Electron Spin Resonance Studies of Radicals derived from Organic Azides

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Photochemically or thermally generated t-butoxyl radicals react with primary or secondary alkyl azides $R^1R^2C(H)N_3$ to afford iminyl radicals $R^1R^2C{=}N\cdot$, the e.s.r. spectra of which have been detected. The iminyl radicals undergo self-reaction at close to the diffusion-controlled rate in solution. Iminyl radicals ($R_2C{=}N\cdot$) were also detected during photolysis of the azines $R_2C{=}N{-}N{=}CR_2$ (R = H or Me), but photolysis of cyclobutanone azine yielded only the spectrum of the 3-cyanopropyl radical, formed by ring-opening of the strained cyclic iminyl radical. In contrast, the 4-cyanobutyl radical undergoes irreversible cyclisation to give the iminyl radical $\overline{CH_2(CH_2)_3C}{=}N\cdot$ with a rate constant of $4.5 \times 10^2\ s^{-1}$ at 259 K. Triorganosilyl radicals add to a variety of organic azides to form adducts which are either 1,3- or 3,3-triazenyl radicals. ^{15}N-Labelling studies establish that the central nitrogen of the original azide gives rise to the largest hyperfine splitting in the triazenyl adducts of MeN_3 or Me_3SiN_3. The available evidence is considered most consistent with formation of a 1,3-triazenyl radical in which the unpaired electron is mainly associated with the central nitrogen and in a σ orbital in the NNN plane. 1-Hydroxy-1-methylethyl radicals react with primary alkyl azides RCH_2N_3 to form dialkylaminyl radicals, which are thought to have the structure $R\dot{N}CH_2C(OH)Me_2$. Other α-hydroxyalkyl radicals behave similarly, and a mechanism related to the acid-catalysed decomposition of azides to give imines is proposed.

RELATIVELY little is known about the reactions of free radicals with organic azides.[1] Alkyl radicals displace organosulphonyl radicals from sulphonyl azides [equation (i)],[2-4] and trichloromethyl radicals induce the decomposition of aryl azides [equations (ii) and (iii)].[5]

$$R^1\cdot + R^2SO_2N_3 \longrightarrow R^1N_3 + R^2\dot{S}O_2 \qquad \text{(i)}$$

$$Cl_3C\cdot + ArN_3 \longrightarrow \underset{(1)}{ArN{=}N{-}\dot{N}CCl_3} \qquad \text{(ii)}$$

$$ArN{=}N{-}\dot{N}CCl_3 \longrightarrow \underset{(2)}{Ar\dot{N}CCl_3} + N_2 \qquad \text{(iii)}$$

$$Me_2\dot{C}OH + XN_3 \longrightarrow Me_2CO + X\dot{N}H + N_2 \qquad \text{(iv)}$$

Although the nature of the products indicated the intermediacy of the aminyl radical (2), the trichloromethyl radical was thought to add to the terminal nitrogen atom of the azide to give the 1,3-disubstituted triazenyl radical (1) rather than the 3,3-substituted radical $Ar(Cl_3C)NN{=}N\cdot$, which would result from addition to the nitrogen attached to the aryl group.[5] Aryl, acyl, and arenesulphonyl azides react with the 1-hydroxy-1-methylethyl radical to give acetone and the appropriate nitrogen-centred radical [equation (iv)].[6]

The aim of the present work was to use e.s.r. spectroscopy to examine the reactions of free radicals with a series of organic azides. A preliminary account of some of our results has already appeared.[7]

RESULTS

E.s.r. spectra were recorded during continuous photochemical or thermal generation of t-butoxyl, triorganosilyl, or 1-hydroxy-1-methylethyl radicals in the presence of the azides in fluid solution. The primary radical sources were di-t-butyl peroxide (photochemical) or di-t-butyl hyponitrite (thermal) with appropriate co-reactants [R_3SiH or $Me_2C(H)OH$] to provide sources of $R_3Si\cdot$ and $Me_2\dot{C}OH$. Methyl radicals, from photolysis of azomethane, did not react with the alkyl azides at a rate sufficient to afford detectable concentrations of radical products; only the spectrum of the methyl radical was observed.

(a) *Reaction of t-Butoxyl Radicals with Alkyl Azides.*—U.v. photolysis of alkyl azides gives rise to imines (3; R = H or alkyl) [equation (v)].[1] In order to avoid mechanistic ambiguities the t-butoxyl radicals were generated thermally at 343 K, since, although reaction (v) may be induced by heating,[1] the thermal rate is negligible at this temperature. Thermolysis of di-t-butyl hyponitrite in the presence of primary or secondary alkyl azides in t-butylbenzene solvent gave rise to e.s.r. spectra which we assign to the iminyl radicals (4; R^1,R^2 = H or alkyl).[8-12]

The same radicals were detected when the t-butoxyl radicals were generated photochemically in cyclopropane solvent, and any α-azidoalkyl radical intermediate [$R^1R^2\dot{C}N_3$] must be very short-lived, since the iminyl radical $H_2C{=}N\cdot$ was the only species detected during the photolysis of di-t-butyl peroxide in the presence of methyl azide even at 133 K. E.s.r. parameters for the iminyl radicals are given in Table 1.

$$R^1R^2R^3CN_3 \xrightarrow{h\nu} \underset{(3)}{R^1R^2C{=}NR^3} + N_2 \qquad \text{(v)}$$

$$Bu^tO\cdot + R^1R^2C(H)N_3 \xrightarrow{k_{vi}} Bu^tOH + \underset{(4)}{R^1R^2C{=}N\cdot} + N_2 \qquad \text{(vi)}$$

The rate of reaction of t-butoxyl radicals with n-butyl azide was measured relative to the rate of abstraction of hydrogen from cyclopentane.[13] The concentrations of iminyl and cyclopentyl radicals were monitored during continuous photolysis of di-t-butyl peroxide in the presence of a mixture of azide and cyclopentane.

Provided that hydrogen abstraction from the azide is

$$Bu^tO\cdot + cyclo{-}C_5H_{10} \xrightarrow{k_{vii}} Bu^tOH + cyclo{-}C_5H_9\cdot \qquad \text{(vii)}$$

TABLE 1

E.s.r. parameters for iminyl radicals $R^1R^2C{=}N\cdot$ derived from alkyl azides $R^1R^2C(H)N_3$

					Hyperfine splittings (G)	
R^1	R^2	Solvent [a]	T/K	g Factor	a(N)	a(H) [b]
H	H	C	220	2.0028 [c]	9.7 [d]	85.2(2) [c]
Me	H	C	220	2.0028 [c]	9.6	77.1(1); [c] 2.55(3)
Et	H	C	220	2.0028 [c]	9.6	79.5(1); [c] 2.75(2); 0.45(3)
Pr^n	H	C	230	2.0029 [c]	9.5	80.4(1); [c] 2.75(2); 0.70(2); 0.35(3)
Me	Me	C	220	2.0029	9.6	1.40(6)
Me	Me	B	343		9.6	1.40(6)
Et	Et	C	220	2.0029	9.6	1.50(4); 0.43(6)
$CH_2(CH_2)_2CH_2$		C	220	2.0029	9.4	4.2(4); 1.90(4)
$CH_2(CH_2)_2CH_2$		B	343		9.4	4.2(4); 1.90(4)

[a] C = generated photochemically in cyclopropane solvent; [azide] *ca.* 1M, $[Bu^tOOBu^t]$ *ca.* 1M. B = generated thermally in t-butylbenzene solvent; [azide] *ca.* 1M, $[Bu^tON{=}NOBu^t]$ *ca.* 1M. [b] Numbers of equivalent nuclei shown in parentheses. [c] Calculated using the Breit–Rabi equation. [d] $a(^{15}N)$ 13.6 G.

concerted with loss of nitrogen or that the fragmentation of $Pr^n(H)\dot{C}N_3$ is irreversible, and that the rate constants describing the removal of $Pr^n(H)C{=}N\cdot$ and the cyclopentyl radical are similar, it may be shown that equation (viii) holds.[13]

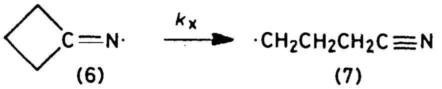
$$(k_{vi}/k_{vii}) = [Pr^n(H)C{=}N\cdot][cyclo\text{-}C_5H_{10}]/[cyclo\text{-}C_5H_9\cdot][Bu^nN_3] \quad \text{(viii)}$$

At 233 K the value of (k_{vi}/k_{vii}) for n-butyl azide was 35 ± 5 and hence $k_{vi}(R^1 = Pr^n, R^2 = H)$ is *ca.* 5×10^6 l mol^{-1} s^{-1}, taking [13b,14] k_{vii} as 1.4×10^5 l mol^{-1} s^{-1} at 233 K.

(b) *Photolysis of Azines.*—The e.s.r. spectrum of the parent iminyl radical, $H_2C{=}N\cdot$, has been detected in the solid state after photolysis of formaldazine monomer at 77 K [equation (ix; R = H)].[15] We have briefly investigated the utility of azine photolysis as a source of iminyl radicals for study by e.s.r. spectroscopy in solution. Photolysis of formaldazine (5; R = H) or acetone azine (5; R = Me) in cyclopropane solvent afforded spectra of the respective iminyl radicals, although the signals were generally much less intense than could be obtained by the azide route. However, azine photolysis has the advantage that the iminyl radicals are formed without the intermediacy of, and in the absence of, other radicals. Azines are often more readily accessible than other iminyl precursors, for example cyclobutanone azine is easily prepared from the ketone. However, photolysis does not yield the spectrum of the iminyl radical (6) but rather that of the ring-opened product, the 3-cyanopropyl radical (7) [equation (x)].

$$R_2C{=}N{-}N{=}CR_2 \xrightarrow{h\nu} 2R_2C{=}N\cdot \quad \text{(ix)}$$

(5)



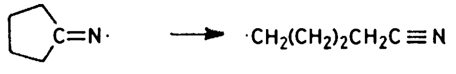
(6) (7)

(x)

The spectrum of (6) could not be detected down to 188 K (in diethyl ether–cyclopropane *ca.* 2 : 1 v/v) below which temperature the azine came out of solution. The radical (7) [$a(2H_\alpha)$ 22.2, $a(2H_\beta)$ 22.7 G, g 2.002 7 at 225 K] was also generated by abstraction of bromine from γ-bromobutyronitrile by photochemically generated triethylsilyl radicals.[16] We estimate that k_x is $>10^3$ s^{-1} at 200 K. When larger alkyl substituents were present in an acyclic azine [*e.g.* in (5; R = Et)], photolysis did not yield detectable concentrations of iminyl radicals.

(c) *Reactions of Iminyl Radicals.*—Iminyl radicals are comparatively unreactive species. Photolysis of the azines (5; R = H or Me) in the presence of trimethyl phosphite afforded only the spectra of the iminyl radicals and no addition to phosphorus [17] was detectable. The radical $H_2C{=}N\cdot$ alone was detected during photolysis of di-t-butyl peroxide and methyl azide in liquid ethylene (*ca.* 10M) between 162 and 206 K, and hence reaction (xi) must be relatively slow.

$$H_2C{=}N\cdot + CH_2{=}CH_2 \longrightarrow H_2C{=}N{-}CH_2\dot{C}H_2 \quad \text{(xi)}$$



(8) (9)

(xii)

We obtained no e.s.r. evidence for ring-opening of the iminyl radical (8), either in solution (generated by the azide route) or in adamantane matrix (generated from cyclopentylamine; *cf.* ref. 10). *X*-Irradiation of cyclopentylamine as a solid solution in adamantane for 1 h at 125 K gave rise to the 1-aminocyclopentyl radical [$a(4H_\beta)$ 27.0, a(N) 4.0, $a(2H'_\beta)$ 4.0 G at 170 K] which was converted into (8) when irradiated with u.v. light.[10] The isotropic e.s.r. signal from (8) decayed slowly at 290 K, but the spectrum of (9) could not be detected amongst signals from other unidentified radicals present at this temperature.

The rates of decay of selected photochemically generated iminyl radicals were measured using kinetic e.s.r. spectroscopy.[18,19] For all radicals decay was a second-order process and the rate constants ($2k_t$), listed in Table 2, are all close to those expected for diffusion-controlled dimerisation to give azine.

TABLE 2

Second-order rate constants for self-reaction of iminyl radicals in cyclopropane at 173 K

Radical [a]	$2k_t$/l mol^{-1} s^{-1}
$H_2C{=}N\cdot$	7.9×10^9
$Pr^n(H)C{=}N\cdot$	5.0×10^9
$Me_2C{=}N\cdot$	9.3×10^8
$\overline{CH_2(CH_2)_3C}{=}N\cdot$	5.8×10^8 [b]

[a] Generally photochemically from the azide (1M) and di-t-butyl peroxide (1M). [b] 1.6×10^9 l mol^{-1} s^{-1} at 259 K.

(d) *Cyclisation of the 4-Cyanobutyl Radical.*—The failure of (8) to undergo ring opening is in accord with the product analysis studies of Ogibin *et al.*,[20] who have obtained evidence for the rapid cyclisation of the 4-cyanobutyl radical (9) to give (8) at 333 K. Using e.s.r. spectroscopy,

$$\underset{(9)}{\cdot CH_2(CH_2)_2CH_2C{\equiv}N} \xrightarrow{k_{xiii}} (8) \qquad \text{(xiii)}$$

$$\left.\begin{array}{l}(8) + (8) \xrightarrow{2k_{xiv}} \qquad \text{(xiv)} \\ (8) + (9) \xrightarrow{k_{xv}} \qquad \text{(xv)}\end{array}\right\} \text{non-radical products}$$

we have investigated the cyclisation of (9) which was generated by photolysis of a mixture of δ-bromovaleronitrile, hexa-n-butylditin, and di-t-butyl peroxide in cyclopropane solvent.* Above *ca.* 220 K the spectra of both (8) and (9) were detected and the rate of cyclisation was measured relative to that of self-reaction of the product iminyl radical (8).[22,23] It may readily be shown that, if (8) and (9) are the only radicals present in significant concentration, equation (xvi) holds. A plot of 1/[(8)]

$$1/[(8)] = (2k_{xiv}/k_{xiii})[(8)]/[(9)] + (k_{xv}/k_{xiii}) \qquad \text{(xvi)}$$

against [(8)]/[(9)] as a function of light intensity yields $(2k_{xiv}/k_{xiii})$.[22,23] At 259 K the value of k_{xiii} was found to be 4.5×10^2 s^{-1}, using our measured value of $2k_{xiv}$ (1.6×10^9 l mol^{-1} s^{-1}).

$$R_3Si\cdot + XN_3 \longrightarrow \underset{(10a)}{R_3Si(X)N{-}N{=}N^{\cdot}} \text{ or } \underset{(10b)}{XN{=}N{-}\dot{N}SiR_3} \qquad \text{(xvii)}$$

(e) *Reaction of Triorganosilyl Radicals with Azides.*—Trimethyl-, triethyl-, and triphenyl-silyl radicals, generated photochemically or thermally, react with a variety of organic azides to afford spectra which show splitting from three non-equivalent nitrogen nuclei and *g* values which are substantially less than 2.002 3. These spectra are ascribed to the triazenyl radicals (10a or b), in which the substituents are attached either to the same nitrogen or to the terminal nitrogens, respectively (see Discussion). The e.s.r. parameters for the radicals (10) are given in Table 3.

TABLE 3

E.s.r. parameters for triazenyl radicals (10) formed by addition of triorganosilyl radicals ($R_3Si\cdot$) to azides (XN_3)

					Hyperfine splittings (G)		
X	R	Solvent [a]	*T*/K	*g* Factor	*a*($N^{central}$)	*a*(N′)	*a*(N″)
Me	Et	C	260	2.0009	17.1	3.6	1.8
Et	Et	C	220	2.0010	17.5	3.5	1.6
Pr^n	Et	C	220	2.0010	17.6	3.6	1.8
Pr^n	Et	B	343	2.0010	17.6	3.6	1.8
Pr^n	Ph	B	343	2.0011	18.0	3.6	1.4
Bu^n	Me	C	230	2.0011	16.8	3.3	1.6
Bu^n	Et	C	230	2.0011	17.2	3.4	1.7
Pr^i	Et	C	210	2.0011	17.0	3.5	1.5
Pr^i	Ph	B	343	2.0011	17.6	3.6	1.2
cyclo-C_5H_9	Et	B	343	2.0010	17.3	4.0	1.5
cyclo-C_5H_9	Ph	B	343	2.0011	17.3	3.6	1.2
Bu^t	Ph	B	343	2.0012	17.8	3.4	1.0
1-Ad [b]	Ph	B	343	2.0011	18.2	3.0	1.0
Bu^{t}OC(O)	Et	B	343	2.0010	20.0	3.8	1.8
Ph	Et	B	343	2.0010	18.1	4.0	1.5
Ph	Ph	B	343	2.0011	18.0	3.6	1.2
$(PhO)_2P(O)$	Ph	B	343	2.0007	22.3 [c]	2.8 [c]	1.2 [c]
Me_3Si	Me	C	285	2.0002	20.6	*d*	*d*
Me_3Si	Et	B	343		20.7	*d*	*d*
Me_3Si	Et	S	330	2.0001	20.6	*d*	*d*
Me_3Si	Ph	B	343	2.0005	21.6	*d*	*d*

[a] C = photochemical generation in cyclopropane solvent; [Bu^{t}OOBu^t] *ca.* 2M, [Et_3SiH] *ca.* 2M or [Ph_3SiH] *ca.* 1M. B = thermal generation in t-butylbenzene solvent; [Bu^{t}ON=NOBu^t] *ca.* 1M, [Et_3SiH] *ca.* 2M or [Ph_3SiH] *ca.* 1M. S = photochemical generation in triethylsilane solvent. The azide concentration was always *ca.* 0.5M. [b] 1-Adamantyl azide. [c] *a*(1P) 28.8 G. [d] Not resolved; peak–peak linewidth *ca.* 2 G.

^{15}N-Labelling experiments showed conclusively that the central nitrogen gives rise to the largest splitting for the adducts of triethyl- or triphenyl-silyl radicals to methyl azide. The azide was prepared by the reaction of dimethyl sulphate with potassium azide which was 92% labelled with ^{15}N in one terminal atom per azide ion. The Figure shows the e.s.r. spectra of the triethylsilyl radical adducts of normal and isotopically labelled methyl azide, together with computer simulations of the different spectra expected from the labelled azide, depending on whether the central nitrogen gives rise to the largest, intermediate, or smallest splitting.

Addition of triethyl- or triphenyl-silyl radicals to trimethylsilyl azide, prepared from the terminally ^{15}N-labelled potassium azide, gave spectra which were indistinguishable from those obtained from unlabelled Me_3SiN_3. We conclude that the splittings shown by (10; X = Me_3Si, R = Et or Ph) are from the central nitrogen atoms and that the other splittings are unresolved.

The spectra of the triazenyl radicals were similar in t-butylbenzene solvent at 343 K (thermal generation) and in cyclopropane over a wide range of temperature (photochemical generation). Primary alkyl azides gave only triazenyl radicals and variable concentrations of iminyl radicals, derived from competitive reaction of the t-butoxyl radicals with the azide, using either photochemical or thermal methods of generation. Secondary and tertiary alkyl azides, t-butoxycarbonyl, trimethylsilyl, and diphenylphosphoryl azides gave, in addition to the triazenyl

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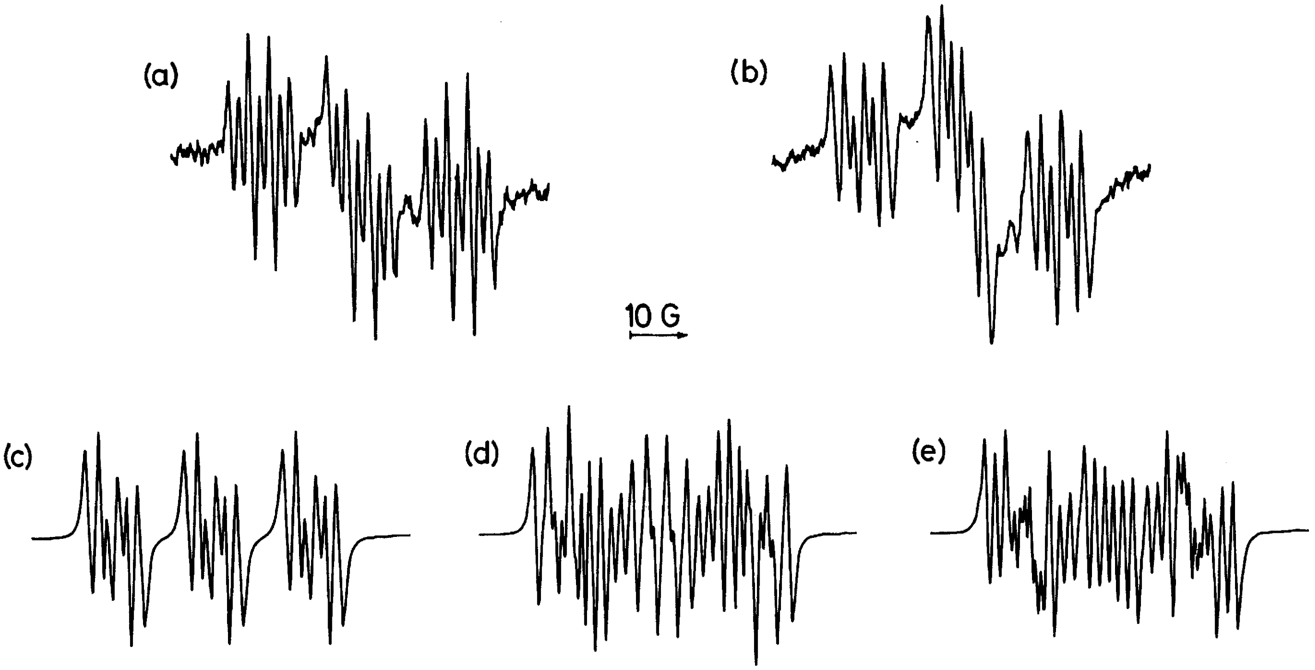
* The rate of cyclisation of the 4-cyanobutyl radical has been measured over a range of temperature by Griller *et al.*[21]

radicals and iminyl radicals (the latter only from secondary alkyl azides) relatively strong signals from other nitrogen-containing radicals most of which were relatively long lived. No special attempts were made to assign these signals,* which were particularly intense when photochemical generation was employed. Phenyl azide underwent rapid photochemical decomposition to form a red-brown solid [24] and its reactions were investigated using only thermal generation methods. In addition to the triazenyl radical (10; X = Me$_3$Si, R = Me) photolysis of a mixture of trimethylsilyl azide, trimethylsilane, and di-t-butyl peroxide in cyclopropane yielded signals which we assign to the persistent triazyl radical (Me$_3$Si)$_2$N$\dot{N}$N(SiMe$_3$)$_2$.[25]

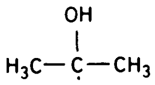
In order to eliminate the possibility that the signals ascribed to triazenyl radicals could be due to *N*-oxyl radicals (compare PhN=N–$\dot{O}$, *g* 2.001 7 [26]), we generated triethylsilyl radicals without the use of oxygen-containing reagents. Photolysis of a rigorously degassed cyclopropane solution containing tetrakis(trimethylsilyl)hydrazine,[27] n-butyl azide, and triethylsilane also gave rise to the e.s.r. spectrum assigned to (10; X = Bu^n, R = Et).



(a) E.s.r. spectrum of the radical (10; R = Et, X = Me) in cyclopropane at 253 K, derived from unlabelled methyl azide. (b) Spectrum of the radical (10; R = Et, X = Me) obtained from labelled methyl azide comprising 46% Me^{14}N^{14}N^{15}N, 46% Me^{15}N^{14}N^{14}N, and 8% Me^{14}N^{14}N^{14}N. Computer simulations of the spectra expected from the labelled radical if N^2 in the azide gives rise to, (c) the largest, (d) the intermediate, and (e) the smallest nitrogen splitting in the triazenyl radical

The e.s.r. spectra of (10) could be observed for long periods of time at high temperatures (353 K), implying that the triazenyl radicals do not readily lose nitrogen. The rate of decay of the signal from (10; X = Bu^n, R = Et) was measured by kinetic e.s.r. spectroscopy [18,19] and at 238 K in cyclopropane, for an initial concentration of 7 × 10^{-8}M, decay was second-order with a rate constant of 2 × 10^9 l mol^{-1} s^{-1}.

(f) *Reaction of* 1-*Hydroxy*-1-*methylethyl Radicals with Alkyl Azides*.—Photolysis at 200—250 K of solutions containing di-t-butyl peroxide (1M), isopropyl alcohol (3M), and an alkyl azide (0.5M) yielded spectra which differed depending on the nature of the azide. With t-butyl azide, only the 1-hydroxy-1-methylethyl radical (11) was detected. Isopropyl and other secondary alkyl azides gave rise to overlapping spectra of (11) and the appropriate iminyl radical [see section (a)]. Methyl azide afforded only the spectrum of H$_2$C=N•, and at high temperatures (*ca.* 270 K) the reagents were rapidly consumed, indicating the occurrence of a chain reaction. However, with primary alkyl azides a dialkylaminyl radical was the major species detected (see Table 4) along with small concentrations of other radicals including (4) and (11). This result was not affected by the presence of piperylene (0.6M) or ethylene (3M) (as potential quenchers of excited triplet and singlet states, respectively), or by replacement of the di-t-butyl peroxide by acetone. Experiments in which the isopropyl alcohol was replaced by cyclopentanol or ethanol also gave similar spectra but replacement by t-butyl alcohol resulted in detection of only the iminyl radical.



$$\mathrm{H_3C{-}\overset{OH}{\underset{\bullet}{C}}{-}CH_3}$$

(11)

The dialkylaminyl radicals were undetectable above 273 K when (11) was generated photochemically, and thermolysis (330—343 K) of a t-butylbenzene solution containing di-t-butyl hyponitrite, n-butyl azide, and isopropyl alcohol afforded no e.s.r. signals. At first, we considered that n-propyl and n-butyl azides were giving rise to Pr$^n_2$N• and Bu$^n_2$N•, respectively, but ethyl azide clearly gave a radical with the structure Me$\dot{N}$CH$_2$R rather than Et$_2$N•. Authentic spectra of the radicals Me$\dot{N}$Et and Me$\dot{N}$Pr^n were obtained by photolysis of di-t-butyl peroxide in the presence of the appropriate tris(dialkylamino)phosphine [equation

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* Many of these e.s.r. spectra probably derived from hydrazyl radicals, formed as secondary products.

(xviii; R = Et or Pr^n)],[19] and the spectral parameters are included in Table 4.

The spectral parameters of $\mathrm{Me\dot{N}Et}$ and $\mathrm{Me\dot{N}Pr^n}$ were solvent dependent, but were significantly different from those of the aminyl radicals derived from ethyl azide in the presence of EtOH or Pr^{i}OH. We conclude that the dialkylaminyl radical formed by photolysis of a mixture of $\mathrm{EtN_3}$, $\mathrm{Bu^tOOBu^t}$, and Pr^{i}OH (EtOH) is not $\mathrm{Me\dot{N}Et}$ or $\mathrm{Me\dot{N}Pr^n}$, but is quite probably $\mathrm{Me\dot{N}CH_2C(OH)Me_2}$ [$\mathrm{Me\dot{N}CH_2C(OH)(H)Me}$]. Analogous assignments of the spectra derived from the other primary alkyl azides are given in Table 4.

$$\mathrm{Bu^tO\cdot} + \mathrm{[Me(R)N]_3P} \longrightarrow \mathrm{Me\dot{N}R} + \mathrm{[Me(R)N]_2POBu^t} \qquad \text{(xviii)}$$

TABLE 4

E.s.r. parameters for dialkylaminyl radicals produced by reaction of hydroxyalkyl radicals with primary alkyl azides

				Hyperfine splittings (G)		
Radical	Alcohol present[a]	T/K	g Factor	a(N)	$a(\mathrm{H}_\beta)$[b]	$\mathrm{d}\lvert a(2\mathrm{H}_\beta)\rvert/\mathrm{d}T$ (mG K^{-1})
$\mathrm{Me\dot{N}CH_2C(OH)(H)Me}$[c]	EtOH	233		15.3	35.6(2); 28.1(3)	−17
$\mathrm{Me\dot{N}CH_2C(OH)Me_2}$	Pr^{i}OH	233	2.0048	15.1	36.7(2); 27.6(3)	−21
$\mathrm{Et\dot{N}CH_2C(OH)Me_2}$	Pr^{i}OH	230		15.0	35.0(2)	
$\mathrm{Pr^n\dot{N}CH_2C(OH)(H)Me}$[c]	EtOH	230		15.0	35.0(2)	
$\mathrm{Pr^n\dot{N}CH_2C(OH)Me_2}$	Pr^{i}OH	233	2.0048	14.9	35.0(2)	−24
$\mathrm{Me\dot{N}CH_2Et}$	None	233	2.0047	14.6	36.3(2); 26.7(3)	*d, e*
$\mathrm{Me\dot{N}CH_2Et}$[f]	EtOH	233	2.0047	15.2	36.9(2); 27.7(3)	−38
$\mathrm{Me\dot{N}CH_2Et}$[f]	Pr^{i}OH	233	2.0047	15.2	36.7(2); 27.6(3)	−39
$\mathrm{Me\dot{N}CH_2Me}$	None	233	2.0047	14.6	35.5(2); 27.1(3)	*d, g*
$\mathrm{Me\dot{N}CH_2Me}$[f]	EtOH	233		15.3	36.7(2); 27.9(3)	−44
$\mathrm{Me\dot{N}CH_2Me}$[f]	Pr^{i}OH	233		15.3	36.5(2); 27.7(3)	−46

[a] Samples contained azide (0.5—1M) or tris(dialkylamino)phosphine (*ca.* 1M), $\mathrm{Bu^tOOBu^t}$ (*ca.* 1M), and (when present) the alcohol (2.5M) in cyclopropane. [b] Numbers of equivalent protons shown in parentheses. [c] The *N*-methylene protons are diastereotopic for this structure; however, magnetic non-equivalence was not detected. [d] The plot of $a(2\mathrm{H}_\beta)$ against temperature showed some curvature. [e] $a(2\mathrm{H}_\beta)$ 38.0 at 188 K, 37.4 G at 213 K. [f] The nitrogen and β-proton splittings for $\mathrm{Me_2N\cdot}$ (generated by photolysis of tetramethyltetrazene) were also higher in the presence of alcohol than in cyclopropane alone; in all solvents g 2.0046. [g] $a(2\mathrm{H}_\beta)$ 37.5 at 188 K, 36.6 G at 213 K.

DISCUSSION

The reaction of t-butoxyl radicals with primary and secondary alkyl azides, which are readily available, provides a useful new route to iminyl radicals. Hydrogen is abstracted from the α-methylene group of n-butyl azide appreciably more readily than from cyclopentane, probably as a result of conjugative stabilisation of the α-azidoalkyl radical or the concerted loss of nitrogen to form the iminyl radical.

Photolysis of azines leads to much lower concentrations of iminyl radicals than does the azide route, but the former source may have certain advantages for some iminyl radicals, since azines are readily prepared from aldehydes or ketones.

Iminyl radicals, like dialkylaminyl radicals,[27] are relatively unreactive and fail to add readily to alkenes or trialkyl phosphites. Ingold and his co-workers [12] have shown that the iminyl radical $\mathrm{(CF_3)_2C{=}N\cdot}$ undergoes self-reaction at the diffusion-controlled rate ($2k_t$ 4×10^9 l mol^{-1} s^{-1} at 238 K), probably to form the ketazine dimer, $\mathrm{(CF_3)_2C{=}N{-}N{=}C(CF_3)_2}$. The rate constants reported here are similarly large and probably also refer to formation of the corresponding azines [equation (xix)].

A first-order decay has been reported for the radical $\mathrm{Bu^t_2C{=}N\cdot}$, and has been ascribed to β-scission to form pivalonitrile [equation (xx)].[12]

The rate constant for fragmentation is given by $\log_{10}(k_{xx}/\mathrm{s}^{-1}) = 14.4 - 71.5/\theta$, where $\theta = 2.303RT$ kJ mol^{-1}. The much more rapid β-scission of the cyclic iminyl radical (6) [equation (x)] may be interpreted in terms of relief of the angle strain present in the four-membered ring. The reverse type of reaction, intramolecular addition to the cyanide function, takes place with the 4-cyanobutyl radical [equation (xiii)] * and the rate constant for cyclisation ($k_{\mathrm{xiii}} = 4.5 \times 10^2$ s^{-1} at 259 K) is significantly less than that for cyclisation of the hex-5-enyl radical (12) [28] at the same temperature (k_{xxi} 1.3×10^4 s^{-1}). The related intermolecular addition reactions (xxii) and (xxiii) are both highly exothermic.[29]

An interesting 1,4-cyanide transfer has been reported recently,[30] and the proposed mechanism involves ring-closure to form an intermediate iminyl radical followed by β-scission of the latter [*e.g.* equation (xxiv)].

Triazenyl Radicals.—The structures of the silyl radical adducts of the azides are not known with complete certainty. The hyperfine splittings appear to be equally consistent with a 3,3-disubstituted triazenyl radical or a 1,3-disubstituted radical in which the unpaired electron is primarily associated with one nitrogen atom. The absence of any resolvable splitting from the protons in the groups X in (10) and the large splitting from a single nitrogen for the adduct of $\mathrm{Me_3Si\cdot}$ to $\mathrm{Me_3SiN_3}$ preclude either a delocalised π-type triaza-allyl structure or a 1,3-triazenyl radical in which the unpaired electron is

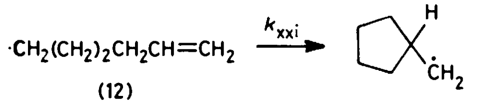
* No signal which might be assigned to the isomeric imidoyl radical $\mathrm{CH_2(CH_2)_3\dot{C}{=}N}$, was detected in fluid solution (or even in adamantane matrix) as a rearrangement product of the iminyl radical (8).

located on the nitrogen carrying the group X. Possible types of electronic structure are shown in (13)—(15).

For (13) it is likely that $a(\mathrm{N}^2)$ would be greater than $a(\mathrm{N}^1)$ (compare[31,32] PhN=N·). In (14) the three nitrogens are involved in a four-electron three-centre (4e : 3c) in-plane (σ) bond and the unpaired electron is in a π orbital whilst in (15) there is a (4e : 3c) π bond and the unpaired electron is in a σ orbital. For both (14) and (15) the unpaired electron is centred mainly on N^2. The extent of bonding between N^1 and N^2 in (14) and (15) is a moot point, although we believe that the azide adducts are better described as acyclic triazenyl radicals rather than triazacyclopropyl radicals, which would presumably possess significant angle strain.

$$2\mathrm{R^1R^2C{=}N\cdot} \longrightarrow \mathrm{R^1R^2C{=}N{-}N{=}CR^1R^2} \qquad \text{(xix)}$$

$$\mathrm{Bu^t{}_2C{=}N\cdot} \xrightarrow{k_{xx}} \mathrm{Bu^t\cdot} + \mathrm{Bu^tC{\equiv}N} \qquad \text{(xx)}$$



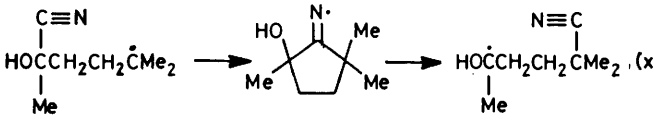
(12)

(xxi)

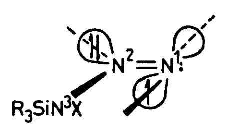
ΔH° / kJ mol⁻¹

$$\mathrm{Me\cdot} + \mathrm{HC{\equiv}N} \longrightarrow \mathrm{Me(H)C{=}\dot{N}} \qquad -135 \qquad \text{(xxii)}$$

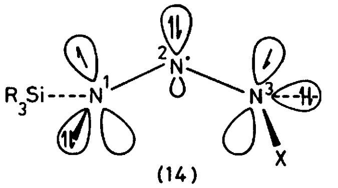
$$\mathrm{Me\cdot} + \mathrm{H_2C{=}CH_2} \longrightarrow \mathrm{MeCH_2\dot{C}H_2} \qquad -101 \qquad \text{(xxiii)}$$



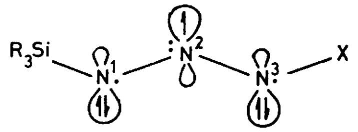
(xxiv)



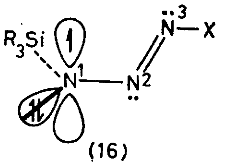
(13)



(14)



(15)



(16)

The nitrogen splittings observed for the triazenyl radicals appear to be inconsistent with the 'perpendicular' triaza-allyl structure (16).

The g-factor of (16) would be expected to be >2.002 3, since the g-factors of certain azoalkyl radicals (*e.g.* $\mathrm{Bu^t{}_2\dot{C}{-}N{=}NBu^t}$), which appear[33] to exist in a similar perpendicular conformation, are normal for carbon-centred species with an α-nitrogen (*ca.* 2.003 0). Attachment of silicon to the radical centre should not decrease g substantially, since the g-factor of $\mathrm{(Me_3Si)_2N\dot{N}SiMe_3}$ (2.004 9)[34] is somewhat lower than that of $\mathrm{Me_2N\dot{N}Me}$ (2.003 8).[35] The g-factors of (13)—(15) could all be less than the free-spin value. For (13), mixing of the empty π* N=N orbital with the singly-occupied σ-orbital by spin-orbit coupling would lead to a low g value along the direction of the N=N bond. Calculations[31] and CIDNP studies[32] suggest that alkyl- and aryl-diazenyl radicals (RN=N·) are σ-radicals with g-factors less than the free-spin value. For (14) and (15), mixing-in of excited states in which the unpaired electron is promoted into the empty σ* or π* orbitals, respectively, could lead to g-factors <2.002 3.

It is difficult to understand why (13) should be relatively stable towards loss of nitrogen, since alkyl-, aryl-, and alkoxy-diazenyl radicals are very short lived in this respect. The 3,3-dimethyltriazenyl radical ($\mathrm{Me_2NN{=}N\cdot}$) is not detected during photolysis of tetramethyltetrazene ($\mathrm{Me_2NN{=}NNMe_2}$) in solution.[34,36] If conjugation of the type represented by canonical structures (17) and (18) were important[7] in stabilising the silyl radical adducts towards loss of nitrogen, we would expect such stabilisation to be even more effective when the silyl ligand is replaced by a methyl group. However, there is some evidence[27] that the $\mathrm{N^2{-}N^3}$ σ bond in $\mathrm{R_3Si(Me)NN{=}N\cdot}$ may be stronger than that in $\mathrm{Me_2NN{=}N\cdot}$.

$$\mathrm{R_3Si(Me)\ddot{N}{-}\ddot{N}{=}\dot{N}\cdot} \longleftrightarrow \mathrm{R_3Si(Me)\overset{+}{N}{=}\ddot{N}{-}\overset{-}{\ddot{N}}\cdot}$$

(17) (18)

An e.s.r. spectrum attributed to the 1,3-dimethyltriazenyl radical has recently been reported[37] and this species was believed to be a triaza-allyl radical, in which the unpaired electron is contained in a π-non-bonding molecular orbital and hence centred mainly on N^1 and N^3. However, we find it difficult to reconcile the reported low g factor (2.002 0) with this electronic structure, since all the σ molecular orbitals would be doubly occupied and the observed *negative g* shift from the free spin value requires mixing-in of an excited state in which the unpaired electron has been promoted into an empty σ-orbital. Molecular orbital calculations[37] predicted a π ground state for the 1,3-dimethyltriazenyl radical, but suggested that when the substituents were changed from CH_3 to H or SiH_3 the σ electronic configuration [*cf.* (15)] would decrease in energy relative to the π configuration. The nitrogen coupling constants predicted for the σ-configuration of the 1,3-dimethyltriazenyl radical were $a(1\mathrm{N}^2)$ 15.6, and $a(2\mathrm{N}^{1,3})$ 1.7 G, similar to those observed for the silyl radical adducts of the azides.

$$Me_3Si\cdot + Ph_2\bar{C}{-}\overset{+}{N}{\equiv}N \longrightarrow \underset{(19)}{Ph_2C{=}N{-}\dot{N}SiMe_3} \qquad (xxv)$$

$$\underset{(20)}{Bu^t(CH_3)C{=}N{-}\dot{N}CMe_3} \qquad \underset{(21)}{Bu^t(CH_3)C{=}N{-}\dot{N}SiMe_3}$$

Hydrazonyl radicals ($R_2C{=}N{-}\dot{N}R$), which are related to 1,3-triazenyl radicals, have been generated by radical addition to diazoalkanes[33,38] and by hydrogen abstraction from hydrazones.[39] The radical (19), formed by the addition of trimethylsilyl radicals to diphenyldiazomethane [equation (xxv)] was thought[38] to have a σ electronic structure on the basis of its e.s.r. spectrum, although the evidence is not entirely convincing.

The e.s.r. spectrum of the radical (20) exhibited a methyl proton splitting of 5.4 G, about six times larger than that shown by (21) and this was thought to be indicative of a σ electronic structure for the latter radical.[39b] However, the *g* factors of (20) and (21) are very similar (*ca.* 2.003 6). At least, we may deduce that replacement of Me_3Si by Me_3C brings about a reduction in the spin density on the three-co-ordinate carbon.

There is little data in the literature regarding the preferred site of radical attack on an alkyl azide, and this might well vary between N^1 and N^3 depending on the nature of the addendum. Radical addition to diphenyldiazomethane appears to take place at both carbon and the terminal nitrogen.[38] The reaction of benzoyl azide with tributyltin hydride produces $Bu_3SnN(H)C(O)Ph$ by a radical chain mechanism,[40] but the authors showed the attack of $Bu^n{}_3Sn\cdot$ on the azide and loss of nitrogen as proceeding in a single step without specifying an intermediate triazenyl radical. Addition could take place more rapidly at N^1 or N^3, and if a 1,3-triazenyl radical were formed it could rearrange either prior to or concerted with loss of nitrogen. Decomposition of a first-formed triazene, $PhC(O)N{=}NN(H)SnBu^n{}_3$, could also be the source of the final product.[41] The reaction of Ph_3SiH with Ph_3SiN_3 yields $(Ph_3Si)_2NH$,[42] possibly by way of a radical chain mechanism. The results of recent product studies[43] have been interpreted in terms of the more ready intramolecular addition of aryl radicals to aryl azides to produce the 3,3-triazenyl radical than to form the 1,3-adduct.

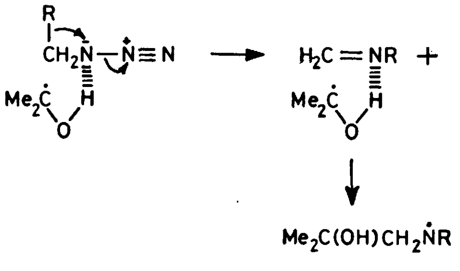
We conclude that the structures (13)—(15) are most likely for the adducts of organosilyl radicals to azides and, on balance, we favour the σ 1,3-triazenyl radical (15).

Reaction of 1-*Hydroxy*-1-*methylethyl Radicals with Alkyl Azides*.—The formation of aminyl radicals during the reaction of 1-hydroxy-1-methylethyl radicals (11) with primary alkyl azides was unexpected. Previous work[1,6] has shown that (11) induces the decomposition of aryl, arenesulphonyl, and acyl azides to give monosubstituted aminyl radicals [equation (iv)] and this reaction may involve a direct transfer of hydrogen from (11) to N^1 or addition of (11) to N^3, followed by intramolecular hydrogen transfer. Diazoalkanes react in a similar way [*e.g.* equation (xxvi)].[44]

$$RC(O)\bar{C}(R){-}\overset{+}{N}{\equiv}N + Me_2\dot{C}OH \longrightarrow RC(O)\dot{C}(R)H + N_2 + Me_2CO \qquad (xxvi)$$

$$RCH_2\bar{N}{-}\overset{+}{N}{\equiv}N \xrightarrow{H^+} R(H)C{=}NH + H_2C{=}NR + N_2 \qquad (xxvii)$$

$$Me_2\dot{C}OH + Bu^tN{=}CH_2 \longrightarrow Bu^t\dot{N}CH_2C(OH)Me_2 \qquad (xxviii)$$



(xxix)

Primary alkyl azides undergo acid-catalysed decomposition at relatively low temperatures to form imines, possibly through the intermediacy of a protonated nitrene [equation (xxvii)].[1] Hydroxyalkyl radicals are known to add to the imine $Bu^tN{=}CH_2$ to give aminyl radicals [equation (xxviii)],[45] and such addition to $RN{=}CH_2$ should be more rapid if R is a primary alkyl group.

Our attempts to generate $Me\dot{N}CH_2C(OH)Me_2$ by addition of (11) to $MeN{=}CH_2$ failed, apparently because of rapid polymerisation of the imine when solutions containing $MeN{=}CH_2$, Pr^iOH, and Bu^tOOBu^t were photolysed at low temperatures. It therefore seems unlikely that the dialkylaminyl radicals derived from ethyl azide could have been formed by radical addition to monomeric $MeN{=}CH_2$, and we favour a mechanism involving direct attack of the hydroxyalkyl radical on the azide [equation (xxix)]. Hydrogen-bonding between (11) and the azide [or even complete proton transfer from (11)] may facilitate loss of nitrogen [*cf.* equation (xxvii)] which may be concerted with migration of the alkyl group from carbon to nitrogen. Carbon–carbon bond formation may accompany or follow migration of R.

Note added in proof: The identity of the dialkylaminyl radicals formed by the reaction of hydroxyalkyl radicals with primary alkyl azides is confirmed by the spectra obtained from neopentyl azide. Thus, photolysis of a cyclopropane solution containing $Bu^tCH_2N_3$, Bu^tOOBu^t, and Pr^iOH gave rise to the spectrum of $Bu^t\dot{N}CH_2C(OH)Me_2$[45] [a(N) 15.0, a(2H) 38.9 G, g 2.004 8 at 307 K]. Replacement of the Pr^iOH by EtOH afforded $Bu^t\dot{N}CH_2CH(OH)Me$,[45] for which the splittings from the diastereotopic methylene protons are markedly different [a(N) 15.1, a(1 H′) 36.3, a(1 H″) 39.9 G, g 2.004 5 at 280 K]. Identical spectra were obtained in independent experiments which involved the addition of the appropriate hydroxyalkyl radical to $Bu^tN{=}CH_2$.[45] The relative intensities of the signal from $Bu^t\dot{N}CH_2C(OH)R_2$ and the weak spectrum of $Bu^t(H)C{=}N\cdot$ (from $Bu^tO\cdot + Bu^tCH_2N_3$) did not vary with the duration of photolysis, lending support to the conclusion that the aminyl radical results from direct attack of the hydroxyalkyl radical on the azide, rather than from addition to $Bu^tN{=}CH_2$ produced by photolysis of the azide.

EXPERIMENTAL

E.s.r. Studies.—The techniques employed for generation and detection of transient free radicals have been described previously.[13b] Rate constants for radical self-reaction were measured by the rotating sector technique.[18,19] Reagent concentrations are given in footnotes to the Tables. Photolysis of the azides alone in solution did not give rise to any e.s.r. signals, although nitrogen was evolved. Care was taken not to photolyse sealed samples for long periods of time when high pressures of nitrogen might build up. Samples were not sealed during experiments involving thermal generation of t-butoxyl radicals from di-t-butyl hyponitrite.

Materials.—Di-t-butyl peroxide, triethylsilane, hexa-n-butylditin, γ- and δ-bromovaleronitrile, and trimethylsilyl, diphenylphosphoryl, and t-butoxycarbonyl azides were commercial products purified before use. Di-t-butyl hyponitrite was prepared by the method of Kiefer and Traylor.[46] Methyl azide was prepared from sodium azide or potassium azide (92 atom% labelled with ^{15}N in one terminal nitrogen) and dimethyl sulphate.[47] The product was pure and not contaminated with dimethyl ether (*cf.* ref. 47). Other primary and secondary alkyl azides were prepared by the method of Lieber *et al.*[48] 3-*Azidopentane*, b.p. 30 °C at 18 Torr, is previously unreported (Found: C, 53.0; H, 9.8; N, 37.1. $C_5H_{11}N_3$ requires C, 53.1; H, 9.8; N, 37.1%). t-Butyl azide was prepared as described by Miller[49] and separated from carbon disulphide using preparative g.l.c. 1-Adamantyl[50] and phenyl[51] azides were prepared by literature methods. ^{15}N-Labelled trimethylsilyl azide was prepared from the 92 atom% $K^{15}N^{14}N_2$ as described for the unlabelled material.[52]

Acetone[53] and cyclobutanone[54] azines were prepared from the ketones. Formaldazine polymer was heated under vacuum to obtain the monomer which was condensed directly into an e.s.r. tube.[15]

Tris-(N-*ethyl*-N-*methylamino*)*phosphine*, b.p. 58 °C at 1.5 Torr, was prepared from ethylmethylamine using the procedure[55] described for $(Me_2N)_3P$ (Found: C, 52.5; H, 12.0; N, 20.1. $C_9H_{24}N_3P$ requires C, 52.7; H, 11.8; N, 20.5%). *Tris*-(N-*propyl*-N-*methylamino*)*phosphine*, b.p. 64—68 °C at 0.15 Torr, was prepared similarly (Found: C, 58.1; H, 12.5; N, 16.9. $C_{12}H_{30}N_3P$ requires C, 58.3; H, 12.2; N, 17.0%).

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