An Example of a Phosphoranyl Radical in a Tetrahedral Configuration

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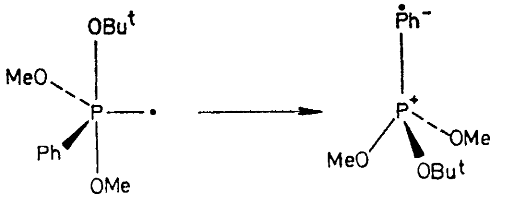
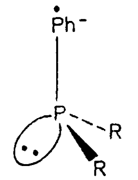
Summary Phosphoranyl radicals with an aryl ligand appear to have a relatively small phosphorus doublet splitting constant, indicating a relation between the a_P and the structure of these radicals.

Recent e.s.r. studies on a number of phosphoranyl radicals report direct evidence for the configuration of the phosphorus atom. The observed large a_P of 600—1300 G,[1] depending on the nature of the substituents, leads to the conclusion that the radicals have a trigonal bipyramidal configuration in which the odd electron is firmly located in an equatorial ligand.



(I)

We now report a phosphoranyl radical (I) related to the trimethoxy(t-butoxy)phosphoranyl radical observed by Davies and his co-workers,[2] in which a methoxy group has been replaced by a phenyl ring. This radical was prepared by photolysis of dimethyl phenylphosphonite in the presence of di-t-butyl peroxide in propane at −80 °C, and has a very small a_P (9·7 G). Using Q = 27·0 G for the phenyl protons (a_H^p = 9·7 G, a_H^m = 0·9 G, a_H^o = 5·5 G) and Q = 40·68 G for phosphorus,[3] due to spin polarization in the P–C$_{phenyl}$ σ-bond, a simple calculation showed that the odd electron is located to a large extent in the phenyl ring. This means that this radical is tetrahedral instead of trigonal bipyramidal.



R = OMe (II)
R = Me (III)

Other attempts to obtain similar phosphoranyl radicals, in which the phenyl group has been replaced by a tolyl or anisyl group, failed under these experimental conditions. In both cases we observed t-butyl radicals (10 lines,

$a_H = 22{\cdot}8$ G). This is caused by β-scission of the phosphoranyl radical.[4]

The dimethyl phenylphosphonite (II, $a_P = 9{\cdot}0$ G, $a_H^p = 5{\cdot}9$ G, $a_H^o = 3{\cdot}9$ G) and the dimethyl phenylphosphine anion radical[5] (III), obtained by electrochemical reduction of the parent compounds in DMF at −60 °C, are closely related to (I). The odd electron is again delocalized in the phenyl ring and the lone pair can be considered as a fourth ligand.

Work has also been done on spirophosphoranyl radicals in a tetrahedral configuration,[6] and here too relatively small a_P's with supplemental fine structure, due to aromatic protons, are observed. PPP–UHF calculations including the five *d*-orbitals of phosphorus, are in good agreement with the measured doublet splitting constants.

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