Hydrogen Randomisation in Negative Ions[1]

By J. H. BOWIE* and B. NUSSEY

(*Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia* 5001)

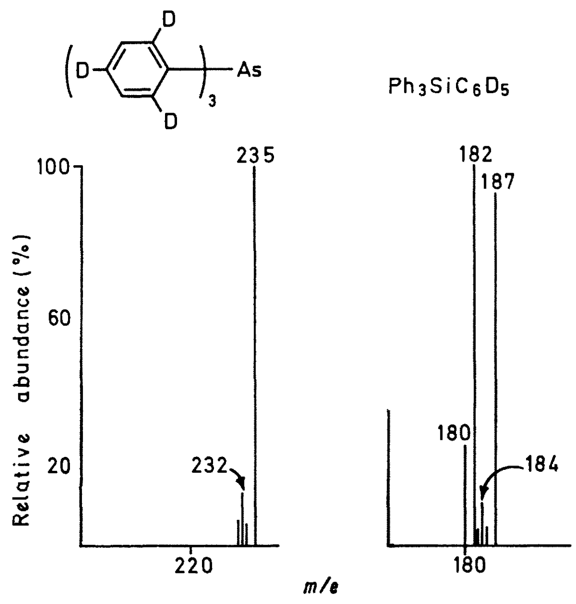
Summary Hydrogen randomisation preceding the fragmentation of the negatively charged molecular ions of triphenylarsine and tetraphenylsilane is reported.

HYDROGEN randomisation often precedes the fragmentation of positively charged molecular ions of aromatic molecules.[2,3] It is of interest to determine whether hydrogen scrambling also occurs in negative ions prior to fragmentation.

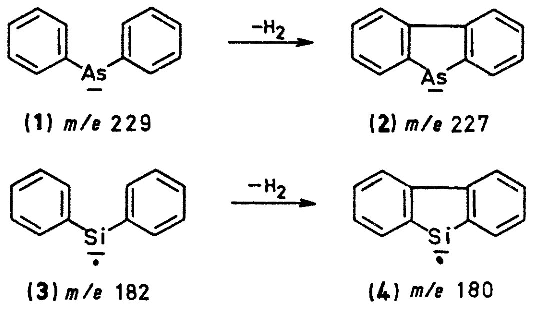
We have attempted to obtain suitable negative-ion spectra for simple aromatic compounds, but have found either that appropriate fragmentations do not occur in these spectra, or that the spectra are not reproducible because of the occurrence of ion–molecule reactions. However, reproducible negative-ion spectra of the tri(tetra)phenyl derivatives of the Group IVA and VA elements may be obtained at 70 ev using sample pressures of 2—3 × 10^{-7} torr. Under these conditions, ion–molecule reactions are kept to an absolute minimum, except in the cases of triphenylamine and tetraphenylmethane.

The base peaks in the spectra of triphenylphosphine, arsine, stibine, and bismuth are $M^{\bar{\cdot}}$–Ph$\cdot$ species and in the latter three cases these are accompanied by $M^{\bar{\cdot}}$–Ph$\cdot$–H_2 peaks [*e.g.* (**1**) → (**2**)]. The partial spectrum (corrected for isotope peaks) of tri[2,4,6-$^2H_3$]phenylarsine is recorded in the Figure. Losses of H_2, HD, and D_2 from *m/e* 235 are observed in the ratio 17 : 51 : 32. The ratio for randomisation is 13.3 : 53·3 : 33·3. This evidence shows that hydrogen scrambling occurs within each benzene ring prior to the process (**1**) → (**2**).

The major peaks in the spectrum of tetraphenylsilane are due to the ions (**3**) and (**4**). The partial spectrum (Figure) of [$^2H_5$-phenyl]triphenylsilane shows that cyclisation and hydrogen randomisation between the benzene rings occur prior to the formation of (**4**). Loss of H_2, HD, and D_2 from *m/e* 187 is in the approximate ratio 22 : 60 : 18 (randomisation requires 22 : 56 : 22).



FIGURE



(**1**) *m/e* 229
(**2**) *m/e* 227
(**3**) *m/e* 182
(**4**) *m/e* 180

As there are no metastable peaks to substantiate the formation of (**2**) from (**1**) or (**4**) from (**3**), it could be argued that (**2**) and (**4**) are not being produced in this way. Even if this is the case, it does not negate the fact that the hydrogens are scrambling before decomposition occurs.

(*Received, October 27th,* 1969; *Com.* 1620.)

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[1] Previous paper: *Austral. J. Chem.*, in the press.

[2] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," ed. F. W. McLafferty, Academic Press, New York, **1963**, ch. 10.

[3] R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrometry*, **1969**, **2**, 137, and references therein.