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THE BEHAVIOUR OF DIPHENYLTHIOPHOSPHINOHYDRAZIDE AND
DIPHENYLPHOSPHINOHYDRAZIDE UNDER ELECTRON IMPACT

By

EMTITAL EL-SAWI and MADINA MOHAMED

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Faculté des Sciences de l'Université d'Ankara
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THE BEHAVIOUR OF DIPHENYLTHIOPHOSPHINOHYDRAZIDE AND DIPHENYLPHOSPHINOHYDRAZIDE UNDER ELECTRON IMPACT

EMTITHAL EL-SAWI* and MADINA MOHAMED

Chemistry Department, University College For Women, Ain Shams University, Heliopolis, Cairo, Egypt.

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The behaviour of diphenylthiophosphinoazide under electron impact is studied. Its molecular ion undergoes fragmentation via four routes. The results indicate that the P–N bond is the easiest bond to be cleaved and in comparison with diphenylphosphinoazide, the P=O bond is weaker than P=S bond.

The behaviour of organophosphorus compounds under electron impact has been extensively investigated1.

The mass spectrum of triphenylphosphine oxide2 was generally similar to that of triphenylphosphine the difference being the relatively more intense M–1+ ion (base peak) and the absence of C₆H₅P⁺ and C₆H₄P⁺ ions in the spectrum of the oxide, while that of the phosphine obviously had no P=O containing ions.

The production of very abundant M–1+ ions from aromatic phosphine oxides2,3 and other pentacovalent phosphorus compounds indicated the formation of bridged (cyclized) ions.

Tris (dimethylamine) phosphine4 was populated with abundant ammonium ions such as Me₂N⁺, and disubstituted phosphorus ions like (Me₂N)₂P⁺. The predominance of these two types of ions supported the hypothesis5 that d–shell participation stabilized the electron deficiency of phosphorus rather than the formation of phosphonium ions.

The present work is directed to study the behaviour of diphenylthiophosphinoazide under electron impact.

* To whom all correspondences should be addressed, Chemistry Department, University College for Women, Ain Shams University, Heliopolis, Cairo, Egypt.
It has been established that the diphenylphosphinohydrazide gives ions of mass 201 as base peak, arising by the loss of the hydrazine moiety from the molecular ion\(^6\). A common feature between the thiophosphinohydrazide and the phosphinohydrazide is the dissociation of the molecular ion \((\text{M}^+)\) to yield the base peak ion by extrusion of the hydrazine moiety \((\text{M}^+-31)\).

\[
\begin{align*}
(\text{C}_6\text{H}_5)_2\overset{\text{P}}{\text{NH}}\overset{\text{H}}{\text{NH}_2} & \quad (\text{Ia}) \\
(\text{C}_6\text{H}_5)_2\overset{\text{S}}{\text{NH}}\overset{\text{H}}{\text{NH}_2} & \quad (\text{Ib})
\end{align*}
\]

However, the modes of dissociation of the molecular ion to yield the second most abundant peak of the diphenylphosphinohydrazide and its this analogue differ considerably from one another. In (Ia), the second most abundant peak being formed through a hydrogen transfer in the molecular ion via a five-membered cyclic transition state as follows:

\[
\begin{align*}
\text{C}_6\text{H}_5\overset{\text{p}=0}{\text{P}}\text{N}\overset{\text{H}}{\text{H}} & \quad \overset{+^+}{\longrightarrow} \quad \text{C}_6\text{H}_5\overset{\text{P}=0-\text{H}}{\overset{+^+}{\text{H}}} + \text{HN=NH}
\end{align*}
\]

In case of the thiohydrazide (Ib), the second most abundant peak being formed by the loss of \(\text{C}_6\text{H}_5\text{S}^-\) moiety from the molecular ion \((\text{M}-\text{C}_6\text{H}_5\text{S})^+\). A possible mechanism for the dissociation of the molecular ion of (Ib) is as follows:

\[
\begin{align*}
\text{S}^9\overset{\text{H}}{\text{H}}\overset{\text{O}_1}{\text{HN}}\overset{\text{H}}{\text{N}_{\text{D}}}\overset{\text{H}}{\text{H}} & \quad \overset{+^+}{\longrightarrow} \quad \overset{\text{S}^9\overset{\text{H}}{\text{H}}\overset{\text{O}_1}{\text{HN}}\overset{\text{H}}{\text{N}_{\text{D}}}}{\text{H}} + \overset{\text{S}^9\overset{\text{H}}{\text{H}}\overset{\text{O}_1}{\text{HN}}\overset{\text{H}}{\text{N}_{\text{D}}}}{\text{H}}
\end{align*}
\]

The one-step loss of \(\text{C}_6\text{H}_5\text{S}^-\) from the \(\text{M}^+\) is apparently preceded by a rearrangement of the phosphine sulfide–thiophosphinite type\(^7\).

The molecular ion of the thiohydrazide (Ib) undergoes fragmentation via four routes, the decomposition pathways which account for all the abundant ions and metastable transitions (marked with an\(^*\)) are summarized in Scheme 1.
Route (a) involves the formation of the phosphothioacetylum ion (M−31) by the loss of the hydrazine moiety. In this case it behaves like the phosphinohydrazide analogues (Ia) This route is supported by the appearance of a strong metastable peak at m/e 189.9.

Route (b) involves the formation of 139 ion (M−C₆H₅S⁻), similar to the behaviour of phosphine sulfides. This one step loss of C₆H₅S⁻ moiety, is apparently preceeded by the phosphine sulfide–thiophosphinate type rearrangement. The appearance of a strong metastable ion at 77.8 supports this route.

Route (c) involves the loss of N₂H₂ moiety to give ions of mass 218 (7.19%) which lose HS⁻ radical to give ions 185. The elimination of HS⁻ radical is apparently preceeded by sulfide-sulphydryl rearrangement. This process is established by a metastable peak at m/e 191.74.

Route (d) involves the break of N−N bond, similar to the behaviour of the phosphinohydrazide analogue (Ia) and acylhydrazides, to give ions of mass 233. This step is substantiated by the presence of a weak metastable peak at m/e 219. The relative intensities of the ions are given (Fig 1).

![Figure 1. Mass spectrum of diphenylthiophosphino hydrazide](image)

The above result reveals that in both hydrazides (Ia, b) the P−N bond is the easiest bond to be cleaved. This finding is in accord with
bond energies\textsuperscript{9,10}. Also the P=S bond is weaker than the P=O bond\textsuperscript{9} This is reflected by the loss of sulfur from the molecular ion, while the elimination of oxygen has not been observed. Reactions of similar nature are known\textsuperscript{7,11,13}.

EXPERIMENTAL

The preparation of diphenylphosphinohydrazide has been reported\textsuperscript{14,15}. Diphenylthiophosphinohydrazide (Ib) was prepared in (70 \%) yield from the reaction of equimolar quantities of chlorodiphenylphosphine and sulphur in dry benzene under reflux for 8 hours to give diphenylthiophosphinochloridate. The solution of the product in dry benzene was added dropwise at room temperature to a stirred solution of hydrazine hydrate (2 mole) in ether. The reaction mixture was refluxed for 5 hours, the product was crystallized from benzene–light petroleum (40–60°C); m.p. 70–71°C Anal. Calcd for C\textsubscript{12} H\textsubscript{13}N\textsubscript{2}PS: N, 11.29; P, 12.50. Found: N, 11.40; P, 12.10.

Mass spectra were obtained with a Dupont 21–492 B mass spectrometer. A 2–4 mg sample of the hydrazide was dissolved in 1.0 ml of methanol, and a suitable aliquot to allow 2–4 ug for analysis was taken. After the solvent was removed in vacuum, the samples were analyzed by direct probe and an ionizing voltage of 75 eV. Source temperature was 260°C and the direct probe temperature for compounds Ia and Ib was 170–190°C.

REFERENCES