Electron Paramagnetic Resonance Study of Spin-trapped Free Radicals in the Hydrosilylation of Septamethylvinyltrisiloxane using Benzophenone as an Initiator

**the late Jeffrey C. Evans, Peter Hupfield and Christopher C. Rowlands***
School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O. Box 912, Cardiff CF1 3TB
Steve E. Cray
*Dow Corning Ltd., Barry, South Glamorgan*

Electron paramagnetic resonance and ENDOR spectroscopy have been used together, with the spin-trapping method to investigate the benzophenone-catalysed addition of a silicon hydride to an alkene. This process is known as hydrosilylation. The paramagnetic adducts detected were characterised and a mechanism proposed for the reaction which is only 30% efficient.

Hydrosilylation[1] involves the terminal addition of a silicon hydride moiety to an unsaturated compound, typically an alkene. The reaction is carried out at elevated temperatures using a catalyst. The most commonly used catalyst is chloroplatinic acid hexahydrate (Speier's catalyst).

$$R_3SiH + {-}CH{=}CH_2 \xrightarrow[\text{Pt}]{\text{heat}} {-}CH_2{-}CH_2{-}SiR_3 \quad (1)$$
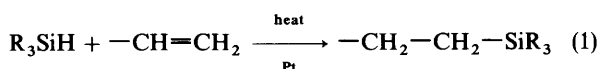
This process is used industrially, as a method for producing silicon polymer paper coatings. These are used to coat 'release' papers which are used in label manufacture, and 'baking' papers which include greaseproof paper and cake cases. There are two disadvantages of this process: (i) the method is substrate-selective owing to the need for high temperatures and (ii) the platinum cannot be recovered from the cured film. Alternative methods which are cheaper and not substrate-selective are being sought.

An alternative method would be to use benzophenone as a photoinitiator. This acts as a free-radical precursor due to its photoreduction in the presence of hydrogen donors.[2,3] An initial investigation into the reaction found that only 30% followed the desired route, when a vinylsilane was used as the terminal alkene.[4]
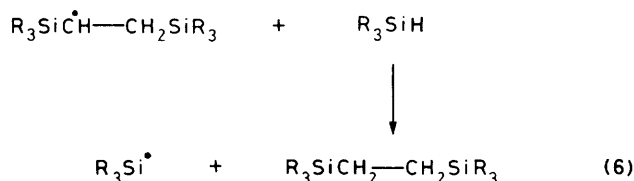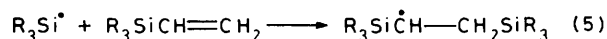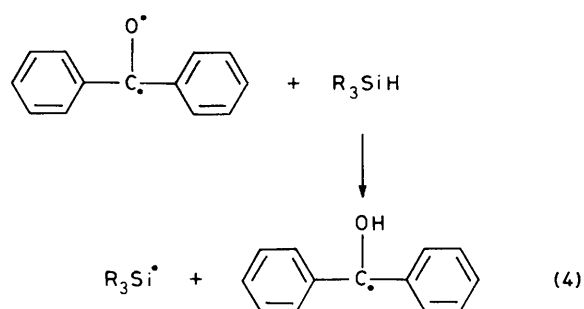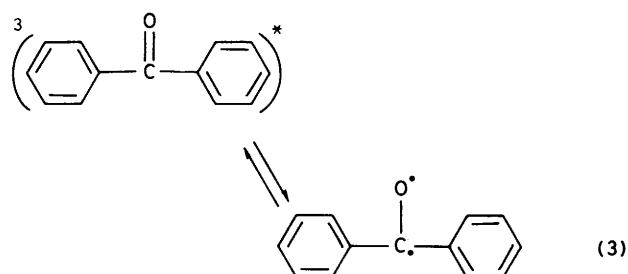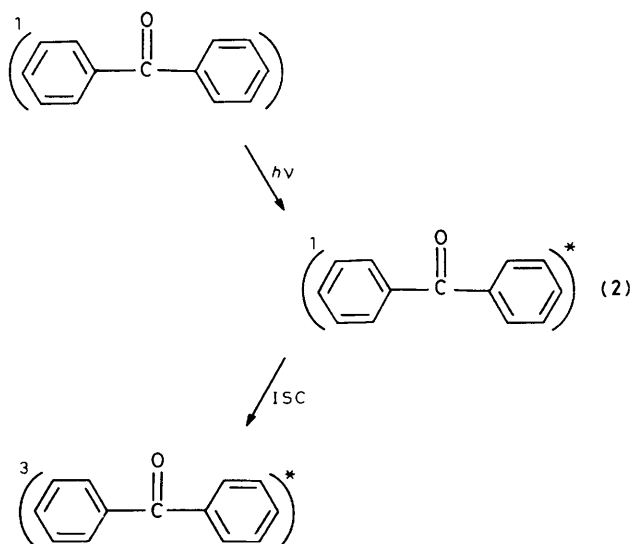
Using EPR and ENDOR spectroscopy in conjunction with the spin-trapping method, an investigation was carried out into the nature of the free radicals present in the system.

The spin-trapping method involves the reaction of the free radical (the spin) with a nitroso or nitrone compound (the trap) to produce a stable nitroxide radical which can then be characterised.[5]

The use of silicon hydrides as photoreducers of benzophenone is not well documented. Flash photolysis studies[6] have shown that photoreduction does occur; however, the free radicals produced, to our knowledge, have not been characterised by the spin-trapping method, and EPR spectroscopy.

The spin-trap tri-t-butyl-nitrosobenzene (BNB) was used to investigate the reaction, due to its photostability; it is unique in that it has two available trapping sites. Primary alkyl radicals undergo addition to the nitrogen (type one) whilst type two involves addition to the oxygen and is characteristic of tertiary alkyl free radicals. Secondary alkyl free radicals undergo both types of addition, producing a mixture of paramagnetic spin adducts.[7]

Experimental

Septamethyltrisiloxane and septamethylvinyltrisiloxane were kindly donated by Dow Corning (Barry, UK), and used as supplied. Triethylsilane, diethylmethylsilane, dimethylphenylsilane, diphenylmethylsilane, tri-t-butyl-nitrosobenzene (BNB) and benzophenone, Aldrich Chemical Co., were used as supplied.

Procedure

In each experiment a spin-trap concentration of 1 mg cm^{-3} and a benzophenone concentration of 0.01 mol dm^{-3} were used, using either the silicon hydride or the vinylsilane as solvent. The solutions were thoroughly degassed down to 10^{-4}–10^{-5} Torr. EPR measurements were made with a Varian E-3 spectrometer at 100 kHz modulation. Third-derivatisation was carried out at 33(1/3) kHz modulation. Sample irradiation was carried out in the spectrometer cavity, using a Bausch and Lomb 150 W xenon lamp.

ENDOR and TRIPLE resonance spectra were recorded using a Varian E109 spectrometer interfaced with a Bruker ENDOR/TRIPLE resonance unit. Temperature regulation was carried out with a modified Oxford instrument.

Results and Discussion

Photoreduction of benzophenone by the silicon hydrides under vacuum and in the presence of BNB produced nine lines due to the ^{14}N ($I = 1$) and two equivalent ^{1}H ($I = 1/2$) nuclei coupling with the unpaired electron [see fig. 1(a)]. Silicon satellite peaks were clearly visible and with the correct intensity (4.7% relative abundance).

The nitrogen and proton hyperfine coupling constants were of the order of 10 and 2.0 G, respectively, suggesting that type-two addition had occurred. This was confirmed by the g values which were in the region of 2.0041.

Type-two Addition

$$ \text{(structure)} \quad -N\!=\!O \ + \ R_3Si^\bullet $$

$$ \downarrow $$

$$ \text{(structure)} \quad -N^\bullet\!-\!O\!-\!SiR_3 \qquad (7) $$
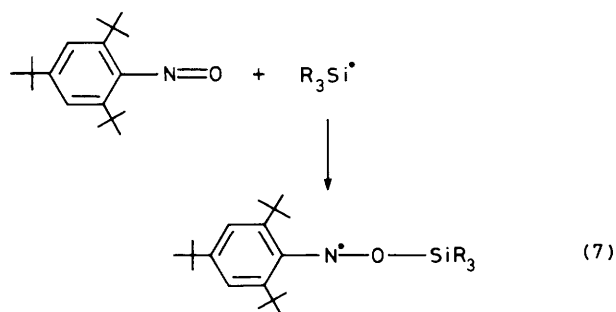
Interestingly the arylsilyl free radicals underwent only type-two addition. This may be due to a steric effect since the radicals are bulky; however, it may be better explained by the oxophilic nature of silicon together with the fact that there are no known stable silicon–nitrogen-bonded spin adducts, at ambient temperatures.
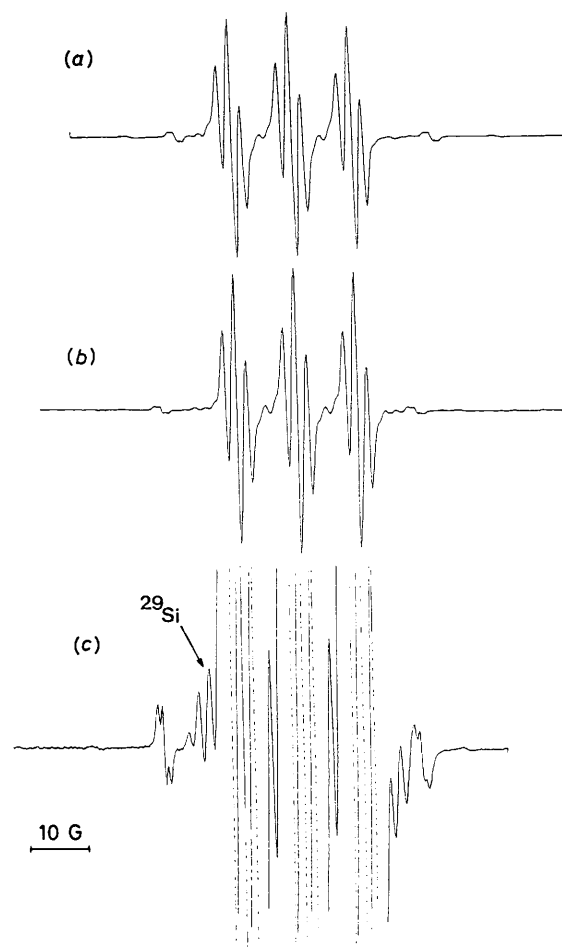

Fig. 1. (a) EPR spectrum obtained after photolysing triethylsilane in the presence of benzophenone and BNB. (b) EPR spectrum obtained after photolysing triethylsilane in the presence of di-t-butyl peroxide and BNB. (c) Triethylsilyl BNB spin adduct at high gain.

The arylsilyl adducts were also generated by photolysing di-t-butyl peroxide in the presence of BNB and a silicon hydride, thus confirming that arylsilyl free radicals were being generated and trapped. The same spectrum was observed [see fig. 1(b)] together with similar hyperfine coupling parameters (see table 1).

$$ Bu^tOOBu^t \xrightarrow{\ h\nu\ } 2 Bu^tO^\bullet \qquad (8) $$

$$ Bu^tO^\bullet \ + \ R_3SiH \longrightarrow Bu^tOH \ + \ R_3Si^\bullet \qquad (9) $$

One interesting feature of these results is the fact that Konaka and Terabe[7] did not observe ^{29}Si satellite peaks

Table 1. EPR parameters (in G) obtained using benzophenone and di-t-butyl peroxide as hydrogen abstractors in the presence of silicon hydrides and BNB

radical	benzophenone			di-t-butyl peroxide		
	a_N	a_H	$a^{29}Si$	a_N	a_H	$a^{29}Si$
Et$_3$Si$^\bullet$	10.34	2.05	10.38	10.36	2.04	10.35
Et$_2$MeSi$^\bullet$	10.32	2.03	10.38	10.38	2.01	10.37
Me$_2$PhSi$^\bullet$	10.32	2.10	10.50	10.36	1.99	10.50
Ph$_2$MeSi$^\bullet$	10.34	2.08	10.48	10.37	2.05	10.49
HSiMe$_2$OMe$_2$Si$^\bullet$	10.38	2.15	10.50	10.40	2.00	10.50
(Me$_3$SiO)$_2$MeSi$^\bullet$	10.38	2.13	10.49	10.40	2.10	10.50

g values were all in the range 2.0041–2.0043.
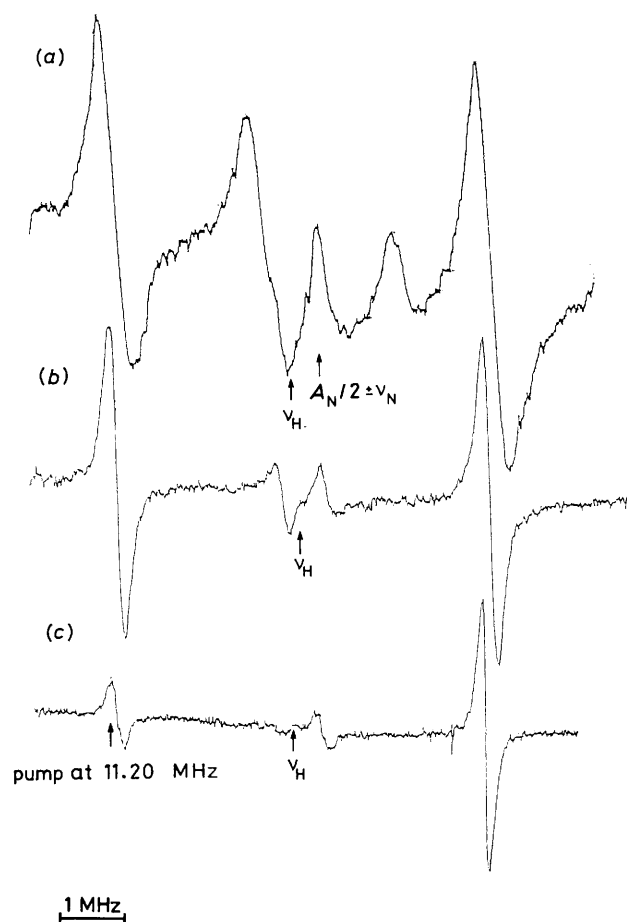
Fig. 2. (a) Computer-averaged ^{14}N and ^{1}H ENDOR spectrum of the triethylsilyl spin adduct at 210 K. (b) ^{1}H ENDOR spectrum of the triethylsilyl spin adduct at 202 K. (c) General TRIPLE resonance spectrum of the triethylsilyl spin adduct at 202 K.

since no hyperfine couplings were cited. However, in our spectra silicon satellites were always clearly visible.

ENDOR and general TRIPLE resonance experiments were carried out on the BNB adducts. In all but one of the experiments both ^{14}N and ^{1}H ENDOR absorptions were observed, with the use of computer-averaging techniques, simultaneously [see fig. 2(a)]. Only one other hyperfine coupling was observed in the ENDOR experiment and this was attributed to the protons associated with the tertiary butyl groups of the spin trap [see fig. 2(b)], which were found to have the same sign as the *meta* protons of the BNB ring. This can be seen from the general TRIPLE spectrum in fig. 2(c). ^{29}Si ENDOR was not observed since the relative abundance of ^{29}Si (4.7%) makes the detection of resonances extremely difficult (see table 2).

During the photoreduction of benzophenone by the silicon hydrides, two possible side-reactions may occur. One

Table 2. ENDOR parameters (in G) of the arylsilyl spin adducts of BNB

radical	a_N	a_H	a_{Bu^t}	T/K
Et$_3$Si˙	10.32	2.01	0.26	210.3
Et$_2$MeSi˙	10.31	1.99	0.23	208.0
Me$_2$PhSi˙	10.31	2.05	0.23	205.6
Ph$_2$MeSi˙	10.32	2.06	0.24	200.3
HSiMe$_2$OMe$_2$Si˙	10.37	2.11	0.25	205.6
(Me$_3$SiO)$_2$MeSi˙	—	2.10	0.27	202.0

involves the formation of benzopinacol *via* the dimerisation of the ketyl radicals generated in eqn (4), and the other involves addition of the arylsilyl free radicals to parent benzophenone.[8,9]
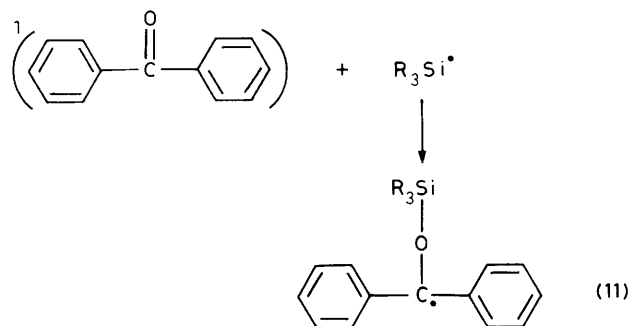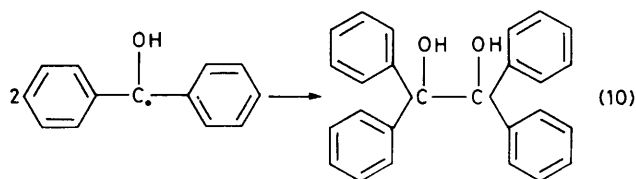
The formation of the benzopinacol can be overcome by irradiation at 250–260 nm, which results in the formation of ketyl radicals. Irradiation of benzopinacol in the presence of a silicon hydride and BNB resulted in the same spectrum as that in fig. 1, and similar hyperfine coupling parameters as in table 1, revealing that the ketyl radicals can abstract from the silicon hydrogen bond *via*
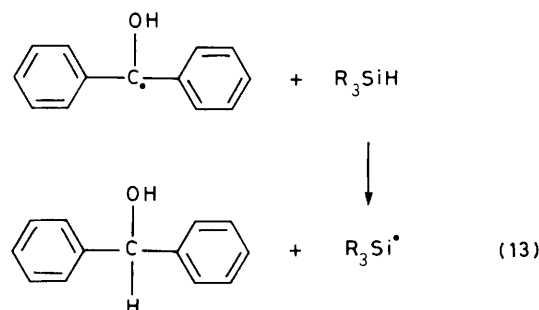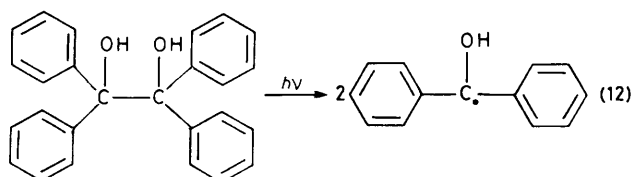
Reaction of the arylsilyl free radicals with parent benzophenone is not considered to be a major reaction step since the silicon hydride and vinylsilane are in large excess with respect to the benzophenone. Indeed, on analysis of the reaction no addition was observed during the hydrosilylation reaction.[4]

The potential of benzophenone as a hydrosilylation initiator was studied in the presence of a silane and a vinylsilane. On irradiating a 1 : 1 mixture it appeared that more than one radical adduct species was present [see fig. 3(a)]. Resolution was enhanced with the use of third-derivatisation as a line-sharpening technique [see fig. 3(b)]. A mixture of adducts
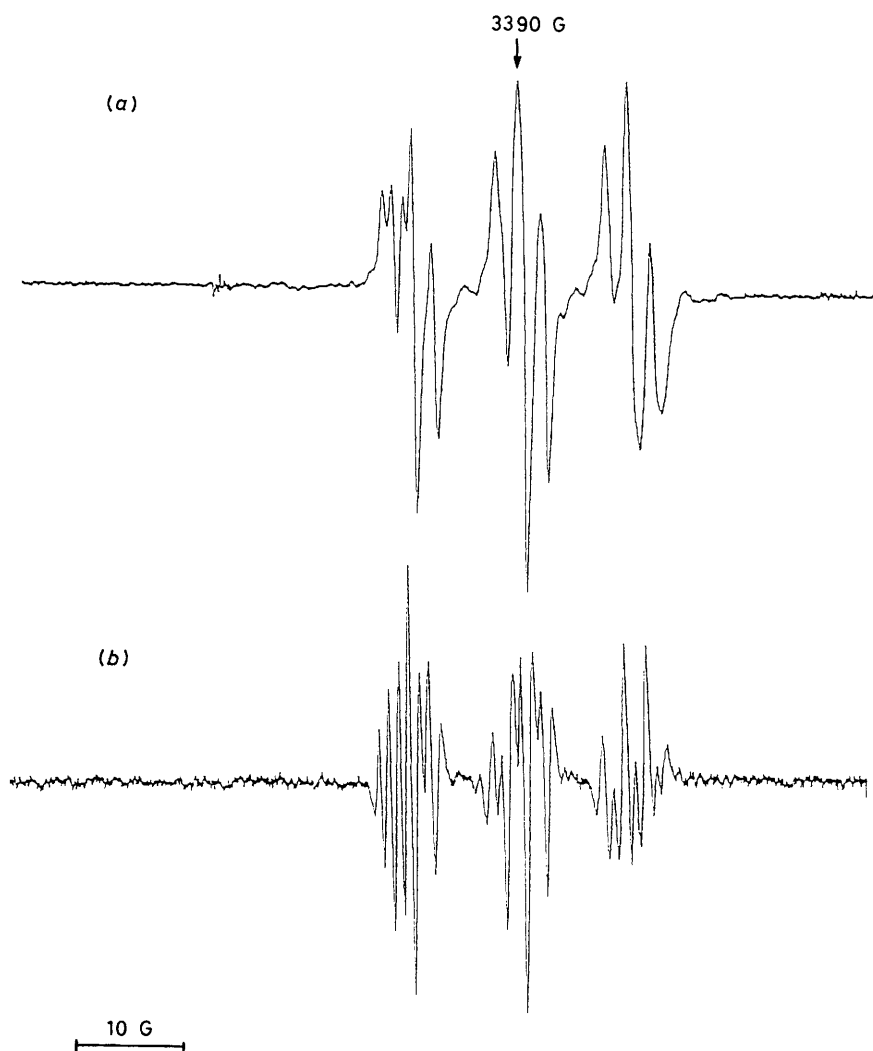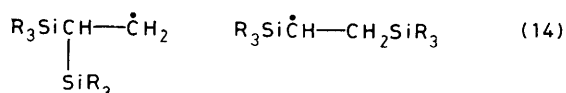
Fig. 3. (*a*) First-derivative EPR spectrum obtained on hydrosilylating septamethyltrisiloxane with septamethylvinyltrisiloxane. (*b*) Third-derivative EPR spectrum obtained on hydrosilylating septamethyltrisiloxane with septamethylvinyltrisiloxane.

could be expected if both α and β addition to the double bond was occurring.
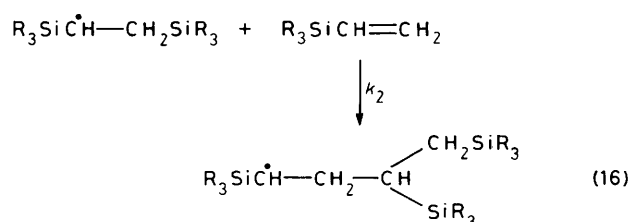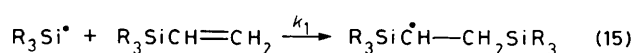
$$R_3SiCH\!-\!\overset{\bullet}{C}H_2 \qquad R_3Si\overset{\bullet}{C}H\!-\!CH_2SiR_3 \qquad (14)$$
$$\quad | \quad$$
$$SiR_3$$

However, on changing the ratio of $-SiH$ to $-CH{=}CH_2$ no change in the EPR spectrum was observed (see fig. 4). This would seem to suggest that the spectrum is only due to the presence of one spin adduct, since the ratio of α to β spin adduct might be expected to change with the changing ratio of starting materials.

ENDOR spectroscopy revealed an additional hyperfine coupling of the order of 0.7 G (see fig. 5). The additional coupling is assigned to the presence of a $-CH$ fragment attached at the oxygen position of the spin trap. This would split the standard nine-line EPR spectrum into 18 lines, as is observed. The ENDOR spectrum also shows the presence of additional t-butyl and $-CH$ couplings, indicating the presence of an additional species, with identical *meta* proton couplings (see table 3). No ^{14}N ENDOR was obtained on any of the spin adducts at these temperatures. This additional species is not visible in the EPR spectrum, even when third-derivatisation is used. This we attribute to both species having almost identical *g* values and hyperfine coupling

parameters. The differences are small enough not to allow differentiation, except with the use of ENDOR. The experimental EPR spectrum can be simulated only when two species are considered to be present (see fig. 6).

The two species are assigned to the following reaction sequence which is known to occur;[4] however, the extent to which it occurs is not fully known:

$$R_3Si^{\bullet} + R_3SiCH{=}CH_2 \xrightarrow{k_1} R_3Si\overset{\bullet}{C}H\!-\!CH_2SiR_3 \quad (15)$$

$$R_3Si\overset{\bullet}{C}H\!-\!CH_2SiR_3 + R_3SiCH{=}CH_2$$

$$\downarrow k_2$$

$$R_3Si\overset{\bullet}{C}H\!-\!CH_2\!-\!\overset{}{C}H\!\overset{\displaystyle CH_2SiR_3}{\underset{\displaystyle SiR_3}{<}} \quad (16)$$

The same results were obtained using di-t-butyl peroxide as the initiator.

A possible reason why changing the ratio of $-SiH$ to $-CH{=}CH_2$ did not alter the EPR spectrum could be that the rates of reactions (15) and (16) do not differ significantly.

Computer simulation (see fig. 6) was used to evaluate the nitrogen couplings of the spin adducts produced in reaction
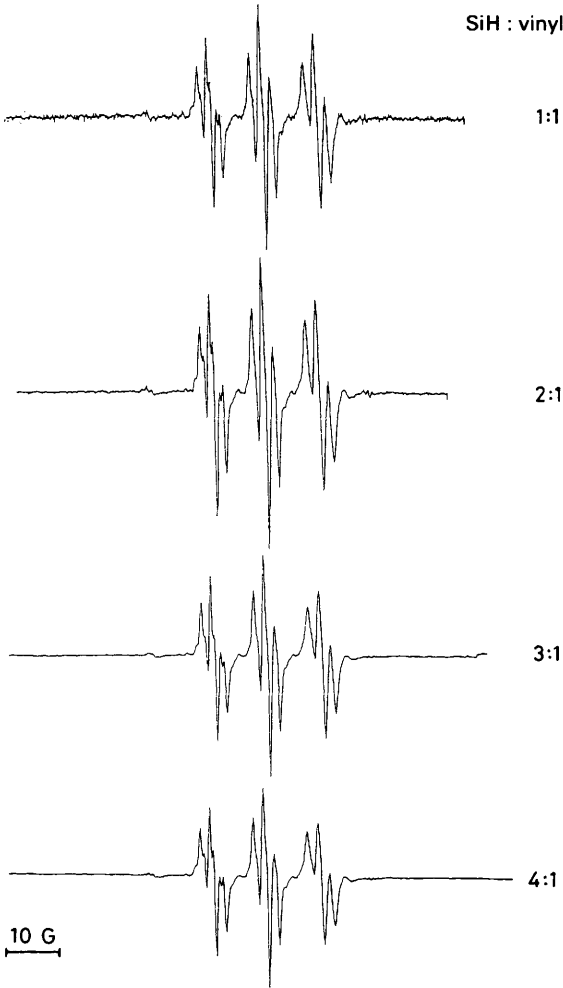
SiH : vinyl

1:1

2:1

3:1

4:1

10 G

Fig. 4. First-derivative EPR spectrum obtained on hydrosilylating different ratios of septamethyltrisiloxane and septamethylvinyltrisiloxane.

(16). The data for the two species are presented in table 4. From the computer simulations it was found that the ratio of the spin adducts was *ca.* 3 : 1 in all cases. The spin adduct in greater concentration was assigned to the β- addition radical

Table 3. ENDOR parameters (in G) for the adducts obtained in the hydrosilylation of septamethylvinyltrisiloxane

radical	species 1			species 2			
	a_H	a_{CH}	a_{Bu^t}	a_H	a_{CH}	a_{Bu^t}	T/K
$Et_3Si^{\cdot}$	1.92	0.71	0.21	—	0.61	0.16	211
$Et_2MeSi^{\cdot}$	1.90	0.70	0.23	—	0.61	0.17	218
$Me_2PhSi^{\cdot}$	1.95	0.72	0.23	—	0.62	0.18	220
$Ph_2MeSi^{\cdot}$	1.94	0.69	0.21	—	0.63	0.17	212
$HSiMe_2OMe_2Si^{\cdot}$	1.93	0.70	0.21	—	0.60	0.16	222
$(Me_3SiO)_2MeSi^{\cdot}$	1.92	0.71	0.22	—	0.61	0.17	215

since the presence of the following reaction would remove the source for formation of the radical species in reaction (16):

$$R_3Si\overset{\bullet}{C}H\!-\!CH_2SiR_3 \quad + \quad R_3SiH$$

$$R_3Si^{\bullet} \quad + \quad R_3SiCH_2\!-\!CH_2SiR_3 \qquad (17)$$
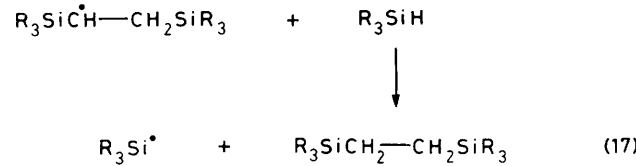
With all these reactions in mind a postulated mechanism for the overall reaction can be constructed:
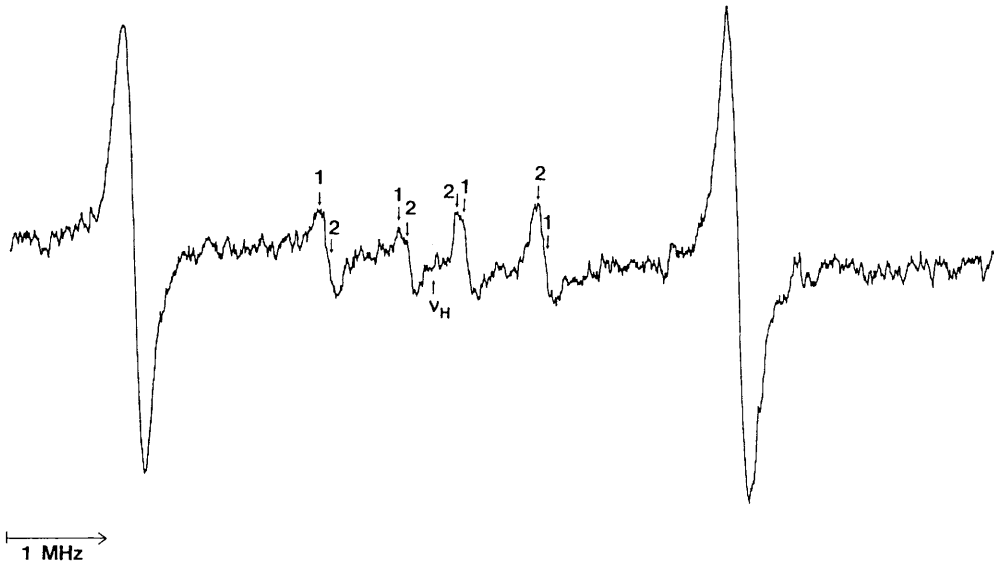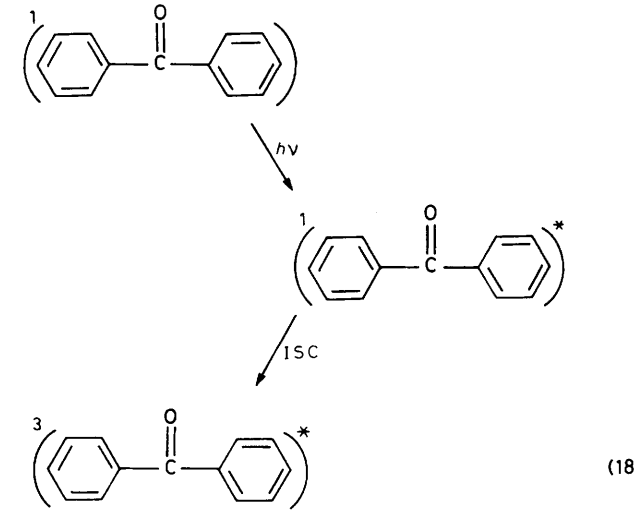
photoinitiation:

$$(18)$$

1 MHz

Fig. 5. ^1H ENDOR of the spin adducts obtained during the hydrosilylation of triethylsilane with septamethylvinylsilane at 211 K.
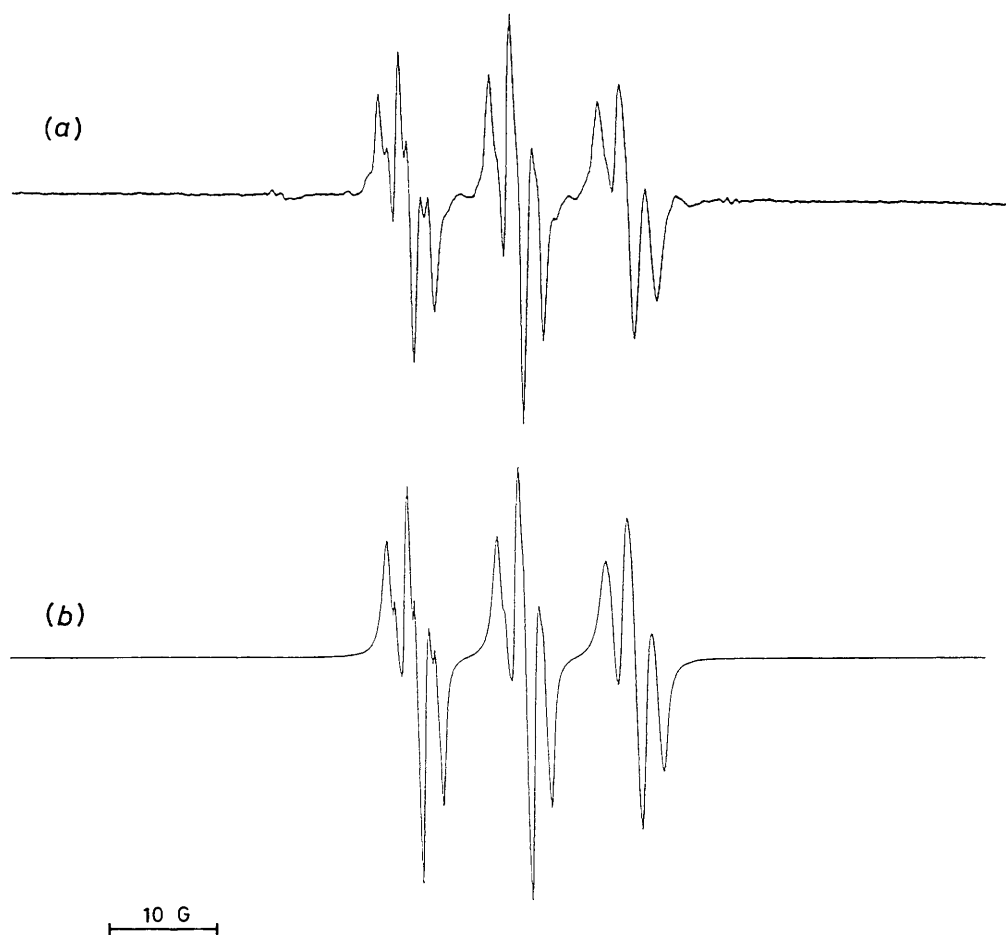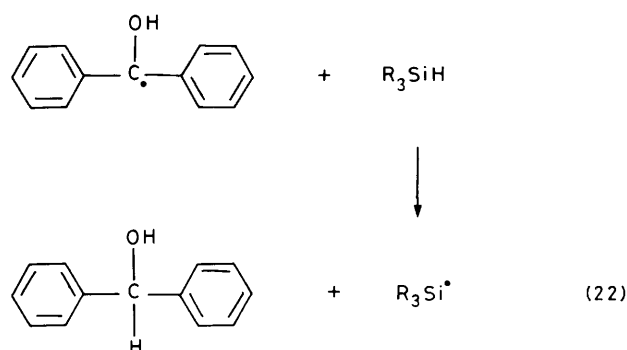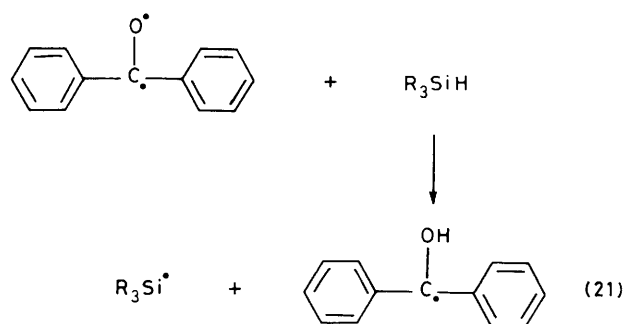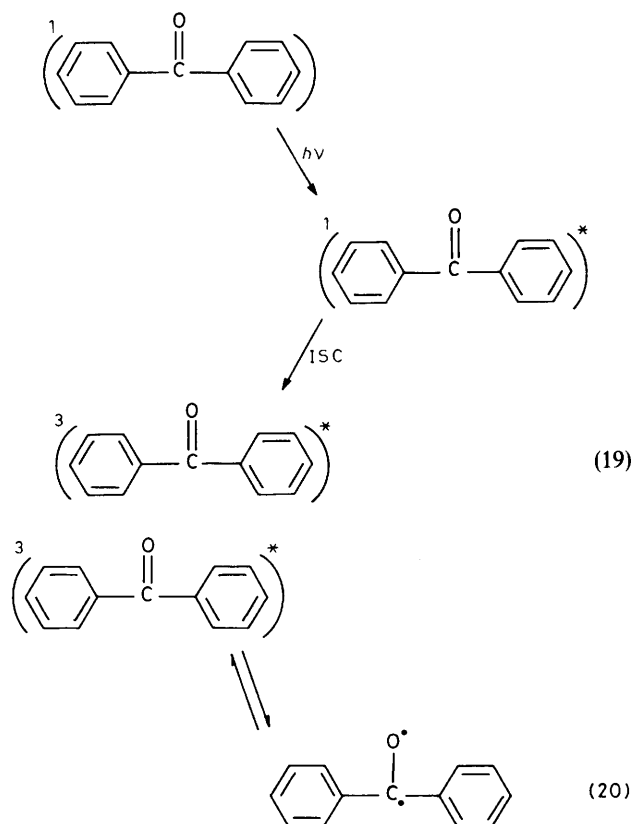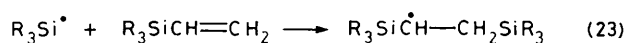
(a)

(b)

10 G

Fig. 6. Computer simulation (b) of the spin-adduct mixture obtained during the hydrosilylation reaction (a).

initiation:

(19)

(20)

(21)

(22)

propagation:

$$R_3Si^\bullet + R_3SiCH{=}CH_2 \longrightarrow R_3Si\overset{\bullet}{C}H{-}CH_2SiR_3 \qquad (23)$$

Table 4. EPR parameters (a values in G) of the two BNB spin adducts obtained using ENDOR analysis and computer simulation

radical	species 1			species 2		
	a_N	a_H	g	a_N	a_H	g
$Et_3Si^{\cdot}$	10.63	1.95	2.0047(4)	10.61	1.94	2.0047(1)
$Et_2MeSi^{\cdot}$	10.63	1.94	2.0047(3)	10.62	1.93	2.0047(0)
$Me_2PhSi^{\cdot}$	10.56	1.97	2.0047(4)	10.56	1.96	2.0047(2)
$Ph_2MeSi^{\cdot}$	10.57	1.96	2.0047(3)	10.55	1.96	2.0047(2)
$HSiMe_2OMe_2Si^{\cdot}$	10.92	1.96	2.0047(4)	10.90	1.94	2.0047(3)
$(Me_3SiO)_2MeSi^{\cdot}$	10.94	1.97	2.0047(5)	10.94	1.96	2.0047(3)
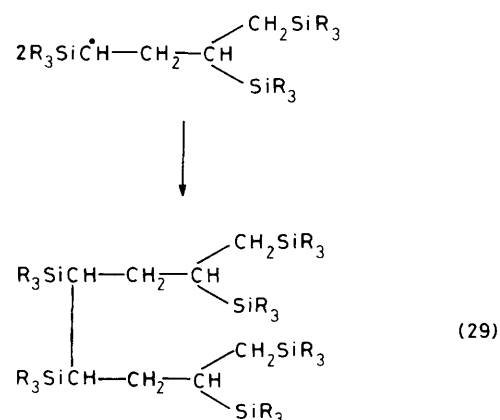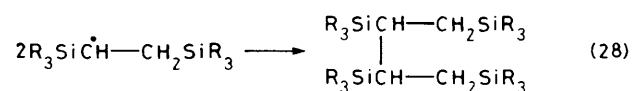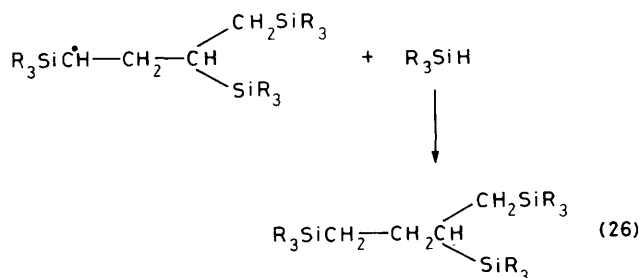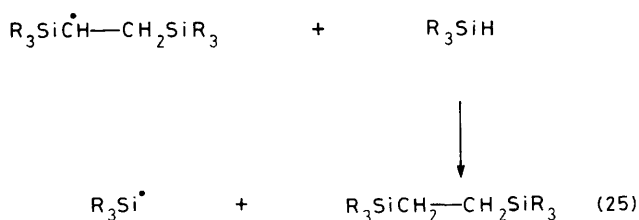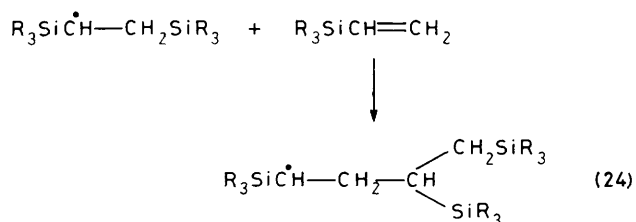
termination:
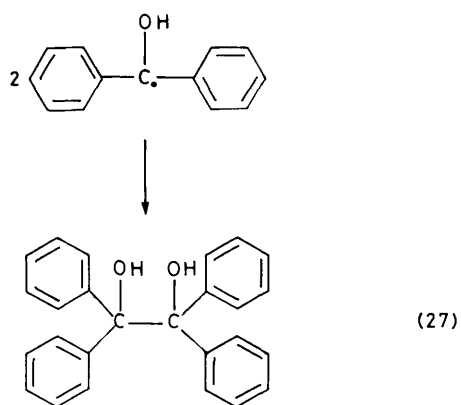
References

1 J. L. Speier, *Adv. Organomet. Chem.*, 1979, **17**, 407.
2 H. Leaver and G. C. Ramsey, *Tetrahedron*, 1969, **25**, 5669.
3 C. R. Morgan, F. Magnotta and A. D. Ketley, *J. Polym. Sci.*, 1977, **A1**, 15, 627.
4 Internal Technical Report, Dow Corning.
5 E. G. Janzen, *Acc. Chem. Res.*, 1971, 30.
6 C. Chatgilialoglu, J. C. Scaiano and K. U. Ingold, *Organometallics*, 1982, **1**, 466.
7 R. Konaka and S. Terabe, *J. Chem. Soc., Perkin Trans. 2*, 1973, 369.
8 C. Chatgilialoglu, K. U. Ingold, J. C. Scaiano and H. Woynar, *J. Am. Chem. Soc.*, 1981, **103**, 3231.
9 J. Cooper, A. Hudson and R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1933.