thick layer of silica gel (Merck 11678) with the eluant light petroleum (b.p. 40—60 °C)–dichloromethane (1:1 to 3:1 v/v) or neat dichloromethane, depending on the behaviour of the desired product. Separations were monitored by t.l.c.

Materials.—Most of the compounds used in this work were obtained commercially and all were purified before use by either distillation or recrystallisation, except t-butyl perbenzoate (B.D.H.) and t-butyl peracetate (Pfaltz and Bauer) which were used as received.

Benzyl iodide was prepared from the alcohol following the procedure reported for 4-methylbenzyl iodide;[33] it was recrystallised from methanol (m.p. 24—25 °C; lit.,[34] 24.5 °C). Ethyl 4-phenylbutanoate was prepared by esterification of the acid (Aldrich) with ethanol using sulphuric acid catalyst (b.p. 76—78 °C at 0.1 Torr; lit.,[34] 130—131 °C at 10 Torr). Diethyl n-hexylphosphonate was prepared from the sodium salt of diethyl phosphite and hexyl bromide according to the method of Kosolapoff[35] (b.p. 115—116 °C at 5 Torr; lit.,[35] 140—144 °C at 17 Torr). n-Hexyl phenyl sulphone[36] was prepared[36b] by refluxing hexyl bromide and sodium benzenesulphinate in ethanol for 6 h (b.p. 125—126 °C at 0.1 Torr; lit.,[36a] 160—161 °C at 2 Torr).

The trimethylamine and pyridine complexes of phenylborane were prepared as described by Hawthorne,[37] by reduction of diethyl phenylboronate in the presence of the appropriate amine.

Tri-n-butylphosphine–phenylborane.[38] Diethyl phenylboronate (44.1 g, 0.248 mol) in dry ether (140 cm^3) was added dropwise under argon to a stirred solution of lithium aluminium hydride (8.4 g, 0.221 mol) and tri-n-butylphosphine (50.2 g, 0.248 mol) in ether (500 cm^3) maintained at −30 to −40 °C. After the addition, the mixture was allowed to warm to room temperature and stirred for a further 1 h. Next day the mixture was cooled in an ice-bath and stirred during careful addition of water (16.5 cm^3). The resulting suspension was filtered, the filtrate was dried ($MgSO_4$), and the ether was evaporated off under reduced pressure to yield the crude product, which was recrystallised from ether–pentane at −78 °C to give the phosphine–borane (36.0 g, 50%), m.p. 44—46 °C (lit.,[38] 44—47 °C); δ(^{31}P) (C_6D_6; proton-decoupled) +7.0 (br q, J_{BP} *ca.* 40 Hz); δ(^{11}B) (C_6D_6) −26.7 (br s) (the peak narrowed when proton decoupling was applied, although phosphorus splitting remained unresolved).

Tri-n-butylphosphine–diphenylborane. Phosphine complexes of diarylboranes appear not to have been isolated previously.[39] The method followed was similar to that described by Jacob[40] for the preparation of pyridine–diphenylborane. A solution of aluminium hydride was prepared by dropwise addition of 99% sulphuric acid (0.83 g, 8.38 mmol) to a stirred solution of lithium aluminium hydride (0.63 g, 16.6 mmol) in dry tetrahydrofuran (30 cm^3) at 0 °C. After further stirring for 30 min at 0 °C, this solution was added dropwise during 10 min from a syringe to a stirred solution of methyl diphenylborinate[40] (9.8 g, 50.0 mmol) and tri-n-butylphosphine (10.9 g, 53.9 mmol) in dry ether (80 cm^3) at 0 °C. Stirring was continued for a further 1.5 h at room temperature, pentane (40 cm^3) was added, and the mixture was filtered through Celite. The filter cake was washed with benzene (80 cm^3) and solvents were removed from the combined filtrate to give an involatile residue from which *tri-n-butylphosphine–diphenylborane* was isolated by h.p.l.c. [light petroleum–dichloromethane (3:1) as eluant] as a colourless viscous oil (Found: C, 77.6; H, 10.4; P, 8.4. $C_{24}H_{38}BP$ requires C, 78.3; H, 10.4; P, 8.4%); δ(^{31}P) (C_6D_6; proton-decoupled) −1.7 (br s); δ(^{11}B) (C_6D_6) −15.1 (br s). In the ^1H n.m.r. spectrum, the integral ratio for the aromatic and aliphatic C–H protons was close to 10:27; the BH proton gave rise to a very broad peak which collapsed to a sharp doublet at δ 3.50 (J_{HP} 17.1 Hz) during ^{11}B decoupling. The i.r. spectrum (liquid film) showed $\nu_{max.}$ 2 300 cm^{-1} (BH).

Analytical Experiments.—In a typical run, tri-n-butylphosphine–phenylborane (2.0092 g, 6.875 mmol) and 1,2,4-trichlorobenzene (0.1505 g) were weighed into a 10 cm^3 flat-bottomed two-necked flask equipped with a magnetic stirrer and a small reflux condenser. The flask was flushed with argon and maintained under argon throughout the reaction. Dry, argon-purged chlorobenzene (1.7 cm^3) was added through a self-sealing rubber septum, followed by n-butyl iodide (0.1594 g, 0.866 mmol) and t-butyl perbenzoate (0.0336 g, 0.173 mmol) using a calibrated microsyringe. The reaction flask was immersed in a thermostatically controlled oil-bath at 110 °C and its contents were stirred during dropwise addition from a tapped syringe of freshly distilled ethyl acrylate (0.6888 g, 6.880

mmol) in chlorobenzene (1.0 cm^3). The addition took 15 min, after which the mixture was stirred at 110 °C for 1 h, allowed to cool to room temperature, and subjected to g.l.c. analysis. The yield of ethyl heptanoate was 58% based on n-butyl iodide.

Reactions between ligated boranes and ethyl 2-bromopropanoate were carried out in a similar way, except that all the reagents were present initially. Pilot experiments were performed in n.m.r. tubes closed with self-sealing rubber caps; quartz n.m.r. tubes were used for reactions initiated by u.v. photolysis of di-t-butyl peroxide.

Product Isolation.—Reactions were carried out in the same general manner as the analytical runs, except that the internal standard was omitted.

Ethyl heptanoate was isolated from the reaction of $Bu^n_3P{\rightarrow}BH_2Ph$ with Bu^nI and ethyl acrylate (molar proportions 8:1:4) in *ca.* 40% yield by spinning-plate chromatography on silica using light petroleum–dichloromethane (3:1) as eluant; analytically pure ester was obtained by h.p.l.c. using dichloromethane as eluant. The yield was not increased when 8 mol equiv. of ethyl acrylate were added slowly and continuously over 1 h using a motor-driven syringe pump.

Ethyl 3-cyclohexylpropanoate was isolated from the reaction of $Bu^n_3P{\rightarrow}BH_2Ph$ with cyclohexyl iodide and ethyl acrylate (molar proportions 8:1:8) in *ca.* 30% yield by spinning-plate chromatography followed by h.p.l.c. as for ethyl heptanoate.

Ethyl 3-[cholest-5-en-3α(β)-yl]propanoate. The epimeric mixture was isolated in *ca.* 50% yield by spinning-plate chromatography (as for ethyl heptanoate) (Found: C, 81.6; H, 11.5%; M^+, 470.4109. $C_{32}H_{54}O_2$ requires C, 81.6; H, 11.6%; *M*, 470.4124). The epimers were separated by h.p.l.c. using light petroleum–dichloromethane (2:1) as eluant; the major component was an oil, whilst the minor epimer was a crystalline solid (m.p. 66—67 °C). In $CDCl_3$ the major component showed δ(^{1}H) 0.67 (s, 18-H_3), 1.01 (s, 19-H_3), 1.26 (t, *J* 7.1 Hz, CH_3CH_2O), 4.12(1) (q, *J* 7.1 Hz, CH_3CH_2O), and 5.25 (m, 6-H); the minor component showed 0.68 (s, 18-H_3), 0.97 (s, 19-H_3), 1.26 (t, *J* 7.1 Hz, CH_3CH_2O), 4.12(4) (q, *J* 7.1 Hz, CH_3CH_2O), and 5.29 (m, 6-H); the CH_3CH_2O quartets were resolved in the 400 MHz spectrum of the epimeric mixture. $CDCl_3$ was used as solvent to facilitate comparison with values in the literature, although the spectra of the two epimers differed more in C_6D_6 as solvent.

Diethyl n-hexylphosphonate was isolated in *ca.* 20% yield from the reaction of $Bu^n_3P{\rightarrow}BH_2Ph$ with Bu^nI and diethyl vinylphosphonate (molar proportions 8:1:4) by spinning-plate chromatography on silica followed by h.p.l.c. using ethyl acetate as eluant.

When the vinylphosphonate was replaced with phenyl vinyl sulphone, n-hexyl phenyl sulphone (*ca.* 40%) was isolated by spinning-plate chromatography followed by h.p.l.c. using light petroleum–ethyl acetate (3:1) as eluant. The ^{1}H n.m.r. spectrum (in $CDCl_3$) was identical with that of the authentic sulphone; δ 0.8—1.8 (m, 11 H), 3.09 (distorted t, CH_2S), and 7.5—7.9 (m, 5 H).[36]

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