Homolytic Reactions of Ligated Boranes. Part 15.[1] Comparative Studies of Amine–Boranes as Donor Polarity Reversal Catalysts for Hydrogen-Atom Abstraction

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ESR spectroscopy has been used to characterise the reactions of the amine–boryl radicals produced by hydrogen-atom abstraction from a variety of amine–borane complexes by photochemically generated t-butoxyl radicals. The complexes $Me_3N{\rightarrow}BH_2R$ (R = Me_2CHCMe_2, Bu^n, Bu^i, Bu^s), 1,1-dimethyl-1,2-azaborolidine, 1-methyl-*cis*-1-azonia-5-boratabicyclo[3.3.0]octane, $Me_2NCH_2CH_2N$-$Me_2{\cdot}2IpcBH_2$ (Ipc = isopinocampheyl), $Me_3SiCH_2NMe_2{\rightarrow}BH_3$, and $Me_3N{\rightarrow}BH_3$ were investigated. All the amine–boryl radicals rapidly abstract halogen from alkyl bromides and chlorides at 170 K. Specific alkyl radicals can be generated for ESR studies at low temperature by UV irradiation of a solution containing Bu^tOOBu^t, $Me_3N{\rightarrow}BH_2Bu^n$, and the corresponding alkyl chloride. The amine–borane complexes act as donor polarity reversal catalysts for the overall abstraction of acidic hydrogen from HCC(O) groups in esters, lactones, ketones, imides, and related compounds. Relative rates of catalysed hydrogen-atom abstraction from $MeCO_2Et$, $MeCH_2CO_2Et$, and Me_2CHCO_2Et have been determined and competitive abstraction from the two different types of α-CH groups in $MeC(O)CHMe_2$ has been similarly quantified. The relative reactivities of the amine–boryl radicals can be understood in terms of a balance between enthalpic, polar, and steric factors and the merits of the different amine–boranes as polarity reversal catalysts for the overall abstraction of hydrogen from acidic C–H groups by alkoxyl radicals are assessed. The origin of the polar effects observed in hydrogen-atom abstraction reactions is discussed in terms of the electronegativity difference between the attacking and departing radicals and a simple approach for the quantitative description of polar effects is outlined.

In Part 12 of this series,[2] we described how amine–alkylborane complexes can function as 'donor' polarity reversal catalysts for hydrogen-atom abstraction from electron-deficient C–H bonds by electrophilic t-butoxyl radicals.

Of the similarly exothermic hydrogen abstraction reactions (1) and (2), in which El$^\bullet$ and Nuc$^\bullet$ are electrophilic and nucleophilic radicals, respectively, reaction (1) is usually the faster because of a favourable charge transfer interaction in the transition state. In the presence of an amine–alkylborane (*e.g.* $Me_3N{\rightarrow}BH_2R$), the slow single step (2) is replaced by the catalytic cycle of reactions (3) and (4), both of which benefit from favourable polar effects because of the strongly nucleophilic character of the amine–alkylboryl radical.

$$Bu^tO^\bullet + H\text{–}Nuc \xrightarrow{fast} Bu^tOH + Nuc^\bullet \quad (1)$$

$$Bu^tO^\bullet + H\text{–}El \xrightarrow{slow} Bu^tOH + El^\bullet \quad (2)$$

$$Bu^tO^\bullet + Me_3N{\rightarrow}BH_2R \longrightarrow Bu^tOH + Me_3N{\rightarrow}\dot{B}HR \quad (3)$$

$$Me_3N{\rightarrow}\dot{B}HR + H\text{–}El \longrightarrow Me_3N{\rightarrow}BH_2R + El^\bullet \quad (4)$$

We have shown previously that amine–alkylboranes efficiently catalyse hydrogen-atom abstraction by t-butoxyl radicals for the α-CH group of esters,[2,3] nitriles,[2,3] and ketones[3] and from cyclopentadiene.[4] However, the catalyst employed in most of this work, trimethylamine–thexylborane† (**1**), although readily prepared,[3] is a moisture sensitive and comparatively unstable compound. In the present paper we describe an ESR spectroscopic study of the reactions of a number of different amine–boryl radicals and assess the relative merits of the parent amine–boranes as donor polarity reversal catalysts.

t-Butoxyl radicals were generated by UV irradiation of samples containing di-t-butyl peroxide (DTBP) [equation (5)]

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^\bullet \quad (5)$$

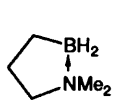
and positioned in the microwave cavity of the spectrometer. In the presence of an amine–borane, reaction (3) takes place rapidly[2] and the subsequent reactions of the derived amine–boryl radical with a third reagent were monitored by ESR spectroscopy.

Results and Discussion

Preparation and Stability of Amine–Boranes.—The amine–boranes (**1**)–(**7**) were investigated in this work. The complex (**1**) was prepared as described previously[2,3] by hydroboration of 2,3-dimethylbut-2-ene, followed by addition of trimethylamine to the thexylborane so formed. This amine–borane reacts rapidly with moist air to give a white solid,[5,6] but can be readily handled neat or as a solution in a dry aprotic solvent using simple syringe techniques.

† The 1,1,2-trimethylpropyl group is referred to as the thexyl group (Thx = Me_2CHCMe_2–).

$Me_3N{\rightarrow}BH_2R$
(1) R = Me_2CHCMe_2 (Thx)
(2) R = Bu^s
(3) R = Bu^i
(4) R = Bu^n



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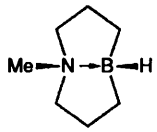

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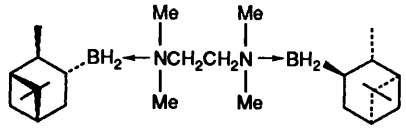

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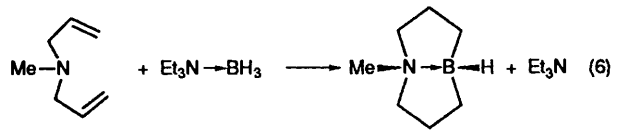
The isomeric trimethylamine–butylboranes (2)–(4) were prepared by reduction of the corresponding tributylboroxine $(RBO)_3$ with $LiAlH_4$ in the presence of excess trimethylamine, using the method of Hawthorne.[7] Although, in common with (1),[3] the complexes (2)–(4) decompose slightly by loss of amine during distillation, they are all much more stable than (1). This is presumably because the strength of the N→B dative bond increases as the bulk of the *B*-alkyl group decreases.

The cyclic amine–alkylborane (5) is reported to be stable towards cold water.[8,9] With the aim of further increasing the stability to be gained from an intramolecular N→B link, the bicyclic amine–dialkylborane complex (6) was prepared by heating $Et_3N{\rightarrow}BH_3$ with *N*-methyldiallylamine, either in refluxing xylene at *ca.* 140 °C or in benzene at *ca.* 190 °C using a pressure vessel [equation (6)]. Only one isomer of the product



(6)

is formed, as judged by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, and this is presumed to be the *cis*-form shown since models indicate that the *trans*-isomer would be more strained.

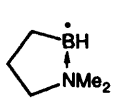
The 1:2 complex of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) with isopinocampheylborane is a surprisingly stable compound[10,11] which is commercially available* and the crystal structure of which has been determined.[12] The optically active complex (7), prepared from (+)-α-pinene, was included in this study because the *B*-alkyl group could in principle serve as a chiral auxiliary capable of inducing enantioselective reactions of the corresponding amine–alkylboryl radical. Trimethylamine–s-butylborane (2) is also of interest in this regard, because it too could be prepared in enantiomerically pure form starting from available[13] optically active s-butylboronic esters.

The air-sensitivity of each of the amine–boranes (1)–(7) was assessed using ^1H and ^{11}B NMR spectroscopy by exposing *ca.* 100 mg of complex to the laboratory atmosphere. The recovered complexes (2)–(7) showed no detectable change in their NMR spectra after 2 h exposure, while (1) had decomposed completely after 15 min.

* Supplied as *R*-Alpine-Boramine® by Aldrich.

Formation of Amine–Boryl Radicals and Their Reactions with Alkyl Halides.—t-Butoxyl radicals abstract hydrogen very rapidly from boron in amine–borane complexes to give the corresponding amine–boryl radicals.[2,3,14] The ESR spectrum of the appropriate amine–alkylboryl radical (8)–(12) was observed during UV irradiation of a cyclopropane or cyclopropane–oxirane solution containing DTBP (*ca.* 20% v/v) and one of the amine-boranes (1)–(5) (*ca.* 1 mol dm^{-3}) at 200—220 K. The lines in these spectra were characteristically broad[2,3,14] and, despite repeated attempts at temperatures between 190 and 260 K, we were unable to detect ESR spectra which could be assigned with certainty to the radicals (13) or (14). This is particularly unfortunate in the case of (13), since the configuration at the boron-radical centre is of some interest and could be deduced from the value of $a(^{11}B)$. The spectroscopic parameters for (8)–(12) are given in Table 1.

$Me_3N{\rightarrow}\dot{B}HR$
(8) R = Thx
(9) R = Bu^s
(10) R = Bu^i
(11) R = Bu^n



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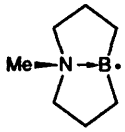

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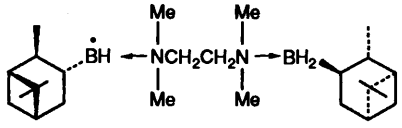
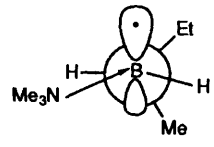


(14)

As reported previously,[2,3,14] the values of $a(^{11}B)$ and $a(H_\alpha)$ for the amine–boryl radicals indicate that the configuration at the boron centre is pyramidal. The magnitude of $a(H_\beta)$ appears to vary with the dihedral angle between the C–H_β bond and the axis of the hybrid orbital of the unpaired electron on boron in a similar way to that found for the less pyramidal alkyl radicals.[15] Thus, the different values of $a(H_\beta)$ shown by (9) and (10) or (11) can be understood in terms of a sterically-induced difference in favoured conformation about the C_β–B bond. The relatively small value of $a(1\text{-}H_\beta)$ for (9) indicates that the preferred conformation is similar to structure (15), where the single β-hydrogen atom lies close to the nodal surface of the SOMO.



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Each of the amine–boryl radicals (8)–(14) abstracts halogen very readily from an alkyl bromide or chloride [equation (7)]. Thus, when the halogenoalkane (*ca.* 1 mol dm^{-3}) is

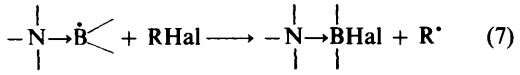

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Table 1. ESR parameters for amine–alkylboryl radicals in cyclopropane.

Radical	T/K	g Factor[a]	Hyperfine splittings[a]/G $a(^{11}B)$	$a(1\text{-}H_\alpha)$	$a(n\text{-}H_\beta)$[b]
$Me_3N{\rightarrow}\dot{B}HMe$[c,d]	199	2.0020	61.6	6.1	14.8(3)
$Me_3N{\rightarrow}\dot{B}HBu^n$	236	2.0022	58.4	6.4	16.4(2)
$Me_3N{\rightarrow}\dot{B}HBu^i$	236	2.0023	58.3	6.4	16.4(2)
$Me_3N{\rightarrow}\dot{B}HBu^s$	237	2.0020	57.9	7.8[e]	7.8[e](1)
$Me_3N{\rightarrow}\dot{B}HThx$[c]	264	2.0021	59.9	9.8	—
(12)[f]	236	2.0019	57.2	g	20.7(2)

[a] Corrected for second-order effects. [b] Value of n given in parentheses. [c] Data from ref. 3. [d] Oxirane solvent. [e] Average of $a(1\text{-}H_\alpha)$ and $a(1\text{-}H_\beta)$ which are equal within the linewidth. [f] Data from ref. 2. [g] Not resolved.

Table 2. Relative rates of halogen abstraction from t-butyl bromide $[k_{(8a)}]$ and n-propyl bromide $[k_{(8b)}]$ by amine–alkylboryl radicals in cyclopropane at 217 K.[a]

Radical	$[k_{(8a)}/k_{(8b)}]$
$Me_3N{\rightarrow}\dot{B}HMe$[b]	1.10
$Me_3N{\rightarrow}\dot{B}HBu^n$	0.67[c]
$Me_3N{\rightarrow}\dot{B}HBu^i$	0.69
$Me_3N{\rightarrow}\dot{B}HBu^s$	0.70
$Me_3N{\rightarrow}\dot{B}HThx$	0.75[d]
(13)[e]	0.62
(14)[f]	0.56

[a] Unless noted otherwise, the concentrations of amine–borane and total alkyl bromide were 1.0 mol dm^{-3} and 0.9–1.0 mol dm^{-3}, respectively. [b] Data from ref. 3. [c] At 173 K, $[k_{(8a)}/k_{(8b)}]$ is 0.55. [d] Ref. 3 gives 0.67 at 173 K. [e] The concentration of (6) was 0.30 mol dm^{-3}. [f] Oxirane solvent; the concentration of (7) was 0.1 mol dm^{-3}.

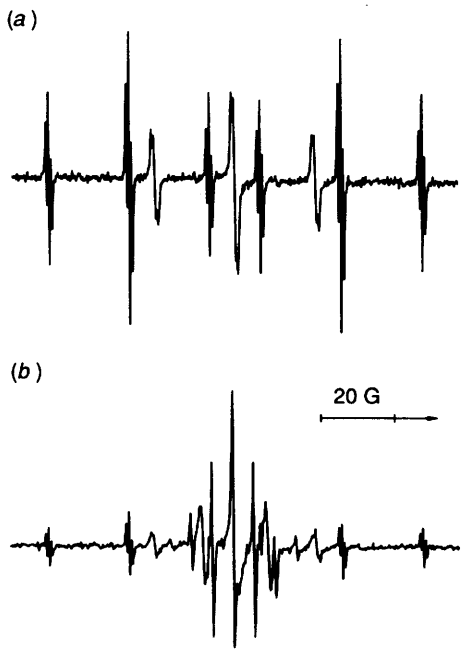
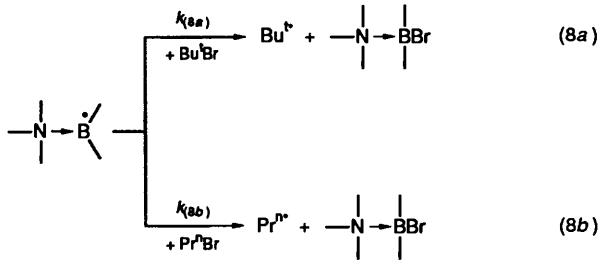


Figure 1. ESR spectra recorded during UV irradiation at 190 K. (*a*) The butyl radical obtained from $Me_3N{\rightarrow}BH_2Bu^n$ (1 mol dm^{-3}), Bu^nCl (1 mol dm^{-3}), and DTBP (17% v/v) in cyclopropane; (*b*) the mixture of radicals obtained from Et_3SiH (1 mol dm^{-3}), Bu^nCl (1 mol dm^{-3}), and DTBP (17% v/v). The gain is slightly lower for (*b*) than for (*a*), otherwise the instrumental conditions are the same.

included with DTBP and the amine–borane, only the ESR spectrum of the corresponding alkyl radical is observed during UV irradiation, even at 170 K. In order to characterise the amine–boryl radicals, the relative rates at which each abstracts bromine from a mixture of t-butyl and n-propyl bromides was determined by measuring the relative concentrations of Bu^t• and Pr^n• produced during UV irradiation [equation (8)].[2,3,14] The values of $[k_{(8a)}/k_{(8b)}]$ obtained at 217 K are given in Table 2. The



amine–alkylboryl radicals are typically unselective in bromine-atom abstraction and this lack of discrimination is probably associated with very high reactivity. For all but $Me_3N{\rightarrow}\dot{B}HMe$, which we have examined previously[3] and in which the radical centre is least congested, Bu^tBr is somewhat less reactive than Pr^nBr, sugesting that steric factors are responsible for the reversal of the normal $R^tBr > R^pBr$ reactivity order.

Probably also for steric reasons, $Me_3N{\rightarrow}\dot{B}HBu^n$ appears to abstract chlorine from alkyl chlorides rather more rapidly than does[3] $Me_3N{\rightarrow}\dot{B}HThx$. Thus, in cyclopropane at 190 K, a strong ESR spectrum of the methyl radical was observed during UV irradiation of a sample containing DTBP (16% v/v), $Me_3N{\rightarrow}BH_2Bu^n$ (1 mol dm^{-3}), and MeCl (1 mol dm^{-3}); the spectrum of $Me_2N{\rightarrow}\dot{B}HBu^n$ was not detected. ESR spectra of the corresponding alkyl radicals were also obtained from similar samples containing Pr^nCl, Bu^nCl, Pr^iCl, Bu^tCl, 2-chloronorbornane,[16] 1-chloroadamantane,[17] or benzyl chloride[18] in place of MeCl (the references cited contain spectra of quality similar to those obtained in the present work).

Halogen abstraction from alkyl bromides using photochemically-generated triethylsilyl radicals is a very useful general method for the production of specific alkyl radicals for ESR studies in solution.[19] However, this method is less suitable for alkyl chlorides, especially at low temperature, because silyl radicals abstract chlorine more slowly than they abstract bromine; ESR spectra are weaker and persistent radicals tend to build up in static samples. UV irradiation of solutions containing DTBP, $Me_3N{\rightarrow}BH_2Bu^n$, and an alkyl chloride provides a general route to alkyl radicals which complements the 'triethylsilane method'[19] for alkyl bromides. Figure 1(*a*) shows the spectrum of the n-butyl radical generated by halogen abstraction from Bu^nCl by $Me_3N{\rightarrow}\dot{B}HBu^n$ at 190 K in cyclopropane. For comparison, Figure 1(*b*) shows the spectrum obtained from a similar sample in which the amine–alkylborane has been replaced by an equal concentration of triethylsilane.

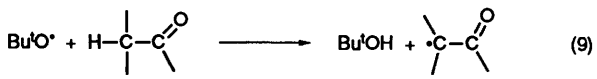
Table 3. Relative rates of α-hydrogen-atom abstraction from esters by amine–boryl radicals at 189 K

Radical	Solvent[a]	Ester reactivity (per molecule)[b]		
		CH_3CO_2Et	$MeCH_2CO_2Et$	Me_2CHCO_2Et
$Me_3N{\rightarrow}\dot{B}HMe$[c]	A	(1)	6.7	7.3
$Me_3N{\rightarrow}\dot{B}HBu^n$	A	(1)	4.1	3.3
$Me_3N{\rightarrow}\dot{B}HBu^i$	A	(1)	3.9	3.0
$Me_3N{\rightarrow}\dot{B}HBu^s$	A	(1)	4.9	2.4
$Me_3N{\rightarrow}\dot{B}HThx$	A	(1)	4.6 (4.5)[c]	0.48 (0.44)[c]
(12)[c]	A	(1)	8.3	9.0
(13)	A	(1)	5.5	5.9
(14)	B	(1)	5.2	1.4
$Me_3N{\rightarrow}\dot{B}H_2$	B	(1)	6.3	7.2
$Me_3SiCH_2NMe_2{\rightarrow}\dot{B}H_2$	B	(1)	7.5	10.3

[a] A = cyclopropane, B = oxirane. [b] Independent of the amine–borane concentration in the range *ca.* 0.10–0.20 mol dm^{-3}. The total ester concentration was *ca.* 1.2 mol dm^{-3}. [c] Data from ref. 2.

The spectrum of $Et_3Si^{\bullet}$ is still apparent, that of $Bu^{n\bullet}$ is much weaker than in Figure 1(*a*), and spectra of persistent radicals are evident.

Hydrogen-Atom Abstraction from Esters.—In contrast to the t-butoxyl radical, the amine–alkylboryl radicals (**8**)–(**14**) readily abstract the acidic hydrogen from α-CH groups in esters and ketones, and the complexes (**1**)–(**7**) all function as efficient donor[2] polarity reversal catalysts for the overall hydrogen-atom transfer reaction (9). Relative rates of α-H-atom



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abstraction from ethyl acetate, propanoate, and 2-methylpropanoate by (**9**)–(**11**), (**13**), and (**14**) were determined as described previously for (**8**) and (**12**),[2] by monitoring the relative concentrations of (ethoxycarbonyl)alkyl radicals produced during UV irradiation of samples containing DTBP, the amine–alkylborane, and mixtures of two esters. The relative radical concentrations were independent of the concentration of amine–alkylborane (0.10–0.20 mol dm^{-3}), confirming that all the t-butoxyl radicals are converted to amine–alkylboryl radicals which then bring about α-H-atom abstraction. The results are given in Table 3.

We have previously ascribed the markedly different selectivities of $Me_2N{\rightarrow}\dot{B}HThx$ (**8**) and the cyclic radical (**12**) to steric effects, because the boron centre in (**8**) is much more congested than that in (**12**). The trends shown by the data in Table 3 can be understood in terms of the decreasing strength of the α-C–H bond along the series $MeCO_2Et > MeCH_2CO_2Et > Me_2CHCO_2Et$, coupled with the increased steric protection which α-methylation affords to the α-C–H group. The reactivity of Me_2CHCO_2Et compared with $MeCO_2Et$ towards $Me_3N{\rightarrow}\dot{B}HR$ decreases with the steric demands of R along the series R = Me > Bu^n, Bu^i > Bu^s > Thx. The cyclic radicals (**12**) and (**13**) both show a greater preference for abstraction from Me_2CHCO_2Et than does $Me_3N{\rightarrow}\dot{B}HBu^n$; (**12**) is even more selective than $Me_3N{\rightarrow}\dot{B}HMe$. Although the *B*-alkyl groups in (**9**) and (**14**) are both secondary, the isopinocampheyl group is evidently the more sterically demanding, with the result that $MeCO_2Et$ and Me_2CHCO_2Et are similarly reactive towards (**14**).

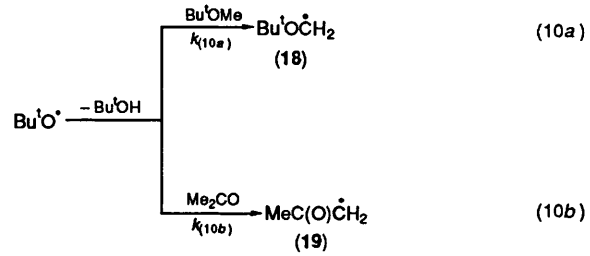
* At 237 K in cyclopropane, (**17**) shows $a(^{11}B)$ 54.7, $a(2\text{-}H_\alpha)$ 10.4 G, and g 2.0022.

$Me_3N{\rightarrow}\dot{B}H_2$ (**16**) $\qquad$ $Me_3SiCH_2NMe_2{\rightarrow}\dot{B}H_2$ (**17**)

Data for the amine-boryl radicals $Me_3N{\rightarrow}\dot{B}H_2$ (**16**)[14] and $Me_3SiCH_2NMe_2{\rightarrow}\dot{B}H_2$ (**17**)* are included in Table 3. Although (**16**) is a rather less effective abstractor of hydrogen from the α-C–H groups of esters than the amine–alkylboryl radicals,[3] even ethyl acetate reacts sufficiently rapidly to afford the ESR spectrum of the corresponding (ethoxycarbonyl)alkyl radical at 189 K. Steric effects are less important than for the reactions of (**8**)–(**11**) and the selectivities of $Me_3N{\rightarrow}\dot{B}H_2$ and $Me_3N{\rightarrow}\dot{B}HMe$ are similar. The 2-methylpropanoate is appreciably more reactive than the acetate towards (**16**) and (**17**), presumably because the bond weakening effect of α-methylation is now dominant.

The proton affinity of $Me_3SiCH_2NMe_2$ is greater than that of trimethylamine[20] and, in the hope that (**17**) might be more nucleophilic than (**16**) and thus abstract acidic hydrogen more rapidly, we examined $Me_3SiCH_2NMe_2{\rightarrow}BH_3$ as a donor polarity reversal catalyst. However, as judged from the intensities of the ESR spectra obtained, the reactivities of (**16**) and (**17**) towards the esters are similar; the selectivities of these two radicals do not differ substantially.

Hydrogen-Atom Abstraction From Ketones.—Because of unfavourable polar effects, the t-butoxyl radical abstracts hydrogen sluggishly from acetone. Thus, UV irradiation of a cyclopropane solution containing DTBP (36% v/v), acetone (0.81 mol dm^{-3}), and t-butyl methyl ether (0.27 mol dm^{-3}) [reactions (10*a*) and (10*b*)] afforded ESR spectra of the radicals (**18**) and (**19**) such that [(**18**)]/[(**19**)] was 10.1 at 190 K. The value of [(**18**)]/[(**19**)] was unchanged when the [DTBP]:[Me_2CO] ratio was doubled, keeping the [Me_2CO]:



(10*a*)

(10*b*)

[Bu^tOMe] ratio constant, showing that reactions of photo-excited ketone are unimportant under these conditions. If the usual assumption is made that the rate coefficients for diffusion-

Table 4. Relative rates of α-hydrogen-atom abstraction $[k_{(12a)}/k_{(12b)}]$ from 3-methylbutan-2-one at 189 K.

Abstracting radical	Solvent[a]	$[k_{(12a)}/k_{(12b)}]$[b]
$Bu^tO^{\bullet}$[c]	A	≤0.1
$Me_3N{\rightarrow}\dot{B}HBu^n$	A	0.60
	B	0.56
$Me_3N{\rightarrow}\dot{B}HBu^i$	A	0.75
$Me_3N{\rightarrow}\dot{B}HBu^s$	A	0.92
$Me_3N{\rightarrow}\dot{B}HThx$	A	7.6
(12)	A	0.7[d]
(13)	A	0.45
(14)	B	4.0

[a] A = cyclopropane, B = oxirane. [b] Independent of the amine–borane concentration in the range 0.23–0.44 mol dm^{-3}; the ketone concentration was generally 0.85 mol dm^{-3}. [c] No amine–borane present. [d] Weak spectra.

controlled reactions between small radicals such as (**18**) and (**19**) are all equal, it follows[21] that the value of $[k_{(10a)}/k_{(10b)}]$ is 30 at 190 K. We have shown previously[22] that $k_{(10a)}$ is given by equation (11), in which $\theta = 2.303RT$ kJ mol^{-1}, and thus the

$$\log_{10}[k_{(10a)}/dm^3\ mol^{-1}\ s^{-1}] = (8.1 \pm 0.5) - (12.6 \pm 2.0)/\theta \quad (11)$$

value of $k_{(10b)}$ is 1.4×10^3 dm^3 mol^{-1} s^{-1} at 190 K. If the *A*-factor for reaction (10*b*) is assumed to be twice that for reaction (10*a*) (for statistical reasons), the activation energy for hydrogen abstraction from acetone would be *ca.* 19 kJ mol^{-1}.

In contrast, UV irradiation of a solution containing DTBP (35% v/v), Me_2CO (0.78 mol dm^{-3}), Bu^tOMe (0.26 mol dm^{-3}), and $Me_3N{\rightarrow}BH_2Thx$ (0.20 mol dm^{-3}) at 190 K, afforded only the ESR spectrum of the acetonyl radical (**19**); (**18**) was not detected. The amine–thexylboryl radical (**8**) must abstract hydrogen from acetone at least 10 times as rapidly as from t-butyl methyl ether. A similar result was obtained with $Me_3N{\rightarrow}BH_2Bu^n$ (**4**) as polarity reversal catalyst. In the absence of DTBP and UV irradiation, acetone (1.0 mol dm^{-3}) showed no sign of reacting with (**4**) (1.0 mol dm^{-3}) in C_6D_6 during 1 h at room temperature or, subsequently, after 1 h at 50 °C, as judged by ^1H NMR spectroscopy.

We have reported that while t-butoxyl radicals abstract an α-hydrogen atom mainly from the isopropyl group of 3-methylbutan-2-one (**20**) to give the radical (**22**), the amine–alkylboryl radical (**8**) abstracts more rapidly from the $CH_3C(O)$ group to give (**21**) [equations (12*a*) and (12*b*)].[2] This difference in selectivity was attributed to steric factors, because the less bulky amine-alkylboryl radical (**12**) was shown to abstract hydrogen mainly from the isopropyl group.[2] We have now obtained higher quality spectra which enable quantitative selectivities for hydrogen-atom abstraction from the ketone (**20**) to be determined.* Relative concentrations of the radicals (**21**) and (**22**) were determined by computer simulation of spectra obtained at 190 K during UV irradiation of cyclopropane or oxirane solutions containing DTBP (35% v/v), 3-methylbutan-2-one (0.85 mol dm^{-3}), and the amine–alkylborane (0.23 mol dm^{-3}). The value of [(**21**)]/[(**22**)] is taken[21] to be equal to $[k_{(12a)}/k_{(12b)}]$ and was unchanged when the amine–alkylborane concentration was increased to 0.44 mol dm^{-3}, showing that all the t-butoxyl radicals are being trapped and converted to amine–alkylboryl radicals which are responsible for hydrogen abstraction. The selectivity of $Bu^tO^{\bullet}$ was determined from experiments in the absence of amine–alkylborane; the results are given in Table 4. Figure 2(*a*) shows part of the spectrum of (**22**), which is the only radical detected when $Bu^tO^{\bullet}$ reacts with the ketone (**20**), and Figures 2(*c*) and 2(*d*) show the same regions of the spectra obtained when abstraction is brought about by $Me_3N{\rightarrow}\dot{B}HThx$ and by $Me_3N{\rightarrow}\dot{B}HBu^n$, respectively.

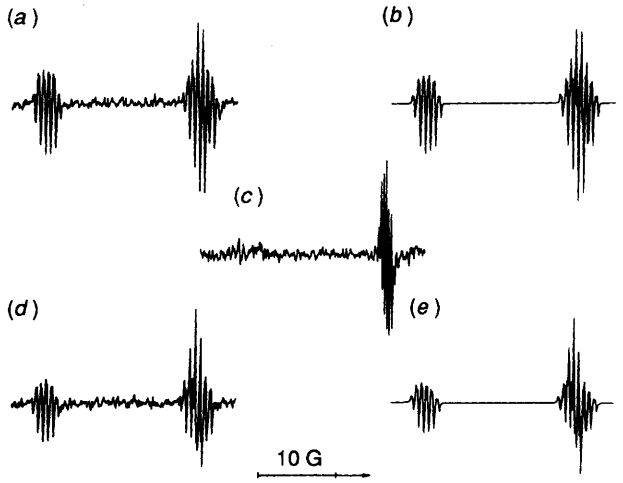
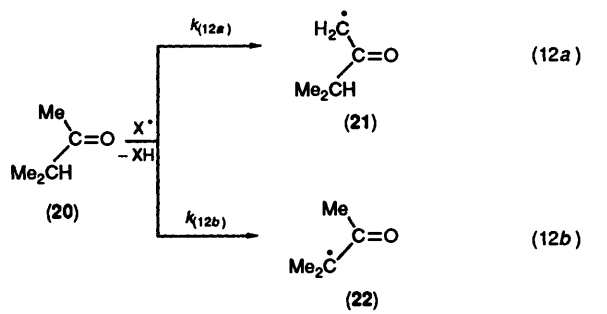


Figure 2. Low field regions from the ESR spectra of (**21**) and (**22**) in cyclopropane at 190 K. The $M_I(2\text{-}H_\alpha) = -1$ lines for (**21**) and the $M_I(6\text{-}H_\beta) = +1$ and +2 lines for (**22**) are shown; computer simulations (including second-order effects) were obtained using the parameters given in the text. (*a*) Hydrogen abstraction by $Bu^tO^{\bullet}$; only (**22**) is detected; (*b*) simulation of (*a*); (*c*) hydrogen abstraction by $Me_3N{\rightarrow}\dot{B}HThx$, [(**21**)]/[(**22**)] = 7.8; (*d*) hydrogen abstraction by $Me_3N{\rightarrow}\dot{B}HBu^n$; (*e*) simulation of (*d*), [(**21**)]/[(**22**)] = 0.56.



The intramolecular selectivities exhibited by the amine–alkylboryl radicals (**8**)–(**14**) parallel the relative reactivities of $MeCO_2Et$ and Me_2CHCO_2Et towards the same radicals (see Table 3). As congestion at the boron-radical centre decreases, so the tendency to abstract the more weakly bound of the two types of α-hydrogen in (**20**) becomes more pronounced. Again, the ligated isopinocampheylboryl radical (**14**) shows a greater preference than $Me_3N{\rightarrow}\dot{B}HBu^s$ for abstraction from the less hindered α-CH group.

Hydrogen-Atom Abstraction From Lactones, Anhydrides, and Related Compounds.—To demonstrate the general utility of amine–alkylboranes as donor polarity reversal catalysts for overall abstraction of hydrogen from acidic C–H groups by t-butoxyl radicals, a selection of carbonyl-containing compounds was examined. UV irradiation at 160–230 K of an oxirane solution containing the carbonyl compound (1 mol dm^{-3}) and DTBP (*ca.* 17% v/v) afforded exclusively or mainly the

* Hyperfine splittings more accurate than those reported previously have been obtained for (**21**) and (**22**). In cyclopropane at 190 K, (**21**) shows splittings of 19.94 (1-H_α), 19.60 (1-H_α), 0.65 (1-H_γ), and 0.28 G (6-H_δ) (*g* 2.0045); (**22**) shows 20.35 (3-H_β), 19.06 (3-H_β), and 0.69 G (3-H_γ) [*g* 2.0042; *g*(**21**)–*g*(**22**) = 0.000 27]. In oxirane at 190 K, (**21**) shows splittings of 19.94 (1-H_α), 19.60 (1-H_α), 0.72 (1-H_γ), and 0.34 G (6-H_δ); (**22**) shows 20.44 (3-H_β), 19.02 (3-H_β), and 0.83 (3-H_γ).

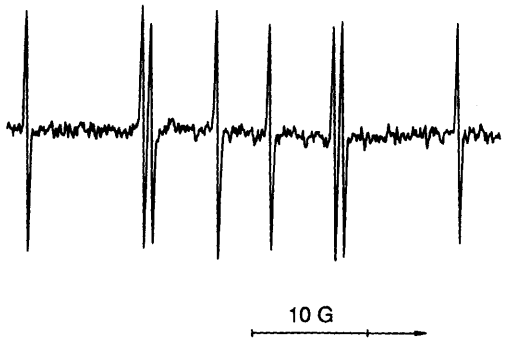
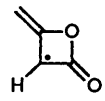


Figure 3. ESR spectrum of the radical (**23**) generated by hydrogen abstraction from diketene by $Me_3N{\rightarrow}\dot{B}HThx$ in oxirane at 190 K.

ESR spectrum of the oxiranyl radical, formed by hydrogen abstraction from the solvent by t-butoxyl radicals. However, in the additional presence of $Me_3N{\rightarrow}BH_2Thx$ (**1**) (*ca.* 0.20 mol dm^{-3}), the only spectrum observed from each compound was one assigned to the corresponding α-carbonyl-substituted radical whose ESR parameters are given in Table 5.*

Spectra were of high quality, as illustrated by the spectrum obtained for the delocalised radical (**23**) derived from diketene (see Figure 3), and this application of polarity reversal catalysis



(**23**)

should prove useful for the generation of carbonyl-conjugated radicals for ESR study in non-aqueous solution.

Choice of Catalyst.—For ESR spectroscopic studies, the complexes $Me_3N{\rightarrow}BH_2Me$, $Me_3N{\rightarrow}BH_2Bu^n$, and $Me_3N{\rightarrow}BH_2Thx$ would appear to be most useful, because of their ready availability and the high reactivity of the derived amine–alkylboryl radicals in hydrogen abstraction from acidic C–H groups and halogen-atom abstraction from alkyl halides. For future synthetic applications of donor polarity reversal catalysis, when thermal stability of the amine–alkylborane will be more crucial, $Me_3N{\rightarrow}BH_2Me$, $Me_3N{\rightarrow}BH_2Bu^n$, $Me_3N{\rightarrow}BH_2Bu^s$, or the bicyclic complex (**6**) appear to offer most promise. At the higher temperatures which are usually appropriate for synthetic chemistry, $Me_3N{\rightarrow}BH_3$ should prove useful. If thermal instability or heterolytic reactivity of $Me_3N{\rightarrow}BH_3$ were to prove a problem, the TMEDA[23] or quinuclidine[24] complexes of borane could be employed. It should be noted that $R_3N{\rightarrow}\dot{B}H_2$ has a greater tendency to add to some unsaturated functional groups (*e.g.* C≡N) than does $R_3N{\rightarrow}\dot{B}HR$.[3,14]

Polar Effects in Hydrogen-Atom Abstraction Reactions.—The results reported here highlight once again the important role played by polar factors in influencing the courses of homolytic reactions between uncharged species.[25,26] Polar effects can be understood in terms of the perturbational interactions between the frontier molecular orbitals of the reacting partners,[27] but the original explanation,[28,29] based on the consideration of charge transfer interactions in the transition state using a valence bond model, still has much to recommend it.

Pauling's pioneering efforts to quantify electronegativity were based on the observation that the bond between two unlike atoms in a molecule A–B is stronger than the (geometric) mean strength of the bonds in the homopolar molecules A–A and B–B.[30] According to Pauling, this extra bond strength should be identified with the 'additional' ionic resonance energy of the A–B bond, which increases with the electronegativity difference between A and B. If the molecule A–B is represented as a hybrid of the canonical structures (**24a–c**), then the additional resonance energy arises because of the increased contribution to the hybrid from one or other of the ionic structures (**24b**) or (**24c**) which occurs when the electronegativities of A and B differ. In Pauling's definition, the bond strengths (in kJ mol^{-1}) for A–B, A–A, and B–B are related to the electronegativity difference between A and B according to

$$\underset{\textbf{(24a)}}{[A\text{–}B]} \longleftrightarrow \underset{\textbf{(24b)}}{[A^{-}B^{+}]} \longleftrightarrow \underset{\textbf{(24c)}}{[A^{+}:B^{-}]}$$

equation (13).[30] More recently, Reddy *et al.*[31] have suggested that a better 'Pauling-type' electronegativity scale might be constructed using equation (14), in which χ now has the units of energy.

$$D_{AB} = (D_{AA}D_{BB})^{\frac{1}{2}} + 125.5(\chi_A - \chi_B)^2 \quad (13)$$

$$D_{AB} = (D_{AA}D_{BB})^{\frac{1}{2}} + 134.1|\chi_A - \chi_B| \quad (14)$$

Since Pauling's original work, many refinements of the concept of electronegativity have been proposed and a variety of alternative ways of defining this property have been put forward, leading to a number of different electronegativity scales.[32] The idea of group electronegativity has been introduced to take account of the fact that the electronegativity of a multivalent atom will depend on the nature of its ligands. Recently, Pearson[33] has developed the general concepts of absolute electronegativity and absolute hardness,† and has discussed the relationship of these properties to bond dissociation energies.

In the same way that the strength of the bond between A and B is increased by ionic resonance when these two atoms or groups differ in electronegativity, so the transition state for hydrogen-atom abstraction from H–B by A$^{\bullet}$ should be subject to similar stabilisation. The extents to (**25c**) and (**25d**) con-

$$\underset{\textbf{(25a)}}{[A^{\bullet}\ H\text{–}B]} \longleftrightarrow \underset{\textbf{(25b)}}{[A\text{–}H\ {}^{\bullet}B]} \longleftrightarrow \underset{\textbf{(25c)}}{[A^{-}H^{\bullet}\ B^{+}]} \longleftrightarrow \underset{\textbf{(25d)}}{[A^{+}H^{\bullet}:B^{-}]}$$

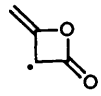
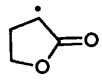
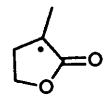
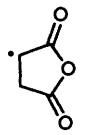
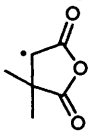
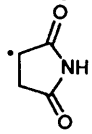
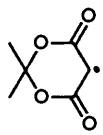
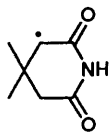
tribute to the hybrid structure of the transition state, and thus the degree to which the transition state is stabilised by ionic resonance, would be expected to depend upon the difference in electronegativity between A and B. If steric and stereoelectronic factors remain constant for a series of isoenthalpic reactions, the larger is $|\chi_A - \chi_B|$ the greater will be the additional ionic resonance energy of the transition state and the smaller should be the activation energy.

The activation energies for a series of reactions of comparable type are generally related to the reaction enthalpies by Evans–Polanyi equations of the form (15), in which α and *C*

* Some of the compounds investigated (*e.g.* diketene) reacted rapidly with $Me_3N{\rightarrow}BH_2Thx$ at room temperature without irradiation. In all experiments the reagents were kept cold and separated by a layer of DTBP during sample preparation. Samples were stored in liquid nitrogen until immediately before insertion into the microwave cavity, when the reagents and solvent were mixed by repeated rapid inversion in a solid CO_2–acetone bath.

† The absolute electronegativity (χ_X) and the absolute hardness (μ_X) of a group X are defined operationally by Pearson in terms of the first ionisation potential [E_i(X)] and the corresponding electron affinity [E_{ea}(X)] of the radical X$^{\bullet}$ in its ground state: $\chi_X = [E_i(X) + E_{ea}(X)]/2$ and $\mu_X = [E_i(X) - E_{ea}(X)]/2$.[33]

Table 5. ESR parameters for radicals obtained by hydrogen-atom abstraction by $Me_3N \rightarrow BHThx$ (**8**) from carbonyl-containing compounds in oxirane.

Radical	T/K	g Factor	Hyperfine splittings/G
	169	2.0035	21.90 (1-H_α), 24.85 (2-H_β)
	166	2.0034	21.8[a] (1-H_α), 21.8[a] (1-H_β), 0.32 (3-H_γ)
	190	2.0032	16.25 (1-H_α), 10.70 (1-H_γ), 10.00 (1-H_γ)
	225	2.0035	20.30 (1-H_α), 41.35 (2-H_β), 1.02 (2-H_γ)
	169	2.0037	37.40 (2-H_β), 21.60 (3-H_β), 0.72 (2-H_γ)
	169	2.0036	20.50 (1-H_α), 34.00 (2-H_β)
	210	2.0035	20.35 (1-H_α), 0.85 (6-H_γ)
	169	2.0037	20.80 (1-H_α), 30.80 (2-H_β), 1.37 (1-H_γ), 0.33 (1-N)
	190	2.0045	19.30 (1-H_α), 0.18 (6-H_ε)
	215	2.037	19.85 (1-H_α)[b]

[a] The α- and β-proton splittings were not resolved within the linewidth. [b] Further splitting into an even number (≥ 6) of lines spaced by 1.2 G, probably arising from coupling to the γ-protons and to nitrogen, was detected.

$$E_a = \alpha \Delta H^\circ + C \qquad (15)$$

are constants.[34] If reactions are to be sufficiently similar for equation (15) to hold, polar effects must either be unimportant or effectively constant for every reaction. The foregoing discussion suggests that Evans–Polanyi relationships for hydrogen-atom abstraction[35] might be usefully extended to take account of differences in polar effects within a series of otherwise similar reactions by inclusion of a term which depends on $(\chi_A - \chi_B)$ and reflects the amount of additional ionic resonance energy of the transition state. In this context, absolute[33] (Mulliken-type)[32] electronegativities of the radicals A$^\bullet$ and B$^\bullet$ would appear to be the most readily applicable.

This approach could be developed by taking into account the structural differences between the A and B moieties in the transition state and in the ground states of the radicals A$^\bullet$ and B$^\bullet$. The ionisation potentials and electron affinities of A$^\bullet$ and B$^\bullet$ might be considered separately, rather than together as the electronegativity, when quantifying the energetic consequences of charge transfer in the transition state. This could be done by considering both absolute electronegativity and absolute hardness.[33] Further, generality might be obtained by taking into account $(D_{AH} + D_{BH})$ as well as $(D_{AH} - D_{BH})$ (*i.e.* ΔH°) because, if other factors remain unchanged, E_a would be expected to decrease as $(D_{AH} + D_{BH})$ decreases, even if ΔH° does not vary.

One failure of an Evans–Polanyi relationship extended to include electronegativity differences would be its inability to predict a relatively low activation energy for the near-thermoneutral abstraction by Bu^{t}O$^\bullet$ of hydroxyl hydrogen from certain alcohols (*e.g.* Bu^{t}CMe$_2$OH) that are not completely hydrogen-bonded in solution.[36,37] The facility of this hydrogen-atom transfer may be associated with the relatively small antibonding interaction between the two RO moieties which carry parallel spins in the transition state.[36,38] However, a factor which appears to have been overlooked previously is the stabilisation of the transition state which would result from hydrogen bonding between the alcohol and the alkoxyl radical.

Experimental

ESR spectra were recorded with Bruker ESP-300 or Varian E-109 instruments operating at *ca.* 9.4 and *ca.* 9.1 GHz, respectively. Samples were sealed in evacuated Suprasil quartz tubes (3 mm i.d. for cyclopropane solvent and 2 mm i.d. for oxirane solvent) and irradiated with UV light (λ *ca.* 240–340 nm) while in the microwave cavity of the spectrometer. The techniques used have been described previously.[3]

Some of the ESR spectra of α-(alkoxycarbonyl)alkyl radicals exhibited CIDEP effects[39] such that corresponding hyperfine lines to low and high field of the spectrum centre were of unequal intensity (E/A polarisation).[39] In these circumstances, relative radical concentrations were determined by taking the average intensity of corresponding low and high field lines.[39]

Materials.—NMR spectra were recorded using Varian XL-200 or VXR-400 instruments, with tetramethylsilane as internal standard (^{1}H, ^{13}C) or $Et_2O \rightarrow BF_3$ as external standard (^{11}B).

Cyclopropane (Argo International) and oxirane (Fluka) were used as received; alkyl halides and t-butyl methyl ether were freshly distilled before use. Most of the carbonyl compounds were obtained from commercial sources and, if liquids, were distilled before use; those which were not available were prepared by standard methods.

Trimethylamine–borane (Aldrich) was purified by sublimation under reduced pressure. *R*-Alpine-Boramine® (**7**) (Aldrich) was recrystallised from diethyl ether. The trimethylamine complexes of thexylborane,[2,3] s-butylborane,[7] isobutylborane,[7] and n-butylborane[7] were prepared by literature methods, as was 1,1-dimethyl-1,2-azaborolidine (**5**).[8]

N,N-*Dimethyl(trimethylsilylmethyl)amine–borane.*—Dimethyl sulphide–borane (2.30 cm^3 of a 10 mol dm^{-3} solution

in excess Me_2S, 23 mmol) was added dropwise to a stirred solution of *N,N*-dimethyl(trimethylsilylmethyl)amine[40] (3.50 g, 27 mmol) in diethyl ether (5 cm^3) cooled in an ice-water bath. After the addition was complete, the mixture was stirred for a further 1 h at room temperature before all volatiles were removed under reduced pressure to yield the amine–borane complex which was purified by sublimation (0.01 Torr, bath temperature 35 °C), m.p. 34–35.5 °C (Found: C, 49.7; H, 13.6; N, 9.5. $C_6H_{20}BNSi$ requires C, 49.7; H, 13.9; N, 9.7%); $\delta_H(C_6D_6)$ 0.08 (s, Me_3Si), 1.97 (s, CH_2), 2.17 (s, Me_2N), and 2.40 (q, $^1J_{BH}$ 96 Hz, BH_3); $\delta_B(C_6D_6)$ −7.6 (q, $^1J_{BH}$ 97 Hz).

1-*Methyl*-cis-1-*azonia*-5-*boratabicyclo*[3.3.0]*octane* (**6**).—*Method A.* A solution of methyldiallylamine (PCR) (4.00 g, 36 mmol) and triethylamine–borane (Aldrich) (4.13 g, 36 mmol) in xylenes (50 cm^3, b.p. 137–140 °C) was heated under reflux with stirring under argon for 5 h (bath temperature 150 °C). The mixture was then distilled at atmospheric pressure under argon (bath temperature 170 °C) and the distillate with a b.p. ≤139 °C was discarded. The residual liquid was distilled under reduced pressure to yield the bicyclic complex (**6**) (0.22 g, 5%) b.p. 53–54 °C at 1.8 Torr (Found: C, 67.8; H, 12.9; N, 11.1. $C_7H_{16}BN$ requires C, 67.3; H, 12.9; N, 11.2%); $\delta_H(C_6D_6)$ 0.70 (2 H, m, CH^AB), 1.27 (2 H, m, CH^BB), 1.58 (4 H, m, CH_2CH_2B), 2.03 (3 H, s, MeN), 2.09 (4 H, m, CH_2N), and 2.84 (1 H, q, $^1J_{BH}$ 99 Hz, BH); $\delta_C(C_6D_6)$ (proton decoupled) 19.8 (br m, CH_2B, poorly resolved ^{13}C–$^{11/10}B$ splitting was evident), 25.8 (CH_2CH_2B), 50.3 (MeN), 63.9 (CH_2N); $\delta_B(C_6D_6)$ 4.1 (d, $^1J_{BH}$ 100 Hz). The ^1H NMR spectrum was assigned with the aid of the ^1H–^{13}C 2D correlated spectrum. Only one isomer of the complex was present, as judged by NMR spectroscopy, and this is assumed to have the *cis*-configuration.

Method B. A higher yield of slightly less pure complex (**6**) was obtained by the following procedure, which is less tedious than that described under Method A. A solution of methyldiallylamine (16.4 g, 148 mmol) and triethylamine–borane (16.5 g, 143 mmol) in benzene (400 cm^3) was stirred and heated in a sealed pressure vessel (Berghof, capacity 750 cm^3) at *ca.* 190 °C for 3.5 h. The solution was allowed to cool to room temperature, benzene and triethylamine were removed using a rotary evaporator, and the residual liquid was distilled under reduced pressure to give (**6**) (2.4 g, 13%) b.p. 58–60 °C at 3.0 Torr.

References

1 Part 14. K. M. Johnson, J. N. Kirwan, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1125.
2 V. Paul, B. P. Roberts, and C. R. Willis, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1953.
3 V. Paul and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1183.
4 V. Paul, B. P. Roberts, and C. A. S. Robinson, *J. Chem. Res. (S)*, 1988, 264.
5 H. C. Brown and G. J. Klender, *Inorg. Chem.*, 1962, **1**, 204.
6 J. E. Douglass, G. R. Roehrig, and O.-H. Ma, *J. Organomet. Chem.*, 1967, **8**, 421.
7 M. F. Hawthorne, *J. Am. Chem. Soc.*, 1961, **83**, 831.
8 Z. Polívka and M. Ferles, *Collect. Czech. Chem. Commun.*, 1969, **34**, 3009.
9 R. M. Adams and F. D. Poholsky, *Inorg. Chem.*, 1963, **2**, 640.
10 H. C. Brown, J. R. Schwier, and B. Singaram, *J. Org. Chem.*, 1978, **43**, 4395; *Inorg. Chem.*, 1979, **18**, 51.
11 B. Singaram and J. R. Schwier, *J. Organomet. Chem.*, 1978, **156**, C1.
12 J. A. Soderquist, S.-J. Hwang-Lee, and C. L. Barnes, *Tetrahedron Lett.*, 1988, **29**, 3385.
13 H. C. Brown and B. Singaram, *J. Am. Chem. Soc.*, 1984, **106**, 1797; H. C. Brown, J. V. N. Vara Prasad, A. K. Gupta, and R. K. Bakshi, *J. Org. Chem.*, 1987, **52**, 310; H. C. Brown and B. Singaram, *Acc. Chem. Res.*, 1988, **21**, 287; D. S. Matteson, *ibid.*, p. 294.
14 J. A. Baban, V. P. J. Marti, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1723.
15 C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535; J. K. Kochi, *Adv. Free-Radical Chem.*, 1975, **5**, 189.
16 T. Kawamura, Y. Sugiyama, and T. Yonezawa, *Mol. Phys.*, 1977, **33**, 1499.
17 P. J. Krusic, T. A. Rettig, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1972, **94**, 995.
18 K. U. Ingold, J. Lusztyk, B. Maillard, and J. C. Walton, *Tetrahedron Lett.*, 1988, **29**, 917.
19 A. Hudson and R. A. Jackson, *Chem. Commun.*, 1969, 1323.
20 K. J. Shea, R. Gobeille, J. Bramblett, and E. Thompson, *J. Am. Chem. Soc.*, 1978, **100**, 1611.
21 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. B*, 1971, 1823.
22 J. A. Baban, J. P. Goddard, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1269.
23 H. C. Brown and L. T. Murray, *Inorg. Chem.*, 1984, **23**, 2746.
24 J. M. Van Paasschen and R. A. Geanangel, *J. Inorg. Nucl. Chem.*, 1976, **38**, 2322.
25 F. Minisci and A. Citterio, *Adv. Free-Radical Chem.*, 1980, **6**, 65.
26 'Substituent Effects in Radical Chemistry,' eds. H. G. Viehe, Z. Janousek, and R. Merényi, Reidel, Dordrecht, 1986.
27 I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, London, 1976, ch. 5.
28 C. Walling and F. R. Mayo, *J. Polymer Sci.*, 1948, **3**, 895.
29 C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957.
30 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 3rd edn., 1960.
31 R. R. Reddy, T. V. R. Rao, and R. Viswanath, *J. Am. Chem. Soc.*, 1989, **111**, 2914.
32 J. Mullay, in 'Electronegativity' (Structure and Bonding Series no. 66), eds. K. D. Sen and C. K. Jørgensen, Springer-Verlag, Berlin, 1987, ch. 1.
33 R. G. Pearson, *J. Am. Chem. Soc.*, 1988, **110**, 7684; *J. Org. Chem.*, 1989, **54**, 1423.
34 D. C. Nonhebel and J. C. Walton, 'Free Radical Chemistry,' CUP, London, 1974.
35 R. Ponec, S. Krupička, and M. Hájek, *Collect. Czech. Chem. Commun.*, 1987, **52**, 547.
36 D. Griller and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 630.
37 I. H. Elson and J. K. Kochi, *J. Org. Chem.*, 1974, **39**, 2091.
38 A. A. Zavitsas, *J. Am. Chem. Soc.*, 1972, **94**, 2779.
39 J. K. S. Wan and A. J. Elliot, *Acc. Chem. Res.*, 1977, **10**, 161; P. J. Hore, C. G. Joslin, and K. A. McLauchlan, *Chem. Soc. Rev.*, 1979, **8**, 29; M. Anpo, K. U. Ingold, and J. K. S. Wan, *J. Phys. Chem.*, 1983, **87**, 1674.
40 J. E. Noll, J. L. Speier, and B. F. Daubert, *J. Am. Chem. Soc.*, 1951, **73**, 3867; Y. Sato, T. Aoyama, and H. Shirai, *J. Organomet. Chem.*, 1974, **82**, 21.

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