

# Studies of the Oxidation of Elemental Phosphorus by Substituted *ortho*-Benzoquinones†

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The phosphorus compounds  $P(O_2C_6R)_2Br$  ( $R = Cl_4, Br_4$  or  $Bu_2H_2$ ) have been prepared by the reaction of  $P_4$ ,  $Br_2$  and the substituted *o*-benzoquinone  $RC_6O_2-o$ . There is no reaction between  $Bu_2H_2C_6O_2-o$ ,  $P_4$  and  $Ph_2Se_2$ , but in the presence of catalytic quantities of  $Br_2$  the product is  $P(O_2C_6H_2Bu_2)_2(SePh)$ . ESR spectra identify the presence of the corresponding *o*-semiquinone species in these reactions. The  $^{13}C$  and  $^{31}P$  NMR spectra of these phosphoranes are reported, and compared with those of  $P(O_2C_6R)X_3$  ( $X_3 = Ph_3, Ph_2Cl, Br_3$  or  $Cl_3$ ) prepared by the reaction of  $PX_3$  and  $RC_6O_2-o$ .

The oxidation of indium(III) and tin(IV) halides by tetrahalogeno-*o*-quinones has been shown to yield the corresponding  $In(cat)X$  and  $Sn(cat)X_2$  species ( $cat = catecholate$ ) as the final product, generally isolated as adducts with neutral or anionic donors,<sup>1,2</sup> and similar reactions were observed with  $Sn(O_2R)$  compounds ( $R = C_6H_4, etc.$ ).<sup>3</sup> With other substituted *o*-quinones, and especially 3,5-di-*tert*-butyl-1,2-benzoquinone (dbbq), ESR spectroscopy demonstrated that the oxidation proceeds by successive one-electron transfers, and the presence of the  $dbbsq^{\cdot-}$  semiquinone radical anion in such reaction mixtures was detected with both indium and tin halides.<sup>4,5</sup>

Another feature of these studies has been the investigation of the oxidation of metallic elements by *o*-benzoquinones. The products in systems involving gallium,<sup>6</sup> indium,<sup>6,7</sup> zinc,<sup>8</sup> cadmium,<sup>8</sup> magnesium<sup>8</sup> and barium<sup>8</sup> are either semiquinone or catecholate compounds, depending on the metal-*o*-quinone combination. In view of these results it seemed reasonable to study analogous reactions with non-metals, and we now report the results of experiments on the oxidation of elemental phosphorus by *o*-quinones. Some earlier work on the reactions of phosphorus(III) compounds has been extended in order to provide the spectroscopic data necessary for the present investigations.

## Experimental

Red phosphorus was purified by treatment with boiling water.<sup>9</sup> Phosphorus tribromide was prepared by treating phosphorus with bromine.<sup>10</sup> Triphenylphosphine (Aldrich) was recrystallized from diethyl ether, and chlorodiphenylphosphine was distilled *in vacuo* before use. Solvents were dried by conventional methods and stored over drying agents. All other compounds were used as supplied. Reactions were carried out in an atmosphere of dry nitrogen unless otherwise stated.

Microanalysis was carried out by Guelph Chemical Laboratories Ltd. or Canadian Microanalytical Services Ltd. Infrared spectra were run on KBr discs on a Nicolet 5DX instrument,  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectra on Varian EM 360 or Bruker AC-300L spectrometers, and ESR spectra on a Varian E12 instrument, using the techniques described earlier.<sup>4</sup>

*Reaction of Phosphorus + Bromine + o-Quinones.*—(i) *Tetrahalogeno-o-quinones.* Red phosphorus (0.198 g, 6.4 mmol

Table 1 Analytical results (%), with calculated values in parentheses

Compound	C	H	P
$P(O_2C_6Cl_4)_2Br \cdot 0.25C_6H_{14}$	25.4 (26.0)		4.40 (4.95)
$P(O_2C_6Br_4)_2Br \cdot 0.25C_6H_{14}$	16.6 (16.6)		3.45 (3.15)
$P(dbc)_2Br^a$	73.2 (72.5)	3.20 (3.65)	5.40 (5.60)
$P(dbc)_2Me$	71.2 (71.6)	8.75 (8.90)	6.65 (6.35)
$P(O_2C_6Cl_4)Ph_3$	56.1 (56.7)	3.00 (3.00)	5.80 (6.10)
$P(O_2C_6Br_4)Ph_3$	41.6 (42.0)	2.25 (2.20)	4.90 (4.50)
$P(dbc)Ph_3$	78.8 (79.6)	6.90 (7.30)	6.60 (6.40)
$P(O_2C_6Cl_4)ClPh_2$	46.9 (46.3)	2.35 (2.15)	6.60 (6.65)
$P(dbc)ClPh_2^b$			
$P(O_2C_6Cl_4)_2(SePh) \cdot 0.25C_6H_{14}$	33.2 (33.4)	1.30 (1.20)	4.35 (4.40)

<sup>a</sup> Br 14.6 (14.5%), <sup>b</sup> Cl 7.40 (8.05%).

calculated as P) was suspended in a solution of  $Y_4C_6O_2-o$  ( $Y = Cl, 3.14$  g, 12.8 mmol;  $Y = Br, 5.42$  g, 12.8 mmol) in hexane (50 cm<sup>3</sup>), and a solution of bromine in slight excess (0.20 cm<sup>3</sup>, 0.59 g, 3.66 mmol, expressed as  $Br_2$ ) in the same solvent added dropwise over 30 min. When the reaction mixture was refluxed, signs of reaction were immediately apparent as the red colour of the phosphorus began to change to a light green. The reaction was stopped when red phosphorus was no longer visible in the reaction flask (*ca.* 6 h). The resultant pale green solid was collected by filtration and washed twice with portions (20 cm<sup>3</sup>) of light petroleum (b.p. 35–60 °C) to remove any unreacted  $Br_2$ ; the final off-white product was dried *in vacuo* for 24 h. The yields were almost quantitative. Analytical results, given in Table 1, implied the presence of hexane in each product, and this was confirmed by the  $^{13}C$  NMR spectrum, with resonances at 13.80, 22.04 and 30.96 ppm, corresponding to  $C^{1,6}$ ,  $C^{2,5}$  and  $C^{3,4}$  respectively. These signals diminished after repeatedly washing the product with light petroleum.

(ii) *dbbq.* Red phosphorus (0.198 g) was refluxed with 3,5-di-*tert*-butyl-*o*-quinone (2.82 g, 12.8 mmol) under conditions identical to those described above. The initially red suspension

† Non-SI unit employed: G = 10<sup>-4</sup> T.

became yellow upon complete addition of the bromine; refluxing was continued for 2 h, after which the resultant solution was filtered, and the solvent removed under vacuum to give a white flaky product, whose  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) showed three signals at  $-2.4$ ,  $-2.0$  and  $-0.73$  ppm (relative to external 85%  $\text{H}_3\text{PO}_4$ ), the intensities of the last two being *ca.* 25% of that of the first. The product was purified by sublimation to yield a waxy solid, which showed a single  $^{31}\text{P}$  resonance (in tetrahydrofuran) at  $-2.37$  ppm, and was identified as  $\text{P}(\text{dbc})_2\text{Br}$  (dbc = 3,5-di-*tert*-butylcatecholate), obtained in almost quantitative yield.

**Methylation Reactions.**—A solution of  $\text{LiMe}$  ( $2\text{ cm}^3$  of a  $1.7\text{ mol l}^{-1}$  solution in  $\text{Et}_2\text{O}$ ,  $3.4\text{ mmol}$ ) was added to a stirred solution containing an equimolar quantity of  $\text{P}(\text{dbc})_2\text{Br}$  ( $1.88\text{ g}$ ,  $3.4\text{ mmol}$ ) in diethyl ether ( $50\text{ cm}^3$ ) at room temperature. The colourless precipitate which resulted was washed, weighed and identified as  $\text{LiBr}$ , formed in quantitative yield (Found: Br, 91.5. Calc.: Br, 92.0%). The filtrate was concentrated by removing some of the ether *in vacuo*, and after 2 d at  $0^\circ\text{C}$  acicular crystals were obtained and identified as  $\text{P}(\text{dbc})_2\text{Me}$ . Yield 70%. In the case of the analogous experiments with  $\text{P}(\text{O}_2\text{C}_6\text{Y}_4)_2\text{Br}$  the yield of  $\text{LiBr}$  was again quantitative, and the products were identified only by their NMR spectra.

**Reactions with Organophosphorus Compounds.**—In each case,  $\text{PPh}_3$  or  $\text{PPh}_2\text{Cl}$  ( $1.0\text{ mmol}$ ) in toluene ( $10\text{ cm}^3$ ) was added dropwise to an equimolar solution of *o*-quinone in the same solvent ( $20\text{ cm}^3$ ) cooled in an acetone–solid  $\text{CO}_2$  bath ( $-78^\circ\text{C}$ ). The reaction caused progressive colour changes from dark red through pale yellow to colourless. The mixture was stirred mechanically for 6 h, after which the mixture was allowed to reach room temperature. The volume of the solution was reduced by *ca.* 80%; subsequent addition of light petroleum ( $20\text{ cm}^3$ ) caused the precipitation of a solid product, which was collected and dried *in vacuo*. The yields of the phosphorus(v) compounds (see Table 1) were almost quantitative.

**Reaction with Diphenyl Diselenide.**—Red phosphorus ( $0.10\text{ g}$ ,  $3.23\text{ mmol P}$ ) was suspended in a solution of  $\text{Cl}_4\text{C}_6\text{O}_2$  ( $0.59\text{ g}$ ,  $6.46\text{ mmol}$ ) and  $\text{Ph}_2\text{Se}_2$  ( $0.50\text{ g}$ ,  $1.62\text{ mmol}$ ) in hexane ( $50\text{ cm}^3$ ), and the mixture refluxed for 24 h. There was no evidence of any reaction at this point. One drop of  $\text{Br}_2$  was then added, and refluxing continued for 6 h at which point a brown compound began to precipitate. This solid was collected by filtration, washed with light petroleum ( $3 \times 20\text{ cm}^3$ ) and dried overnight *in vacuo*. The product was identified as  $\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)_2(\text{SePh})$ , obtained in almost quantitative yield. The  $^1\text{H}$  NMR spectrum revealed the presence of hexane in the final product [ $\delta$  0.72 (t), 1.07 (s) and 2.51 (s)], and the analytical results agree with the formula  $\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)_2(\text{SePh})\cdot 0.25\text{-C}_6\text{H}_{14}$ .

## Results and Discussion

**Preparations.**—The reaction between red phosphorus, bromine and a substituted *o*-quinone is a simple direct route to the bromobis(catecholato)phosphorane compounds. The formulation of the products was established by the analytical data, and by spectroscopy (see below). This direct 'one-pot' synthesis may have some advantages over the previous route<sup>10</sup> which involves the reaction of phosphorus pentahalide with a 1,2-diol. In addition, the  $\text{P}(\text{O}_2\text{R})_2\text{Br}$  products are themselves useful intermediates to such compounds as  $\text{P}(\text{O}_2\text{R})_2\text{Me}$ , otherwise obtained from the reaction of  $\text{PMeCl}_2$  with the appropriate catechol.<sup>11</sup> There is no reaction between phosphorus and quinones in the absence of bromine, even in the presence of an agent such as  $\text{Ph}_2\text{Se}_2$ , but catalytic quantities of  $\text{Br}_2$  are sufficient to promote reaction under these conditions. The product of this reaction is the  $\text{P}(\text{O}_2\text{R})_2(\text{SePh})$  derivative, and similar compounds could no doubt be prepared by

analogous routes. The significance of the presence of  $\text{Br}_2$  is shown by the fact that the reactions reported here involve red phosphorus; when white phosphorus was used in the synthesis of  $[\text{NHEt}_3][\text{P}(\text{O}_2\text{R})_3]$  salts, UV irradiation was necessary to achieve reaction.<sup>12</sup>

The reaction of phosphorus(III) compounds ( $\text{PX}_3$ ; X = organic or inorganic group) with *o*- or *p*-quinones is a well established route to  $\text{P}(\text{O}_2\text{R})\text{X}_3$  species,<sup>13,14</sup> and gave products whose NMR spectra, reported below, were helpful in confirming the identity of the  $\text{P}(\text{O}_2\text{R})_2\text{Br}$  species.

**Spectroscopic Results.**—The characterization of the products as phosphoranones depended on both IR and NMR spectra. The most important feature of the IR spectra is that in each case the strong  $\nu(\text{C}=\text{O})$  vibration of the original *o*-quinones at *ca.*  $1700\text{ cm}^{-1}$  is absent for the products, being replaced by  $\nu(\text{C}-\text{O})$  modes seen as a pair of absorptions at  $1440 + 1200\text{ cm}^{-1}$ .

The  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra are summarized in Table 2. We should note that the  $^1\text{H}$  NMR spectra confirm the presence of  $\text{C}_6\text{H}_5$  groups in the appropriate systems, with typical multiplets in the  $\delta$  6.6–7.9 region. In addition, *tert*- $\text{C}_4\text{H}_9$  resonances are observed as singlets at  $\delta$  1.10 + 1.40 for dbc derivatives, with small variations from one compound to another. Finally, the  $\text{P}(\text{O}_2\text{R})_2\text{Me}$  products show the  $^1\text{H}$  resonances of the  $\text{PCH}_3$  group for  $\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)_2\text{Me}$  at 2.20 (d) ( $J_{\text{PH}} 20\text{ Hz}$ ), for  $\text{P}(\text{O}_2\text{C}_6\text{Br}_4)_2\text{Me}$  at 2.38 (d) ( $J_{\text{PH}} 22\text{ Hz}$ ) and for  $\text{P}(\text{dbc})_2\text{Me}$  at 2.24 (d) ( $J_{\text{PH}} 22\text{ Hz}$ ).

The  $^{13}\text{C}$  NMR resonances are in good agreement with those reported previously for substituted catechol derivatives of indium and tin.<sup>1,2,4,5</sup> The most important point in the present results, as in the previous work, is that there are large changes for  $\text{C}^{1,2}$  (for  $\text{Y}_4\text{C}_6\text{O}_2$ ), or  $\text{C}^1$  and  $\text{C}^2$  (for dbbq), between the quinone ( $\delta$  *ca.* 140 ppm) and the corresponding catecholate. There appears to have been no previous report of  $^{13}\text{C}$  NMR spectra for  $\text{P}(\text{O}_2\text{R})_2\text{X}$  or  $\text{P}(\text{O}_2\text{R})\text{X}_3$  compounds, and some interesting correlations can be seen in these results. In the  $\text{Y}_4\text{C}_6\text{O}_2$  derivatives (Y = Cl or Br),  $\text{C}^{3,6}$  and  $\text{C}^{4,5}$  are consistently more deshielded for Y = Cl, but this effect is reversed at  $\text{C}^{1,2}$ . For the  $\text{P}(\text{O}_2\text{C}_6\text{Y}_4)\text{X}_3$  compounds, the sequence at  $\text{C}^{1,2}$  is  $\text{Cl}_3 < \text{Ph}_3 \leq \text{Br}_3 < \text{ClPh}_2$ , suggesting that both electronegativity and inductive effects influence the deshielding of these carbon nuclei.

The  $^{31}\text{P}$  chemical shifts are in the range reported for phosphorus(v) compounds, and the changes in resonance frequency are readily identified. For the three  $\text{P}(\text{cat})_2\text{X}$  compounds, replacement of Br by  $\text{CH}_3$  produces an upfield shift, most markedly so for the dbc derivative. In the  $\text{P}(\text{O}_2\text{C}_6\text{Y}_4)\text{X}_3$  series, the downfield shifts are in the sequence  $\text{Br}_3 > \text{ClPh}_2 > \text{Ph}_3 > \text{Cl}_3$ , and in this group phosphorus is less shielded in  $\text{Cl}_4\text{C}_6\text{O}_2$  derivatives than in  $\text{Br}_4\text{C}_6\text{O}_2$  compounds, but this effect is reversed in  $\text{P}(\text{O}_2\text{C}_6\text{Y}_4)_2\text{Br}$  and  $\text{P}(\text{O}_2\text{C}_6\text{Y}_4)_2\text{Me}$ . No detailed analysis of these results is attempted here, since it is known that  $^{31}\text{P}$  NMR frequencies are dependent on both ligand electronegativity and molecular geometry, and Holmes<sup>14–16</sup> has shown in an extensive series of structural determinations of phosphoranones and related compounds that a change of ligand almost invariably produces a significant change in the detailed stereochemistry at the phosphorus atom.

**Reaction Pathway.**—The ESR measurements point to the overall mechanism of the oxidation of  $\text{P}_4$  on  $\text{PX}_3$  by *o*-quinones. When  $\text{P}_4$  was stirred with a solution of  $\text{Cl}_4\text{C}_6\text{O}_2$  and  $\text{Br}_2$  in toluene (mole ratio  $\text{P}_4:\text{Cl}_4\text{C}_6\text{O}_2:\text{Br}_2 = 0.5:4:1$ ) at  $0^\circ\text{C}$  the resultant solution showed a triplet resonance centred at  $g = 2.003$ , with  $A_p = 3.0\text{ G}$ . On warming to room temperature (*ca.*  $20^\circ\text{C}$ ) over a period of 5 min this signal disappeared. Similar experiments involving equimolar quantities of  $\text{PCl}_3$  and  $\text{Cl}_4\text{C}_6\text{O}_2$ ,  $\text{Br}_4\text{C}_6\text{O}_2$ , or dbbq mixed in toluene–methylene chloride solution (1:1, v/v) at  $-60^\circ\text{C}$  gave ESR spectra similar to those reported by Klimov *et al.*<sup>17</sup> for two of these systems in

**Table 2** Carbon-13 and  $^{31}\text{P}$  NMR spectra of phosphorane derivatives; values in ppm relative to  $\text{SiMe}_4$  ( $\delta = 0$ ) ( $^{13}\text{C}$ ) or 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ )

(a) Tetrahalogenoquinone derivatives		Diolato			PPh		$^{31}\text{P}$ -{H}	
Compound	Solvent	C <sup>1,2</sup>	C <sup>3,6</sup>	C <sup>4,5</sup>	C <sup>1'</sup>	Others	Solvent *	$\delta$
$\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)_2\text{Br}$	$(\text{CD}_3)_2\text{SO}$	141.3	122.0	113.0			thf	-3.02
$\text{P}(\text{O}_2\text{C}_6\text{Br}_4)_2\text{Br}$	$(\text{CD}_3)_2\text{SO}$	146.5	120.6	109.1			thf	-1.93
$\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)_2\text{Me}$	$(\text{CD}_3)_2\text{SO}$	142.4	124.3	113.4		28.2 (P-CH <sub>3</sub> )	thf	-5.82
$\text{P}(\text{O}_2\text{C}_6\text{Br}_4)_2\text{Me}$	$(\text{CD}_3)_2\text{SO}$	148.0	121.3	108.5		27.8 (P-CH <sub>3</sub> )	thf	-4.45
$\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)\text{Cl}_3$	$\text{CH}_2\text{Cl}_2$	138.8	127.1	115.3			$\text{CH}_2\text{Cl}_2$	-21.75
$\text{P}(\text{O}_2\text{C}_6\text{Br}_4)\text{Cl}_3$	$\text{CH}_2\text{Cl}_2$	140.7	122.0	106.5			$\text{CH}_2\text{Cl}_2$	-23.96
$\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)\text{Br}_3$	$\text{Et}_2\text{O}$	142.3	121.1	114.1			thf	10.95
$\text{P}(\text{O}_2\text{C}_6\text{Br}_4)\text{Br}_3$	$\text{Et}_2\text{O}$	146.2	119.7	109.0			thf	9.55
$\text{PCl}(\text{O}_2\text{C}_6\text{Cl}_4)\text{Ph}_2$	$\text{CDCl}_3$	145.8	123.2	115.5	135.8	129.0-134.0	$\text{CDCl}_3$	-1.54
$\text{PCl}(\text{O}_2\text{C}_6\text{Br}_4)\text{Ph}_2$	$\text{CDCl}_3$	147.1	119.4	106.9	136.8	128.9-134.0	$\text{CDCl}_3$	-4.51
$\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)\text{Ph}_3$	$\text{CDCl}_3$	142.4	122.5	115.3	137.8	128.3-132.3	$\text{CDCl}_3$	-3.55
$\text{P}(\text{O}_2\text{C}_6\text{Br}_4)\text{Ph}_3$	$(\text{CD}_3)_2\text{SO}$	144.7	116.7	113.8	133.4	128.6-132.0	$\text{CDCl}_3$	-6.94
$\text{P}(\text{O}_2\text{C}_6\text{Cl}_4)(\text{SePh})$	$(\text{CD}_3)_2\text{SO}$	141.2	122.1	113.2		127.8-130.8	$(\text{CD}_3)_2\text{SO}$	27.28

(b) dbbq derivatives		dbc										PPh		$^{31}\text{P}$	
Compound	Solvent	C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	C <sup>5</sup>	C <sup>6</sup>	C <sup>7</sup>	C <sup>8</sup>	C <sup>9</sup>	C <sup>10</sup>	C <sup>1'</sup>	Others	Solvent	$\delta$
$\text{P}(\text{dbc})_2\text{Br}$	$(\text{CD}_3)_2\text{SO}$	141.4	144.3	139.9	110.2	134.5	113.1	34.7	33.9	31.5	29.5			Toluene	-2.37
$\text{P}(\text{dbc})_2\text{Me}$	$(\text{CD}_3)_2\text{SO}$	142.2	145.3	140.1	110.8	135.3	113.4	34.4	33.8	31.4	29.9		29.2 (P-CH <sub>3</sub> )	thf	-22.61
$\text{P}(\text{dbc})\text{Cl}_3$	$\text{CH}_2\text{Cl}_2$	142.6	144.6	141.7	109.5	136.4	116.8	34.7	34.1	31.1	29.1			$\text{CH}_2\text{Cl}_2$	-10.34
$\text{P}(\text{dbc})\text{Br}_3$	$\text{CH}_2\text{Cl}_2$	142.3	144.6	140.5	109.4	136.5	116.9	34.7	34.5	31.3	29.0			$\text{CH}_2\text{Cl}_2$	-28.16
$\text{P}(\text{dbc})\text{ClPh}_2$	$\text{CDCl}_3$	140.0	144.5	139.1	117.1	130.1	120.3	35.5	34.2	31.4	29.7		128.6-133.0	thf	-3.60
$\text{P}(\text{dbc})\text{Ph}_3$	$\text{CDCl}_3$	144.1	145.1	140.3	105.8	132.4	114.0	34.8	34.1	31.9	29.7	142.5	127.6-132.4	Toluene	-22.58

\* thf = Tetrahydrofuran.

toluene ( $\text{Cl}_4\text{C}_6\text{O}_2$ , dbbq). The  $A_p$  values deduced from these spectra were 3.17 ( $\text{Cl}_4\text{C}_6\text{O}_2$ ), 3.10 ( $\text{Br}_4\text{C}_6\text{O}_2$ ) and 3.77 G (dbbq), and in this last system,  $A_H^4 = 3.77$  G; these results are very similar to those reported by Klimov *et al.* The signals appear to be infinitely stable at  $-60^\circ\text{C}$ , but disappear as the solution warms to *ca.*  $20^\circ\text{C}$ .

In addition to these and other studies<sup>18,19</sup> of *o*-quinone systems, there have been investigations of the corresponding reactions with *p*-quinones by a variety of techniques, again including ESR and UV-VIS spectroscopy.<sup>20,21</sup> The absence of clear evidence for the presence of  $\text{PX}_3^{+}$  species was taken to exclude the possibility of one-electron-transfer processes in these *p*-quinone studies, although the ESR evidence points to semiquinone radicals being formed. The present and earlier *o*-quinone studies clearly indicate that one-electron transfer does indeed take place in the first stages of the reaction between an *o*-quinone and  $\text{PX}_3$ . The identifiable coupling between the semiquinone and phosphorus, and the ligand dependence of  $A_p$ , favours the formation of an intermediate **1** stabilized by the solvent cage, and by the low temperature. There seems to be no reason to invoke the radical cation **2** proposed by Klimov *et al.*,<sup>17</sup> since there is no obvious oxidant to explain the electron-removal process postulated by these authors. On warming, **1** would easily and rapidly yield the phosphorane product by internal electron transfer and ring closure.

In the experiment involving elemental phosphorus there is again ESR evidence for a semi-*o*-quinone species coupled to phosphorus. Since the reaction only proceeds in the presence of

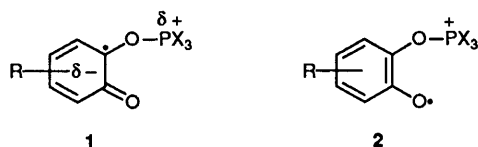
$\text{Br}_2$ , it is likely that this involves the intermediate formation of either  $\text{PBr}$  or  $\text{PBr}_3$  which then reacts with the *o*-quinone. We do not have any evidence at this point to allow these possibilities to be distinguished.

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