An Electron Spin Resonance Study of the Addition Reactions of Arylsilyl and Diphenylphosphino-radicals to *para*-Quinones

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Arylsilyl radicals were found to add to a carbonyl oxygen of various *p*-quinones to produce siloxy-substituted phenoxyl radicals. Likewise the reaction of diphenylphosphino-radical with *p*-quinones produced similar phenoxyl radicals. For the unsymmetrical 2,6-di-t-butyl-*p*-benzoquinone both possible isomers of the triphenylsilyl adduct were observed, but while 4-triphenylsiloxy-2,6-di-t-butylphenoxyl radical persisted for months its isomer decayed within seconds. t-Butoxyl and carbon radicals did not appear to add to *p*-quinones. Consequently *p*-quinones appear to be excellent preferential spin traps for silyl and phosphino-radicals in solution.

As a continuing e.s.r. investigation of the elusive arylsilyl radicals in liquid solution, we have studied the addition of some of these arylsilyl radicals to benzophenone[1] and to phenyl t-butyl nitrone.[2] In both cases, the silyl adduct radicals are not particularly persistent and disappear within seconds after the source of generating the arylsilyl radical is removed.

Our interest in the chemically induced dynamic electron and nuclear polarisation of quinone systems[3,4] has led us to consider the possibility of ' polarized ' arylsilyl–quinone adduct radicals.

We report here the conventional e.s.r. study of such adducts between a series of arylsilyl radicals and various substituted *p*-benzoquinones. Although protonated semiquinone radicals have been found to decay at almost diffusion-controlled rates[5] these arylsilyl semiquinone radicals are very persistent at room temperature even over 12 months.

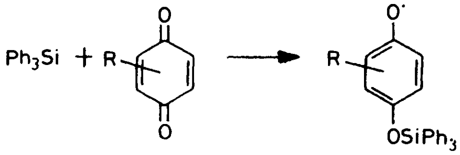
Since phosphorus-substituted quinones are of some interest in biological studies[6] we have studied the addition of diphenylphosphino-radical to quinones. While the additions of diphenylphosphino-radicals to carbon double bonds are quite common[7] few e.s.r. investigations of the adduct radicals have been reported. The diphenylphosphino–quinone adducts are found to be less persistent than the silyl adducts.

RESULTS AND DISCUSSION

Additions of Arylsilyl Radicals to Quinones.—All sample solutions at room temperature did not give any dark e.s.r. signals. Upon photolysis of the benzene solutions of a silane, quinone, and di-t-butyl peroxide (BOOB) well resolved e.s.r. spectra were obtained. Solutions without the silane did not produce any detectable concentrations of radicals. Photolysis of solutions of quinone and silane without di-t-butyl peroxide produced in some cases very weak spectra of a mixture of radicals (*e.g.* duroquinone in diphenylsilane) while in other cases no e.s.r. spectrum was obtained (*p*-benzoquinone in diphenylsilane). It is reasonable to conclude that the observed spectra are due to the arylsilyl adducts of quinones generated through the typical reactions (1)—(3). Reactions (1) and (2) have been documented in the literature.[8] When the quinones used in reaction (3) are symmetrically substituted (*e.g.* duroquinone and anthraquinone), only one type of silyl adduct can be expected (Table 1). However, for quinones with unsymmetrical substitutions such as 2,6-dimethyl-*p*-benzoquinone and 2,6-di-t-butyl-*p*-benzoquinone, the addition may lead to two different isomers.

$$\mathrm{BOOB} + h\nu \longrightarrow 2\mathrm{BO}^{\bullet} \qquad (1)$$

$$\mathrm{BO}^{\bullet} + \mathrm{Ph_3SiH} \longrightarrow \mathrm{BOH} + \mathrm{Ph_3Si}^{\bullet} \qquad (2)$$



(3)

Thus when the triphenylsilyl radical adds to 2,6-di-t-butyl-*p*-benzoquinone both isomers (I) and (II) were observed at −20 °C using di-t-butyl peroxide as solvent. The e.s.r. parameters of adducts (I) and (II) are given in Table 1. The assignments of the e.s.r. parameters to radicals (I) and (II) are consistent with those of 4-t-butoxy-2,6-di-t-butylphenoxyl[9] and 3,5-di-t-butylphenoxyl radicals.[10] At 300 K and under continuous irradiation, the steady state concentration of adduct (I) was more than an order of magnitude higher than that of adduct (II). Furthermore, upon termination of irradiation, adduct (II) was found to decay within seconds while adduct (I) persisted over 12 months. Because of the high persistency of the radical (I), it was possible to build up a high concentration of the radical by pro-

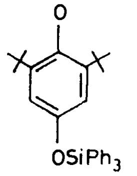
TABLE 1

E.s.r. parameters of the arylsilyl and the diphenylphosphino radical adducts of various *p*-quinones in benzene solution

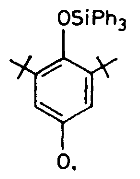
Adduct	Coupling constants (mT)	g
(I)	$a^{\mathrm{H(2)}}_{meta}$ 0.13, $a^{29}\mathrm{Si}$ 1.15	2.0047
(II)	$a^{\mathrm{H(2)}}_{ortho}$ 0.41	2.0047
(III)	$a^{\mathrm{H(6)}}_{\mathrm{HC_3}}$ 0.55, $a^{\mathrm{H(2)}}_{meta}$ 0.13	2.0048
(IV)	Not observed	
(V)	$a^{\mathrm{H(2)}}_{meta}$ 0.13, $a^{\mathrm{H(2)}}_{\mathrm{SiH_2}}$ 0.040	2.0047
(VI)	$a^{\mathrm{H(2)}}_{meta}$ 0.14, $a^{\mathrm{H(1)}}_{\mathrm{SiH}}$ 0.055	2.0047
(VII)	$a^{\mathrm{H(2)}}_{meta}$ 0.11, $a^{31}\mathrm{P(1)}$ 0.31	2.0047
Tetramethyl-4-triphenylsiloxyphenoxyl	$a^{\mathrm{H(6)}}_{ortho}$ 0.59, $a^{\mathrm{H(6)}}_{meta}$ 0.15	2.0047
10-Triphenylsiloxyanthracen-9-oxyl	$a^{\mathrm{H(4)}}$ 0.30, $a^{\mathrm{H(4)}}$ 0.08	2.0046

longed photolysis. This in turn allowed us to observe the weak ^{29}Si splittings reported in Table 1.

In the addition of the triphenylsilyl radical to 2,6-dimethyl-*p*-benzoquinone, only one adduct isomer was observed even at lower temperatures. A typical e.s.r. spectrum of the adduct radical is shown in Figure 1.



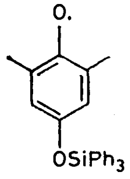
(I)



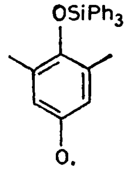
(II)

The spectrum is assigned to radical (III). The e.s.r. parameters of 4-methoxy-2,6-dimethylphenoxyl[11] radical are similar to those reported in Table 1 for radical (III). It is not quite clear whether the failure to observe the isomer adduct (IV) means that the addition is specific to give adduct (III) only or the isomer (IV) is so reactive that it cannot be observed in steady state experiments. We are inclined to believe that the first interpretation of a small rate of formation of isomer (IV) is more reasonable. The possible hydrogen bonding between the carbonyl oxygen and the hydrogen of the *ortho*-methyl[12] may reduce the rate of formation of isomer (IV).

FIGURE 1 The room temperature e.s.r. spectrum of the triphenylsilyl radical adduct of 2,6-dimethyl-*p*-benzoquinone



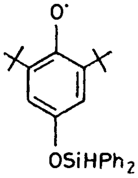
(III)



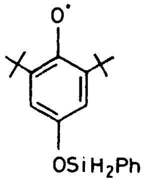
(IV)

However it must be pointed out that triphenylsilyl radicals do add to duroquinone and the resultant radicals are found to be persistent over several days. Similarly the triphenylsilyl adduct of 9,10-anthraquinone is persistent for several days. The e.s.r. parameters of both adducts are given in Table 1.

The additions of diphenyl and phenylsilyl radicals to 2,6-di-t-butyl-*p*-benzoquinone were studied using diphenyl- and phenyl-silane respectively. In each case only one isomer adduct was observed. With diphenylsilyl adduct, a triplet with fine doublet splitting was featured in the e.s.r. spectrum, while the spectrum of the phenylsilyl adduct displayed a triplet with smaller triplet splittings. These smaller splittings were due to the proton(s) of the diphenyl- and phenyl-silyl moieties. The coupling constants of the adducts (V) and (VI) are reported in Table 1. Compared with the triphenylsilyl adduct (I), adducts (V) and (VI) are much less persistent.



(V)



(VI)

When unsubstituted *p*-benzoquinone was used, the e.s.r. spectrum of the triphenylsilyl adduct was not observed. Instead the e.s.r. spectrum of the protonated semiquinone radical, resulting from hydrogen abstraction by triplet benzoquinone was observed. We did not observe protonated semiquinone radical with any of the substituted quinones. This suggests that the rate of hydrogen abstraction from silane by triplet-substituted quinone is slower than the rate of hydrogen abstraction by t-butoxyl radical in reaction (2) above, which rate in turn is less than the rate of hydrogen abstraction by the triplet unsubstituted *p*-benzoquinone. This conclusion is consistent with the reported difference in hydrogen abstraction rates by different triplet quinones.[13]

The arylsilyl adducts of 2,6-di-t-butyl-*p*-benzoquinone are *para*-substituted 2,6-di-t-butylphenoxyl radicals. Thus their e.s.r. parameters are similar (Table 2). The higher values of a^{H}_{meta} for the arlysiloxy-substituted phenoxyl radicals compared to the alkoxy-substituted phenoxyl radicals are in agreement with the higher electronegativity of silicon. The high persistency of the triphenylsilyl adduct of di-t-butylquinone is comparable with the long life-time of 4-t-butoxy- and 4-t-butoxy-

TABLE 2

Hperfine coupling constants of some *para*-substituted 2,6-di-t-butylphenoxyl radicals

Substituent	a^{H}_{meta}/mT	a_{para}/mT	Ref.
OBu$^{\mathrm{t}}$	0.10		9
OMe	0.10	$a^{\mathrm{H}}_{\mathrm{OCH_3}}$ 0.16	9
Ac	0.22	$a^{\mathrm{H}}_{\mathrm{CH_3}}$ 0.028	9
OSiPh$_3$	0.13		This work
OSiHPh$_2$	0.14	$a^{\mathrm{H}}_{\mathrm{SiH}}$ 0.055	This work
OSiH$_3$Ph	0.14	$a^{\mathrm{H}}_{\mathrm{SiH_2}}$ 0.040	This work

2,6-di-t-butylphenoxyl radicals which have been isolated in pure form.[9] The observed decrease, with increasing number of hydrogen atoms on silicon, in the life-time of the arylsilyl adducts of the quinones is similar to the increase in the decay rate of 4-alkyl-2,6-di-t-butylphenoxyl radicals.[14] However the mechanism for the decay of 4-arylsiloxy-substituted phenoxyl radicals may not be the same as that of their carbon analogues.

In a previous study [2] we showed that arylsilyl radicals could be trapped by phenyl t-butyl nitrone to form nitroxides. The arylsilyl adduct radicals were not very persistent and they disappeared seconds after the source of generating the arylsilyl radical is removed. The identification of the trapped radicals was tentative because it was based only on the β-hydrogen splitting constants which were considerably higher than those of their carbon analogues.[2] The results of the present study suggest that 2,6-di-t-butyl-*p*-benzoquinone is a better spin trap than phenyl t-butyl nitrone for silyl radicals. The arylsilyl adducts of the quinone are more persistent. The observation of ^{29}Si splitting and the hyperfine splittings of the proton(s) on the diphenyl- and phenyl-silyl moieties (Table 1) provide positive identification of the radicals being trapped. In addition 2,6-di-t-butyl-*p*-benzoquinone appears to be a specific spin trap for the silyl radicals because the addition of hydrocarbon and butoxyl radicals to quinones did not produce any observable e.s.r. spectrum.

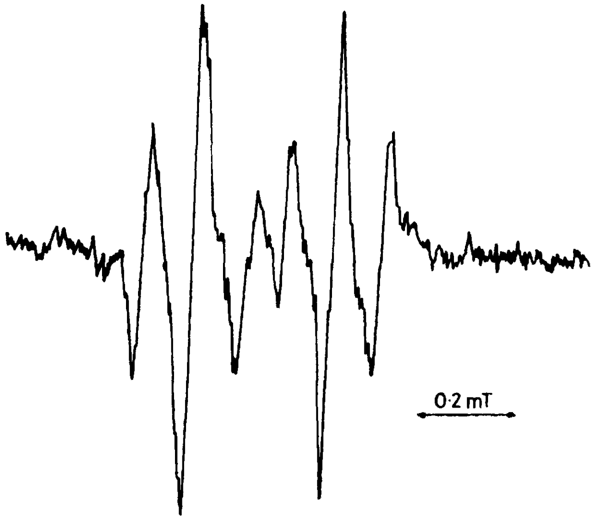
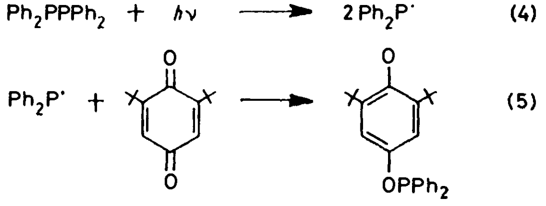


FIGURE 2 The room temperature spectrum of the diphenylphosphino radical adduct of 2,6-di-t-butyl-*p*-benzoquinone



(VII)

Addition of Diphenylphosphino-radical to 2,6-*Di-t-butyl*-p-*benzoquinone*.—A benzene solution containing 2,6-di-t-butyl-*p*-benzoquinone and tetraphenyldiphosphine did not give any e.s.r. signal in the dark. During irradiation the spectrum shown in Figure 2 was observed. Benzene solutions of either the quinone only or the diphosphine only did not produce any observable photo-e.s.r. signal. It is concluded that the observed spectrum is due to the diphenylphosphino-adduct of the quinone *via* reactions (4) and (5). The primary photochemical split of tetraphenyldiphosphine to two diphenylphosphino-radicals has been established.[7] Radical (VIII) could also be formed by homolytic substitution reaction on the phosphorus of the diphosphine by excited quinone[15] [reaction (6)]. The addition of the diphenylphosphino-radical to di-t-butyl-*p*-benzoquinone would lead to two possible isomers. However only one of the isomers was observed and the e.s.r. spectrum was

$$(\text{Quinone})^{*} + \text{Ph}_2\text{PPPh}_2 \longrightarrow (\text{VII}) + \text{Ph}_2\text{P}^{\bullet} \quad (6)$$

assigned to radical (VII) on the basis of the e.s.r. parameters which are reported in Table 1. The phosphorus splitting constants (0.31 mT) for radical (VII) may be compared with phosphorus splitting constants reported by Allen and Bond.[6] They observed that the phosphorus splitting constants in semiquinone phosphate radicals vary between 0.13 and 2.0 mT depending on the size of the substituents *ortho* to the phosphate group.

Diphenylphosphino-radical adducts of duroquinone and 2,6-dimethyl-*p*-benzoquinone were also observed. Their e.s.r. spectra are much more complex than silyl analogues. In general these phosphino–quinone adducts are less persistent than the silyl adducts.

EXPERIMENTAL

2,6-Di-t-butyl-*p*-benzoquinone (Aldrich) was purified by vacuum sublimation and triphenylsilane (Alfa) by zone refinement. All other quinones, phenyl- and diphenylsilane, as well as tetraphenyldiphosphine were used without further purification.

Between 0.02 and 0.05M solution of each of the silane and quinone was prepared in benzene. Di-t-butyl peroxide (0.2 cm^3) was added to the solution (2 cm^3). The solution was placed in 4-mm i.d. Pyrex tubing, degassed, and sealed under vacuum. In most experiments degassing did not have any noticeable effect on either the resolution or the stability of the radicals.

Samples were irradiated within the microwave cavity of Varian E-3 spectrometer with 100 kHz modulation. The light source was a 200 W super-pressure mercury lamp equipped with Pyrex optics. The magnetic field and *g* values were measured using an aqueous solution of Fremy's salt.

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