

An Electron Spin Resonance Study of the Group IVB Organometallic Adducts of 2,6-Di-*t*-butylbenzoquinone

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2,6-Di-*t*-butylbenzoquinone can interact with group IVB organometallic compounds to give the stable substituted phenoxyl radicals detectable by e.s.r. The strong bonding between silicon and oxygen atoms together with the unusual stability of the resulting phenoxyl radicals show that 2,6-di-*t*-butylbenzoquinone is an excellent spin trap of organosilyl radicals. This quinone has also been used successfully to trap both diphenylphosphino and phenylthiyl radicals.

SEVERAL recent publications have been concerned with the e.s.r. spectra of transient species formed by the reactions of group IVB metal-centred radicals with radical compounds.¹⁻⁷ The greater stability of phenoxyl radicals by comparison with carbon-centred radicals promoted us to explore the possibility of using a 1,4-quinone as an efficient spin trap of various organometal-centred radicals.⁸

The trapping ability of 2,6-di-*t*-butylbenzoquinone towards group IVB metal-centred, organophosphino, and organothiyl radicals has been investigated. The unusual stability of organosilyl spin adducts of various quinones is discussed.

EXPERIMENTAL

2,6-Di-*t*-butylbenzoquinone, tetrafluoro-1,4-benzoquinone, and anthraquinone were obtained from Aldrich and vacuum sublimed. Fisher spectroanalysed benzene was refluxed over molecular sieves and distilled prior to use. Di-*t*-butyl peroxide (MCB), trimethylsilane (PCR), triphenylsilane (PCR), diphenylsilane (PCR), hexamethylditin (Alfa), hexamethyldilead (Alfa), hexaphenyldilead (Alfa), dimethyl disulphide (Aldrich), diethyl disulphide (Eastman), di-*n*-propyl disulphide (Eastman), di-*t*-butyl disulphide (MCB), and tetraphenylbiphosphine (K and K) were used without further purification. Triethylgermane was a gift from Dr. Mochida. *t*-Butyl $\beta\beta$ -dimethylperbutanoate was prepared by the method of Bartlett and Hiatt.⁹ Fluorodimethylsilane was prepared from 1,1,2,2-tetramethyldisiloxane and boron trifluoride.¹⁰ Diphenyl disulphide was prepared by the oxidation of benzenethiol with lead tetraacetate.¹¹

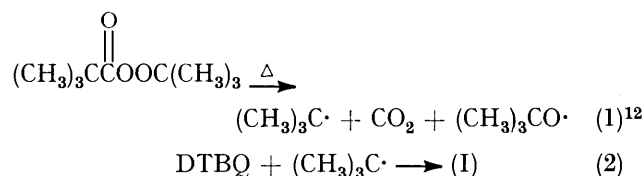
A standard sample consisted of benzene (1 ml), di-*t*-butyl peroxide (0.1 ml), and quinone (5 mg), and organometallic compound (5 mg) and was degassed by four freeze-thaw cycles and sealed with a residual pressure of 10^{-4} mmHg at liquid nitrogen temperature.

E.s.r. spectra were obtained on a Bruker 420 spectrometer with 100 kHz modulation. Magnetic field and microwave frequency were monitored by a Bruker n.m.r. oscillator and a Hewlett-Packard 5342A microwave frequency counter, respectively. The temperature was regulated by a Varian temperature controller. The light source was a HBO 200 W super pressure mercury lamp.

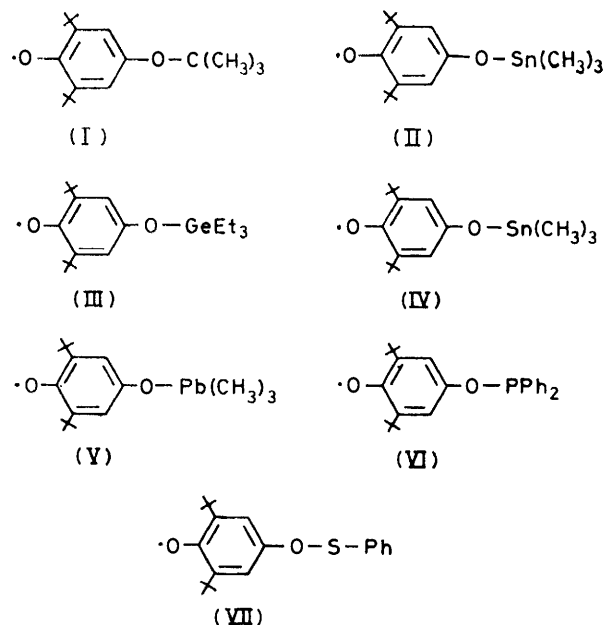
RESULTS AND DISCUSSION

*Formation and Observation of 2,6-Di-*t*-butylbenzoquinone (DTBQ) Spin Adducts.*—A. *Spin adducts of group IVB metal-centred radicals.* 1. *t*-Butyl adduct (I). When a frozen benzene solution of DTBQ and *t*-butyl

$\beta\beta$ -dimethylperbutanoate, prepared at -190 °C in the dark, was allowed to warm in the cavity of an e.s.r. spectrometer, the intense e.s.r. spectrum of *t*-butyl adduct was observed [reactions (1) and (2)]. The



observed hyperfine splitting constant is consistent with that resulting from $\text{K}_3\text{Fe(CN)}_6$ oxidation of the corresponding phenol.¹³ The e.s.r. parameters of (I) are given in Table I.



2. Trimethylsilyl adduct (II). By photolysing a benzene solution of DTBQ and trimethylsilane in the presence of di-*t*-butyl peroxide, an intense e.s.r. spectrum with a triplet splitting of 0.112 mT as shown in Figure a was observed. When fluorodimethylsilane instead of trimethylsilane was present, an additional doublet of multiplets, presumably hyperfine splittings from fluorine and six methyl protons on the silicon atom, appeared (Figure b). This observation confirmed the formation of organosilyl adducts *via* hydrogen abstraction followed

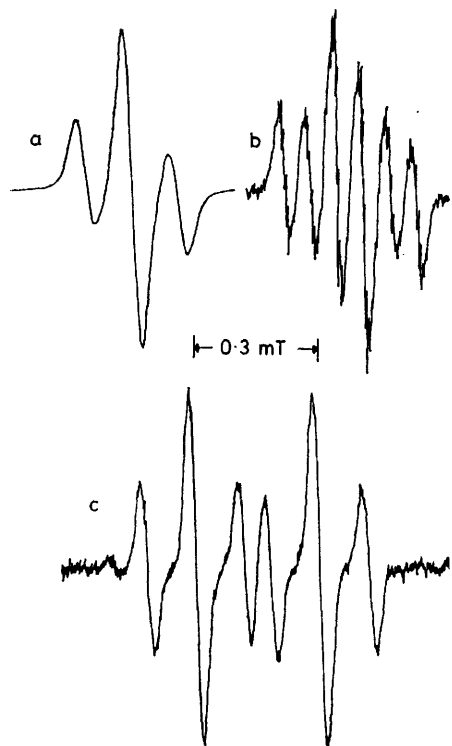
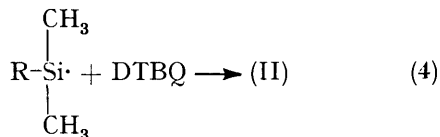
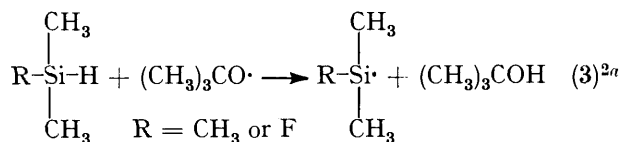
TABLE I

E.s.r. parameters of group IVB organometallic containing phenoxy radicals in benzene at 20 °C

M	$\cdot\text{OC}_6\text{H}_2-(2,6\text{-Bu}^t_2)-4\text{-OM}(\text{CH}_3)_3$			$\cdot\text{OC}_6\text{H}_2-(2,6\text{-Bu}^t_2)-4\text{-M}(\text{CH}_3)_3$		
	<i>g</i>	a_M/mT	a_H^m/mT	<i>g</i>	a_M/mT	a_H^m/mT
C	2.004 67		0.098	2.004 57		0.167 ^c
Si	2.004 64	0.75 (0.49%) ^a	0.112		1.24 ^d (0.81%) ^a	0.20 ^d
Ge	2.004 52 ^b	0.110 ^b (0.13%) ^a	0.076 ^b		0.29 ^c (0.34%) ^a	0.17 ^d
Sn	2.004 37	1.123 (0.07%) ^a	0.058			
Pb	2.003 53	1.696 (0.06%) ^a	<0.03			

^a The spin densities on the *ns* orbital of the metal. They were estimated from the splitting for a *ns* electron on a metal atom (152.5 for ²⁹Si, 8.50 for ⁷³Ge, 1 540.0 for ¹¹⁹Sn, and 2 870.0 mT for ²⁰⁷Pb, data taken from R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, **95**, 2459; J. H. Mackey and D. E. Wood, *Mol. Phys.*, 1970, **18**, 783. ^b Data are for triethylgermyl adduct. ^c 0.041 mT was resolved for nine *para*-methyl protons. ^d Data taken from G. A. Razuvaev, N. S. Vasileiskaya, E. P. Oleinik, D. V. Muslin, E. S. Klimov, and N. N. Vavilina, *Zhur. Org. Khim.*, 1974, **10**, 2257.

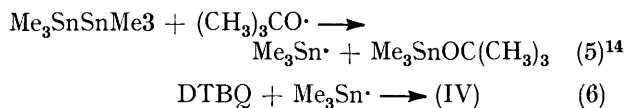
by the addition of the resultant silyl radical onto the quinone [reactions (3) and (4)]. The stability of organosilyl adduct depends on both quinone and silyl radical. A detailed account of this together with the unusual features of various organosilyl adducts of different quinones will be given later.



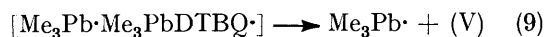
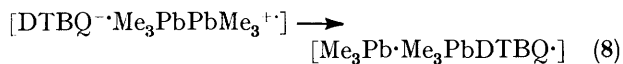
E.s.r. spectra of 2,6-di-*t*-butylbenzoquinone spin adducts of (a) trimethylsilyl radical, (b) dimethylfluorosilyl radical, and (c) diphenylphosphino radical in benzene at 20 °C

3. Triethylgermyl adduct (III). No e.s.r. signal was detected when a frozen benzene solution of DTBQ, triethylgermane, and di-*t*-butyl peroxide was warmed in the e.s.r. cavity. An intense signal was recorded immediately after the incidence of the light. The signal once formed is stable for a while even after the light was removed. On top of the triplet *meta*-proton hyperfine splittings, an additional decet of germanium-73 ($I = 9/2$; 7.61%) was observed in support of the formation of (III).

4. Trimethylstannyl adduct (IV). When a benzene solution of DTBQ, hexamethylditin, and di-*t*-butyl peroxide was photolysed at 20 °C, a radical species was detected. Besides the main triplet spectrum, a satellite doublet from tin-117 and -119 was observed. It was assigned as adduct (IV) [reactions (5) and (6)].

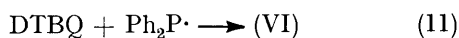
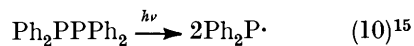


5. Trimethylplumbyl adduct (V). A frozen benzene solution of DTBQ and hexamethyldilead was placed in a precooled e.s.r. cavity. Thermostatted nitrogen was allowed to pass the sample holder. At the thaw temperature (*ca.* 6 °C) of the solution, an e.s.r. signal of a singlet with a satellite doublet was observed. The singlet splits into a very small resolved triplet (0.029 mT) when hexaphenyldilead was used. The observed signal was assigned to adduct (V) formed *via* the previously reported electron transfer mechanism [reactions (7)–(9)].



B. Spin adduct of diphenylphosphino radical (VI). A well resolved e.s.r. spectrum was observed when a benzene solution of DTBQ and tetraphenylbiphosphine was irradiated with a Pyrex filtered light. The observed additional doublet due to phosphorus-31 supported the formation of adduct (VI) probably *via* the homolytic

dissociation of the P-P bond followed by spin trapping of DTBQ [reactions (10) and (11)]. The e.s.r. spectrum is shown in Figure c, and the e.s.r. parameters are given in Table 2.



C. *Spin adduct of phenylthiyl radical (VII)*. A weak e.s.r. signal was detected by u.v. photolysis a benzene solution of DTBQ, diphenyl disulphide, and di-*t*-butyl peroxide. It was assigned as adduct (VII) from the resolved additional quartet (0.14 mT) when dimethyl disulphide was used. A much stronger signal was observed with di-*t*-butyl disulphide was used. However,

to the *para*-position of the phenyl ring are included for comparison. Several trends in the e.s.r. parameters were noted. (1) Both *meta*-proton and metal hyperfine splittings decrease significantly when an oxygen atom was introduced between the phenoxy part and the metal. This indicates that some spin density has moved from both the phenoxy group and the metal atom into the inserted oxygen atom. (2) A drastic decrease of *meta*-proton hyperfine splittings occurred when the metal went down the periodic table from silicon to lead. This should reflect on the *g* factors if the magnitude of the spin density on the phenoxy oxygen is the major factor determining the *g* factor. Indeed, a regular decrease in the *g* factors was observed for this series. Although the spin densities of the *ns* orbital also decreased in the series,

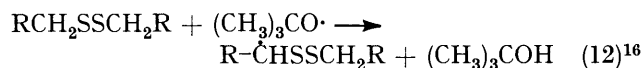
TABLE 2

E.s.r. parameters of the silicon-, phosphorus-, and sulphur-containing phenoxy radicals in benzene at 20 °C

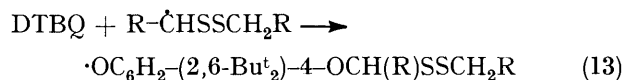
M	<i>n</i>	·OC ₆ H ₂ -(2,6-Bu ^t) ₂ -4-OMPh _n			·OC ₆ H ₂ -(2,6-Bu ^t) ₂ -4-MPh _n	
		<i>g</i>	<i>a</i> _M /mT	<i>a</i> _{H^m} /mT	<i>a</i> _M /mT	<i>a</i> _{H^m} /mT
Si	3	2.004 69	0.746	0.119	1.24 ^a	0.20 ^a
P	2	2.004 69	0.299	0.118	0.68 ^b	0.16 ^b
S	1	2.004 68		0.103		0.14 ^c

^a Data are for trimethylsilyl-substituted phenoxy radical and are taken from footnote *d* to Table 1. ^b Data taken from E. Müller, H. Eggenberger, and K. Scheffler, *Annalen*, 1962, **658**, 103. ^c Data taken from E. Müller, H. B. Stegmann, and K. Scheffler, *Annalen*, 1961, **645**, 79.

for disulphides with the hydrogen available at the α -carbon, the alkyl radicals resulting from hydrogen abstraction added to DTBQ were observed [reactions (12) and (13)]. The identification of adduct (VIII) was furnished by the observed additional proton splitting.



R = Me or Et

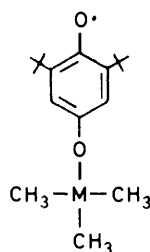


(VIII)

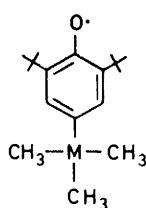
(*a*_H 0.1 mT)

II. E.s.r. Parameters and the Nature of Bonding of Organometallic Adducts of 2,6-Di-*t*-butylbenzoquinone.—

A. *Group IVB organometallic adducts*. The e.s.r. para-



M = C, Si, Ge, Sn, Pb



M = C, Si, Ge

eters of 2,6-di-*t*-butylbenzoquinone spin adducts of Group IVB metal-centred radicals are given in Table 1. The corresponding e.s.r. parameters of phenoxy radicals with group IVB metal-centred radicals directly attached

the relatively small percentages (0.06—0.49%) may not account totally for the observed trend in *g*.

The failure of the e.s.r. observation of an organolead adduct of acetone or benzophenone has been ascribed to the weak lead-oxygen bond.^{2f} The detection of the e.s.r. signal of 2,6-di-*t*-butylbenzoquinone spin adducts of trimethyl- and triphenyl-lead may be reasonably attributed to the stability of the resulting phenoxy radicals.

B. *Diphenylphosphino and phenylthiyl adducts*. E.s.r. parameters of the silicon-, phosphorus-, and sulphur-containing phenoxy radicals are given in Table 2. A similar decrease in both *meta*-proton and metal hyperfine splittings was observed when an oxygen atom was placed between the phenoxy group and the metal. However, no variation in the *g* factors was noticed when both the metal (from silicon to phosphorus to sulphur in the same row of the periodic table) and the number of substituents on the metal were changed. This is in accordance with the very small change in *meta*-proton hyperfine splittings in the same series. Both observations seem to suggest that the involvements of Si-O, P-O, and S-O bond formations on the spin distribution are roughly the same.

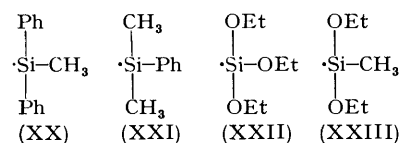
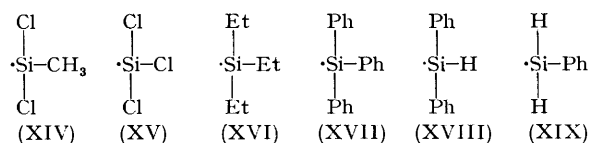
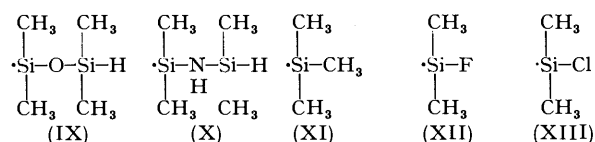
Quinone Adducts of Organosilyl Radicals.—A number of organosilyl radicals have been trapped by nitrene¹⁷ and various carbonyl compounds¹⁻⁷ in solution. The silyl radicals (IX)—(XXIII) have now been trapped by a single precursor, 2,6-di-*t*-butylbenzoquinone. The hyperfine splittings of some representative adducts are given in Table 3. Presumably the strong bonding between silicon and oxygen together with the two highly sterically protective *t*-butyl groups in positions 2 and 6 promote the unusual stability of the resultant silicon-

TABLE 3

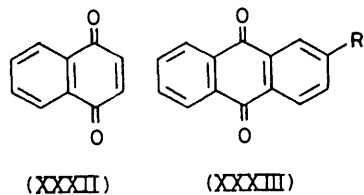
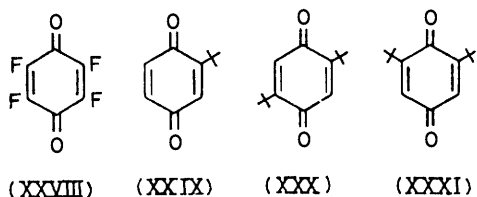
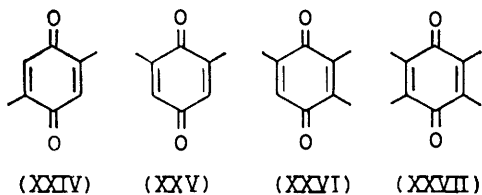
Hyperfine splitting constant (mT) of organosilyl adducts of p-quinones in benzene at 20 °C

Quinone Alkyl groups	·OC ₆ H ₂ (2,6-Bu ^t) ₂ -4-OSiR ¹ ₂ R ²					9-OC ₁₄ H ₈ -10-OSiR ¹ ₂ R ²					·OC ₆ F ₄ -4-OSiR ¹ ₂ R ²						
	R ¹	R ²	A _H ³	A _H ^{Si-H}	A _F ^{Si-F}	A _H ^{Si-CH₃}	A _H ¹	A _H ²	A _H ³	A _H ⁴	A _H ^{Si-H}	A _F ^{Si-F}	A _F ¹	A _F ²	A _H ^{Si-H}	A _F ^{Si-F}	A _H ^{Si-CH₃}
CH ₃ CH ₃			0.112			<0.002	0.110	0.314	0.105	0.275			1.388	0.423			<0.003
CH ₃ F			0.131		0.061	0.007	0.086	0.321	0.086	0.287	0.081		1.442	0.457		0.065	<0.004
Ph Ph			0.118				0.087	0.319	0.087	0.283			1.421	0.442			
Ph H			0.119	0.047			0.086	0.319	0.086	0.282	0.016		1.415	0.434	0.051		

containing phenoxy radicals. For example, the triphenylsilyl adduct of 2,6-di-*t*-butylbenzoquinone is stable for years.

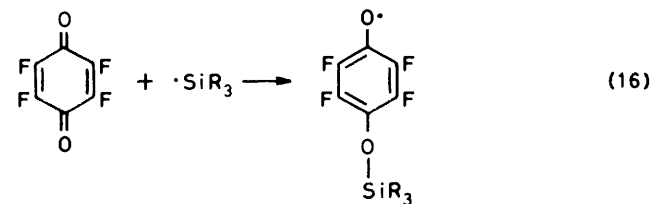
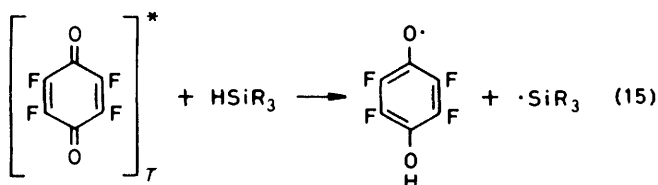
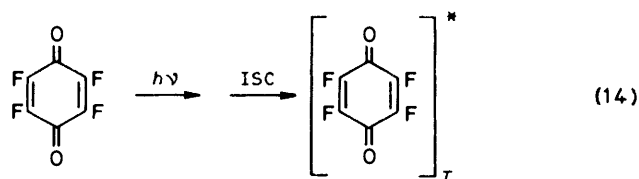


Various 1,4-quinones (XXIV)—(XXXIII) have also been investigated. These successfully trapped triethyl silane and formed adducts detected by e.s.r. The stereo-protective groups seem necessary to explain the future of benzoquinone and 2-methylbenzoquinone to trap the silyl radical. Besides 2,6-di-*t*-butylbenzo-

R = H, CH₃, Et, Bu^t

quinone, two other quinones, anthraquinone and tetrafluoroquinone, merit further consideration. The hyperfine splittings of some spin adducts of these two quinones are also given in Table 3.

When a benzene solution of anthraquinone, triethylsilane, and di-*t*-butyl peroxide flowed through the e.s.r. cavity, an intense e.s.r. signal of the silyl adduct was detected immediately after the incidence of the light. Meanwhile a very strong blue light was emitted. Excitation at 450 nm gave the maximum emission at 402 nm. This blue light has been observed for all silanes. A similar, although weaker, blue light was also observed for other quinones. A further study to identify the system responsible for emitting the light is in progress.



For tetrafluorobenzoquinone, the spin adduct is more transient and a semiquinone radical is always present. The silyl adduct can be observed in the absence of the di-*t*-butyl peroxide. A possible reaction route is (14)—(16).

The well resolved hyperfine splittings of proton and fluorine on silicon as shown in Table 3 clearly confirmed the formation of silyl adducts. This is another advantage of using quinone as a spin trap for silyl radicals.

Conclusions.—2,6-Di-*t*-butylbenzoquinone has been demonstrated to be an efficient spin trap of group IVB metal-centred, organophosphino, and organothyl radicals. The strong bonding between silicon and oxygen together with the two stereo-protective *t*-butyl groups

rendered this quinone an especially superior trap for organosilyl radicals.

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