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STUDIES ON PHOSPHENIUM CATIONS

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INTRODUCTION

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

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(NR2)3. From (a) and PCl3, 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 NEt3 to form dimers V.

PHOSPHENIUM CATIONS

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

 \underline{A} is a red glassy substance and can remain for at lest 5 days at 10°C under N₂ in desiccator. The chemical shift of \underline{A} in ³¹P NMR appeared at 261. 9ppm, between 111~560ppm, the characteristic shift values of phosphenium cations ^[7].

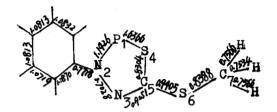
$$\underline{A} + P(NR_2)_3 ---- VI$$

<u>A</u> reacts with P(NR₂)₃ to give complex VI, the J value of which is 625 Hz, larger than $336\sim506$ Hz reported in literature ^[7].

The stabilization of \underline{A} is coming from the Ph substituent on N. If Ph group is absent, the cation will become unstable, but its complex $V\!R$ also can be obtained in the presence of NEt_3 .

The equivalent conductance of \underline{A} , (b), (e) and (d) was measured. The result shows that the equivalent conductance of \underline{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).

The atomic gross overlap population of \underline{A} , obtained from extend Huckel 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: P_1 : + 0.36263; N_1 -- N_1 : + 0.52144; and CH_3S_{-1} : + 0.11992.

THE REACTIONS OF PHOSPHENIUM CATION A

We preliminaryly studied the reactions of $\underline{\Lambda}$ and compared them with the reactions of neutral compounds. $\underline{\Lambda}$ participates in Staudinger reaction [7] with N₃SiMe₃ at room temperature, but neutral compounds can accomplish this reaction only in reflux.

$$\underline{A} + N_3 \text{SiNe}_3 \xrightarrow{\mathbf{r} \cdot \mathbf{t}} \mathbf{W}$$

$$(b) + N_3 \text{SiNe}_3 \xrightarrow{\mathbf{reflux}} \mathbf{IX}$$

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

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

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

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

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

$$\underline{A}$$
 + $X = NMe_2$, OMe

$$N-N-Ph$$

$$NeS-CP^+-P(NEt_2)_3 \cdot AlCl_4 VI$$

$$\begin{array}{c|c}
N - N - Ph \\
\downarrow & \downarrow & \downarrow & \downarrow \\
NeS - C & P + 0 & C1 \\
S & C1 & A1C14 & X
\end{array}$$

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