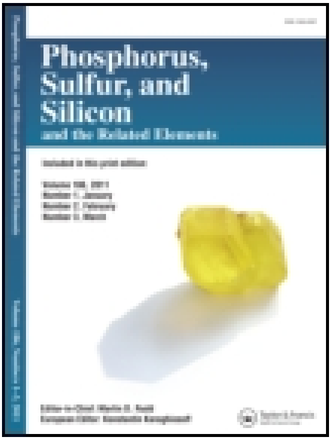

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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New Type of Phosphorus Compounds Containing Sulfur and Selenium

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To cite this article: Masaaki Yoshifuji (1999) New Type of Phosphorus Compounds Containing Sulfur and Selenium, Phosphorus, Sulfur, and Silicon and the Related Elements, 144:1, 557-560, DOI: 10.1080/10426509908546305

To link to this article: http://dx.doi.org/10.1080/10426509908546305

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 557-560
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New Type of Phosphorus Compounds Containing Sulfur and Selenium

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New type of phosphorus compounds containing the P=S or P=Se groups were prepared by utilization of sterically protecting group carrying amino groups with the aid of intramolecular coordination effect.

Keywords: intramolecular coordination; organophosphorus compounds

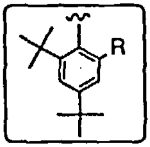
INTRODUCTION

Various types of low-coordinated phosphorus compounds have been isolated, by utilizing the 2,4,6-tri-*t*-butylphenyl group (abbreviated as Ar) as a kinetically stabilizing group. Concerning the chemistry of P=S and P=Se compounds, we introduced the stabilizing aromatic groups, bearing a functional group with coordination ability at their *o*-position, estimating the through-space electronic effect of the lone pair on the phosphorus. Chalcogenophosphoranes [$R\text{-}P(=X)_2$] and chalcogenophosphines [R-P(=X)] are among those and are predicted to be reactive due to their polarized canonical structures with positively charged phosphorus and negatively charged chalcogen atom.

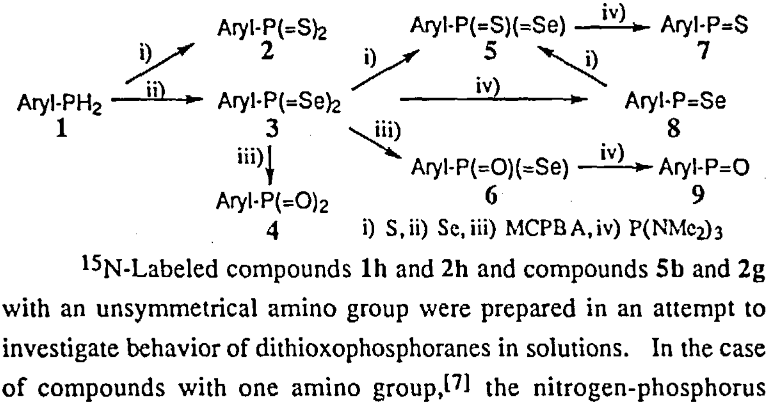
Sterically Protecting Groups Carrying Amino Group

By use of this kind of stabilizing groups carrying nitrogen, we have isolated dichalcogenophosphoranes and chalcogenophosphines, starting from the corresponding phosphonous dichlorides, and they were analyzed by NMR, IR, as well as X-ray crystallography. In the case of

Mx, (Aryl, R = a),[1,2] compounds **2**, **3**, **5**, **7**, **8** were obtained. Similarly, in the case of **d—f**,[3–6] the reactions of the corresponding phosphines **1** with sulfur or selenium gave the desired dichalcogenophosphoranes **2** or **3** as very stable compounds. These compounds were analyzed by NMR as well as X-ray crystallography, indicating that the lone pair electrons coordinate on the phosphorus atom, intramolecularly.

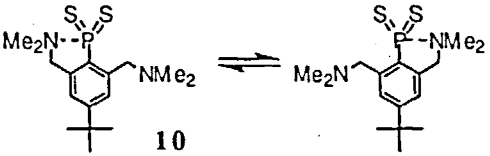


Aryl
a: NMe_2
b: $NMe\textit{i}Pr$
c: $N(CH_2)_5$
d: CH_2NMe_2
e: CMe_2NMe_2
f: $CMe_2CH_2NMe_2$
g: $CH_2NMe\textit{i}Pr$
h: $CH_2{}^{15}NMe_2$
i: CH_2OMe
j: CH_2SMe
k: CH_2SeMe
x: OMe
y: O*i*Pr
z: OPh



i) S, ii) Se, iii) MCPBA, iv) $P(NMe_2)_3$

^{15}N-Labeled compounds **1h** and **2h** and compounds **5b** and **2g** with an unsymmetrical amino group were prepared in an attempt to investigate behavior of dithioxophosphoranes in solutions. In the case of compounds with one amino group,[7] the nitrogen-phosphorus coordination seems to be strong and no appreciable exchange reaction appeared to occur on the NMR time scale at room temperature, whereas such exchange reaction was fast in **10** with two amino groups.



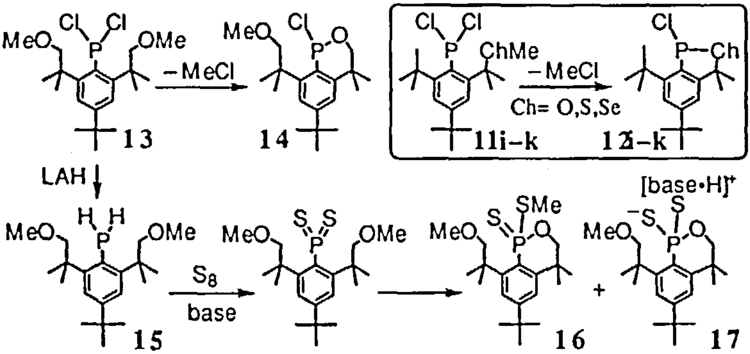
10

Utilizing an efficient coordination ability of **d—f**, compounds **4** were formed as crystals by oxidation of diselenoxophosphoranes **3** with

MCPBA. Furthermore, the deselenation reaction with $P(NMe_2)_3$ was applied to prepare chalcogenophosphines **7**—**9**, starting from the corresponding dichalcogenophosphoranes **5**, **3**, and **6**, respectively. Compounds **8d**—**f** and **7d**—**f** are stable toward oxygen in the air, while oxophosphines **9d**—**f** were not stable enough toward aerial treatment and gave the corresponding phosphinic esters with alcohols.

Sterically Protecting Groups Carrying Alkoxy Group

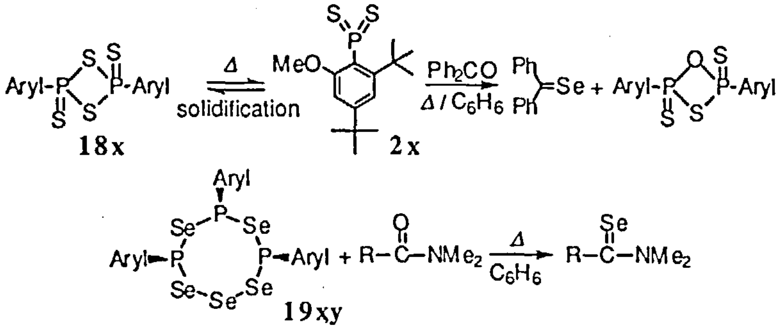
On the other hand, as for the sterically protecting groups **i**—**k**, the corresponding phosphonous dichloride **11** were not stable during the isolation process, due to the intramolecular cyclization reactions with elimination of methyl chloride to give **12**.



Furthermore, the sulfurization reactions with elemental sulfur of the corresponding primary phosphines **1i**—**k** failed to give the desired dichalcogenophosphoranes **2i**—**k**. At −78 °C, the primary phosphine **15** was prepared and the sulfurization reaction in the presence of organic bases such as DBU, gave cyclization reaction product **16** and **17**.

Heterocycles as Sulfurization and Selenation Reagents

By use of heterocyclic compounds containing phosphorus and sulfur or selenium, with protecting group x,y carrying alkoxy groups, were used as sulfurization or selenation reactions.[8,9] Reaction of **18x** with benzophenone in refuxing benzene gave thiobenzophenone, while the reaction of **19x,y**[10] with amides gave selenoamides under similar conditions. Thermolysis of **18** and **19** appeared to generate intermediarte dichalcogenophosphorane and chalcogenophosphine.



Acknowledgments

The support of our work by the Ministry of Education, Science, Sports and Culture, Japanese Government, is greatly acknowledged. The author thanks those whose names are given in the list of references for their dedicated collaboration.

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