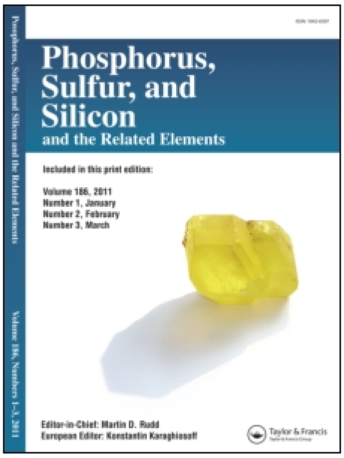

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Oxidation of Triarylphosphines, Tetraaryldiphosphine and Cyclopolyphosphanes. Electrochemical and ESR Studies

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OXIDATION OF TRIARYLPHOSPHINES, TETRAARYLDIPHOSPHINE AND CYCLOPOLYPHOSPHANES. ELECTROCHEMICAL AND ESR STUDIES.

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Abstract Electrochemical oxidation of a series of triarylphosphines and tetraaryldiphosphines was investigated by pulse voltammetry and cyclic voltammetry. Phosphines and diphosphines bearing only very bulky aryl groups (Mesityl, Duryl, Xylyl) show a reversible one-electron oxidation process. The resultant cation radicals are very persistent and their ESR features are easily obtained at room temperature. Unlike their nitrogen analogs, triarylphosphoniumyl radicals and tetraaryldiphospine cation radicals both exhibit a pyramidal geometry.

INTRODUCTION

Phosphoniumyl radicals, $L_3P^{+\bullet}$, are involved in many chemical or electrochemical processes. These species are highly reactive and very short-lived in solution, thus making their ESR study very difficult. Most of the ESR studies dealing with $L_3P^{+\bullet}$ have been performed in matrices[1] and the radicals were generated by gamma or X irradiation of the parent L_3P compounds.
We have studied the electrochemical oxidation of a series of triarylphosphines, tetraaryldiphosphines and two cyclopolyphosphanes in order to estimate the influence of steric crowding both on the oxidation potentials of the starting materials and on the half-life of the resultant cationic species.

ELECTROCHEMICAL OXIDATION

The oxidation was studied by pulse voltammetry, P.V., and cyclic voltammetry, C.V., in butyronitrile or methylene chloride solution at room temperature using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The results obtained appear in Table 1.

TABLE 1 Oxidation potentials[a] (P.V.) for some triarylphosphines ,tetraaryldiphosphines and cyclopolyphosphanes.

Compound[c]	$E_{1/2}$	I_{cp}/I_{ap} (C.V.)	Scan rate ($V.s^{-1}$)
Ph_3P ,1,	1.33	0	100
Ph_2PMes ,2,	1.06	0	100
$PhPMes_2$,3,	0.92	0.23	5
$PMes_3$,4,	0.75	0.87	0.1
$PDur_3$,5,	0.64	0.93	0.1
PXy_3 ,6,	0.86	1.0	0.1
Ph_2PPPh_2 ,7,	1.1	0	100
Xy_2PPXy_2 ,8,	0.77	0.92	0.1
Mes_2PPMes_2 ,9,	0.67	0.95	0.1
E_2PPE_2 ,10,	0.56	1.0	0.1
$(BisP)_4$,11,	0.67[b]	1.0	0.1
$(BisP)_3$,12,	1.24[b]	0	100

a : in volts / s.c.e. b : in methylene chloride c : Mes = mesityl, Dur = duryl, Xy = xylyl, E = 2,4,6,- triethylphenyl .

peak appearing at the less anodic potential is always the more intense. The one-electron nature of the reversible oxidation processes was demonstrated by, (i) a peak separation close to that anticipated for a Nernstian process (58 mV), (ii) comparison with a reference compound (ferrocene) and (iii) by bulk coulometry experiments[2] for compounds **4**, **5**, **9** **and** **10**.

There is a significant decrease in the oxidation potentials as the number of bulky substituents attached to the phosphorus increases. This result could be accounted for by the flattening of the pyramidal geometry of the starting compounds[3] induced by the bulky substituents. This flattening is accompanied by an increase of the 3p character of the SOMO thus making easier the removal of an electron.

On the other hand the tetraaryldiphosphine radical cations are stabilized by spin and charge delocalization and thus the tetraaryldiphosphine are easier to oxidize than the corresponding

TABLE 2 E.S.R. features of cation radicals of triarylphosphines, tetraaryldiphosphines and cyclopolyphosphanes.

Cation radical[a]	A_P	**g**	**T (K)**
$Ph_3P^{+\bullet}$	291.0	2.0040	73
$PhPMes_2^{+\bullet}$	278.7	2.0041	293
$PMes_3^{+\bullet}$	240.1	2.0052	293
$PXy_3^{+\bullet}$	244.1	2.0050	288
$PDur_3^{+\bullet}$	236.8	2.0052	293
$Xy_2PPXy_2^{+\bullet}$	171	2.0060	291
$Mes_2PPMes_2^{+\bullet}$	170	2.0063	290
$(BisP)_4^{+\bullet}$	56.4	2.0103	293
$(BisP)_3^{+\bullet}$	48.3	2.0095	253

a : Bis = $HC(SiMe_3)_2$

phosphines.
Tetrabisylcyclotetraphosphane, **11**, and tribisylcyclotriphosphane, **12**, also exhibit two oxidation peaks. However, whereas the first oxidation process is relatively easy and completely reversible for **11**, it occurs at a much more anodic potential and is irreversible at room temperature for **12**.

ESR STUDIES

It is worth mentioning that while the first oxidation process is completely irreversible for the triphenylphosphine, **1** and the tetraphenyldiphosphine **7** it becomes partially or completely reversible by increasing the number of bulky substituents attached to the phosphorus atoms. This result indicates that for the bulky phosphines and diphosphines the primary oxidation process generates persistent cationic species and actually acquisition of liquid solution ESR data was possible for all the studied compounds except **1** and **7**. The ESR features of some typical cation radicals observed are listed in Table 2.
The principal feature of the ESR spectra of triaryphosphoniumyl radicals[4] comprises a doublet A_P = 290 to 236 G, g =

2.0040 to 2.0052. The relatively large isotropic phosphorus splitting indicates that unlike the triarylammoniumyl radicals which are planar the phosphorus analogs retain a pyramidal geometry which is progressively flattened as the steric hindrance of the aryl substituents increases.

For cation radicals derived from **4, 5 and 6** the anisotropic components of the hyperfine splitting tensor were deduced from the frozen solution ESR spectra . The 3s and 3p character of the SOMO's were estimated from the isotropic and anisotropic components of the phosphorus splitting thus permitting to calculate a bending angle close to 10° which is only half the value in the starting materials.

Owwing to the magnitude of the phosphorus hyperfine splitting, second order splitting was clearly resolved for radicals derived from **8 and 9**. The resultant four line spectra yielded A_P close to 170 G. and a g value close to 2.0060. The large phosphorus splitting observed for these radicals clearly indicates that the phosphorus centers are highly pyramidal thus suggesting that the energy required to make the two phosphorus centers planar is too large to be compensated by any three electron stabilization.

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