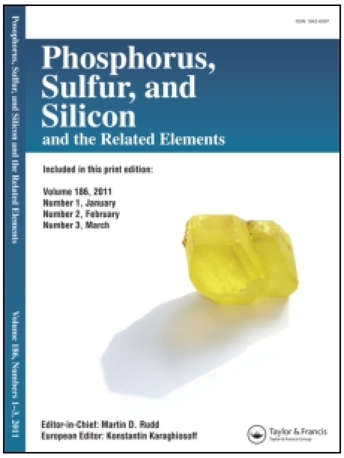

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SOME REACTIONS OF DIPHOSPHENES AND RELATED SPECIES

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Abstract Some reactions of diphosphenes and the related species involving oxidation, reduction, alkylation, sulfurization, and $^6\eta$-coordination are described.

INTRODUCTION

Phosphorus(III) compounds with a p_π-p_π bonding have been of interest because of their unusual chemical and physical nature.[1] By introducing an extremely bulky group, 2,4,6-tri-*tert*-butylphenyl (hereafter, Ar stands for $2,4,6\text{-Bu}^t{}_3C_6H_2$), we have been successful in preparation and characterization of some unusual phosphorus compounds.[2]

PREPARATION OF SOME UNSYMMETRICAL DIPHOSPHENES

We reported the preparation and characterization of a symmetrical diphosphene (1a) *via* the dechlorination of the corresponding phosphonous dichloride (2a) with magnesium metal,[3] δ_P 492.4 ppm.

$$\underset{(2a)}{ArPCl_2} \quad + \quad Mg \longrightarrow \underset{(1a)}{ArP=PAr}$$

Alternatively, the symmetrical 1a and unsymmetrical diphosphenes (1b-d) were prepared by the dehydrochlorination reaction of the phosphine (3) with the corresponding phosphonous dichlorides (2a-d) in the presence of a base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or triethylamine (a: Ar' = Ar = $2,4,6\text{-Bu}^t{}_3C_6H_2$; b: Ar' = $2,4\text{-Bu}^t{}_2\text{-}6\text{-MeC}_6H_2$; c: Ar' = $2,4,6\text{-Me}_3C_6H_2$; d: Ar' = C_6H_5).[4]

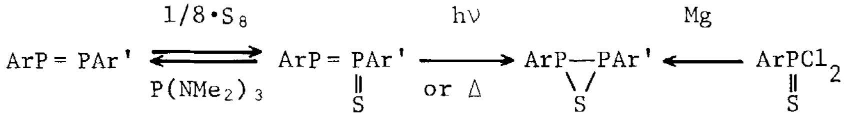
$$\underset{(3)}{ArPH_2} \quad + \quad \underset{(2a\text{-}d)}{Ar'PCl_2} \xrightarrow{\text{base}} \underset{(1a\text{-}d)}{ArP=PAr'}$$

^{31}P NMR spectra of 1a-d were recorded to show that the chemical shifts of the diphosphenes are extremely low (δ_P 450 - 550 ppm) with large spin-spin coupling constants $^1J_{PP}$ (550 - 585 Hz for 1b-d) indicating a very strong interaction between the adjacent phosphorus atoms.

Raman and IR spectra of 1a-d showed a band at 620 - 610 cm^{-1} tentatively assignable to $\nu_{P=P}$. The ESCA spectrum[5] of 1a indicated that the phosphorus 2p binding energy $E_b(P_{2p})$ is the lowest among those for the common organophosphorus compounds (130.4 eV). *ab initio* Calculation of HP = PH (44-31G*) with polarization function indicated that the P-P bond has normal double bond character[4] and the energy-optimized geometry agreed with the observed X-ray structure of 1a (r_{PP} = 2.03 Å).

REACTION OF DIPHOSPHENES AND RELATED SPECIES

The phosphonothioic dichloride 6 was allowed to react with magnesium unexpectedly to give a thiadiphosphirane 4a, which is extraordinarily stable to air, light, and heat. The structure of 4a was confirmed by an X-ray analysis (r_{PP} = 2.25 Å, r_{PS} = 2.10 Å), δ_P -65.1 ppm.[6]



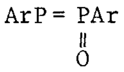
$$\mathrm{ArP{=}PAr'}\ \underset{\mathrm{P(NMe_2)_3}}{\overset{1/8\cdot\mathrm{S_8}}{\rightleftarrows}}\ \mathrm{ArP{=}}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{P}}\mathrm{Ar'}\ \xrightarrow[\text{or }\Delta]{h\nu}\ \underset{\underset{\mathrm{S}}{\backslash\,/}}{\mathrm{ArP{-}PAr'}}\ \xleftarrow{\mathrm{Mg}}\ \mathrm{Ar}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{P}}\mathrm{Cl_2}$$

(1a-c) (5a-c) (4a-c) (6)

When the diphosphene 1a was allowed to react with elemental sulfur in triethylamine, a yellow intermediate 5a was obtained which isomerized to 4a by heat or light. The structure of 5a was analyzed by means of NMR, IR, UV, and finally by X-ray analysis, δ_P 255.8 ppm and 247.8 ppm with $^1J_{PP}$ = 629.9 Hz; r_{PP} = 2.05 Å and r_{PS} = 1.93 Å.[7] The monosulfide 5a reacted with hexamethylphosphorous triamide to give 1a, whereas 4a resisted the desulfurization reaction. Very similarly, some unsymmetrical thiadiphosphiranes 4b,c were prepared from the corresponding unsymmetrical diphosphenes 1b,c *via* 5b,c.[8]

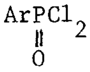
4b,c: δ_P -67 - -82 ppm with $^1J_{PP}$ = 233 - 245 Hz; 5b,c: δ_P 250 - 228 ppm, $^1J_{PP}$ = 604 - 625 Hz.

The diphosphene 1a was allowed to react with *m*-chloroperbenzoic acid to give 3 and a mixed anhydride which indicated the intermediacy of a diphosphene 1-oxide 7.[9] Alternatively the phosphonic dichloride 8 was allowed to react with magnesium to give an orange crystal, 7, the structure of which was identified by spectroscopic analyses, δ_P 206.5 and 69.8 ppm with $^1J_{PP}$ = 683.6 Hz. The oxide 7 was very sensitive to moisture giving the phosphine 3 and phosphonic acid 10.



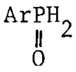
$\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{{=}PAr}$

(7)



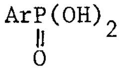
$\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{Cl_2}$

(8)



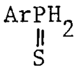
$\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{H_2}$

(9)



$\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OH)_2}$

(10)



$\mathrm{Ar}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{P}}\mathrm{H_2}$

(11)

The phosphine 3, which was alternatively and more conveniently prepared from the reaction of 2a with $LiAlH_4$, reacted with one equivalent of H_2O_2 to give the corresponding primary phosphine oxide 9, δ_P -10.0 ppm, $^1J_{PH}$ = 490.7 Hz.

Similarly the phosphine 3 reacted with elemental sulfur[10] to give the corresponding primary phosphine sulfide 11 as the first stable primary phosphine sulfide, δ_P -24.7 ppm with $^1J_{PH}$ = 466.3 Hz.

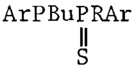
The diphosphene 1a reacted with lithium aluminum hydride or Vitride to give diastereomeric mixture of diphosphanes 12A,B, *dl* as major and *meso* as minor, which were analyzed by the coupling constants in NMR and the hyper fine splitting constants of ESR signals observed during the reaction in terms of angular interactions of the conformers.[11]

ArPHPHAr

(12A,B)

ArPBuP(R)Ar

(13)



$\mathrm{ArPBu}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{P}}\mathrm{RAr}$

(14)

$(\mathrm{ArP{=}PAr})(\mathrm{Cr(CO)_3})_n$

(15, n = 1; 16, n = 2)

The diphosphene 1a reacted with butyllithium to give a phosphinophosphide which afforded dialkylated diphosphanes 13 after quenching the phosphide with various alkyl halides and **13** were monosulfurized with sulfur to give **14**.[12]

The diphosphene **1a** reacted with hexacarbonylchromium(0) in refluxing dioxane to give the mono η^6-$Cr(CO)_3$ complex (**15**), δ_P 503.2 ppm and 475.6 ppm with $^1J_{PP} = 590.8$ Hz and the bis η^6-$Cr(CO)_3$ complex (**16**), δ_P 499.7 ppm.[13]

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