An Electron Spin Resonance Study of Radical Addition to Alkyl Isocyanides

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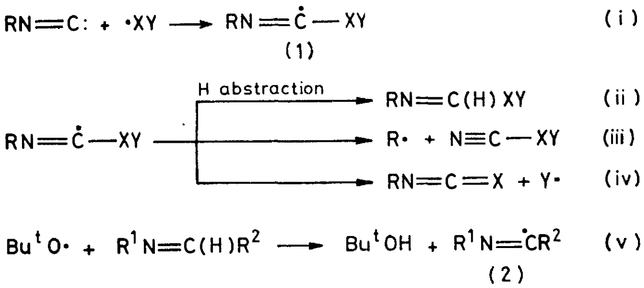
Using e.s.r. spectroscopy, a variety of types of free radical (Z·) have been shown to add to the terminal carbon of alkyl isocyanides (RNC) to form imidoyl radical adducts ($RN{=}\dot{C}Z$). At 253 K the rate constants for radical addition to Bu^tNC are in the order $k(Ph\cdot) > k(Bu^tO\cdot) > k(Me\cdot)$, and $k(Bu^tO\cdot) = 6 \times 10^5$ l mol^{-1} s^{-1}. The imidoyl adducts are σ-radicals in which the unpaired electron occupies an orbital orthogonal to the N=C π-orbital. The magnitudes of $a(^{13}C_\alpha)$ and $a(N_\beta)$ are markedly dependent upon the nature of Z, and $a(^{13}C_\alpha)$ increases with the electronegativity of Z. The radical $Bu^tN{=}\dot{C}SiEt_3$ appears to be close to linear at C_α, whilst $Bu^tN{=}\dot{C}OR$ is bent. There appear to be two contributions, of opposite sign, to $a(N_\beta)$, a positive one resulting from direct overlap of the orbital of the unpaired electron with that of the lone pair on nitrogen, and a negative one resulting from spin-polarisation of the N_β–C_α σ-bonding orbital. The β-scission of some imidoyl radicals has also been studied using e.s.r. spectroscopy. Radicals of the type $RN{=}\dot{C}XBu^t$ (X = O or S) undergo X–C cleavage to form RNCX and $Bu^t\cdot$, whilst the radicals $RN{=}\dot{C}Y$ (Y = MeS, Et_3Si, or Ph) undergo cleavage to produce R· and N≡CY. At 243 K the rate constants for β-scission were *ca.* 1.4×10^5 ($Bu^tN{=}\dot{C}SiEt_3$), 3.1×10^5 ($Bu^tN{=}\dot{C}SBu^t$), and 3.6×10^3 s^{-1} ($Bu^tN{=}\dot{C}OBu^t$).

CHEMICAL evidence suggests that a variety of reactive free radicals add to the terminal carbon atom of an isonitrile to form an imidoyl radical (1) [reaction (i)].[1-4] The imidoyl radical may subsequently abstract hydrogen to form the product of α-addition of HXY to the isocyanide [reaction (ii)], or it may undergo unimolecular β-scission to yield either the radical R· [reaction (iii)] or, if X = O or S, the radical Y· [reaction (iv)].[1]



$$RN{=}C{:} + \cdot XY \longrightarrow RN{=}\dot{C}{-}XY \quad (i)$$
(1)

H abstraction

$$RN{=}\dot{C}{-}XY \longrightarrow RN{=}C(H)XY \quad (ii)$$

$$RN{=}\dot{C}{-}XY \longrightarrow R\cdot + N{\equiv}C{-}XY \quad (iii)$$

$$RN{=}\dot{C}{-}XY \longrightarrow RN{=}C{=}X + Y\cdot \quad (iv)$$

$$Bu^tO\cdot + R^1N{=}C(H)R^2 \longrightarrow Bu^tOH + R^1N{=}\dot{C}R^2 \quad (v)$$
(2)

The purpose of our work was to make use of e.s.r. spectroscopy to confirm that radical addition to alkyl isocyanides gives rise to imidoyl radicals, and to examine the structures and subsequent transformations of these adducts. A preliminary communication of part of this work has already appeared.[5] The only previous report of the e.s.r. spectra of imidoyl radicals is that by Danen and West,[6] who generated species of the type (2; R^1 and R^2 = alkyl) by abstraction of hydrogen from aldimines using photochemically generated t-butoxyl radicals [reaction (v)].

The imidoyl † radicals (2) exhibited g factors of 2.001 6, less than the free-spin value (2.002 3), and relatively small splittings from β-hydrogens in the group R^2. These e.s.r. parameters were considered to be consistent with the formulation of (2) as 'σ-type' radicals.[6]

RESULTS

E.s.r. spectra were recorded during continuous photochemical generation [7] of a variety of free radicals in the presence of a series of alkyl isocyanides in cyclopropane solvent. At low temperatures (*ca.* 160 K) an e.s.r. spectrum assigned to the imidoyl radical (1) was usually the only signal apparent, although at higher temperatures radicals formed by the β-scission of (1) could often also be detected. The spectroscopic parameters of the imidoyl radicals are given in Table 1.

The imidoyl radicals had g factors within the range 2.001 1—2.002 0, less than the free-spin value of 2.002 3. The e.s.r. spectra of some of the imidoyl adducts were sufficiently intense to allow determination of $a(^{13}C_\alpha)$ without isotopic enrichment,[5] but in order to confirm our earlier [5] measurement of $a(^{13}C_\alpha)$ for $Bu^tN{=}\dot{C}SiEt_3$ and to detect ^{13}C splitting for other radicals, we employed t-butyl isocyanide containing 47% $Bu^tN^{13}C$ and 53% $Bu^tN^{12}C$. To verify that the spectrum detected during photolysis of di-t-butyl peroxide in the presence of t-butyl isocyanide was due to the imidoyl adduct (3), we generated this radical by an alternative route; an identical spectrum was obtained during photolysis of a mixture of bis(trimethylsilyl) peroxide and $Bu^tN{=}C(H)OBu^t$ [reaction (vi); *cf.* ref. 6]. The silyl peroxide, rather than di-t-butyl peroxide, was employed so that t-butoxyl radicals were not produced in the system.‡

Photolysis of azomethane in the presence of t-butyl isocyanide (*ca.* 1M) between 170 and 253 K showed only the spectrum of the methyl radical, and hence Me· does not add at a rate sufficient to give rise to a detectable concentration of $Bu^tN{=}\dot{C}Me$.

When phenyl radicals (produced by photolysis of a

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† Danen and West [6] referred to (2) as an iminoyl radical; we feel that these species are more correctly described as imidoyl radicals.

‡ It is just conceivable that a small amount of t-butyl isocyanide could be present in or formed from $Bu^tN{=}C(H)OBu^t$, and this would make the result ambiguous if di-t-butyl peroxide were employed as the source of hydrogen-abstracting radicals.

[1] For a review see T. Saegusa and Y. Ito in 'Isonitrile Chemistry', ed. I. Ugi, Academic Press, New York, 1971, ch. 4.

[2] R. E. Banks, R. N. Haszeldine, and C. W. Stephens, *Tetrahedron Letters*, 1972, 3699.

[3] L. A. Singer and S. S. Kim, *Tetrahedron Letters*, 1974, 861.

[4] S. S. Kim, *Tetrahedron Letters*, 1977, 2741.

[5] P. M. Blum and B. P. Roberts, *J.C.S. Chem. Comm.*, 1976, 535.

[6] W. C. Danen and C. T. West, *J. Amer. Chem. Soc.*, 1973, 6872.

[7] R. W. Dennis, I. H. Elson, B. P. Roberts, and R. C. Dobbie, *J.C.S. Perkin II*, 1977, 889.

TABLE 1

E.s.r. parameters for imidoyl radicals in cyclopropane

Radical[a]	T/K	g Factor	Hyperfine splittings (G) $a(N_\beta)$	$a(^{13}C_\alpha)$	Others
$Bu^tN{=}\dot{C}OSiMe_3$	188	2.0013	*b*	116.0	*b*
$Bu^nN{=}\dot{C}OSiMe_3$	177	2.0011	*c*		*c*
$Bu^tN{=}\dot{C}OBu^t$	180	2.0016	*d*	108.0	*e*
$Bu^tN{=}\dot{C}O[^2H_9]Bu^t$	185		*d*		*f*
$EtMe_2CN{=}\dot{C}OBu^t$	188	2.0014		109.0	
$Bu^tN{=}\dot{C}OCMe_2Et$	179	2.0015			
$MeN{=}\dot{C}OBu^t$	190	2.0013	$\leqslant 0.2$[g]		0.75 (3 H); 0.13 (9 H)
$Bu^tN{=}\dot{C}SCF_3$	185		5.8	92.4	
$Bu^tN{=}\dot{C}SCH_3$	270	2.0012	4.4		
$Bu_tN{=}\dot{C}SBu^t$	188	2.0014	5.0	76.0	
$Bu^tN{=}\dot{C}P(\overline{-OCH_2CMe_2NH})_2$	200	2.0016	6.7	46.0	139.9 (1P)[h]
$Bu^tN{=}\dot{C}P(\overline{-OCH_2CMe_2O})_2$	196	2.0016	8.6	41.5	147.9 (1P)[h]
$Bu^nN{=}\dot{C}P(\overline{-OCH_2CMe_2O})_2$	187	2.0013	8.5		147.0 (1P)
$Bu^tN{=}\dot{C}P(O)(OEt)_2$	177	2.0014	7.5		127.4 (1P)[h]
$Bu^tN{=}\dot{C}SiEt_3$	178	2.0014	8.6	29.8	
$MeN{=}\dot{C}SiEt_3$	171	2.0011	8.0		
$Bu^nN{=}\dot{C}SiEt_3$	181	2.0011	7.7		
$Me_3SiN{=}\dot{C}SiMe_3$	217	2.0018	8.7		*i*
$Bu^tN{=}\dot{C}Ph$	213	2.0020			
$Bu^nN{=}\dot{C}CH_3$[j]	173	2.0016	1.75		8.55 (3 H)
$Bu^tN{=}\dot{C}Bu^t$[j]	173	2.0016	1.80		
$Bu^nN{=}\dot{C}Bu^t$[j]	173	2.0016	1.20		

[a] Photochemical sources of radical addenda: ROOR (RO·); RSSR (RS·); $R_3SiH + Bu^tOOBu^t$ ($R_3Si\cdot$); $(EtO)_2P(O)H + Bu^tOOBu^t$ [$(EtO)_2\dot{P}O$]; $(\overline{XCMe_2CH_2O-})_2PH + Bu^tOOBu^t$ [$(\overline{XCMe_2CH_2O-})_2P\cdot$, X = O or NH]; $Ph_3As + Bu^tOOBu^t$ (Ph·). [b] Unresolved, linewidth 1.6 G. [c] Some poorly resolved further splitting was apparent; three or five lines spaced by *ca.* 0.7 G. [d] Detailed analysis was not possible, but $a(N_\beta)$ is probably $\leqslant 0.3$ G. [e] Spectrum appeared as a multiplet of at least 20 lines, equally spaced by 0.15 G. It seems likely that $a(OBu^t) = 0.15$ G and that the protons of the *N*-t-butyl group give rise to resolvable splitting which must be a multiple of the line spacing. [f] Spectrum appeared as a multiplet of at least 11 lines, equally spaced by 0.3 G. [g] $MeN{=}\dot{C}OC_4D_9{}^t$ showed a 1 : 3 : 3 : 1 quartet with no further resolvable splitting and a linewidth of 0.4 G. [h] Some poorly resolved further splitting was apparent, probably arising from the *N*-t-butyl protons. [i] Multiplet of at least 11 lines, equally spaced by 0.42 G. [j] Results from ref. 6.

mixture of di-t-butyl peroxide and triphenylarsine[8]) were generated in the presence of t-butyl isocyanide, a weak, broad signal was detected (g 2.002 0, linewidth *ca.* 8 G).* The same spectrum was obtained when dicumyl peroxide was photolysed in the presence of $Bu^tN{=}C(H)Ph$, and the signal is ascribed to the imidoyl radical (4) [equation (vii)]. The assignment of this spectrum to (4) was confirmed by its replacement by the signal from the t-butyl radical at higher temperatures [reaction (viii)].

$$Me_3SiO\cdot + Bu^tN{=}C(H)OBu^t \longrightarrow Me_3SiOH + \underset{(3)}{Bu^tN{=}\dot{C}OBu^t} \qquad \text{(vi)}$$

$$PhMe_2CO\cdot + Bu^tN{=}C(H)Ph \longrightarrow PhCMe_2OH + \underset{(4)}{Bu^tN{=}\dot{C}Ph} \qquad \text{(vii)}$$

$$Bu^tN{=}\dot{C}Ph \longrightarrow Bu^t\cdot + N{\equiv}CPh \qquad \text{(viii)}$$

Fragmentation of Imidoyl Radicals.—Whilst the imidoyl radical was usually the only species detected at low temperatures (<153 K), in many cases the spectrum of this adduct was progressively replaced at higher temperatures by that of a radical product of fragmentation. The radicals produced by β-scission are listed in Table 2.

The rate constants for β-scission of selected imidoyl radicals were obtained relative to those for self-reaction of the product alkyl radicals, by measurement of the steady-state concentrations of imidoyl and alkyl radicals at different incident light intensities.[9,10] Thus, if the t-butyl radical is formed from (3) [equation (ix)] and destroyed by reactions (x) and (xi) it may readily be shown that equation (xii) holds.

$$Bu^tN{=}\dot{C}OBu^t \xrightarrow{k_\beta} Bu^tNCO + Bu^t\cdot \qquad \text{(ix)}$$

$$\left.\begin{array}{l} Bu^t\cdot + Bu^tN{=}\dot{C}OBu^t \xrightarrow{k_x} \\ Bu^t\cdot + Bu^t\cdot \xrightarrow{2k_t} \end{array}\right\} \begin{array}{l}\text{non-radical} \\ \text{products}\end{array} \qquad \begin{array}{r}\text{(x)} \\ \text{(xi)}\end{array}$$

The slope of a plot of $(1/[Bu^t\cdot])$ against $[Bu^t\cdot]/[(3)]$ for different light intensities is equal to $(2k_t/k_\beta)$ Measurements were made over the temperature range 216—253 K

$$1/[Bu^t\cdot] = (k_x/k_\beta) + (2k_t/k_\beta)\,[Bu^t\cdot]/[(3)] \qquad \text{(xii)}$$

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* The spectrum of $Ph_2\dot{A}s(OBu^t)_2$ was also observed.[8]

[8] E. Furimsky, J. A. Howard, and J. R. Morton, *J. Amer. Chem. Soc.*, 1973, **95**, 6574.

[9] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1972, 747.

[10] G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 8784.

and the results are summarised by equation (xiii), in which $\theta = 2.303RT$ kJ mol^{-1}.

$$\log_{10}[(k_\beta/2k_t)/\text{mol l}^{-1}] = 1.1 - 34.2/\theta \qquad \text{(xiii)}$$

The rate constant for self-reaction of t-butyl radicals has been measured previously and found to correspond to that for a diffusion-controlled process.[11,12] Bennett and Summers [11] measured $2k_t$ as 1.1×10^{10} l mol^{-1} s^{-1} at 298 K with an activation energy of 4.3 kJ mol^{-1} in either isobutane or cyclopentane as solvent. The choice of an activation energy for the particular medium employed in our experiments (*ca.* 1M-Bu^{t}NC + *ca.* 1M-Bu^{t}OOBu^t in cyclopropane) is somewhat arbitrary, but a value of 6 kJ mol^{-1} seems reasonable, and if we assume $2k_t$ is 1.1×10^{10} l mol^{-1} s^{-1} at 298 K we may derive equation (xiv). Combining equations (xiii) and (xiv) we obtain equation (xv) for the rate constant for β-scission of $\mathrm{Bu^tN{=}\dot{C}OBu^t}$.

$$\log_{10}(2k_t/\text{l mol}^{-1}\text{ s}^{-1}) = 11.1 = 6.0/\theta \qquad \text{(xiv)}$$

$$\log_{10}(k_\beta/\text{s}^{-1}) = 12.2 - 40.2/\theta \qquad \text{(xv)}$$

TABLE 2

Radicals formed by β-scission of imidoyl radicals in cyclopropane

Imidoyl radical	Radical product of β-scission	T/K [a]	Rate constant for β-scission k_β/s^{-1}	k_β[b]/s^{-1} at 243 K
$\mathrm{Bu^tN{=}\dot{C}OBu^t}$	$\mathrm{Bu^t\cdot}$	223—293	*c*	3.6×10^3
$\mathrm{Bu^tN{=}\dot{C}O[^2H_9]Bu^t}$	$\mathrm{[^2H_9]Bu^t\cdot}$ [d]			
$\mathrm{EtMe_2\dot{C}N{=}COBu^t}$	$\mathrm{Bu^t\cdot}$ [e]		3.0×10^3 (243 K)	3.0×10^3
$\mathrm{MeN{=}\dot{C}OBu^t}$	$\mathrm{Bu^t\cdot}$	223—283		
$\mathrm{Bu^tN{=}\dot{C}OCMe_2Et}$	$\mathrm{EtMe_2C\cdot}$ [f]		4.5×10^3 (245 K)	3.8×10^3
$\mathrm{Bu^tN{=}\dot{C}SBu^t}$	$\mathrm{Bu^t\cdot}$	163—213	2.0×10^3 (183 K)	3.1×10^5
$\mathrm{Bu^tN{=}\dot{C}SCMe_2Et}$	$\mathrm{EtMe_2C\cdot}$			
$\mathrm{Bu^tN{=}\dot{C}SMe}$	$\mathrm{Bu^t\cdot}$	265—295		
$\mathrm{Bu^tN{=}\dot{C}SiEt_3}$	$\mathrm{Bu^t\cdot}$	163—205	1.5×10^3 (190 K)	1.4×10^5
$\mathrm{EtMe_2CN{=}\dot{C}SiEt_3}$	$\mathrm{EtMe_2C\cdot}$			
$\mathrm{Bu^tCH_2Me_2CN{=}\dot{C}SiEt_3}$	$\mathrm{Bu^tCH_2\dot{C}Me_2}$ [g]			
$\mathrm{Bu^nN{=}\dot{C}SiEt_3}$	$\mathrm{Bu^n\cdot}$	253—273	*ca.* 2×10^5 (255 K) [h]	7×10^2
$\mathrm{Bu^tN{=}\dot{C}Ph}$ [i]	$\mathrm{Bu^t\cdot}$			

[a] Approximate temperature range over which e.s.r. spectra of the imidoyl adduct and of the radical formed by β-scission were both readily detectable. This gives a qualitative measure of the relative ease of β-scission of the imidoyl radical. [b] Calculated by taking $\log_{10}(A/\text{s}^{-1}) = 12.2$, the value measured for fragmentation of $\mathrm{Bu^tN{=}\dot{C}OBu^t}$. [c] Measured over a range of temperatures (see text). [d] Small concentrations of incompletely deuteriated radicals were also detected (see Experimental section). [e] No trace of $\mathrm{EtMe_2C\cdot}$ could be detected. [f] No trace of $\mathrm{Bu^t\cdot}$ could be detected. [g] At 233 K, $a(6\ \mathrm{H}_\beta)$ 22.9, $a(2\ \mathrm{H}_\beta)$ 12.4 G. [h] Very approximate value, signals were very weak at this temperature. [i] Generated by photolysis of $\mathrm{PhMe_2COOCMe_2Ph}$ or $\mathrm{Me_3SiOOSiMe_3}$ in the presence of $\mathrm{Bu^tN{=}C(H)Ph}$.

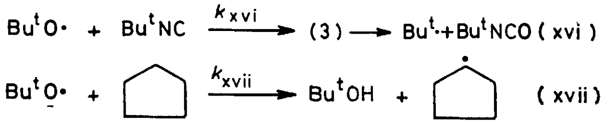
The rate constants for β-scission of some other imidoyl radicals were measured similarly, and we have assumed that equation (xiv) applies to the self-reaction of n-butyl and t-pentyl radicals. The most reliable experimental rate constant is given in Table 2, and that at 243 K has been calculated by assuming an A factor of $10^{12.2}$ s^{-1} for all fragmentation processes.

The e.s.r. spectrum of the imidoyl radical $\mathrm{Bu^tN{=}\dot{C}OSiMe_3}$ remained strong at high temperatures and no radical product of fragmentation was detectable even at 273 K. This imidoyl radical decayed by a second-order process, and at 200 K the rate constant was measured by kinetic e.s.r. spectroscopy [13] and found to be 3×10^8 l mol^{-1} s^{-1}. The reaction presumably corresponds to formation of the C_α–C_α coupled dimer at close to the diffusion-controlled rate.

Although $\mathrm{Bu^tN{=}\dot{C}SiEt_3}$ underwent ready β-scission to give t-butyl radicals at low temperature (see Figure), the adducts of phosphorus-centred radicals with t-butyl isocyanide were more stable towards fragmentation. For example, β-scission of $\mathrm{Bu^tN{=}\dot{C}P(\overline{-OCH_2CMe_2O})_2}$ was not sufficiently rapid to give rise to a detectable concentration of t-butyl radicals below 260 K.

Both t-butoxyl and trimethylsiloxyl radicals underwent addition to methyl isocyanide to give imidoyl adducts and no signal from $\cdot\mathrm{CH_2NC}$ was detected.

Photolysis of di-t-butyl peroxide in the presence of a mixture of t-butyl isocyanide and cyclopentane above *ca.* 255 K gave rise to the spectra of both t-butyl and cyclopentyl radicals, and the spectrum of the imidoyl radical (3) was very weak or undetectable.



The ratio $(k_{\mathrm{xvi}}/k_{\mathrm{xvii}})$ will be equal to $[\mathrm{Bu^t\cdot}][\text{cyclo-}\mathrm{C_5H_{10}}]/[\text{cyclo-}\mathrm{C_5H_9\cdot}][\mathrm{Bu^tNC}]$, provided that the rate constants for removal of the two alkyl radicals are similar [14] and that the addition of t-butoxyl radicals to t-butyl isocyanide is effectively irreversible. For values of $[\text{cyclo-}\mathrm{C_5H_{10}}]/[\mathrm{Bu^tNC}]$ in the range 1.0—3.1, the ratio $(k_{\mathrm{xvi}}/k_{\mathrm{xvii}})$ was 2.25 ± 0.15 independent of temperature within experimental error between 260 and 290 K. The value [15] of k_{xvii} is 8.8×10^5 l mol^{-1} s^{-1} at 294 K and, if we assume an A factor of 10^9 l mol^{-1} s^{-1}, the temperature dependence of this rate constant may be expressed by equation (xviii). It follows that k_{xvi} is *ca.* 6.3×10^5 l mol^{-1} s^{-1} at 253 K and that the activation energy for the addition of $\mathrm{Bu^tO\cdot}$ to $\mathrm{Bu^tNC}$ is *ca.* 17 kJ mol^{-1}.

$$\log_{10}(k_{\mathrm{xvii}}/\text{l mol}^{-1}\text{ s}^{-1}) = 9.0 - 17.2/\theta \qquad \text{(xviii)}$$

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[11] J. E. Bennett and R. Summers, *J.C.S. Perkin II*, 1977, 1504.

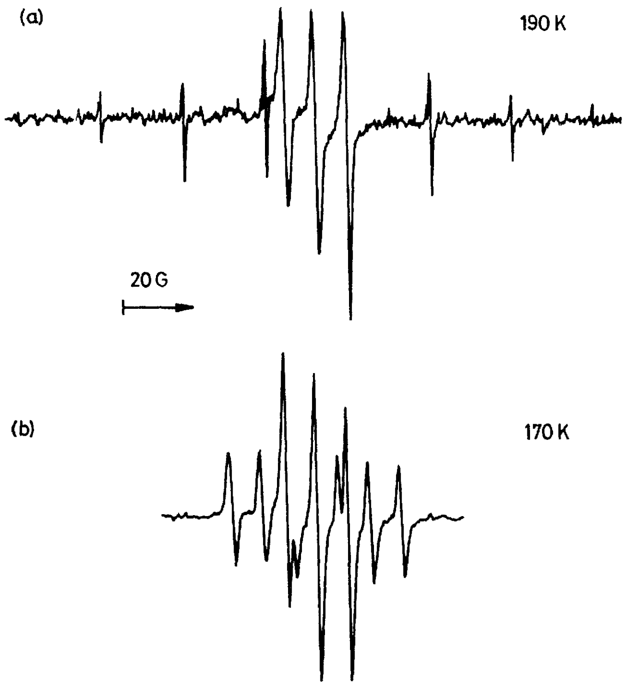
[12] H. Schuh and H. Fischer, *Internat. J. Chem. Kinetics*, 1976, **8**, 341.

[13] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902.

[14] D. Griller and K. U. Ingold, *Internat. J. Chem. Kinetics*, 1974, **6**, 453.

[15] H. Paul, R. D. Small, jun., and J. C. Scaiano, *J. Amer. Chem. Soc.*, 1978, **100**, 4520.

At high temperatures the e.s.r. spectrum of $\mathrm{Bu^tN{=}\dot{C}SPe^t}$ was replaced by that of the t-pentyl radical, produced by C–S bond cleavage. The radical $\mathrm{Bu^tN{=}\dot{C}SMe}$ did not undergo fragmentation at a detectable rate below 260 K. At higher temperatures the imidoyl radical spectrum was partially replaced by that of the t-butyl radical, although the imidoyl adduct was still readily detectable at 295 K. Although the spectrum of $\mathrm{Bu^tN{=}\dot{C}SCF_3}$ became progressively weaker as the temperature was increased, it was replaced not by the signal from the trifluoromethyl radical but by a five-line spectrum (intensities *ca.* 1 : 2 : 3 : 2 : 1, line spacing 9.0 G at 270 K) centred at *g* 2.001 0. The same spectrum was obtained when trifluoromethyl radicals (from photolysis of $\mathrm{CF_3I + Me_3SnSnMe_3}$) were generated in the presence of t-butyl isocyanide. The identity of the radical giving rise to this signal is not known at present, although the radical is probably produced by the reaction of trifluoromethyl radicals with the isocyanide. The *g* factor is in the range expected for a σ-radical, possibly of the type $\mathrm{Bu^tN{=}\dot{C}X}$, but when the experiment was repeated with ^{13}C labelled isocyanide the spectrum obtained showed $a(^{13}\mathrm{C})$ 9.0 G, which is not in agreement with such a formulation.



E.s.r. spectra obtained during the reaction of photochemically generated triethylsilyl radicals with t-butyl isocyanide in cyclopropane: (a) with $\mathrm{Bu^tN^{12}C}$ at 190 K; (b) with $\mathrm{Bu^tN^{13}C + Bu^tN^{12}C}$ (47 : 53) at 170 K

We have also shown by e.s.r. spectroscopy that trimethylsilyl radicals (from photolysis of $\mathrm{Bu^tOOBu^t + Me_3SiH}$) add to trimethylsilyl cyanide * to form the imidoyl radical (5). After a short period of photolysis the e.s.r. spectrum of the extremely long lived radical [17] $\mathrm{(Me_3Si)_2\dot{C}N(SiMe_3)_2}$ became apparent and grew steadily in intensity whilst irradiation continued.

$$\mathrm{Me_3Si\cdot + Me_3SiC{\equiv}N \longrightarrow \underset{(5)}{Me_3Si\dot{C}{=}NSiMe_3}} \qquad \text{(xix)}$$

DISCUSSION

The results obtained using e.s.r. spectroscopy confirm that a variety of free radicals add to alkyl isocyanides to produce imidoyl radicals which may undergo subsequent β-scission.

(i) *Radical Addition to Isocyanides.*—t-Butoxyl radicals add to t-butyl isocyanide and abstract hydrogen from cyclopentane at similar rates and the activation energies for the two reactions are very similar. On the basis of product analysis Singer and Kim [3] concluded that at 398 K t-butoxyl radicals abstract hydrogen from cumene and add to t-butyl isocyanide at similar rates. At 294 K cyclopentane and cumene are equally reactive towards t-butoxyl radicals.[15]

Addition of methyl radicals to t-butyl isocyanide was undetected by e.s.r. spectroscopy even at 253 K, although this reaction seems likely to be as favourable thermodynamically as the addition of t-butoxyl radicals. The rate constant for the overall reaction (xx) in the gas phase is given by equation (xxi).[18]

$$\mathrm{Me\cdot + MeNC \xrightarrow{k_{xx}} MeCN + Me\cdot} \qquad \text{(xx)}$$

If the formation of the intermediate imidoyl radical (6) is essentially irreversible and the only fate of (6) is to

$$\log_{10}(k_{xx}/\mathrm{l\ mol^{-1}\ s^{-1}}) = 9.25 - 32.6/\theta \qquad \text{(xxi)}$$

give MeCN and Me·, then k_{xx} corresponds to the rate constant for addition of methyl radicals to methyl isocyanide [equation (xxii)].†

$$\mathrm{Me\cdot + MeNC \longrightarrow \underset{(6)}{MeN{=}\dot{C}Me}} \qquad \textit{(xxii)}$$

At 253 K k_{xx} would be 3×10^2 l mol^{-1} s^{-1} and we estimate that our inability to detect $\mathrm{Bu^tN{=}\dot{C}Me}$ in solution at this temperature implies that the rate constant for addition of methyl radicals to $\mathrm{Bu^tNC}$ is less than *ca.* 5×10^2 l mol^{-1} s^{-1}.

Kim [4] has recently reported that the rate constant for addition of phenyl radicals to t-butyl isocyanide is *ca.* 10^8 l mol^{-1} s^{-1} at 373 K and, assuming an *A* factor of 10^9 l mol^{-1} s^{-1}, this would be *ca.* 3×10^7 l mol^{-1} s^{-1} at 253 K. At this temperature the rate constant for addition of t-butoxyl radicals is *ca.* 6×10^5 l mol^{-1} s^{-1}, and thus phenyl radicals add more rapidly to t-butyl isocyanide than do t-butoxyl or methyl radicals, a result also noted by Kim.[4]

(ii) *Structures of Imidoyl Radicals.*—Imidoyl radicals

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* A very small equilibrium concentration of the isocyanide (*ca.* 0.15 mol % at 298 K) is present along with the more stable cyanide.[16] However, the concentration of $\mathrm{Me_3SiNC}$ is so small that it is unlikely that (5) is formed by addition of $\mathrm{Me_3Si\cdot}$ to the isocyanide, even though this may be more reactive than the cyanide.

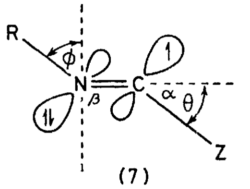
† Shaw and Pritchard [18] estimate that reaction (xxii) is exothermic by between 20 and 40 kJ mol^{-1}

[16] M. R. Booth and S. G. Frankiss, *Spectrochimica Acta*, 1970, **26A**, 859.

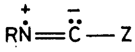
[17] R. A. Kaba, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1974, **96**, 6202.

[18] D. H. Shaw and H. O. Pritchard, *Canad. J. Chem.*, 1967, **45**, 2749.

are isoelectronic with the more familiar vinyl and acyl radicals. The low g factors exhibited by the imidoyl adducts are characteristic of ' σ-radicals ', in which the unpaired electron resides in a σ-orbital orthogonal to an adjacent filled π-orbital.[19] Danen and West [6] carried out preliminary INDO molecular orbital calculations for the imidoyl radical $HN{=}\dot{C}H$ and concluded that a configuration with the hydrogens *cis* was the most stable. However, the calculated values of $a(N_\beta)$ were an order of magnitude larger than those observed [6] (1.2—1.9 G) for radicals of the type $RN{=}\dot{C}R$ (R = alkyl).

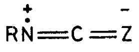


(7)



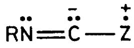
$R\overset{+}{\dot{N}}{=}\overset{-}{\ddot{C}}{-}Z$

(8)



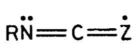
$R\overset{+}{\dot{N}}{=}C{=}\overset{-}{Z}$

(9)



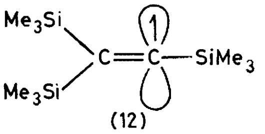
$R\ddot{N}{=}\overset{-}{\ddot{C}}{-}\overset{+}{\dot{Z}}$

(10)



$R\ddot{N}{=}C{=}\dot{Z}$

(11)



(12)

We have also performed INDO calculations for $HN{=}\dot{C}H$ assuming a planar structure and using fixed standard bond lengths.[20] Calculations were carried out for (7; R = Z = H) with all possible combinations of θ and ϕ, where these angles were varied in 10° steps between 0 and 90° and 0 and 180°, respectively. The minimum energy configuration was found to be that for which $\theta = 50$ and $\phi = 30°$, that is a *trans*-configuration. The most stable *cis*-configuration ($\theta = 40$, $\phi = 130°$) was less stable by 10 kJ mol^{-1}, and the most stable configuration linear at C_α ($\theta = 0$, $\phi = 30°$) was less stable by 46 kJ mol^{-1}. These calculations cannot be said to establish a *trans*-configuration for $HN{=}\dot{C}H$ on energetic grounds; however, only for *trans*-configurations was the predicted value $a(N_\beta)$ in reasonable agreement with that obtained experimentally [6] for $RN{=}\dot{C}R$. For the *trans*-configuration ($\theta = 50$, $\phi = 30°$) $a(N_\beta)$ was +7.7 G, and for ($\theta = 40$, $\phi = 70°$) $a(N_\beta)$ had fallen to +3.9 G, whereas for all *cis*-configurations investigated $a(N_\beta)$ was +10 to +36 G. With substituents more bulky than hydrogen, steric effects should also favour a *trans*-configuration, and we suggest that this structure is the one adopted by the acyclic imidoyl radicals reported in this paper. The larger values of $a(N_\beta)$ predicted for *cis*-configurations are expected because the overlap between the orbital of the unpaired electron on C_α with that of the lone pair on N_β (pseudo-π overlap) should be favoured by this geometry.

The magnitudes of both $a(C_\alpha)$ and $a(N_\beta)$ are markedly dependent upon the nature of the substituent on C_α. The value of $a(C_\alpha)$, which is expected to be positive, will depend upon the hybridisation of the semi-occupied orbital on carbon [related to θ in (7)] and upon the spin density in this orbital, which in turn depends on the extent of delocalisation of the unpaired electron onto N_β and the ligand Z. Such delocalisation may be represented as contributions from the canonical structures (8)—(11), and will vary in extent with the angles θ and ϕ and with the nature of Z.

As the ligand Z becomes more electronegative the C-2p character of the C–Z σ-bond would be expected to increase,[21] leading to an increase in the C-2s character of the semi-occupied orbital and to an increase in the angle θ. The magnitude of $a(^{13}C_\alpha)$ should thus increase with the electronegativity of Z, in accord with the experimental observations (see Table 1). For the radical (7; R = Bu^t, Z = Me_3SiO) the angle θ must be relatively large, since the value of $a(^{13}C_\alpha)$ corresponds to a spin density of *ca.* 0.1 in the C-2s orbital. The electronegativity of the Et_3Si group is much lower and $a(^{13}C_\alpha)$ for (7; R = Bu^t, Z = Et_3Si) is only 29.8 G, close to the value (28.1 G) reported [22] for the vinyl radical (12), which was thought to have a linear arrangement of bonds about C_α.

It seems reasonable that θ should be close to zero for (7; R = alkyl, Z = R_3Si), although increased contributions from canonical structures (9) and (11) would serve to reduce the spin density on carbon and thus to reduce $a(^{13}C_\alpha)$. Relatively large contributions from (9) and (11) might be expected because of the presence on silicon of empty 3d-orbitals.*

The magnitude of $a(N_\beta)$ for (7) will depend mainly upon the relative size of two contributions of opposite sign. The size of the positive contribution will depend upon the spin density in and hybridisation of the ' lone pair ' orbital on nitrogen. It will thus depend upon the angles θ and ϕ and on the nature of Z, particularly on the ability of Z to stabilize negative charge on C_α and thus the unpaired electron on N_β, as represented by canonical structures (8) and (9). Although the angle θ changes considerably [as judged from $a(^{13}C_\alpha)$] with the electronegativity of Z, the most important effect determining the size of the positive contribution appears to be the ability of Z to stabilise an adjacent carbanionic centre.

There will also be a negative contribution to $a(N_\beta)$ resulting from spin-polarisation of the N–C σ-bonding electrons by the unpaired electron on C_α. The size of this contribution should depend to a lesser degree than

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* In fact the acceptor orbitals may not be Si-3d, but rather a suitable combination of σ^* Si–R orbitals which can serve the same function.[23]

[19] R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, 1967, **71**, 14.

[20] J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory ', McGraw-Hill, New York, 1970.

[21] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

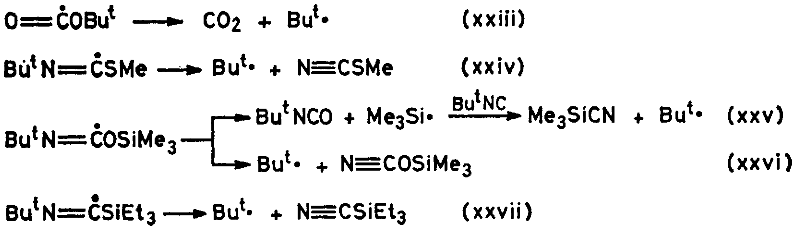
[22] D. Griller, J. W. Cooper, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1975, **97**, 4269.

[23] K. J. Shea, R. Grobeille, J. Bramblett, and E. Thompson, *J. Amer. Chem. Soc.*, 1978, **100**, 1611.

the positive component upon the hybridisation of the orbitals of the unpaired electron and the lone pair (that is on θ and ϕ). In the discussion which follows we assume that the negative contribution to $a(\mathrm{N}_\beta)$ and the hybridisation of the orbital of the lone pair (*i.e.* ϕ) are independent of the nature of Z. For the radical $\mathrm{Bu^tN{=}\dot{C}OBu^t}$ $a(\mathrm{N}_\beta)$ is *ca.* 0, and the positive and negative contributions must cancel. Sulphur should be better than oxygen at stabilising an adjacent carbanionic centre [24] and the positive contribution dominates for $\mathrm{Bu^tN{=}\dot{C}SBu^t}$, for which $a(\mathrm{N}_\beta)$ is (+) 5.0 G. The value of θ in the latter radical should also be more favourable (assuming a *trans*-configuration) for pseudo-π overlap. Although θ is larger in $\mathrm{Bu^tN{=}\dot{C}SCF_3}$ and the geometry is less favourable for pseudo-π overlap, the $\mathrm{CF_3S}$ substituent is expected to be better than $\mathrm{Bu^tS}$ at stabilising an adjacent carbanionic centre, accounting for the increase in $a(\mathrm{N}_\beta)$ to (+) 5.8 G.

The radical $\mathrm{Bu^tN{=}\dot{C}SiEt_3}$, if linear at C_α, has the optimum geometry for pseudo-π overlap and also the silicon (like S and P) stabilises an adjacent negative charge,[24] resulting in the relatively high value of $a(\mathrm{N}_\beta)$ [(+) 8.6 G]. The small magnitude of $a(\mathrm{N}_\beta)$ for $\mathrm{Bu^tN{=}CR}$ (*ca.* 1.5 G [6]), in which θ is presumably intermediate between zero and its value in $\mathrm{Bu^tN{=}\dot{C}SBu^t}$, appears to stem from the poor ability of the alkyl substituent, compared with RS or $\mathrm{R_3Si}$, to stabilise a negative charge on C_α.

(iii) *Fragmentation of Imidoyl Radicals.*—Imidoyl radicals of the type $\mathrm{RN{=}\dot{C}OR^t}$ undergo ready β-scission to give RNCO and $\mathrm{R^t}$. The rate constant for fragmentation of $\mathrm{Bu^tN{=}\dot{C}OBu^t}$ is $3.6 \times 10^3\ \mathrm{s^{-1}}$ at 243 K, very close to that ($2.3 \times 10^3\ \mathrm{s^{-1}}$) for β-scission of the related t-butoxycarbonyl radical [9] [equation (xxiii)].*



$$\mathrm{O{=}\dot{C}OBu^t} \longrightarrow \mathrm{CO_2 + Bu^t\cdot} \qquad \text{(xxiii)}$$

$$\mathrm{Bu^tN{=}\dot{C}SMe} \longrightarrow \mathrm{Bu^t\cdot + N{\equiv}CSMe} \qquad \text{(xxiv)}$$

$$\mathrm{Bu^tN{=}\dot{C}OSiMe_3} \longrightarrow \mathrm{Bu^tNCO + Me_3Si\cdot} \xrightarrow{\mathrm{Bu^tNC}} \mathrm{Me_3SiCN + Bu^t\cdot} \qquad \text{(xxv)}$$

$$\mathrm{Bu^tN{=}\dot{C}OSiMe_3} \longrightarrow \mathrm{Bu^t\cdot + N{\equiv}COSiMe_3} \qquad \text{(xxvi)}$$

$$\mathrm{Bu^tN{=}\dot{C}SiEt_3} \longrightarrow \mathrm{Bu^t\cdot + N{\equiv}CSiEt_3} \qquad \text{(xxvii)}$$

Radicals of the type $\mathrm{RN{=}\dot{C}SR^t}$ undergo a similar fragmentation to give RNCS and $\mathrm{R^t\cdot}$; however $\mathrm{Bu^tN{=}\dot{C}SBu^t}$ undergoes β-scission more rapidly than $\mathrm{Bu^tN{=}\dot{C}OBu^t}$. This is surprising since fragmentation of $\mathrm{Bu^tN{=}\dot{C}OBu^t}$ would be expected to be appreciably more exothermic than β-scission of $\mathrm{Bu^tN{=}\dot{C}SBu^t}$, on account of the relatively weak C=S π-bond in $\mathrm{Bu^tN{=}C{=}S}$.[25,†]

The imidoyl radical $\mathrm{Bu^tN{=}\dot{C}SMe}$ is more stable towards fragmentation than is $\mathrm{Bu^tN{=}CSBu^t}$, presumably because of the greater strength of the S–alkyl bond in the former. At relatively high temperatures $\mathrm{Bu^tN{=}\dot{C}SMe}$ undergoes C–N cleavage to give t-butyl radicals and, presumably, methyl thiocyanate [equation (xxiv)].

The radical $\mathrm{Bu^tN{=}\dot{C}OSiMe_3}$ does not undergo fragmentation to give a detectable concentration of t-butyl radicals, even at 273 K. t-Butyl radicals could result from either C–N or Si–O cleavage, since the trimethylsilyl radicals formed in the latter process would react with the isocyanide to produce t-butyl radicals *via* an unstable imidoyl radical [equation (xxv)].

The resistance to Si–O cleavage may be ascribed to the great strength of this bond [27] (*ca.* 498 kJ mol^{-1} in $\mathrm{Me_3SiOH}$). In sharp contrast to the low rate of reaction (xxvi), the imidoyl radical $\mathrm{Bu^tN{=}\dot{C}SiEt_3}$ undergoes very rapid β-scission with C–N cleavage [equation (xxvii)].

It is not clear whether or not C–N cleavage is thermodynamically more favourable for $\mathrm{Bu^tN{=}\dot{C}SiEt_3}$ than for $\mathrm{Bu^tN{=}\dot{C}OSiMe_3}$, but it is worth noting that the unpaired spin density on nitrogen is probably greater in the former radical.

EXPERIMENTAL

E.s.r. Studies.—Samples were sealed under vacuum in 4 mm o.d. Suprasil tubes and irradiated, whilst in the cavity of a Varian E-4 spectrometer, with light from either a Philips SP 500 or CS 500 W/2 mercury discharge lamp using fused silica optics. Spectra were recorded during continuous photolysis and incident light intensities were varied using metal gauze screens of different transmittance. Radical concentrations were determined by comparison with a standard solution of diphenylpicrylhydrazyl in carbon tetrachloride, using a synthetic ruby fixed to the inside of the cavity to provide a standard reference signal. Relative radical concentrations were measured by electronic integration of suitable derivative signals, followed by manual integration of the absorption peaks so obtained. g Factors ($\pm 0.000\,1$) were determined by measurement of the microwave frequency and the magnetic field, and were

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* The rate constant for reaction (xxiii) was determined relative to that for self-reaction of t-butyl radicals and k_{xxiii} was given by $\log_{10}\,[(k_{\mathrm{xxiii}}/2k_t)/\mathrm{mol\ l^{-1}}] = 2.6 - 42.1/\theta$.[9] Combining this result with equation (xiv) gives a revised value of k_{xxiii} given by $\log_{10}\,(k_{\mathrm{xxiii}}/\mathrm{s^{-1}}) = 13.7 - 48.1/\theta$.

† The enthalpy changes for the overall reactions of $\mathrm{Bu^tO\cdot}$ and $\mathrm{Bu^tS\cdot}$ with MeNC may be calculated from enthalpies of formation.

	$\Delta H^{\ominus}$/kJ mol^{-1}
$\mathrm{Bu^tO\cdot + MeNC \longrightarrow Bu^t\cdot + MeNCO}$	−147
$\mathrm{Bu^tS\cdot + MeNC \longrightarrow Bu^t\cdot + MeNCS}$	−43

The following standard enthalpies of formation (kJ mol^{-1}) were used:[25,26] $\mathrm{Bu^t\cdot}$, +35.6; $\mathrm{Bu^tO\cdot}$, −94.1; $\mathrm{Bu^tS\cdot}$, +58.6; MeNC, +151; MeNCO, −126; MeNCS, +131.

[24] I. Fleming, *Chem. and Ind.*, 1975, 449 and references contained therein.

[25] S. W. Benson, *Chem. Rev.*, 1978, **78**, 23.

[26] H. E. O'Neal and S. W. Benson in 'Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. 2, ch. 17; S. W. Benson, personal communication.

[27] R. A. Jackson in 'Essays in Free Radical Chemistry', Chem. Soc. Special Publication No. 24, The Chemical Society, London 1970, ch. 12.

calculated using the Breit–Rabi equation when large hyperfine splittings from ^{31}P or ^{13}C were present. The second-order rate constant for the self-reaction of $\text{Bu}^t\text{N}{=}\dot{\text{C}}\text{OSiMe}_3$ was measured using kinetic e.s.r. spectroscopy.[13,28]

Solutions, in cyclopropane solvent, were generally 0.5—1M in isocyanide and in the primary photochemical source of radicals (peroxide, disulphide, or azomethane). When triethylsilane was also present its concentration was *ca.* 1M. Photolysis of the isocyanides alone did not give rise to any e.s.r. signals.

Materials.—The preparations of those compounds which were not obtained commercially are given below. Methyl isocyanide,[29] t-pentyl isocyanide,[30] bis(trimethylsilyl) peroxide,[31] azomethane,[32] $(\overline{\text{OCMe}_2\text{CH}_2\text{O}}\text{–})_2\text{PH}$,[33] and $(\overline{\text{HNCMe}_2\text{CH}_2\text{O}}\text{–})_2\text{PH}$[34] were prepared by methods described in the literature. A mixture of $\text{Bu}^t\text{N}^{13}\text{C}$ and $\text{Bu}^t\text{N}^{12}\text{C}$ was prepared by the reaction of t-butyl iodide with labelled silver cyanide (made from KCN containing 47% ^{13}C).[35]

N-Benzylidene-t-butylamine was prepared by the method of Emmons[36] and purified by preparative g.l.c. in order to remove traces of benzaldehyde, which gave rise to the e.s.r. signal of the benzoyl radical when peroxides were photolysed in the presence of the distilled, but still impure, product.

t-Butyl (N-*t-butyl*)*formimidate* was prepared by heating a mixture of t-butyl isocyanide (2 g), t-butyl alcohol (1.8 g), and copper(II) oxide (0.1 g) in a sealed thick-walled glass tube for 5 h at 110 °C (*cf.* ref. 37). The product was purified by distillation, b.p. 142—145 °C at 760 Torr (Found: C, 68.8; H, 12.2; N, 8.6. $\text{C}_9\text{H}_{19}\text{NO}$ requires C, 68.7; H, 12.2; N, 8.9%), δ_H (C_6D_6) 1.12 (9 H, s, NBu^t), 1.45 (9 H, s, OBu^t), and 7.40 (1 H, s, CH).

[$^2\text{H}_{18}$]Di-t-butyl peroxide was synthesised from [$^2\text{H}_{10}$]t-butyl alcohol ($\geqslant$99 atom % D) by the method reported for the unlabelled compound.[38] The only source of exchangeable hydrogen was the 83% solution of H_2O_2 in H_2O which was diluted with D_2O to produce a 27% solution; all other reagents were fully deuteriated. The mass spectrum of the product indicated that the ratio $[\text{C}_8\text{D}_{18}\text{O}_2] : [\text{C}_8\text{D}_{17}\text{HO}_2]$ was 2.9 : 1, and thus photolysis would yield $\text{t-C}_4\text{D}_9\text{O}\cdot$ and $\text{t-C}_4\text{D}_8\text{HO}\cdot$ in the ratio 6.8 : 1. The synthesis of fully deuteriated peroxide would require the use of D_2O_2 in D_2O.

We are grateful to Mr. C. J. Cooksey for preparing t-pentyl isocyanide and ^{13}C labelled t-butyl isocyanide.

[8/125 *Received, 25th January,* 1978]

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