#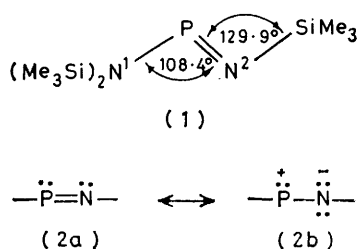 An Electron Spin Resonance Study of Radical Addition to Bis(trimethylsilyl)amino(trimethylsilylimino)phosphine, $(Me_3Si)_2NP=NSiMe_3$

By **Brian P. Roberts** * and **Karamjit Singh**, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ
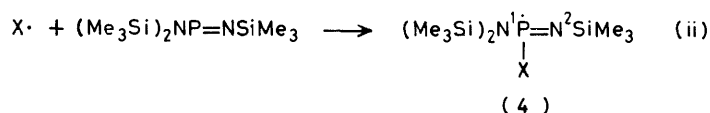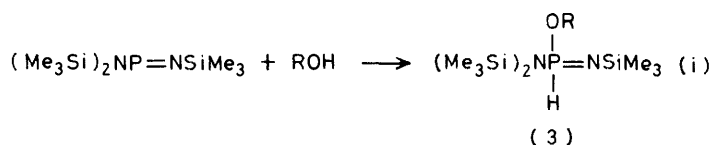
Alkoxyl, alkyl, and acyl radicals add rapidly to phosphorus in the phospha(III)azene $(Me_3Si)_2NP=NSiMe_3$ to give phosphorimidoyl radicals $X[(Me_3Si)_2N]\dot{P}=NSiMe_3$ (4; X = RO, R, or RCO) which are nitrogen analogues of the phosphonyl radicals $Y_2\dot{P}=O$. The solution e.s.r. spectra of the phosphorimidoyl radicals are characterised by large values of $a(^{31}P)$ [519 G for (4; X = Bu^{t}O) at 173 K] which are indicative of a pyramidal geometry at phosphorus. The phosphorimidoyl radicals are relatively persistent [$t_{1/2}$ ca. 25 s for the decay of (4; X = Bu^t) at 292 K] and their addition to ethylene could not be detected by e.s.r. spectroscopy. This lack of reactivity is ascribed mainly to steric shielding of the radical centre by the bulkyl trimethylsilyl groups.

It is now some years since compounds of the type $R_2NP=NR$, which contain two-co-ordinate phosphorus-(III), were first reported.[1-3] These phospha(III)azenes are stabilised by trimethylsilyl or t-butyl substituents on nitrogen and the compound (1)[4] is a yellow-green, moisture-sensitive liquid that dimerises[5] only very slowly at room temperature in the absence of catalysts.

$$(Me_3Si)_2N^1 \underset{108 \cdot 4}{\overset{P}{\diagup}} \underset{N^2}{\overset{129 \cdot 9}{\diagdown}} SiMe_3$$

(1)

$$-\ddot{\overset{..}{P}}=\ddot{N}- \longleftrightarrow -\overset{+}{\ddot{P}}-\overset{-}{\underset{..}{N}}-$$

(2a)   (2b)

The PN^2 bond in (1) may be represented as a hybrid of the structures (2a and b) and, in accord with this description, the phosphazene undergoes ready nucleophilic attack at phosphorus.[3] For example, oxidative addition of alcohols to (1) gives the phospha(V)azenes (3).[1,3]

We now report that free radicals also add rapidly to (1) to give a novel series of phosphorimidoyl radicals (4) which are nitrogen analogues of the phosphonyl radicals $Y_2\dot{P}=O$.

$$(Me_3Si)_2NP=NSiMe_3 + ROH \longrightarrow (Me_3Si)_2N\overset{\overset{OR}{|}}{\underset{\underset{H}{|}}{P}}=NSiMe_3 \quad (i)$$

(3)

$$X\cdot + (Me_3Si)_2NP=NSiMe_3 \longrightarrow (Me_3Si)_2N^1\overset{\overset{|}{}}{\underset{\underset{X}{|}}{\dot{P}}}=N^2SiMe_3 \quad (ii)$$

(4)

RESULTS

Radical addenda were generated thermally in the presence of (1) using benzene solvent. When a solution containing (1) (ca. 0.6M) and di-t-butyl hyponitrite (TBHN) (ca. 0.5M), as a source of t-butoxyl radicals,[6] was heated to ca. 333 K under nitrogen in the cavity of the spectrometer,

an e.s.r. spectrum which we assign to the adduct (4; X = Bu^{t}O) was observed. The spectrum shows a large phosphorus hyperfine splitting (511 G) and coupling to two non-equivalent nitrogen nuclei (see Figure 1); the spectro-
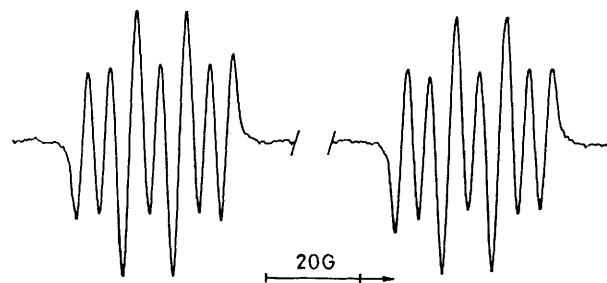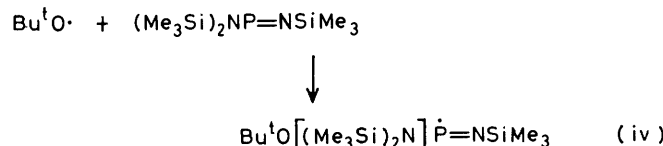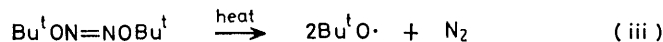
scopic parameters are included in the Table. No e.s.r. signals were detected in the absence of TBHN.

When appropriate reagents were present in addition to TBHN, the t-butoxyl radical was converted into a second

$$Bu^tON=NOBu^t \xrightarrow{heat} 2Bu^tO\cdot + N_2 \quad (iii)$$

$$Bu^tO\cdot + (Me_3Si)_2NP=NSiMe_3$$

$$\downarrow$$

$$Bu^tO[(Me_3Si)_2N]\dot{P}=NSiMe_3 \quad (iv)$$

radical addendum and the spectrum of the adduct of the latter to (1) was detected. For example, in the presence of triethyl phosphite t-butyl radicals are formed [equation (v)][7] and a spectrum which we assign to (4; X = Bu^t) was observed alongside that of (4; X = Bu^{t}O).

$$Bu^tO\cdot + (EtO)_3P \longrightarrow Bu^t\cdot + (EtO)_3P=O \quad (v)$$

Although a quantititative analysis is not straightforward, because the adducts (4; X = Bu^{t}O or Bu^t) are fairly persistent (see Table), it is clear that the addition reaction (iv) must be very rapid since reaction (v) is known[7,8] to take place at close to the diffusion-controlled rate in solution. Thermolysis of t-butyl perpivalate, Bu^{t}C(O)OOBu^t, at 338 K in the presence of (1) with t-butylbenzene solvent,
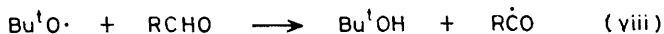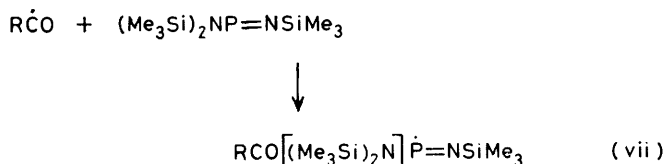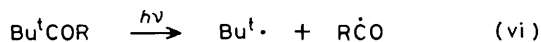
Phosphorimidoyl radicals $X[(Me_3Si)_2N^1]\dot{P}=N^2SiMe_3$ generated by addition to $(Me_3Si)_2NP=NSiMe_3$

Addendum radical X·	Source of X·ᵃ	Solvent ᵇ	T/K	g Factor ᶜ	Hyperfine splittings (G)			Approx. lifetime ᵈ (5)
					a(P) ᶜ	a(N¹)	a(N²)	
BuᵗO·	A	C₆H₆	336	2.0023	511.4	10.6	4.8	
BuᵗO·	B	C₃H₆	173	2.0023	518.9	10.6	4.8	26 (228 K)
BuᵗO·	B	C₃H₆	192	2.0023	517.1	10.6	4.8	
EtO·	B	C₃H₆	191	2.0023	514.0	9.9	4.6	
(Me₃Si)₂N·	C	C₃H₆	250	2.0025	501.8	10.0 ᵉ	4.4	3 000 (275 K) ᶠ
(Me₃Si)₂N·	C	C₆H₆	340	2.0024	501.3	10.0 ᵉ	4.4	
Cl₃C·	D	C₃H₆	275	2.0037	436.4	6.4 ᵍ	4.6 ᵍ	1.5 (262 K)
Buᵗ·	E	C₆H₆	336	2.0032	336.5	5.2 ᵍ	4.0 ᵍ	
Buᵗ·	F, G	C₃H₆	184	2.0032	338.6	5.2 ᵍ	4.0 ᵍ	44 (278 K) ᶠ
Prⁱ·	H	C₃H₆	299	2.0029	337.8	5.4 ᵍ,ʰ	4.2 ᵍ,ʰ	3 (278 K)
[²H₇]Prⁱ·	I	C₃H₆	298	2.0029	337.5	5.4 ᵍ	4.2 ᵍ	
MeC(O)	J	C₃H₆	203	2.0028	251.2	ca. 5.2 ᵍ	ca. 4.3 ᵍ	<1 (193 K)
BuᵗC(O)	K	C₆H₆	333	2.0028	243.0	5.2 ᵍ	4.3 ᵍ	
BuᵗC(O)	L	C₃H₆	184	2.0027	243.3	5.2 ᵍ	4.3 ᵍ	<1 (193 K)

ᵃ Solutions containing (1) and the reagents indicated where photolysed or heated: A = TBHN + heat; B = ROOR + hν; C = no reagent + hν; D = CCl₄ + Me₆Sn₂ + hν; E = TBHN + (EtO)₃P + heat; F = BuᵗN=NBuᵗ, Buᵗ₂CO, BuᵗCHO, or BuᵗC(O)Me + hν; G = BOOB + (EtO)₃P + hν; H = PrⁱN=NPrⁱ or PrⁱBr + hν; I = [²H₇]PrⁱBr + hν; J = BuᵗC(O)Me + hν; K = TBHN + BuᵗCHO + heat; L = Buᵗ₂CO + hν. ᵇ Benzene or cyclopropane. ᶜ Calculated using the Breit–Rabi equation. ᵈ Time for the e.s.r. spectrum to decay to approximately half its original intensity after photochemical generation had ceased; temperatures are given in parentheses. ᵉ Coupling to two equivalent nitrogen nuclei. ᶠ Negligible radical decay after 3 days at 193 K. ᵍ Obtained by computer simulation. ʰ Splitting of 4.4 G from one proton also present.

afforded spectra of both t-butyl and t-butoxyl radical adducts.

Radical addenda were also generated photochemically in the presence of (1) using cyclopropane solvent. These experiments served to confirm the assignments of the thermally-generated adducts and allowed spectra to be recorded over a wide range of temperatures. Thus, photolysis of azo-(1,1-dimethylethane) (BuᵗN=NBuᵗ), di-t-butyl ketone (Buᵗ₂C=O), pivalaldehyde (BuᵗCHO), or pinacolone (BuᵗCOMe) in the presence of (1) gave rise to the spectrum assigned above to (4; X = Buᵗ). With the azoalkane, (4; X = Buᵗ) was the only adduct detected, but with the

$$Bu^tCOR \xrightarrow{h\nu} Bu^t\cdot + R\dot{C}O \qquad (vi)$$

$$R\dot{C}O + (Me_3Si)_2NP=NSiMe_3$$

$$\downarrow$$

$$RCO[(Me_3Si)_2N]\dot{P}=NSiMe_3 \qquad (vii)$$

$$Bu^tO\cdot + RCHO \longrightarrow Bu^tOH + R\dot{C}O \qquad (viii)$$

carbonyl compounds spectra ascribed to the acyl radical adducts (4; X = RCO) were also observed [equations (vi) and (vii)]. These adducts could also be generated thermally by heating a benzene solution containing (1), TBHN and an aldehyde [reaction (viii) followed by (vii)].
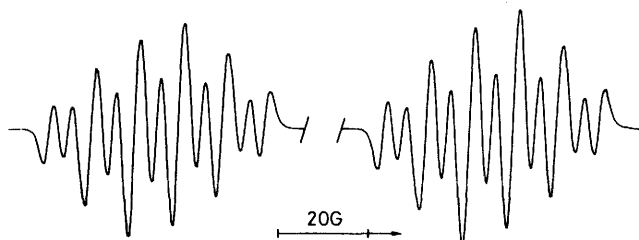

FIGURE 2   E.s.r. spectrum of [4; X = (Me₃Si)₂N] generated by photolysis of (1) in cyclopropane at 294 K

It has been reported [1] that (1) is light sensitive (see, however, ref. 2) and photolysis of (1) alone in cyclopropane afforded the spectrum, shown in Figure 2, which was always present alongside that of the adduct of X· when the latter was generated photochemically. On the basis of the e.s.r. parameters (see Table) we assign this spectrum to the radical [4; X = (Me₃Si)₂N]. The intensity of this spectrum increased with the duration of photolysis, but the radical is extremely long-lived at low temperatures and its rate of photochemical production must be relatively small.* In view of the electronic similarity of RO and (Me₃Si)₂N groups, it is likely that the larger nitrogen splitting for (4; X = RO) should be assigned to N¹.

Photolysis of di-t-butyl peroxide (BOOB) in the presence of (1) afforded (4; X = BuᵗO) and similarly the spectrum of (4; X = EtO) was detected during photolysis of a solution containing (1) and diethyl peroxide.

The isopropyl adduct, generated by photolysis of mixtures of PrⁱN=NPrⁱ † or PrⁱBr ‡ and (1) showed (apart from ³¹P splitting) the six line spectrum expected if a(N¹) ≃ a(N²) ≃ a(1H) ≃ 4.8 G and the proton splitting presumably arises from the methine hydrogen of the isopropyl group. This analysis was confirmed by photolysing a mixture of [²H₇]-PrⁱBr and (1) which gave rise to a five-line spectrum, similar to that of (4; X = Buᵗ), expected if the difference between a(N¹) and a(N²) is not resolved (see Figure 3).

The structures of the alkyl radical adducts were confirmed by generating (4; X = Prⁱ) independently by photolysis of (5) [10] in cyclopropane. Stronger spectra were obtained when hexamethylditin was also present to scavenge bromine atoms and/or provide a source of Me₃Sn· which would be expected to abstract bromine from (5).

Although dialkoxyphosphonyl radicals add rapidly to

* A weak signal from the very persistent phosphinyl radical [(Me₃Si)₂N]₂P· [9] was often detected in photochemical experiments with (1). The origin of this radical is not clear but it quite likely arises from a trace impurity of [(Me₃Si)₂N]₂PCl(or Br) [precursors of (1)]. Certainly photolysis of the chlorophosphine alone or with other reagents in cyclopropane gave rise to a very intense spectrum of the phosphinyl radical [a(P) 91.6 G, a(N) not resolved, g 2.0050 at 249 K].

† Photolysis of PrⁱN=NPrⁱ alone in cyclopropane afforded the e.s.r. spectrum of the isopropyl radical.
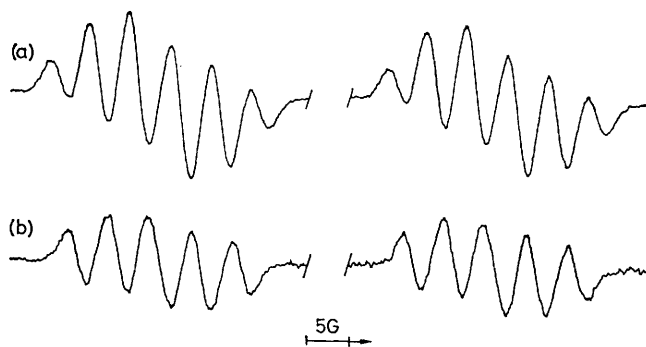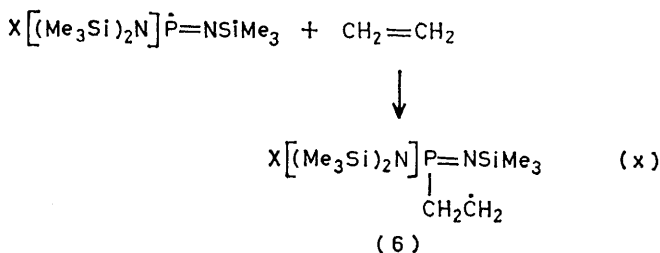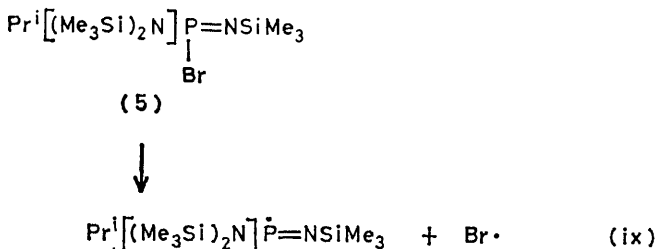
‡ Photolysis of (1) and BuᵗBr gave rise to (4; X = Buᵗ).

FIGURE 3 E.s.r. spectra in cyclopropane at 297 K of (a) (4; X = Pr^i) and (b) (4; X = [^{2}H$_7$]Pr^i), generated by photolysis of mixtures of (1) and Pr^{i}Br or [^{2}H$_7$]Pr^{i}Br, respectively

ethylene,[11] the analogous reaction of (4) [equation (x)] could not be detected by e.s.r. spectroscopy. Thus, photolysis of ethylene solutions containing (5) and hexamethylditin or BOOB and (1) afforded only the spectra of (4; R = Pr^i) or (4; R = Bu^{t}O), respectively, and no β-substituted ethyl

$$Pr^i[(Me_3Si)_2N]\underset{\underset{(5)}{\overset{|}{Br}}}{P}=NSiMe_3$$

$$\downarrow$$

$$Pr^i[(Me_3Si)_2N]\overset{\cdot}{P}=NSiMe_3 \quad + \quad Br\cdot \qquad (ix)$$

$$X[(Me_3Si)_2N]\overset{\cdot}{P}=NSiMe_3 \quad + \quad CH_2=CH_2$$

$$\downarrow$$

$$X[(Me_3Si)_2N]\underset{\underset{(6)}{\overset{|}{CH_2\overset{\cdot}{C}H_2}}}{P}=NSiMe_3 \qquad (x)$$

radicals (5) [nor adducts of these with (1)] were detected between 173 and 233 K.

DISCUSSION

The rapidity of radical addition to (1) was not unexpected in view of the known high reactivity of three-co-ordinate phosphorus(III) compounds towards homolytic addition [equation (xi)].[8,12] Addition to (1) takes

$$X\cdot \quad + \quad PX_3 \quad \longrightarrow \quad \overset{\cdot}{P}X_4 \qquad (xi)$$
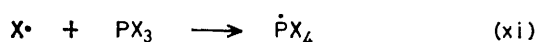
place at phosphorus and addition to N^2, to produce phosphinyl radicals which would show phosphorus hyperfine splittings of ca. 70—90 G, was not detected.

The magnitude of a(P) for the phosphorimidoyl radicals increases with the electronegativity of the group X, for example [4; X = Bu^{t}O, (Me$_3$Si)$_2$N, or Bu^t] show splittings of 511, 501, and 337 G, respectively. Increasing ligand electronegativity results in concentration of P-3p character in the P-X bond and conse-

quently leads to an increase of P-3s character in the orbital of the unpaired electron and, assuming orbital following, to an increase in the deviation from planarity at phosphorus. A similar trend is shown by the isotropic phosphorus splittings of the phosphonyl radicals (EtO)$_2\overset{\cdot}{P}$=O, (Me$_2$N)$_2\overset{\cdot}{P}$=O, and (n-C$_6$H$_{13}$)$_2\overset{\cdot}{P}$=O (689, 524, and 350 G, respectively)[13] and ligand electronegativity effects are again responsible for the differences. Extrapolating from [4; X = (Me$_3$Si)$_2$N] and (4; X = RO) we would predict that (RO)$_2$P=NSiMe$_3$ would show a(P), ca. 526 G, less than that (ca. 689 G) shown by (RO)$_2\overset{\cdot}{P}$=O, again in accord with expectation based on group electronegativities.

However, [4; X = RC(O)] exhibits an unexpectedly low value of a(P) (ca. 250 G), less than that (ca. 338 G) shown by (4; X = R). Possibly conjugative delocalisation of the unpaired electron by the C=O group [see (7a—c)], resulting in reduction of spin population on
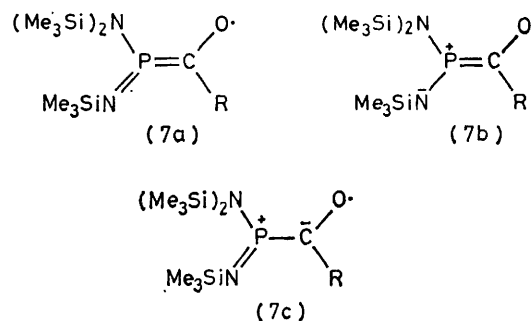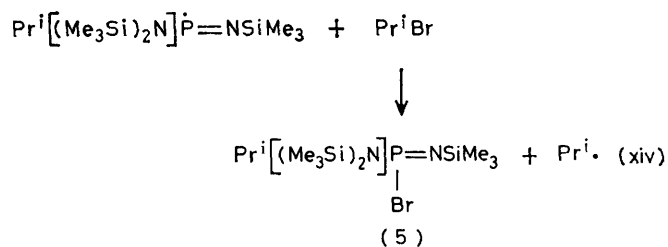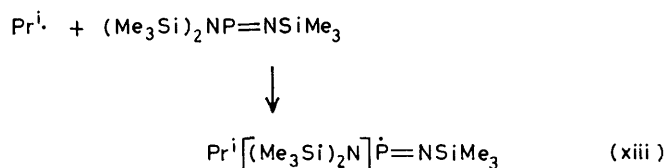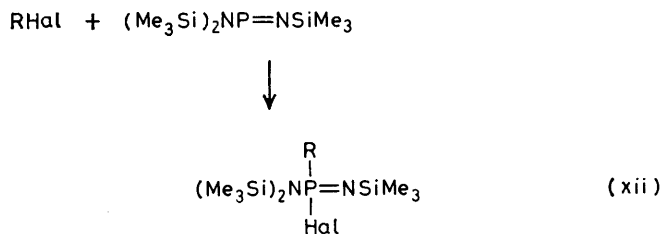

and in flattening at phosphorus, is responsible for this apparent anomaly. The electronic structure of [4; X = RC(O)] thus appears to be related to that of (Me$_3$Si)$_2$NP(=NSiMe$_3$)$_2$, in which the phosphorus and three nitrogen atoms are coplanar.[14]

Hyperfine splitting from the methine proton in (4; X = Pr^i) would be expected since splitting of a similar magnitude is found for β-protons in alkylphosphonyl radicals, for example (n-C$_6$H$_{13}$)$_2\overset{\cdot}{P}$=O.[13] The splittings from the three-co-ordinate nitrogens in [4; X = RO or (Me$_3$Si)$_2$N] are similar to those in (Me$_2$N)$_2\overset{\cdot}{P}$=O which shows a(2N) 12.0 G.[13]

Phosphonyl radicals Y$_2\overset{\cdot}{P}$=O undergo self-reaction at close to the diffusion-controlled rate in solution if Y is not bulky,[15] and presumably the much longer lifetimes of (4) under comparable conditions may be ascribed to steric protection of the radical centre preventing dimerisation. The radicals [(Me$_3$Si)$_2$N]$_2\overset{\cdot}{P}$=NSiMe$_3$ and Bu^t[(Me$_3$Si)$_2$N]-$\overset{\cdot}{P}$=NSiMe$_3$ are particularly long-lived (see Table) as would be expected. Similarly, the failure of (4; X = Bu^{t}O or Pr^i) to add to ethylene is probably due mainly to steric shielding of the radical centre by the bulky trimethylsilyl ligands. However, an unhindered phosphorimidoyl radical Y$_2\overset{\cdot}{P}$=NR might be expected to add less rapidly than the corresponding phosphonyl radical Y$_2\overset{\cdot}{P}$=O because of the lower electrophilicity of the former.

A number of alkyl halides undergo oxidative addition

to (1) [equation (xii)] [10] and either heterolytic (nucleophilic substitution) or homolytic mechanisms could be operative. The addition of isopropyl bromide is accelerated by u.v.–visible irradiation of the reaction mixture [10] and, although the mechanism was not discussed, a radical chain process in which (4; R = Pr^i) abstracts bromine from Pr^{i}Br seems likely. The prob-

RHal + (Me$_3$Si)$_2$NP=NSiMe$_3$

$\downarrow$

$$\underset{\underset{\text{Hal}}{|}}{\overset{\overset{\text{R}}{|}}{(\text{Me}_3\text{Si})_2\text{NP=NSiMe}_3}} \qquad (\text{xii})$$

Pr^i· + (Me$_3$Si)$_2$NP=NSiMe$_3$

$\downarrow$

Pr^i[(Me$_3$Si)$_2$N]Ṗ=NSiMe$_3$ $\qquad$ (xiii)

Pr^i[(Me$_3$Si)$_2$N]Ṗ=NSiMe$_3$ + Pr^{i}Br

$\downarrow$

$$\underset{\underset{\text{Br}}{|}}{\text{Pr}^i[(\text{Me}_3\text{Si})_2\text{N}]\text{P=NSiMe}_3} \; + \; \text{Pr}^i\cdot \quad (\text{xiv})$$

(5)

able propagation steps are shown in equations (xiii) and (xiv). Dialkoxyphosphonyl radicals, (RO)$_2$Ṗ=O, also abstract halogen from alkyl halides.[11a]

EXPERIMENTAL

Radicals were generated directly in the e.s.r. spectrometer cavity using standard 4 mm o.d. Suprasil sample tubes. The techniques have been described previously.[16,17] All manipulations were carried out under vacuum or an atmosphere of dry nitrogen.

Thermal Generation.—Benzene solutions (total volume *ca.* 500 μl) contained (1) (*ca.* 100 μl) and TBHN (*ca.* 50 mg). When other reagents were present (see Results section) these (*ca.* 100 μl) were added immediately before beginning the experiment. The sample tubes were stoppered, but sufficient space was available such that high internal pressures could not develop even if all the TBHN decomposed. Tubes were inserted into the cavity at room temperature and the temperature was then increased until acceptable signal strength was obtained (40—60 °C).

Photochemical Generation.—Cyclopropane or ethylene solutions (total volume *ca.* 500 μl) contained (1) (*ca.* 100 μl), the primary source of addenda (*ca.* 100 μl), and any other reagent (*ca.* 100 μl; see Results section). Sample tubes were sealed under vacuum and stored in liquid nitrogen before being thawed at −80 °C immediately prior to the experiment. Full light intensity from the Philips CS 500 W/2 lamp was seldom required (or desirable) since the adducts (4) were quite persistent. Low light intensity (*ca.* 3% of maximum) was used initially and increased if necessary.

Materials.—Bis(trimethylsilyl)amino(trimethylsilylimino)phosphine (1) was prepared by the method of Scherer and Kuhn [2] starting with either PCl$_3$ or PBr$_3$. Compound (5) was prepared by irradiation through silica of a mixture of (1) and isopropyl bromide with unfiltered light from a Thorn 250 W ME/D mercury arc lamp.[10]

Di-t-butyl hyponitrite (TBHN),[6] 1,1,1′,1′-tetramethylazoethane,[18] 1,1′-dimethylazoethane,[19] and di[bis(trimethylsilyl)amino]chlorophosphine [2] were prepared by literature methods. All other reagents and solvents were commercial materials, the majority of which were purified before use.

REFERENCES

[1] E. Niecke and W. Flick, *Angew. Chem., Int. Ed. Engl.,* 1973, 12, 585.
[2] O. J. Scherer and N. Kuhn, *Chem. Ber.,* 1974, 107, 2123.
[3] E. Niecke and O. J. Scherer, *Nachr. Chem. Tech.,* 1975, 23, 395.
[4] S. Pohl, *Z. Naturforsch., Teil B,* 1977, 32, 1344.
[5] E. Niecke, W. Flick, and S. Pohl, *Angew. Chem., Int. Ed. Engl.,* 1976, 15, 309.
[6] H. Kiefer and T. G. Traylor, *Tetrahedron Lett.,* 1966, 6163.
[7] A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.,* 1971, 10, 738; *J. Chem. Soc., Perkin Trans. 2,* 1972, 993.
[8] B. P. Roberts and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. 2,* in the press.
[9] M. J. Gynane, A. Hudson, M. F. Lappert, P. P. Power, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.,* 1976, 623.
[10] E. Niecke and W. Bitter, *Chem. Ber.,* 1976, 109, 415.
[11] (a) A. G. Davies, D. Griller, and B. P. Roberts, *J. Am. Chem. Soc.,* 1972, 94, 1782; (b) I. G. Neil and B. P. Roberts, *J. Organomet. Chem.,* 1975, 102, C17.
[12] B. P. Roberts, *Adv. Free Radical Chem.,* 1980, 6, 225.
[13] B. P. Roberts and K. Singh, *J. Organomet. Chem.,* 1978, 159, 31.
[14] S. Pohl and B. Krebs, *Chem. Ber.,* 1977, 110, 3183.
[15] D. Griller, B. P. Roberts, A. G. Davies, and K. U. Ingold, *J. Am. Chem. Soc.,* 1974, 96, 554.
[16] R. W. Dennis, I. H. Elson, B. P. Roberts, and R. C. Dobbie, *J. Chem. Soc., Perkin Trans. 2,* 1977, 889.
[17] P. M. Blum and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2,* 1978, 1313.
[18] J. C. Stowell, *J. Org. Chem.,* 1967, 32, 2360.
[19] R. Renaud and L. C. Leitch, *Can. J. Chem.,* 1954, 32, 545.