

AN ESR STUDY OF THE REACTIONS OF ALKALI METALS WITH SOME PHOSPHOLES AT LOW TEMPERATURES

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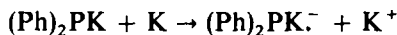
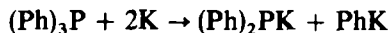
Abstract—The reactions of sodium, potassium and lithium at -80° with 1-methyl-2,5-diphenylphosphole, 1,2,5-triphenylphosphole and pentaphenylphosphole in ether solvents to give radical anions have been studied using ESR spectroscopy. Analysis of the spectra with the aid of spin density calculations shows that the monoanion radicals are formed initially. The reactions are compared with the corresponding reactions with phosphines, and the stability of the phosphole anions is interpreted in terms of an aromatic ring system. An unusual varying linewidth effect is also reported.

INTRODUCTION

THE REACTION of aryl phosphine oxides and phosphines with alkali metals to give coloured solutions was first noted by Hein *et al.*¹ Subsequent studies of the reactions involved with the phosphine oxides using ESR spectroscopy produced conflicting results,² but the main products of such reactions appear to be either the monoanion or a monoanion formed by cleavage of a phosphorus-phenyl bond.

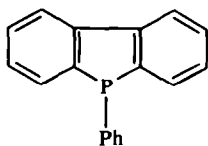
The first ESR study of the reaction of triphenylphosphine with alkali metals³ was reported as giving the monoanion in which the unpaired electron was confined to one phenyl ring.

On re-investigation of this reaction,⁴ a more careful study by Britt and Kaiser showed that the radical observed was in fact the phenyl-cleaved product, the reaction scheme being

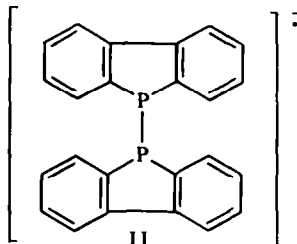


The radical formed on reaction with potassium was stable at -20° , however the radicals formed on reaction with sodium and lithium were unstable above -50° .

A similar stepwise reaction was also found⁵ with phenylbiphenylenephosphine (I), although the dimer-radical (II) was also formed.



I

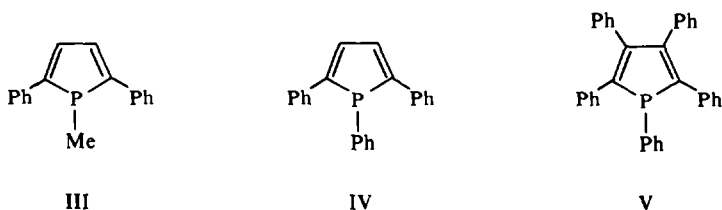


II

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The phosphine (I) is a particularly interesting species, since it may also be regarded as a dibenzophosphole. Experimental evidence seems to favour an aromatic-type phosphole ring system,^{6,7} although some doubt does remain. It may be expected that if I were reacting as a dibenzophosphole and not as a tertiary phosphine then the extra stability conferred by virtue of a delocalised system would prevent loss of a Ph group and perhaps result in the formation of the monoanion.

In order to investigate the possibility of monoanion formation in the phosphole system, we have studied the reaction in 1,2-dimethoxyethane (DME) and in tetrahydrofuran (THF) of Na, K and Li with 1-methyl-2,5-diphenylphosphole (III), 1,2,5-triphenylphosphole (IV) and pentaphenylphosphole (V).



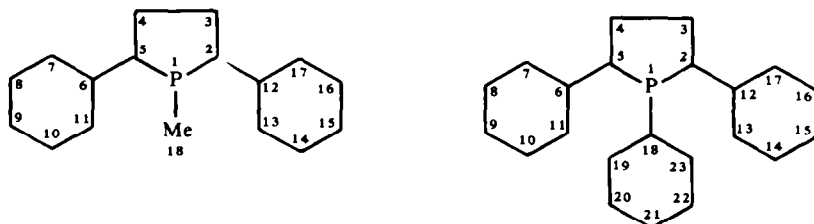
The reactions at room temperature have been reported previously.⁸ No reaction was apparent with Na or Li, but reactions of IV and V with K gave a complex series of radicals of unknown structure but which apparently results from cleavage of a Ph group and subsequent reaction of the Ph moiety. Phosphole III, with no P-Ph linkage, gave no signals. On prolonged contact with K, IV and V gave signals attributable to radicals of the type $R_2PK\cdot$, although no definite identification was possible.

RESULTS

The reactions with Li were very slow and no radicals were observed after several weeks. Reaction of Na and K with all three phospholes was rapid and gave intense blue solutions.

Reactions of III with Na and K in DME and Na in THF, gave an intense spectrum consisting of a well-resolved doublet, separation 23.5G, one component of which is shown in Fig. 1. Each component was split into at least 35 lines arranged in 6 main groups.

The large splitting can be assigned to the phosphorus nucleus, and analysis of the fine structure gave the assignments shown in Table 1, together with the spin densities calculated for the monoanion by the McLachlan method using the McConnell relation $a_i^H = Q_{CH}^H \rho_i^\pi$, with $Q_{CH}^H = 23G$. (The numbering system is shown below).



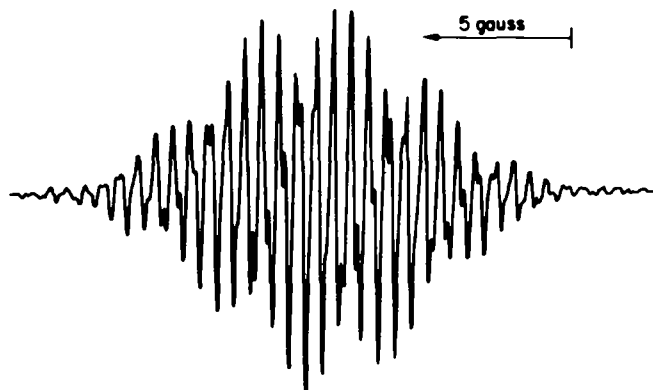


FIG 1. One component of the spectrum of (III) with K in DME at -60° .

Reaction of III with K in THF gave a much less intense signal which, although superficially similar to that above, was less well-resolved and exhibited an unusual temperature-dependent varying linewidth effect.

TABLE I

Phosphole	Position	$a_{\text{H}}^{\text{calc.}}$ (gauss)	$a_{\text{H}}^{\text{exp.}}$ (gauss)
III	3.4.18	2.60*	2.48 (6 lines)
	7. 9. 11. 13. 15. 17	1.34	1.31 (7 lines)
	8. 10. 14. 16	0.51	0.62 (5 lines)
IV	3. 4. 7. 9. 11. 13. 15. 17	2.30	2.26 (9 lines)
	8. 10. 14. 16	0.78	0.43 (5 lines)

* Calculated for the 3.4 positions only.

At -65° (Fig. 2a) the highfield component was much less well-resolved than the lowfield component, and was distinctly asymmetric. At -55° (Fig. 2b) both components had similar structures with the lowfield group of lower intensity. At -50° (Fig. 2c) the spectrum was almost the reverse of that at -65° , with nearly all the resolution on the lowfield group having been lost. At -40° the spectrum was again similar to that at -65° . In certain spectra run at -45° (Fig. 2d) in which both components were of similar appearance, there were clear indications of groupings similar to those in Fig. 1, with the same group separation. The large splitting constant varied from 24G at -65° to 28G at -30° .

Reaction of IV with both metals in DME and with IVa in THF gave an intense spectrum (Fig. 3) consisting again of a doublet, separation 26.5G, with some fine structure, although less well-resolved than that obtained from III. With K in THF, a similar spectrum was obtained but with the doublet separation 28.1G. The measured and calculated splitting constants are given in Table 1.

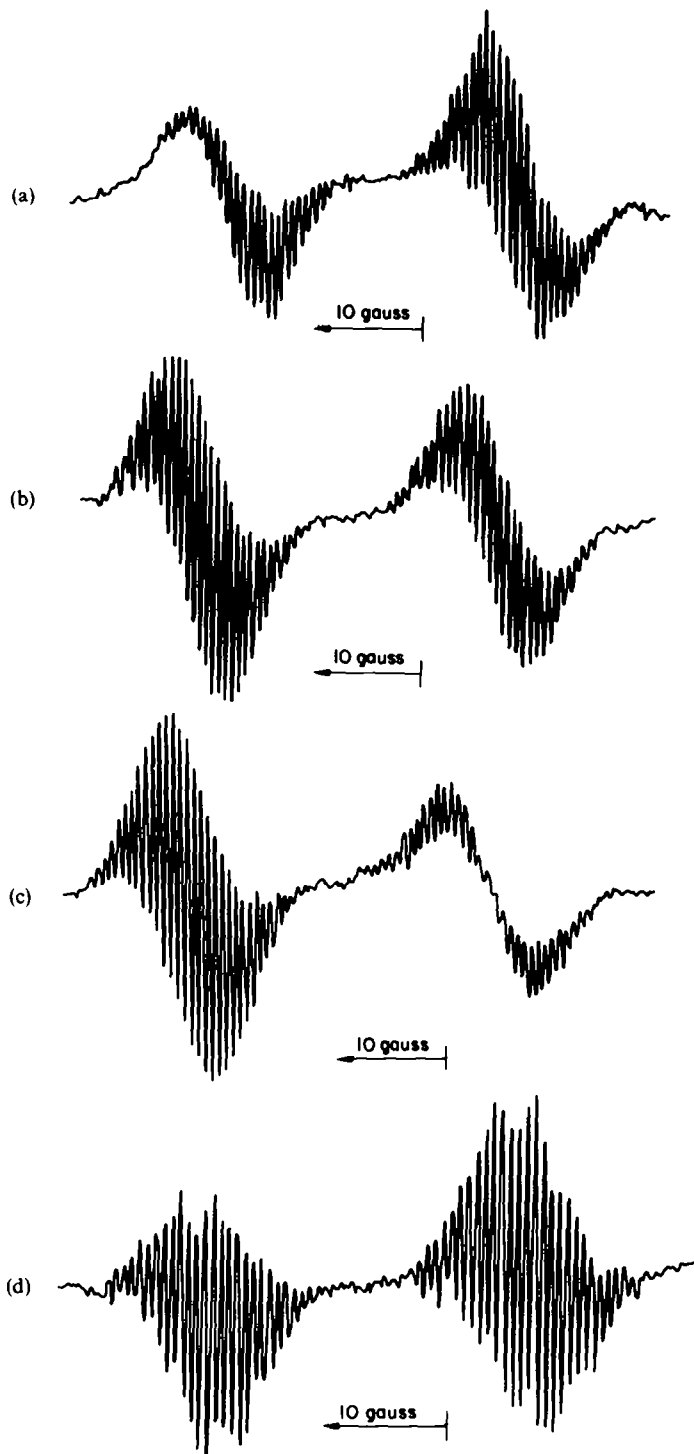


FIG 2. Spectrum of (III) with K in THF at: (a) -65° ; (b) -55° ; (c) -50° ; (d) -45° .

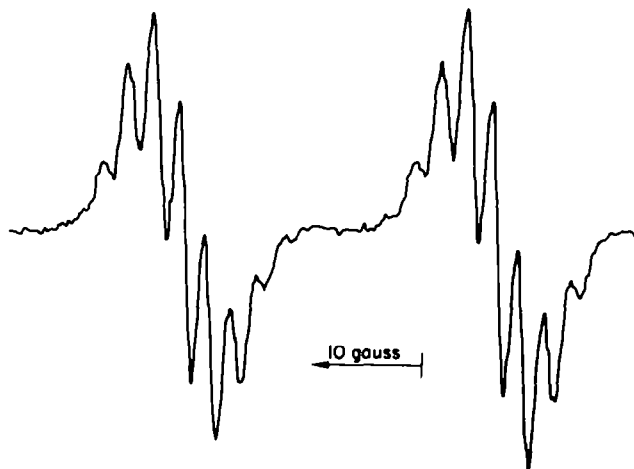


FIG 3. Spectrum of (IV) with K in DME at -60° .

Reaction of V with both Na and K in both DME and THF gave an intense, featureless doublet (Fig. 4), separation 31.3G. No analysis was attempted for this species.

All the radicals were stable for several days at -80° . Above -30° the radicals decomposed rapidly; ultimately, IV and V gave the radicals obtained on reaction at room temperature.

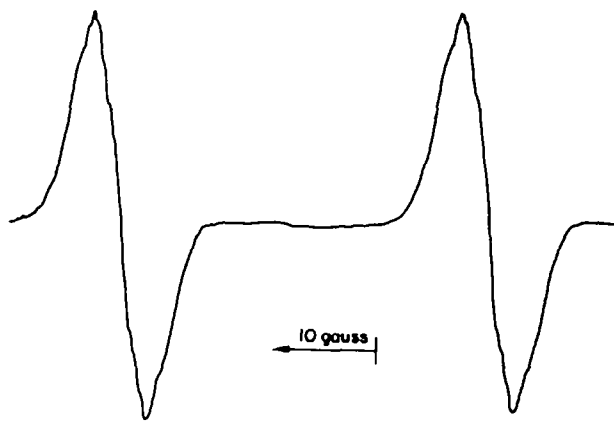


FIG 4. Spectrum of (V) with K in DME at -60° .

DISCUSSION

The good agreement of the measured splitting constants of III and IV with those calculated for the monoanions suggests that these radicals are, in fact, the monoanions, no Ph cleavage having occurred in IV. Although no calculations were possible, it seems likely that the radical from V is also the monoanion.

No signals analogous to those seen on reaction of IV and V at room temperature were observed until the temperature was raised above -30° . Thus the Ph cleavage reaction appears to be a second, distinct step, in contrast to the reaction with triphenylphosphine⁴ and with I.⁵

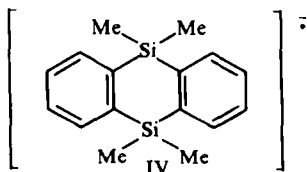
The large doublet splitting can be assigned to the phosphorus nucleus. The increase in value on going from III to IV to V despite the more extended delocalised system is consistent with the increased steric crowding round the phosphole ring pushing the Ph rings out of the plane and increasing localisation of the unpaired electron in the phosphole ring. In this respect it is interesting to note that no splittings are observed from the central Ph ring in IV, suggesting that this ring is pushed out of the plane, allowing the other two rings to remain in the plane.

The values of the phosphorus splittings are significantly higher than those observed in other organic π -radicals, including the phosphines, and in fact are very similar in magnitude to the splittings in the radical ions from the phosphorin series.¹⁰ As the phosphorin ring system may be regarded as a true aromatic system, analogous to that in pyridine, the large phosphorus splittings point to some aromatic character in the phosphole ring. This is supported by considerations of the Me splittings in III. If a Q_{PP}^P value of 25G is assumed,^{10d} the phosphorus splitting of 23.5G gives a phosphorus spin density of about 0.1. The Me splitting of 2.48G then suggests a $Q_{PCH_3}^H$ value of about 25G. The corresponding $Q_{CCH_3}^H$ values for aromatic systems lie in the range 18–38G,¹¹ and the corresponding Q_{NMe}^H value of 24.5G calculated for the 10-methylphenothiazine cation¹² is very close. Therefore the Me group would appear to be attached to a 'normal' aromatic ring.

The greater stability of the phosphole ring to one-electron addition compared with triphenylphosphine supports the above evidence for aromatic character in the phosphole system. In this respect, the cleavage reaction of I appears to be anomalous, this system reacting as a tertiary phosphine. There is, in fact, some thermochemical evidence that conjugation of phosphorus with the rest of this molecule is small.⁷

The complex varying linewidth effect found in the spectrum of III on reaction with K in THF apparently arises from ion-pairing of the monoanion of III with the K^+ gegenion. The similarity of the spectrum at -45° (Fig. 2d) with that in Fig. 1 suggests that these radicals have the same basic structure. Ion-pairing has been observed¹³ in the spectra of the anions of 1,2,5-triphenylphosphole oxide and pentaphenylphosphole oxide formed from reaction of the neutral molecules with K, Na and Li, and is also probably responsible for the increase of the phosphorus splitting constant of the anion of IV with K in THF compared with that in DME. No unusual effects were observed with V, probably due to the steric effect of the Ph rings not allowing close proximity of the gegenion with its solvent shell.

Rationalisation of the temperature dependent linewidth effect is, however, extremely difficult owing to the low intensities and the relatively poor resolution of the spectra. In a study of the 5,5,10,10-tetramethyl-5,10-dihydrosilanthrene anion (VI)¹⁴



alternating linewidths were ascribed to the K^+ gegenion oscillating between the silicon atoms, and being associated with the silicon d-orbitals. A similar mechanism may be operative here, with the K^+ gegenion taking up positions on either side of the phosphole ring and associating itself with the phosphorus d-orbitals. This mechanism would produce complex linewidth effects if the configuration about the phosphorus were non-planar, making the two sites non-equivalent. The situation would be further complicated by restricted rotation of the Me group.

EXPERIMENTAL

Spectra were recorded using a Decca Radar X3 spectrometer and a Newport Instruments Type F 11-inch electromagnet with a field homogeneity of 20 mG. A Decca variable temperature accessory MW235 was employed for the low-temperature work, and with this system the temperatures obtained were accurate to $\pm 2^\circ$.

DME and THF were purified by distillation from Na followed by degassing over LAH. Final drying was achieved by formation of the anthracene anion in the solvent.

K and Na were purified by distilling into the reaction vessel through two constrictions. Li was introduced into the vessel in the form of chips.

The reactions were carried out in a solid CO_2 /acetone bath at -80° and the spectra run at -60° .

McLachlan spin density calculations were performed on an IBM 360/44 computer using a programme written by D. H. Levy⁹ in Fortran II for an IBM 7090 and modified for the 360.

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