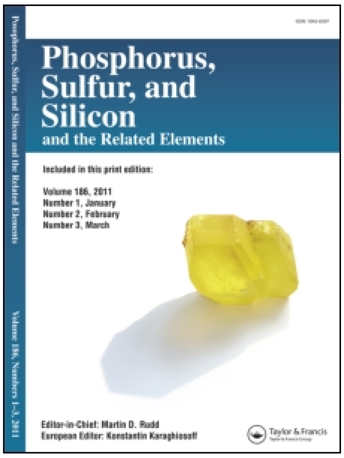

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Some New Protective Groups for Stabilizing Low Coordinated Phosphorus Compounds

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SOME NEW PROTECTIVE GROUPS FOR STABILIZING LOW COORDINATED PHOSPHORUS COMPOUNDS

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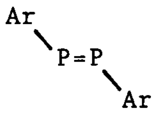
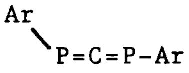
Abstract Sterically stabilized diphosphenes and 1,3-diphosphaallenes by 2,4-di-t-butylphenyl or 2,4,6-tri-t-pentylphenyl groups were prepared.

INTRODUCTION

2,4,6-Tri-t-butylphenyl (Ar) group is one of the most useful protective groups for stabilizing low coordinated phosphorus compounds of current interest. For example, unusual organophosphorus compounds such as diphosphene (**1a**; ^{31}P NMR, δ_P 490.3)[1] and 1,3-diphosphaallene (**2a**; δ_P 141.7)[2] have been prepared and isolated as stable compounds.



(**1a**)

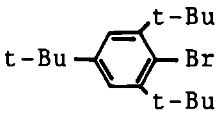


(**2a**)

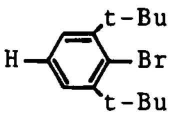
We were interested in some other sterically bulky groups than Ar which might serve as alternative protective groups for kinetically stabilized multiple bonded compounds involving heavier main group elements.

PREPARATION OF 2,6-DI-t-BUTYLBROMOBENZENE

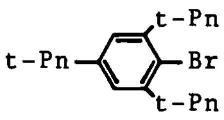
Attempts were made to remove the p-t-butyl group from 2,4,6-tri-t-butylbromobenzene (**3a**). Fuming nitric acid in acetic acid was allowed to react with (**3a**) resulting in the ipso nitration at the p-position to give 2,6-di-t-butyl-4-nitrobromobenzene, which was reduced to the corresponding aniline. The aniline was deaminated to afford 2,6-di-t-butylbromobenzene (**3b**) (AxBr; x stands for xylyl).[3]



(**3a**)

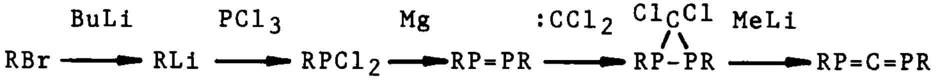


(**3b**)



(**3c**)

2,6-Di-t-butylphenylphosphonous dichloride (**4b**; δ_P 148.9) was prepared starting from (**3b**) by the lithium-halogen exchange followed by quenching with phosphorus trichloride.



$$\underset{(3)}{RBr} \xrightarrow{BuLi} RLi \xrightarrow{PCl_3} \underset{(4)}{RPCl_2} \xrightarrow{Mg} \underset{(1)}{RP{=}PR} \xrightarrow{:CCl_2} \underset{(6)}{\overset{Cl\ C\ Cl}{RP-PR}} \xrightarrow{MeLi} \underset{(2)}{RP{=}C{=}PR}$$

a:R=2,4,6-$Bu^t{}_3C_6H_2$, **b**:R=2,6-$Bu^t{}_2C_6H_3$, **c**:R=2,4,6-$Pn^t{}_3C_6H_2$

When the dichloride (**4b**) was allowed to react with magnesium metal, the diphosphene (**1b**; δ_P 488.7) was obtained as a stable P=P compound. The diphosphene (**1b**) was then allowed to react with dichlorocarbene to give the corresponding diphosphirane (**6b**; δ_P -67.1), which was converted by methyllithium[4] to 1,3-bis(2,6-di-t-butylphenyl)-1,3-diphosphaallene (**2b**; δp 142.4). The 2,6-di-t-butylphenyl moiety is more simplified protective group than 2,4,6-tri-t-butylphenyl and shows that o-t-butyls are essential to function largely in stabilizing multiple bonds involving low coordinated phosphorus atoms.

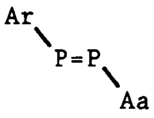
PREPARATION OF 2,4,6-TRI-t-PENTYLBROMOBENZENE

1,3,5-Tri-t-pentylbenzene was prepared by the conventional Friedel-Crafts reaction of benzene with t-pentyl chloride catalyzed by aluminum chloride and the bromide (**3c**) (AaBr; a stands for amyl) was obtained by the bromination of the benzene with bromine using trimethyl phosphate as a solvent. The corresponding phosphonous dichloride (**4c**; δp 149.3) was prepared in a similar manner described above. The dichloride (**4c**) gave the diphosphene (**1c**; δp 490.8) as a very stable diphosphene. The diphosphirane (**6c**; δp -69.0) was similarly obtained by the reaction of (**1c**) with dichlorocarbene and was converted to the corresponding diphosphaallene (**2c**; δp 142.2) stabilized by the 2,4,6-tri-t-pentylphenyl group. The reaction of (**1c**) with dichlorcarbene was reluctant compared with that of (**1a**) indicating that Aa is more sterically bulky than Ar from a point of view of reactivity as well as molecular model consideration.

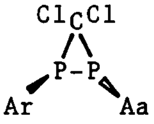
UNSYMMETRICAL DIPHOSPHENE AND DIPHOSPHAALLENE

The unsymmetrical diphosphene bearing Ar and Aa groups was prepared by the reaction of a mixture of (**4a**) and (**4c**) with magnesium together with symmetrical diphosphenes (**1a**) and (**1c**). Those three diphosphenes thus obtained were separated through column chromatography over siliga gel using pentane as an eluent.

$(4a) + (4c) + 2Mg \longrightarrow (8) + (1a) + (1c)$



(8)



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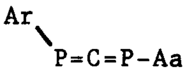

(10)

The unsymmetrical diphosphene (**8**; δ_P 491.2, 489.9 ^1J 582.9 Hz) was then converted to the corresponding diphosphirane (**9**; δ_P -67.8, -68.4, ^1J 137.7 Hz), which afforded the unsymmetrical 1,3-diphosphaallene (**10**; δ_P 142.5, 142.4, ^2J 18.5 Hz) by the reaction with methyllithium. The coupling constant $^2J_{P=C=P}$ for 1,3-diphosphaallene was observed for the first time.

CONCLUSION

The diphosphenes and 1,3-diphosphaallenes with Aa or Ax thus obtained were stable enough to permit isolation and were fully spectroscopically characterized. Both Ax and Aa groups have turned out to be also useful and promising as well as Ar for the further studies of chemistry on multiple bonding involving heavier main group elements of current interest.

REFERENCES

1. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981); 104, 6167 (1982).
2. M. Yoshifuji, K. Toyota, and N. Inamoto, J. Chem. Soc., Chem. Commun., 1984, 689; H. H. Karsch, H.-U. Reisacher, and G. Müller, Angew. Chem., Int. Ed. Engl., 23, 618 (1984).
3. W. Rundel, Chem. Ber., 101, 2956 (1968).
4. M. Yoshifuji, S. Sasaki, T. Niitsu, and N. Inamoto, Tetahedron Lett., 30, 187 (1989); M. Gouygou, C. Tachon, R. El Ouatib, O. Ramarijaona, G. E.-Moghadam, and M. Koenig, Tetrahedron Lett., 30, 177 (1989).