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SHORT COMMUNICATION

Mass spectra of triphenyl derivatives of Group VA elements

A recent publication[1] on the mass spectra of diphenyl and dibenzo compounds prompts us to report our findings on the mass spectra (Atlas CH-4) of triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine and triphenylbismuthine. It was concluded[1] that compounds containing two or more aromatic rings (bonded to a common atom) underwent condensation of the rings in the *ortho* positions giving unstable semi-aromatic ions which subsequently eliminated characteristic groups to give a fully aromatic configuration. Similar processes observed in the mass spectra of triphenylamine and triphenylphosphine were alluded to, and the conclusion drawn that all compounds containing two or more aromatic groups might be expected to behave in a similar fashion.

Examination of the 70 eV mass spectra obtained from the triphenyl derivatives of the group VA elements reveals that they can be classed into three categories. The first consists of those compounds in which the dominant peak in the spectrum is that of the molecular ion in addition to an appreciable $M-1$ peak. The compounds comprising this category are triphenylamine and triphenylphosphine. The second group, consisting of triphenylarsine and triphenylstibine, have the phenylmetal cation as the dominant peak in the spectrum; and finally, the dominant peak in the spectrum of triphenylbismuthine is that of the Bi^+ ion. These compounds exhibit increasingly abundant molecular ions as one proceeds, in the group, from bismuth to nitrogen. This is presumably a reflection of the corresponding increase in the strength of the carbon–heteroatom bond.

The mass spectrum of triphenylamine provides evidence for the occurrence of two principal fragmentation paths:

$$\begin{tikzcd}
\substack{\text{m/e } 244 \\ (24.7\%)} & \substack{M\ (\text{m/e } 245) \\ (100\%)} \arrow[l, "-\mathrm{H}", "m^*"'] \arrow[r, "-C_6H_5"] & \substack{\text{m/e } 168 \\ (6.1\%)} \arrow[r, "-\mathrm{H}", "m^*"'] \arrow[dr] & \substack{\text{m/e } 167 \\ (20.9\%)} \arrow[r, "-\mathrm{H}", "m^*"'] & \substack{\text{m/e } 166 \\ (12.8\%)} \\
 & & & \substack{\text{m/e } 141^{\star} \\ (12.9\%)} &
\end{tikzcd}$$

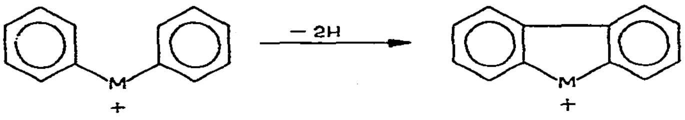
m^* = transition supported by an appropriate metastable peak

Similar evidence for two principal fragmentation paths is found in the mass spectrum of triphenylphosphine

$$\begin{tikzcd}
\substack{\text{m/e } 261 \\ (12.9\%)} & \substack{M\ (\text{m/e } 262) \\ (100\%)} \arrow[l, "-\mathrm{H}", "m^*"'] \arrow[r, "-C_6H_5"] & \substack{\text{m/e } 185 \\ (7.0\%)} \arrow[r, "-2\mathrm{H}", "m^*"'] \arrow[dr, "-\mathrm{H}", "m^*"'] & \substack{\text{m/e } 183 \\ (42.6\%)} \\
 & & & \substack{\text{m/e } 184 \\ (9.5\%)}
\end{tikzcd}$$

[★] Identified as $C_{11}H_9$ by use of a double focus mass spectrometer.

The formation of the dibenzoheterocyclic cation (II) (M = P) from the corresponding cation (I) in a one-step process involving the simultaneous loss of two hydrogen atoms is substantiated by the observation of an appropriate metastable peak. An identical "*ortho* coupling" occurs in the instances when M is arsenic or antimony. While this "*ortho* coupling" is a one-step process in the cases cited, the available evidence indicates that a stepwise loss of hydrogen atoms occurs for the nitrogen compound and that there is no coupling in the bismuth compound. An examination of the mass spectra of the fully phenylated derivatives of B(III), Ga(III), Hg(II), C(IV), Si(IV), Ge(IV), Sn(IV), and Pb(IV) in addition to $[(C_6H_5)_3Sn]_2$ revealed no evidence for "*ortho* coupling".



(I) (II)

The results of the present study indicate that one-step "*ortho* coupling" identical to that found in triphenylphosphine occurs only in the corresponding arsenic and antimony derivatives and not in a wide variety of fully phenylated elements as previously anticipated[1].

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1 J. H. D. ELAND AND C. J. DANBY, *J. Chem. Soc.*, (1965) 5935.

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