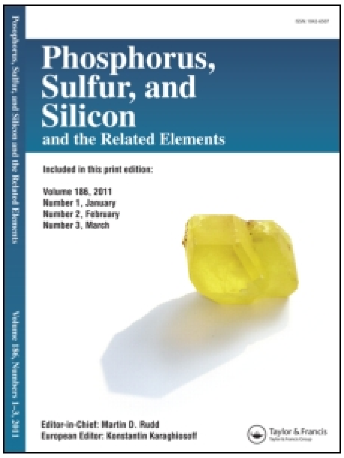


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Studies on Phosphenium Cations

Jinglin Zhang[a]; Tianbao Huang[a]; Haiyan Lu[a]
[a] Institute of Organic Synthesis, Central China(Huazhong) Normal University, Hubei, China

To cite this Article Zhang, Jinglin , Huang, Tianbao and Lu, Haiyan(1993) 'Studies on Phosphenium Cations', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 79 — 82

To link to this Article: DOI: 10.1080/10426509308032363

URL: http://dx.doi.org/10.1080/10426509308032363

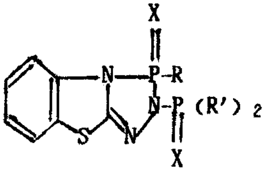
Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 79–82
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES ON PHOSPHENIUM CATIONS

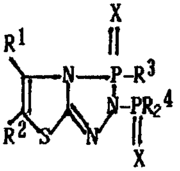
JINGLIN ZHANG, TIANBAO HUANG AND HAIYAN LU
Institute of Organic Synthesis, Central China(Huazhong) Normal University,
Wuhan, Hubei, 430070, China

INTRODUCTION

Corresponding phosphenium cations which could not be formed from 2, 3-2(H) −1, 3-benzothiazolo or 1, 3-thiazolo] -[2, 3-d] , [1, 2, 4, 3] -triazaphospholes, as I and II, were firstly synthesized in our lab.[1-4]



I

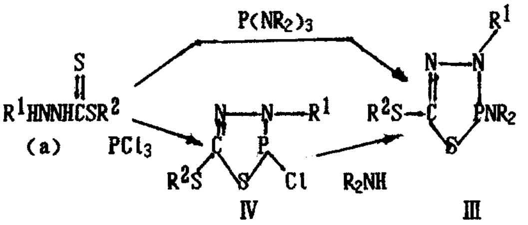


II

It was perhaps due to the presence of conjugation[5], dispersed in whole molecule, not concentrated only in the triazaphosphole ring. So we have to turn our study up on the single hetero-rings.

5-METHYLTHIO-3-DIALKYLAMINO-4, 1, 2, 3, -THIODIAZAPHOSPHOLES[6]

These compounds III containing sulfur and double bond in the ring are prepared from (a) and $P(NR_2)_3$. From (a) and PCl_3, corresponding chlorides IV are obtained.

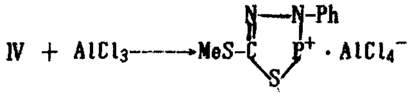


The reaction is some complicated according to the different substituents. Whatever happens, the base peaks of III. IV in MS are either N=P- containing molecular ions or phosphenium molecular ions. It is easy to react IV with NEt_3 to form dimers V.

$$\mathrm{IV} + \mathrm{NEt_3} \longrightarrow \mathrm{V}$$

PHOSPHENIUM CATIONS

Phosphenium cation A can be given rise from the reaction of IV with anhydrous $AlCl_3$



A

A is a red glassy substance and can remain for at lest 5 days at 10℃ under N_2 in desiccator. The chemical shift of A in ^{31}P NMR appeared at 261. 9ppm, between 111~560ppm, the characteristic shift values of phosphenium cations[7].

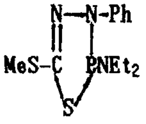
$$\underline{A} + P(NR_2)_3 \longrightarrow \mathrm{VI}$$

A reacts with $P(NR_2)_3$ to give complex VI, the J value of which is 625 Hz, larger than 336~506 Hz reported in literature[7].

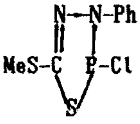
The stabilization of A is coming from the Ph substituent on N. If Ph group is absent, the cation will become unstable, but its complex VII also can be obtained in the presence of NEt_3.

$$\mathrm{VI} + AlCl_3 + NEt_3 \longrightarrow \mathrm{VII}$$

The equivalent conductance of A,(b),(e) and (d) was measured . The result shows that the equivalent conductance of A is 40 times larger than (b) and (c), but 3 times smaller than (d). This means that the positive charge surely localizes on P, but does not completely localize on it as in (d).



(b)

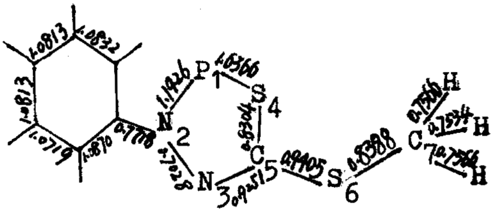


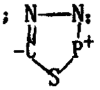
(c)

$Ph_3P^+CH_2PhBr^-$

(d)

The atomic gross overlap population of A, obtained from extend Hückel molecular orbital calculation is as below:



This picture shows that the double bond of N_3--C_5 is largely migrated to the N_2-P_1, specially to the P_1-S_4, within the ring. The dispersion of positive charge in $\underline{A}$ is: Ph: + 0.36263;  : + 0.52144; and CH_3S-: + 0.11992.

THE REACTIONS OF PHOSPHENIUM CATION $\underline{A}$

We preliminaryly studied the reactions of $\underline{A}$ and compared them with the reactions of neutral compounds. $\underline{A}$ participates in Staudinger reaction[7] with N_3SiMe_3 at room temperature, but neutral compounds can accomplish this reaction only in reflux.

$$\underline{A} + N_3SiMe_3 \xrightarrow{r \cdot t} \text{VIII}$$

$$(b) + N_3SiMe_3 \xrightarrow{reflux} \text{IX}$$

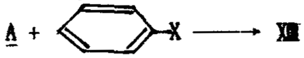
$\underline{A}$ can add to tetrachloro-ortho-quinone(e) or 2,3-butanedione(f) at 0℃ or room temperature separately. Neutral compound can only add to (e) at 50℃ but cannot react with (f).

$$\underline{A} + (e) \xrightarrow{50^\circ C} \text{X}$$

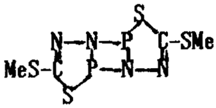
$$(b) + (e) \xrightarrow{50^\circ C} \text{XI}$$

$$\underline{A} + (f) \xrightarrow{r \cdot t} \text{XII}$$

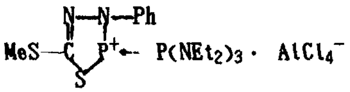
In aromatic substitution, $\underline{A}$ can substitutes para-H in N, N-dimethylaniline and anisole.



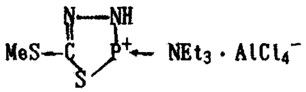
X=NMe_2, OMe



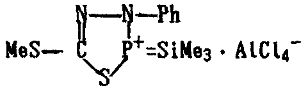
V



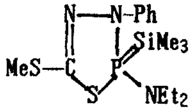
VI



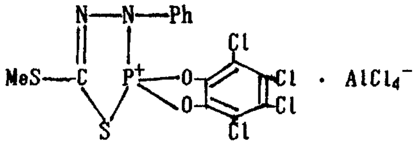
VII



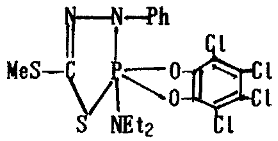
VIII



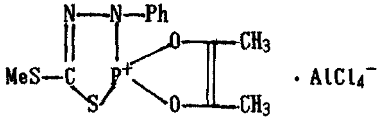
IX



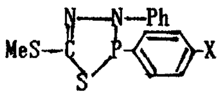
X



XI



XII



XIII

References

1、J. L. Zhang, Z. S. Cao, Synthesis, 11, 1067 (1985)

2、J. L. Zhang, Z. S. Cao, Kexue Tongbao, 6, 432 (1986)

3、J. L. Zhang, Z. S. Cao, Huaxue Xuebao, 44 (1), 51 (1981)

4、J. L. Zhang, W. Xu, Phos.Sul. and Silc., 46, 7 (1987)

5、Z. S. Cao, J. L. Zhang, F. F. Xu, Chin. J. Microw. Radio-Freq.Spect., 3 (2), 99 (1986)

6、T. B. Huang, J, L.Zhang, Q. C. Zhou, 2nd. Nat. Conf. on Phos. Chem., 149(1991)

7、A. H. Cowley, R. A. Kemp, Chem. Rev., 85, 367 (1985)