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Synthesis and Reactivity of Cyclic (R_3P-PR_3) Dications

Roger Alder^a; Chris Harris^a

^a School of Chemistry, University of Bristol, Bristol, U.K.

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SYNTHESIS AND REACTIVITY OF CYCLIC $(R_3P-PR_3)^{++}$ DICATIONS

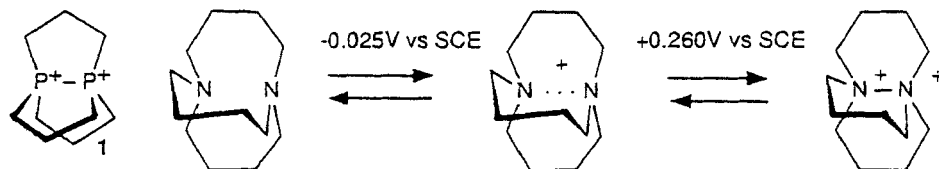
ROGER ALDER AND CHRIS HARRIS

School of Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

Abstract The synthesis and reactivity of a novel bicyclic system containing directly bonded phosphonium centres is discussed.

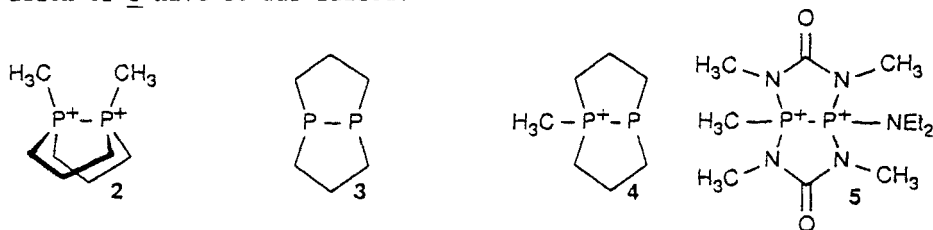
INTRODUCTION

1,5-Diphospha[3.3.3]propellane dication salts, 1, and related species, may have a rich redox chemistry comparable to that observed for related nitrogen species.¹



SYNTHESIS

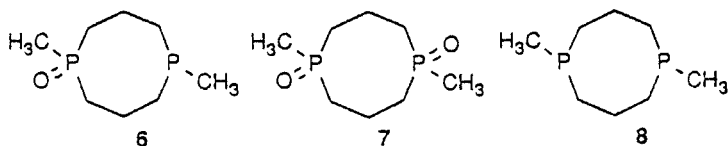
Alkylation of diphosphine 3² to the known monomethylated ion 4² followed by second alkylation with methyl trifluoromethanesulphonate, or direct dialkylation of 3 with methyl trifluoromethanesulphonate, gives 2 in quantitative yield. Attempts to prepare 1 by cycloalkylation of 3 have so far failed.



The synthesis and properties of 2 may be compared with those of 5,³ the only compound with directly bonded phosphonium centres previously reported.

Reactivity of 2

Compound 2 is exceptionally sensitive to water. Hydrolysis cleaves the P-P bond and gives the diphosphine mono-oxide 6. Compound 6 can be converted into 7 or 8.



High field ^1H -NMR studies carried out on diphosphine 8 show that the methyl groups take up a transconformation, which indicates that the hydrolysis of dication 2 must proceed via apical attack of water.

REFERENCES

1. R.W. Alder, *Tetrahedron*, 1990, 46, 683-713.
2. R. Issleib and P. Thoraus, *Phosphorus and Sulphur*, 1978, 4, 137-144.
3. D. Schomberg, G. Bettermann, L. Ernst, and R. Schmutzler, *Angew. Chem. Int. Ed. Engl.*, 1985, 24, 975.