Electron Spin Resonance Spectra of Some Phosphole Oxide Anions

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Summary The formation of radical anions in the reactions of the phosphole oxides (I) and (II) with lithium, potassium, and sodium in both 1,2-dimethoxyethane and tetrahydrofuran have been studied using e.s.r. spectroscopy.

THE reactions of alkali metals with phosphine oxides to give radical anions have been studied using e.s.r. spectroscopy by various workers.[1,2,3] The radical formed has been ascribed to the monoanion only if no phenyl substituents are present; if such substituents are present, cleavage of a phenyl group may occur. Some confusion exists over the conditions for monoanion formation, the type of reaction occurring being dependent on the solvent and the alkali metal.

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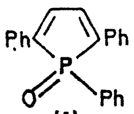
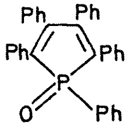
To clarify this situation, we have examined the reaction of the phosphole oxides (I) and (II) with lithium, potassium, and sodium in both 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF).



(I)



(II)

Reaction at room temperature in each case gave dark blue solutions exhibiting intense e.s.r. spectra. (I) gave spectra with a large hyperfine splitting characteristic of a phosphorus doublet together with some fine structure, the structure being dependent on the metal used (Figure 1—3).

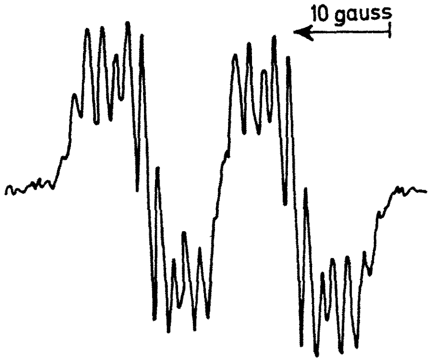


FIGURE 1. *E.s.r. spectrum from phosphole* (I) *on reaction with lithium.*

(II) gave, with all three metals, a featureless doublet with no fine structure. The spectra were identical in all the solvents. Owing to the complexity and poor resolution of the spectra, no analysis of the proton splittings was possible. The phosphorus hyperfine splittings are given in the Table.

	Ap (*gauss*)	
Metal	(I)	(II)
Li	14·95	15·25
K	16·22	16·40
Na	15·75	16·11

On further reaction of (I) and (II) with potassium, the solution became red-brown and a new, complex, asymmetric signal was obtained with no clear phosphorus doublet and with average line separations of *ca.* 1·75 G and with *g* 2·0027. The form of the spectrum varied from run to run. No further signals were seen with lithium or sodium.

The line separation and *g*-value of the secondary radicals formed on reaction with potassium are similar to those formed on reaction of potassium with certain phospholes at room temperature,[4] the radicals (of unknown structure) being formed after cleavage of a phosphorus–phenyl bond. No such cleavage was found on reaction with sodium or lithium.

The primary radicals therefore appear to be the monoanions, phenyl cleavage only occurring on further reaction with potassium. The reactions are therefore less complex than those occurring with phosphine oxides, as the formation of the monoanion is not dependent on the metal or the solvent. This increased stability of the monoanions may be ascribed to increased delocalisation of the unpaired electron over the phosphole ring; the large phosphorus splittings, which are of a similar magnitude to those found in the spectra of phosphorin anions,[5,6] support the idea of an aromatic phosphole ring.

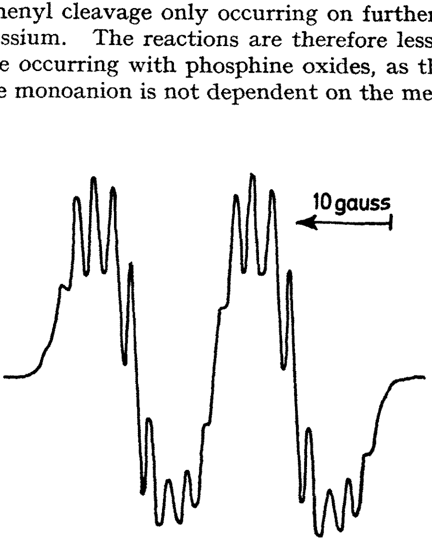


FIGURE 2. *E.s.r. spectrum from phosphole* (I) *on reaction with potassium.*

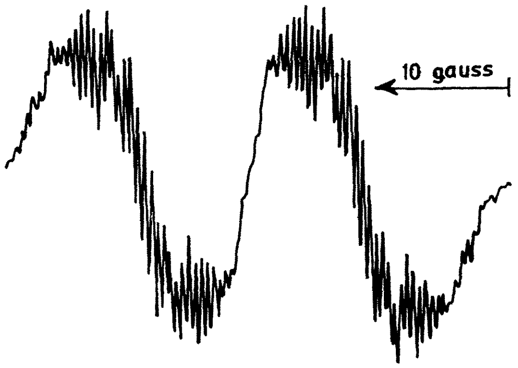


FIGURE 3. *E.s.r. spectrum from phosphole* (I) *on reaction with sodium.*

The effect of the sodium gegenion on the fine structure and the effect of each of the gegenions on the phosphorus splitting indicates a high degree of ion-pairing. The change in the fine structure may arise from gegenion splittings, from a change of the proton splittings, or both. The significant change in the phosphorus splitting indicates close association of the gegenion with the phosphorus nucleus, possibly *via* the phosphorus *d* orbitals. The e.s.r. spectra, however, do not provide any evidence for this.

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