Homolytic Reactions of Ligated Boranes. Part 7.[1] An Electron Spin Resonance Study of the t-Butyl Isocyanide–Boryl Radical

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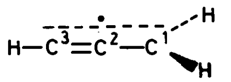
Photochemically generated alkoxyl or cyclopropyl, but not n-propyl, radicals abstract hydrogen from t-butyl isocyanide–borane (TBIB) to give the corresponding isocyanide–boryl radical $Bu^tNC\rightarrow\dot{B}H_2$ (**1**), which has been studied in solution using e.s.r. spectroscopy. The structure and electronic configuration of (**1**) is discussed in relation to the isoelectronic propargylic radical $Bu^tC\equiv C\text{–}\dot{C}H_2$. On the basis of qualitative considerations and molecular orbital calculations it is concluded that (**1**) is probably bent at nitrogen, unlike propargylic radicals which have a linear $C\text{–}C\equiv C\text{–}\dot{C}$ skeleton, and that the spin population on the β-carbon atom in (**1**) is much larger than that in $Bu^tC\equiv C\text{–}\dot{C}H_2$. In contrast with saturated ligated boryl radicals, (**1**) does not abstract halogen from alkyl bromides, as judged by e.s.r. spectroscopy, and this low reactivity is probably a consequence of unpaired electron delocalisation in the isocyanide–boryl. The t-butyl radical is formed in lower yield along with (**1**) when dialkyl peroxides are photolysed in the presence of TBIB. β-Scission of (**1**) is not the source of $Bu^{t\bullet}$ and other possible origins are discussed. γ-Radiolysis of polycrystalline TBIB affords $Bu^{t\bullet}$ at 77 K, presumably by dissociative electron capture. One-electron reduction of TBIB in a methanol glass at 77 K or by $Me_2\dot{C}OH$ in solution also yields $Bu^{t\bullet}$.

Alkyl isocyanides, in common with other Lewis bases (L) such as amines, phosphines, sulphides, and carbon monoxide, form well defined complexes of the type $L\rightarrow BH_3$ with borane. These same donors would be expected to bind effectively to the boryl radical ($H_2B^\bullet$) and we have recently studied a variety of such adducts. The ligated boryls $R_3N\rightarrow\dot{B}H_2$, $R_3P\rightarrow\dot{B}H_2$, and $R_2S\rightarrow\dot{B}H_2$ are isoelectronic analogues of the saturated carbon-centred radicals $R_3C\text{–}\dot{C}H_2$, $R_3Si\text{–}\dot{C}H_2$, and $R_2P\text{–}\dot{C}H_2$, respectively.[1–4] Isocyanide–boryl radicals $RNC\rightarrow\dot{B}H_2$ are isoelectronic counterparts of the *unsaturated* propargylic radicals $RC\equiv C\text{–}\dot{C}H_2$ and here we report an e.s.r. study of the isocyanide–boryl (1) derived from t-butyl isocyanide–borane (TBIB).

$Bu^tN\equiv C\rightarrow\dot{B}H_2$

(1)



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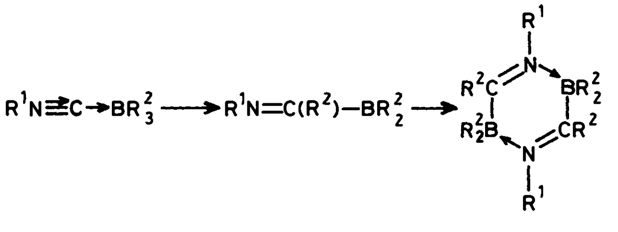
The structures and electronic configurations of propargylic radicals have been investigated in some detail using both experimental and theoretical methods. E.s.r. spectroscopic studies[5–7] and molecular orbital calculations[6–8] at various levels of theory lead to the conclusion that the propargyl radical itself is best represented by the structure (2), in which the broken line signifies delocalisation through the three C-$2p_\pi$ orbitals. The HCCC fragment is linear and linearity is preserved when C(3) is alkylated. The unpaired electron is delocalised by conjugation, but to a lesser extent than in the allyl radical.

Although alkyl isocyanide complexes of borane[9–13] and of trialkylboranes[14] have been described in the literature, these adducts are thermally labile and one mode of their decomposition evidently involves 1,2-shift of a group from boron to the attached carbon atom, followed by dimerisation of the product to give a 2,5-diboradihydropyrazine (3; R^2 = H or alkyl).[9,13,15,16]



(1)

(3)

Work with the borane complexes of methyl and t-butyl isocyanides has been confined to spectroscopic studies and, in particular, the gas-phase microwave spectra[10,11] of both these molecules indicate a linear CNCB skeleton. However, neither adduct has been fully characterised in the condensed phase. The t-butyl isocyanide–trimethylborane complex[14] has been prepared as a crystalline solid, although this is thermally unstable and, encouraged by this result, we have now isolated and characterised t-butyl isocyanide–borane, an isoelectronic analogue of 4,4-dimethylpent-2-yne ($Bu^tC\equiv CMe$).

Results and Discussion

t-Butyl isocyanide reacts smoothly with dimethyl sulphide–borane in pentane to afford TBIB [equation (2)], which could

$$Bu^tNC + Me_2S\rightarrow BH_3 \longrightarrow Bu^tNC\rightarrow BH_3 + Me_2S \qquad (2)$$

be purified by careful vacuum sublimation at 50 °C. *B*-Trideuteriated TBIB was prepared in a similar fashion from $Me_2S\rightarrow BD_3$, and $Bu^tN^{13}C\rightarrow BH_3$ was obtained from the ^{13}C-labelled isocyanide. Naturally occurring boron consists of 80.2% ^{11}B (I 3/2) and 19.8% ^{10}B [I 3, $\gamma(^{10}B)/\gamma(^{11}B)$ 0.335] and TBIB containing 97.5 atom% ^{11}B was sometimes used in order to simplify and intensify the e.s.r. spectra.

The molecular structure of TBIB was confirmed by ^1H and ^{11}B n.m.r. spectroscopy and by i.r. spectroscopy. Although the isocyanide–borane was unchanged after being heated for 1 h at 50 °C, the solid decomposed rapidly, sometimes violently, at *ca.* 85 °C and fell to a pale yellow liquid consisting of a mixture of products [probably including (3; R^1 = Bu^t, R^2 = H)] which was not examined in detail. TBIB decomposes more rapidly in solution to give a more complex mixture of products. Thus,

Table 1. E.s.r. parameters for the t-butyl isocyanide–boryl radical

Radical	Solvent[a]	T/K	g Factor[b]	Hyperfine splittings (G)[b] $a(2\mathrm{H}_\alpha)$	$a(^{11}\mathrm{B})$	$a(^{14}\mathrm{N})$	$a(^{13}\mathrm{C}_\beta)$
$\mathrm{Bu^tNC{\rightarrow}\dot{B}H_2}$	A	213		12.14	6.82	12.14	
	A	191	2.0023	12.13	6.85	12.13	
$\mathrm{Bu^tNC{\rightarrow}\dot{B}D_2}$	A	212	2.0023	1.88[c]	6.26	12.27	
	A	190	2.0023	1.85[c]	6.26	12.21	
$\mathrm{Bu^tN^{13}C{\rightarrow}\dot{B}H_2}$	A	213		12.15	6.83	12.15	7.60
	A	191		12.15	6.88	12.15	7.59
$\mathrm{Bu^tNC{\rightarrow}\dot{B}H_2}$	B	273		12.05	6.90	12.05	
	B	220	2.0023	12.10	6.90	12.10	
	B	200		12.10	6.90	12.10	
$\mathrm{Bu^tNC{\rightarrow}\dot{B}D_2}$	B	273		1.90[c]	6.35	12.18	
	B	220		1.85[c]	6.35	12.15	
	B	200		1.90[c]	6.34	12.10	
$\mathrm{Bu^tN^{13}C{\rightarrow}\dot{B}H_2}$	B	273		12.15	6.90	12.15	7.60
	B	220		12.10	6.90	12.10	7.85
	B	200		12.10	7.00	12.10	8.00
$\mathrm{Bu^tCC{-}\dot{C}H_2}$	A	260		18.4[d]			
	A	220	2.0027	18.4[d]			
	A	180		18.4[d]			

[a] A = [^{2}H$_8$]toluene, B = [^{2}H$_8$]toluene–CD$_2$Cl$_2$ (1:1 v/v). [b] g Factors are considered accurate to ±0.000 05, hyperfine splittings to ±0.05 G. [c] $a(2\mathrm{D}_\alpha)$. [d] No further fine structure (linewidth *ca.* 1.8 G); the spectrum was insufficiently intense to permit detection of ^{13}C satellites without isotopic enrichment.

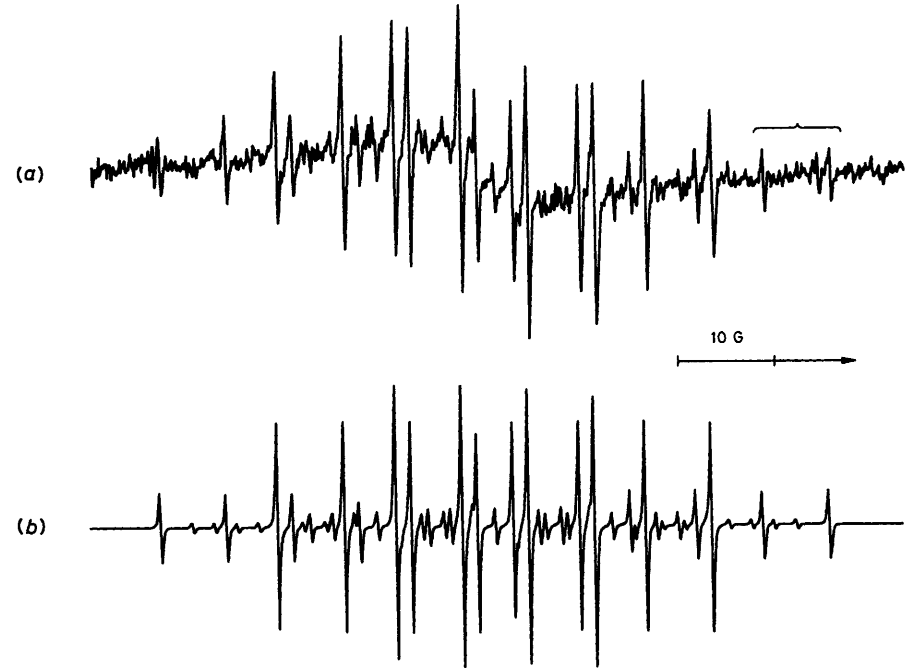


Figure 1. (*a*) E.s.r. spectrum obtained during u.v. irradiation of a [^{2}H$_8$]toluene solution containing TBIB (80.2 atom% ^{11}B, 19.8 atom% ^{10}B) and DTBP at 200 K; the microwave power is 5 mW. The region indicated is shown expanded in Figure 2. (*b*) Computer simulation of the spectrum of (**1**) as a mixture of the ^{11}B- and ^{10}B-containing radicals using $a(2\mathrm{H}_\alpha)$ 12.13, $a(^{14}\mathrm{N})$ 12.13, $a(^{11}\mathrm{B})$ 6.84, and $a(^{10}\mathrm{B})$ 2.29 G. The linewidth is 0.30 G and the lineshape is 50% Gaussian (50% Lorentzian)

when a [^{2}H$_8$]toluene solution of TBIB (initially 0.5M) was heated at 50 °C under dry argon, ^{1}H n.m.r. spectroscopy showed that 80% of the isocyanide–borane had decomposed after 20 min. Solid TBIB was unchanged after storage for 8 weeks in a sealed container at 4 °C.

When a toluene solution containing TBIB (*ca.* 0.15M) and di-t-butyl peroxide (DTBP) (*ca.* 15% v/v) was exposed to u.v. light (λ 240—340 nm) whilst the sample was in the microwave cavity of an e.s.r. spectrometer, the spectrum shown in Figure 1(*a*) was obtained. The pattern of stronger lines can be analysed as a ^{11}B quartet of 1:3:4:3:1 quintets, arising from accidentally equal coupling to one ^{14}N nucleus and to two equivalent protons, and we attribute this spectrum to the isocyanide–boryl radical (**1**) [equations (3) and (4)]. This assignment was confirmed by the

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\,\mathrm{Bu^tO\bullet} \quad (3)$$

$$\mathrm{Bu^tO\bullet} + \mathrm{Bu^tNC{\rightarrow}BH_3} \longrightarrow \mathrm{Bu^tNC{\rightarrow}\dot{B}H_2} + \mathrm{Bu^tOH} \quad (4)$$

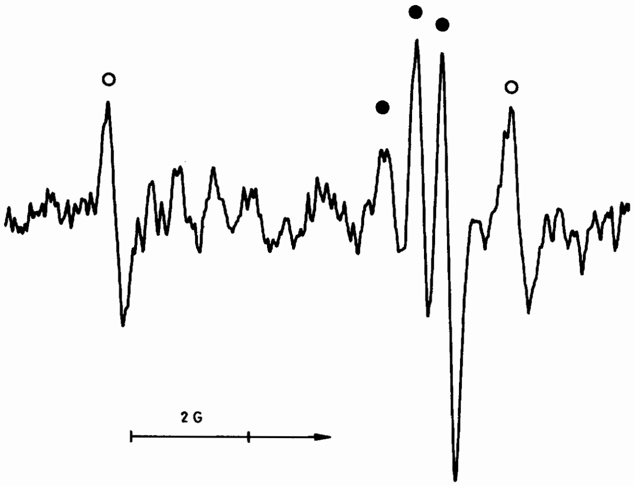


Figure 2. Expansion at 215 K of the region indicated in Figure 1(*a*); the microwave power is 1 mW. The last two lines of $\mathrm{Bu^tNC\rightarrow{}^{11}\dot{B}H_2}$ (open circles), and the three most intense of the four second-order components of line 7 of the t-butyl radical (filled circles) are visible

e.s.r. spectra obtained from ^{11}B-enriched TBIB and from the *B*-deuteriated material. The same spectra were observed in [$^2H_8$]toluene solvent and in mixtures of toluene or deuteriated toluene with CD_2Cl_2 (1:1 v/v) in which TBIB is more soluble; all the e.s.r. parameters are given in Table 1.

TBIB must be very reactive towards hydrogen abstraction by t-butoxyl radicals since no spectrum of the benzyl radical was detectable alongside that of (**1**) between 195 and 270 K in toluene solvent, even though the molar concentration of the latter was at least 20 times that of TBIB. Competitive hydrogen abstraction from toluene was sometimes just evident in similar experiments with $\mathrm{Bu^tNC\rightarrow BD_3}$. The value of $[\mathrm{Bu^tNC\rightarrow\dot{B}H_2}]/[\mathrm{Bu^tNC\rightarrow\dot{B}D_2}]$ was measured during photolysis of DTBP in the presence of a mixture of TBIB and $\mathrm{Bu^tNC\rightarrow BD_3}$ (molar ratio 1:2.0—1:5.4; both compounds contained 97.5 atom% ^{11}B) in [$^2H_8$]toluene–CD_2Cl_2 (1:1 v/v) at 210 K. Assuming that the relative concentrations of the two isocyanide–boryl radicals are equal to their relative rates of formation, (k_H/k_D) for reaction (4) was found to be 2.4 ± 0.2 from the slope of the straight-line plot of $[\mathrm{Bu^tNC\rightarrow\dot{B}H_2}]/[\mathrm{Bu^tNC\rightarrow\dot{B}D_2}]$ against $[\mathrm{TBIB}]/[\mathrm{Bu^tNC\rightarrow BD_3}]$. Such a small isotope effect is to be expected for a rapid, exothermic hydrogen-atom abstraction proceeding through an early transition state.

A weak spectrum of the t-butyl radical is visible in Figure 1(*a*) together with that of (**1**) and the presence of $\mathrm{Bu^{t\bullet}}$ is more obvious in Figure 2, which was recorded under different conditions. In toluene at 215 K, the value of [(**1**)]/[$\mathrm{Bu^{t\bullet}}$] (hereafter referred to as *r*) is *ca.* 2.5. The t-butyl radical was still present when DTBP was replaced with [$^2H_{18}$]DTBP or di-t-pentyl peroxide ($\mathrm{Pe^tOOPe^t}$) and does not, therefore, originate from the peroxide, as it might if free isocyanide were present and reacted through the intermediate imidoyl radical (**4**) as shown in equation (5).[17] U.v. irradiation of TBIB alone in toluene afforded no e.s.r. spectra.

$$\mathrm{Bu^tO\bullet + Bu^tNC \longrightarrow \underset{(4)}{Bu^tN{=}\dot{C}OBu^t} \longrightarrow Bu^t\bullet + Bu^tNCO} \qquad (5)$$

With TBIB (0.5M) and DTBP (15% v/v) in [$^2H_8$]toluene–CD_2Cl_2 (1:1 v/v) at 220 K, the value of *r* was 4.4 ± 0.4 and at 273 K this had decreased only to 2.5 ± 0.3, whilst the absolute concentration of t-butyl radicals remained almost constant. On the basis of the small temperature dependence of *r*, we can exclude thermally induced β-scission of (**1**) [equation (6)] as the

$$\mathrm{Bu^tNC\rightarrow\dot{B}H_2 \longrightarrow Bu^t\bullet + NCBH_2} \qquad (6)$$

major source of $\mathrm{Bu^{t\bullet}}$, provided that the *A* factor for this fragmentation is 'normal' (*i.e.* close to 10^{13} s^{-1}).[18,19] Support for this conclusion was obtained by photolysis of bis(cyclopropylformyl) peroxide (0.25M) and TBIB (0.5M) in [$^2H_8$]toluene–CD_2Cl_2 (1:1 v/v). At 220 K, (**1**) was detected showing that cyclopropyl radicals also abstract hydrogen from the isocyanide–borane [equations (7) and (8)],[20] although the spectrum was

$$\mathrm{cyclo\text{-}C_3H_5C(O)OOC(O)C_3H_5\text{-}cyclo} \xrightarrow{h\nu} \mathrm{2\ cyclo\text{-}C_3H_5\bullet + 2CO_2} \qquad (7)$$

$$\mathrm{cyclo\text{-}C_3H_5\bullet + Bu^tNC\rightarrow BH_3} \longrightarrow \mathrm{Bu^tNC\rightarrow\dot{B}H_2 + cyclo\text{-}C_3H_6} \qquad (8)$$

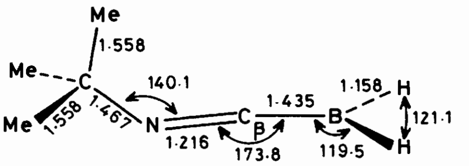
rather weaker than that obtained with DTBP as primary radical source. Although the t-butyl radical was also just detectable in these experiments, the value of *r* (12.5 ± 1) was much larger than that obtained using DTBP, while the rate coefficient for reaction (**6**) must be essentially unchanged, again indicating that β-scission of (**1**) is not the source of $\mathrm{Bu^{t\bullet}}$. We return later to the possible origins of $\mathrm{Bu^{t\bullet}}$.

For comparison with (**1**), we have generated the isoelectronic propargylic radical (**5**) by hydrogen abstraction from 4,4-dimethylpent-2-yne [equation (9)]. The e.s.r. parameters are

$$\mathrm{Bu^tO\bullet + Bu^tC{\equiv}CMe \longrightarrow \underset{(5)}{Bu^tC{\equiv}C{-}\dot{C}H_2} + Bu^tOH} \qquad (9)$$

included in Table 1 and agree closely with those obtained for other 3-alkylated propargyl radicals.[5,6]

Molecular Orbital Calculations.—Spin-unrestricted Hartree–Fock (UHF) molecular orbital calculations were carried out for $\mathrm{Bu^tNC\rightarrow\dot{B}H_2}$ and $\mathrm{MeNC\rightarrow\dot{B}H_2}$ at the semi-empirical MNDO level[21,22] and for the latter radical at the *ab initio* level using the standard 6-31G* basis set available within the GAUSSIAN 82 package.[23] Geometries were fully optimised within C_s symmetry and the resulting molecular structures are all remarkably similar, considering the different levels of theory. In each structure the configuration at boron is effectively planar (sum of the bond angles is 360.0°) and the CNC_β angle is 139 ± 1°; the results are summarised in Table 2 and the MNDO-optimised geometry of (**1**) is shown in (**6**) (bond lengths are in Å, bond angles in degrees). Geometry optimisation with the further constraint of linearity at nitrogen yields structures which are again planar at boron and almost exactly linear at C_β (see Table 2). These linear structures are less stable than the bent equilibrium configurations by 26—27 kJ mol^{-1} at the MNDO



(**6**)

Table 2. Calculated hyperfine splitting constants and other properties of isocyanide–boryl radicals $RNC_\beta \rightarrow \dot{B}H_2$ (R = Me or Bu^t)

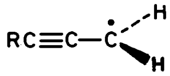
R	Method^a	$C\hat{N}C_\beta$ (°)	Relative energy^b (kJ mol^{-1})	Hyperfine splittings (G) calculated by the INDO (MNDO) methods^c $2H_\alpha$	^{11}B	$^{13}C_\beta$	^{14}N	CH_3^{d}	Other geometrical parameters^e B–H	B–C	N–C_β	HBC	BCN	μ/D
Bu^t	A	140.1^f	0	−9.5 (−6.2)	+10.7 (+7.0)	−3.1 (+23.1)	+26.7 (+30.6)		1.158	1.435	1.216	119.5	173.8	2.1
Bu^t	A	180.0^g	+27.1	−10.5 (−9.2)	+12.7 (+12.2)	−6.3 (+9.5)	+11.7 (+13.4)		1.158	1.420	1.202	119.5	179.6	3.3
Me	A	137.9^f	0	−9.2 (−6.2)	+10.4 (+6.8)	−2.3 (+23.8)	+27.8 (+29.1)	+7.9 (+0.2)	1.158	1.435	1.218	119.4	174.2	1.8
Me	A	180.0^g	+26.2	−10.0 (−9.0)	+12.3 (+11.7)	−5.5 (+10.5)	+10.5 (+12.4)	+16.2 (+7.6)	1.158	1.420	1.202	119.4	179.7	2.8
Me	B	138.0^f	0^h	−9.4 (−6.0)	+12.0 (+6.8)	−1.0 (+26.4)	+24.4 (+30.5)	+5.8 (−0.6)	1.188	1.482	1.181	118.3	176.4	3.0
Me	B	180.0	+11.2^i	−10.9 (−9.1)	+15.1 (+12.5)	−4.9 (+13.3)	+8.6 (+11.0)	+12.2 (+5.6)	1.189	1.490	1.160	117.7	180.0	4.9

^{a} Method used for geometry optimisation; A = MNDO, B = UHF/6-31G*. ^{b} For MNDO calculations this corresponds to the difference in enthalpies of formation of the bent and linear forms; for the *ab initio* calculations it is the difference in total energies. ^{c} Calculated without annihilation of the small amounts of quartet-state contamination ($\langle S^2 \rangle$ *ca.* 0.76). There is no established scaling factor to convert computed B-2*s* spin populations to coupling constants; a value of 720.8 G was used for both MNDO and INDO calculations.[28] ^{d} For R = CH_3 only; mean value. ^{e} Bond lengths in Å, bond angles in degrees. ^{f} All positive normal vibrational frequencies. ^{g} One negative normal vibrational frequency. ^{h} Total energy −157.717 142 hartree. ^{i} Total energy −157.712 876 hartree.

level, but by only 11 kJ mol^{-1} at the UHF/6-31G* level, although the latter value is raised to 15 kJ mol^{-1} when electron correlation is included as a Møller-Plesset correction taken to third-order (UMP3/6-31G*//UHF/6-31G*).[23] These results indicate that the barrier to inversion at nitrogen is probably not very large for isocyanide–boryls in solution. Similar calculations for the isoelectronic propargylic radicals predict a collinear geometry for the C–C≡C–$\dot{C}H_2$ skeleton, in confirmation of previous work. Reassuringly, in contrast to (**1**), TBIB was predicted to prefer a linear arrangement of the CNCB moiety at the MNDO level.

The hyperfine splitting constants computed for the bent equilibrium structures of $RNC \rightarrow \dot{B}H_2$ using the INDO[24] and MNDO[22] methods (see Table 2) are not all in good agreement with experiment. However, it must be remembered that if bending at nitrogen is not energetically demanding, the time-average CNC_β angle could be appreciably closer to 180° than to its equilibrium value. A particular consequence of this is that the value of *a*(N) calculated for the equilibrium structure will be an overestimate of the experimental value. The observed nitrogen hyperfine splitting for (**1**) shows no measurable variation over the accessible temperature range.

There is a wide discrepancy between the values of $a(^{13}C_\beta)$ calculated using the INDO or MNDO methods. Thus, while INDO predicts small *negative* values of $a(^{13}C_\beta)$, those computed by MNDO are larger and *positive*. The SOMO calculated by the INDO method has only a relatively small contribution from the C_β-$2p_\pi$ orbital;* the resulting positive spin density at C_β is thus small and is evidently less than the negative spin density induced by spin-polarisation. In valence bond terms, propargylic radicals and isocyanide–boryl radicals may be described as resonance hybrids of the canonical structures shown in (**7a**—**d**) and (**8a**—**d**), respectively. The INDO result for $RNC \rightarrow \dot{B}H_2$ corresponds to a hybrid which has only a small contribution from structure (**8d**), while the MNDO result is equivalent to a hybrid rich in (**8d**).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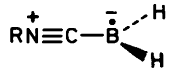
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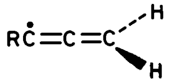
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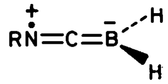
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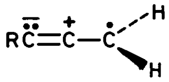
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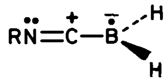
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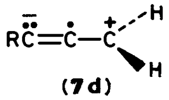
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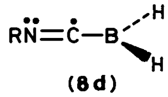
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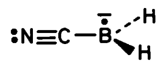
We have previously reported the e.s.r. spectrum of the cyanoborane radical anion (**9**), which was generated by hydrogen-atom abstraction from the cyanotrihydroborate anion.[25] The splitting constants for (**9**) [$a(2H_\alpha)$ 15.8, $a(^{11}B)$ 14.3,

$$\mathrm{Bu^tO\bullet + H_3BCN^- \longrightarrow NC{-}\dot{B}H_2^- + Bu^tOH} \qquad (10)$$

(**9**)

and *a*(N) 3.0 G at 252 K] indicate that the extent of unpaired electron delocalisation onto the cyano group is similar to that in the isoelectronic cyanomethyl radical NC–$\dot{C}H_2$ and that the contribution from structure (**10c**) is small.[25] However, it would be expected that *N*-protonation of (**9**), to give the simplest isocyanide–boryl $HNC \rightarrow \dot{B}H_2$, will stabilise (**10c**) in relation to (**10a** and **b**) and thus result in a shift of π spin population from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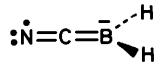
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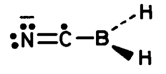
(10c)

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* The distinction between σ and π orbitals is not strictly possible because the CBH_2 plane is not a symmetry plane of the radical. Nevertheless, it is useful to retain this classification for purposes of qualitative description.

N and B to the central carbon atom; *N*-alkylation of (**9**) should have a similar effect. Indeed, the small value of $a(^{11}B)$ for (**1**) compared with that for (**9**), while $a(2H_\alpha)$ for the former is only 30% less than for the latter, suggests that the π spin population on C_β is substantially larger in the isocyanide–boryl than in the cyanoborane radical anion, since positive spin population on C_β will give rise to a *negative* contribution to $a(^{11}B)$ because of spin polarisation of the C–B σ bonding electrons.

In summary, while propargylic radicals can be adequately represented as hybrids of (**7a** and **b**) with negligible contributions from (**7c** and **d**), structure (**8d**) appears to be relatively important for the isoelectronic isocyanide–boryl radicals. This is reasonable since no formal charge separation is involved in (**8d**), while it is in (**7d**). In molecular orbital language, inclusion of (**8d**) reflects the delocalisation of the unpaired electron from boron into the NC π^* orbital of the isocyanide moiety resulting in a build-up of positive spin population on C_β and a tendency for bending at nitrogen. Although the sign of $a(^{13}C_\beta)$ for (**1**) is not known with certainty, its magnitude (*ca.* 7.8 G) is considerably smaller than that of $a(^{13}C_\beta)$ for the propargyl radical (**2**) (-18.1 G).[7] This difference is in accord with a significant positive contribution to $a(^{13}C_\beta)$ for (**1**), arising from the relatively large π spin population on C_β. The *ab initio* calculations predict a negative spin density at the C_β nucleus in bent $MeNC\rightarrow\dot{B}H_2$ corresponding to $a(^{13}C)$ -2.1 G, which is close to the value obtained by the INDO method. The value of $a(^{13}C_\alpha)$ for (**2**) (33.9 G) is nearly five times as large as $a(^{11}B)$ for (**1**), again indicating a substantial shift of π spin population from the α to the β atom on going from the propargyl radical to the isocyanide–boryl.

The smaller value of $a(^{11}B)$ for $Bu^tNC\rightarrow\dot{B}D_2$ compared with that for the protiated radical at the same temperature is in accord with a planar equilibrium geometry at boron and arises because of the smaller amplitude of out-of-plane vibration in the deuteriated species. The magnitude of the α-proton splitting (presumably negative) for (**1**) is appreciably smaller than that for (**5**) and, although the 'excess charge effect' may account in part for the difference,[25,26] this result provides further evidence that the π spin population on boron is less than that on the α-carbon in the isoelectronic analogue.

Reaction of (**1**) *with Alkyl Halides.*—Amine–, phosphine–, and sulphide–boryl radicals rapidly abstract halogen from alkyl bromides [equation (11)].[1–3,27] The isocyanide–boryl radical

$$L\rightarrow\dot{B}H_2 + RBr \longrightarrow R\cdot + L\rightarrow BH_2Br \qquad (11)$$

(**1**) is much less reactive since its e.s.r. spectrum was still observed up to 273 K in the presence of n-propyl bromide (1.5M) and $Pr^{n\cdot}$ was not detectable. In similar experiments, (**1**) did not react with Pr^nCl as judged by e.s.r. spectroscopy; the value of *r* was unaffected by the presence of either halide. Only the spectrum of $Pr^{n\cdot}$ was detected during u.v. irradiation of a $[^2H_8]$toluene–CD_2Cl_2 solution containing dibutanoyl peroxide (0.25M) and TBIB (0.5M) between 210 and 273 K, confirming that this alkyl radical does not react with the isocyanide–borane under the experimental conditions.

The relatively low reactivity of (**1**) towards alkyl halides compared with the saturated ligated boryl radicals is in accord with conjugative delocalisation of the unpaired electron away from boron as discussed before.

Electron Addition to TBIB.—An intense e.s.r. spectrum of the t-butyl radical was observed between 77 and 160 K from a polycrystalline sample of TBIB which had been exposed to γ-rays (^{60}Co source, dose *ca.* 1 Mrad) at 77 K. At temperatures above *ca.* 170 K, the spectrum of $Bu^{t\cdot}$ decayed and was replaced by new unidentified e.s.r. signals which were not investigated further. *B*-Trideuteriated TBIB gave similar results and the high-temperature spectrum was essentially superimposable on that obtained from the protiated material. This suggests that the isocyanide–borane undergoes dissociative electron capture to give $Bu^{t\cdot}$ and the cyanoborohydride anion [equation (12)].[28]

$$Bu^tNC\rightarrow BH_3 \xrightarrow{+e^-} Bu^t\cdot + NCBH_3^- \qquad (12)$$

Further evidence for the unstable nature of the TBIB radical anion was obtained by u.v. irradiation of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) and the isocyanide–borane in a methanol glass at 77 K. This technique involves photoinduced electron transfer from TMPD to a reducible substrate [equation (13)]; the e.s.r. spectrum of the diamine

$$TMPD \xrightarrow{h\nu} TMPD^{\cdot+} + e^- \qquad (13)$$

radical cation is broad and unobtrusive at low temperature.[29] As with γ-radiolysis, a strong spectrum of the t-butyl radical was observed and no signals which might be attributed to the TBIB radical anion were detected. U.v. irradiation of TBIB alone in a methanol glass at 77 K did not afford the e.s.r. spectrum of the t-butyl radical.

In this context, we recall that the reaction of the borane radical anion with t-butyl isocyanide in fluid solution also affords the t-butyl radical with no e.s.r. evidence for an intermediate imidoyl radical (which would presumably be indistinguishable from the TBIB radical anion) [equation (14)].

$$Bu^tNC + H_3B^{\cdot-} \longrightarrow [Bu^tN\dot{C}BH_3^-] \longrightarrow Bu^t\cdot + NCBH_3^- \qquad (14)$$

The chemical properties of the triethylsilyl radical are similar in many ways to those of $H_3B^{-\cdot}$ and the imidoyl adduct of the former with t-butyl isocyanide is sufficiently stable to be detected at low temperatures, although it does break down readily in an analogous manner to the TBIB radical anion above *ca.* 180 K [equation (15)].[17]

$$\begin{tikzcd} Bu^tNC + Et_3Si\cdot \arrow[r] & Bu^tN\dot{C}SiEt_3 \arrow[d] & \\ & Bu^t\cdot + NCSiEt_3 & (15) \end{tikzcd}$$

The Origin of the t-Butyl Radical.—As discussed before, β-scission of (**1**) cannot be the major source of the t-butyl radical which is detected alongside the former, especially when dialkyl peroxides are used as the primary photochemical source of radicals. Furthermore, with DTBP as primary source the steady-state concentration of (**1**) during continuous u.v. irradiation of a $[^2H_8]$toluene solution at 200 K was proportional to the square-root of the incident light intensity, indicating that (**1**) is removed by radical–radical reactions. When the light was shuttered, its spectrum decayed within the fall-time of the instrument (0.3 s).

There are a number of possible sources of the t-butyl radical and some of the more reasonable ones are considered below.

It is feasible that *photolysis* of (**1**) could give $Bu^{t\cdot}$, although in our previous studies of transient photochemically generated radicals we have not encountered a precedent for this type of transformation. Moreover, at 273 K with 0.5M-TBIB in $[^2H_8]$toluene–CD_2Cl_2, *r* showed only a small *decrease* from 2.6 ± 0.3 to 1.8 ± 0.3 as the concentration of DTPB was increased from 5 to 60% v/v. If photolysis of (**1**) is the source of $Bu^{t\cdot}$, the value of *r* would be expected to *increase* as the concentration of light-absorbing peroxide increases.

It seems likely that the t-butyl radical arises as a result of electron transfer to TBIB [see equation (12)], although the identity of the electron donor(s) remains in doubt. The most obvious candidate would be a photoexcited state of the peroxide, but in the gas phase the excited singlet state of DTBP is dissociative and in solution also it is thought to be too short-lived to participate in such bimolecular processes.[30,31]

The relative concentration of the t-butyl radical is very different (smaller) when bis(cyclopropylformyl) peroxide is the primary radical source, suggesting that the electron donor might be a nucleophilic radical which is formed more efficiently when DTBP is the primary radical source. At 220 K for a [$^2H_8$]toluene–CD_2Cl_2 solution containing $Bu^tNC\rightarrow BD_3$ and DTBP, the value of $[Bu^tNC\rightarrow \dot{B}D_2]/[Bu^{t\bullet}]$ was 2.8 ± 0.3, while in a similar experiment with TBIB the value of r was 4.4 ± 0.4 (see above). This result provides some evidence that the reaction leading ultimately to $Bu^{t\bullet}$ is in competition with the formation of (**1**) by reaction (4).

To obtain support for the proposed electron-transfer route to the t-butyl radical, Pe^tOOPe^t was photolysed in the presence of TBIB (0.2M) in propan-2-ol–toluene (1:1 v/v). At *ca.* 230 K, strong spectra of both $Bu^{t\bullet}$ and $Me_2\dot{C}OH$ (a good electron donor) were observed, but that of (**1**) was absent. We interpret this result in terms of reactions (16) and (17), with the former competing effectively with hydrogen abstraction from TBIB. In a control experiment when TBIB was replaced by Bu^tNC, only $Me_2\dot{C}OH$ (and not $Bu^{t\bullet}$) was detected.

$$Pe^tO\bullet + Me_2CHOH \longrightarrow Pe^tOH + Me_2\dot{C}OH \qquad (16)$$

$$\begin{array}{c} Me_2\dot{C}OH + Bu^tNC\rightarrow BH_3 \\ \Big\downarrow \\ Bu^t\bullet + NCBH_3^- + Me_2CO + H^+ \end{array} \qquad (17)$$

Experimental

E.s.r. spectra were recorded during continuous u.v. irradiation of samples positioned in the microwave cavity of a Varian E-109 or E-4 spectrometer operating at *ca.* 9.1 GHz.[32] The light source was a 500 W mercury discharge lamp (Osram HBO-500W/2) in an Oriel Universal 1 KW housing equipped with an f0.7 Aspherab fused silica condensing lens. The slightly converging beam from this was focused onto the sample, using a fused silica lens (focal length 10 cm, diameter 7.5 cm), after passage through a 3 cm pathlength cell filled with an aqueous solution containing $NiSO_4\cdot7H_2O$ (0.38M), $CoSO_4\cdot7H_2O$ (0.07M), and sulphuric acid (0.04M). The intensity of the incident light could be reduced by positioning bronze mesh screens (30, 10, or 3% transmittance) in the beam.

Samples were prepared using a vacuum line and were sealed in evacuated Suprasil quartz tubes (4 mm o.d., 3 mm i.d.); these were stored in liquid nitrogen and thawed in a solid CO_2–acetone slush bath just prior to recording spectra. A standard Varian variable-temperature unit was used and the sample temperature during irradiation was determined as described previously.[32]

Photoelectron detachment experiments with TMPD were carried out as described by Campion and Williams;[29] methanol glasses containing TMPD and TBIB (0.2 and 1 mol%, respectively, based on MeOH) were photolysed at 77 K using the standard Varian liquid nitrogen Dewar accessory. In γ-radiolysis experiments, polycrystalline TBIB contained in sealed, evacuated Suprasil tubes (3 mm o.d., 2 mm i.d.) was irradiated at 77 K with a ^{60}Co source for *ca.* 1 h (dose *ca.* 1 Mrad). Spectra were recorded initially at 77 K and then transferred to the variable-temperature unit.

g-Factors and hyperfine splittings were derived from the measured microwave frequency and the line positions, the latter obtained using a Varian E-500 gaussmeter and corrected for the field difference between the probe and the sample using the pyrene radical anion (*g* 2.002 71) as standard.[33] Best-fit e.s.r. parameters were usually computed using Preston's program ESRLSQ.[34]

Materials.—N.m.r. spectra were recorded at ambient temperature in C_6D_6 using a Varian XL-200 instrument; the standards were tetramethylsilane (^1H, internal) or $BF_3\cdot Et_2O$ (^{11}B, external). The thermal decomposition of TBIB was followed in [$^2H_8$]toluene with a probe temperature of 50 °C. I.r. spectra were obtained using a Perkin-Elmer 983 instrument.

All solvents were dried before use; although TBIB does not appear to be particularly air-sensitive, all operations involving boron-containing compounds were conducted under dry argon. Di-t-butyl peroxide (Aldrich) was washed with aqueous silver nitrate solution, then with water, dried ($MgSO_4$), passed down a column of basic alumina (activity 1), and finally distilled (b.p. 46—47 °C at 76 Torr). [$^2H_{18}$]DTBP,[17] di-t-pentyl peroxide,[35] bis(cyclopropylformyl) peroxide,[27,36] dibutanoyl peroxide,[37] and 4,4-dimethylpent-2-yne[38] were prepared by literature methods. Dibutanoyl peroxide was purified by chromatography through silica gel (CH_2Cl_2 eluant), δ_H 0.70 (t, 6 H, *J* 7.4 Hz), 1.42 (sextet, 4 H, *J* 7.3 Hz), and 1.95 (t, 4 H, *J* 7.3 Hz). Dimethyl sulphide–borane was obtained commercially (Aldrich); the ^{11}B-enriched (97.5 atom%) and *B*-trideuteriated materials were prepared as described previously.[1] t-Butyl isocyanide (Aldrich) was used as received; $Bu^tN^{13}C$ was prepared according to the method of Nef[17,39] from t-butyl iodide and labelled silver cyanide, itself prepared from $K^{13}CN$ (Aldrich; 99 atom% ^{13}C).

t-Butyl Isocyanide–Borane (*TBIB*).—Dimethyl sulphide–borane (1.0 cm^3 of 10M solution in Me_2S) was added dropwise during 10 min to a stirred solution of t-butyl isocyanide (0.83 g, 0.010 mol) in pentane (10 cm^3). During the addition the reaction flask was cooled in a bath at −30 °C and afterwards the mixture was stirred for a further 30 min at the same temperature. The mixture was then allowed to warm to room temperature, and the precipitate was removed by filtration and dried under reduced pressure. The crude product was purified by vacuum sublimation (0.01 Torr; bath temperature 50 °C) to give microcrystalline *t-butyl isocyanide–borane* [m.p. *ca.* 85 °C (decomp.)] (Found: C, 61.8; H, 12.6; N, 14.6. $C_5H_{12}BN$ requires C, 61.9; H, 12.5; N, 14.5%), δ_H 0.57 (t, 9 H, $^3J_{NH}$ 2.3 Hz) and 1.47 (q, 3 H, $^1J_{BH}$ 94 Hz); δ_B −43.1 p.p.m. (q, $^1J_{BH}$ 94 Hz). The i.r. spectrum (Nujol mull) showed strong absorption bands at 2 351 (B–H stretch) and 2 258 cm^{-1} (N≡C stretch); the latter band was also shown by $Bu^tNC\rightarrow BD_3$, but the former band was replaced by a B–D stretch at 1 785 cm^{-1}. The isotopically labelled materials were prepared by similar routes starting from $Me_2S\rightarrow{}^{11}BH_3$ (97.5 atom% ^{11}B), $Me_2S\rightarrow{}^{11}BD_3$ (also 97.5 atom% ^{11}B), or $Bu^tN^{13}C$ (by reaction with $Me_2S\rightarrow{}^{11}BH_3$); $Bu^tNC\rightarrow{}^{11}BD_3$ showed δ_B −44.3 p.p.m. (br s).

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