Mass Spectra of Sila-cyclobutane and -cyclobutene Derivatives †

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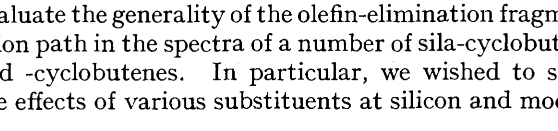
The mass spectra of (*i*) silacyclobutane and some 1,1-disubstituted derivatives containing chloro-, methyl, or methoxy-groups, (*ii*) 1,1,2-trimethyl-1-silacyclobutane, and (*iii*) 1,1-dimethyl-1-silacyclopentane are characterised by reasonably abundant parent molecular ions $P^{+\cdot}$ and a fragmentation scheme dominated by the elimination of ethylene from $P^{+\cdot}$. The cleavage of a Si–C ring bond leading to three-co-ordinate silicon ions is an important first step in the fragmentation of types (*i*) and (*ii*). For $R_3MSiMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$ (R_3M = Ph_3Si, Ph_3Ge, or Me_3Sn), $P^{+\cdot}$ ions are also abundant but the elimination of ethylene is unimportant. Most of the major fragment ions observed are produced with cleavage of the M–Si bond. Alternative fragmentation paths to ethylene elimination are also preferred for 1,1-dimethyl- and 1,1-diphenyl-1,2-dihydro-1-silacyclobutabenzene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane; the most important involve loss of Me· from the methyl compounds and benzene from the phenyl derivative: abundant $P^{+\cdot}$ ions are observed.

REPORTS of the spectra of 1-silacyclobutane,[1] 1,1-dimethyl-1-silacyclobutane,[2] 1-silacyclopentane,[3] some mono- and di-methyl-substituted 1-silacyclopentanes,[2] 1,1,2-trimethyl-1-silacyclopentane,[4] and 1-methylsilacyclohexane [2] have emphasised two features. First, relatively abundant $P^{+\cdot}$ ions and, second, a dominant fragmentation path involving the elimination of olefin molecules from $P^{+\cdot}$ ions. The latter is most unusual in the mass spectra of organometallic main-group compounds; [5,6] $P^{+\cdot}$ ions, being odd-electron species, usually prefer to fragment by losing odd-electron species to give even-electron ions. Analogous decompositions have been reported in the spectra of 1-germacyclopentane,[3,7] and some other mono- and di-substituted germanium derivatives.[7] The study of deuteriated germacyclopentanes such as (**I**) showed that the olefin lost was CH_2CD_2 and specifically contained either C(2) and C(3), or C(4) and C(5).



(I)

As part of our continuing interest in organosilicon chemistry [8] and the mass spectra of main-group 4 metal compounds,[9] the present work was undertaken to evaluate the generality of the olefin-elimination fragmentation path in the spectra of a number of sila-cyclobutanes and -cyclobutenes. In particular, we wished to study the effects of various substituents at silicon and modific-

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† No reprints available.

[1] J. Laane, *J. Amer. Chem. Soc.*, 1967, **89**, 1144.

[2] N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, V. M. Vdovin, and T. N. Arkhipova, *J. Gen. Chem.* (*U.S.S.R.*), 1966, **36**, 99.

[3] A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1965, **87**, 2920.

[4] T. W. Dolzine, A. K. Holand, and J. P. Oliver, *J. Organometallic Chem.* 1974, **65**, C1.

[5] M. R. Litzow and T. R. Spalding, 'Mass Spectrometry of Inorganic and Organometallic Compounds,' Elsevier, Amsterdam, 1973.

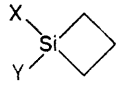
[6] M. I. Bruce in 'Mass Spectrometry,' ed. D. H. Williams, *Specialist Periodical Reports*, The Chemical Society, London, 1971, vol. 1, and 1973, vol. 2.

[7] A. M. Duffield, C. Djerassi, P. Mazerolles, J. Dubac, and G. Manuel, *J. Organometallic Chem.*, 1968, **12**, 123.

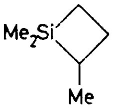
[8] C. S. Cundy, C. Eaborn, and M. F. Lappert, *J. Organometallic Chem.*, 1972, **44**, 291; C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organometallic Chem.*, 1973, **11**, 253.

[9] M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, *J. Organometallic Chem.*, 1971, **29**, 195.

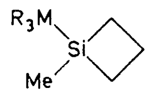
ations of the four-membered ring structure. To this end we prepared compounds (II)—(XI) and 1,1-dimethyl-1-silacyclopentane, (XII), and recorded their spectra. The chemistry of some of these compounds, especially in a transition-metal context, has been studied.[8]



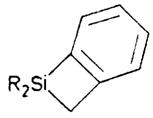
	X	Y
(II)	H	H
(III)	Cl	Cl
(IV)	Me	Me
(V)	OMe	OMe
(VI)	Me	OMe
(VII)	Me	Cl



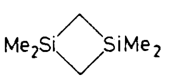
(VIII)



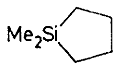
(IX) $R_3M = Ph_3Si$, Ph_3Ge, or Me_3Sn



(X) R = Me or Ph



(XI)



(XII)

RESULTS AND DISCUSSION

The monoisotopic ion abundances of (II)—(IV), (VIII)—(X), and (XII), and the polyisotopic ion abundances of (V)—(VII) and (XI) for ions of greater than 0.25% of the total ion current carried by ions of $m/e \geqslant 28$, together with assigned metastable supported transitions, are in Supplementary Publication No. SUP 21620 (16 pp.).*

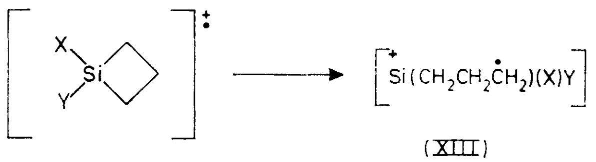
Polyisotopic spectra have previously been reported in detail for compounds (II),[1] (IV), and (XII).[2] Reasonable agreement was found between the polyisotopic spectra obtained in this and the previous work on (II). Good correspondence was observed between the present and previous spectra of (IV) and (XII). Such differences in the abundance of ions as were observed can largely be ascribed to the different instruments and conditions used. Partial polyisotopic spectra have also been reported for (III), (IV), and (VI).[10] Whilst the spectrum of (VI) is in reasonable agreement with the present study, there is divergence with regard to the species assigned as base peaks for (III) and (IV). For (III),[10] no base peak was given but the sequence for the ion $[Si(CH_2)Cl_2]^{+\cdot}$ containing either or both ^{35}Cl and ^{37}Cl was given as m/e 116, 114, and 112 in the ratio 12 : 70 : 10. Since $P^{+\cdot}$ for $^{28}Si(^{12}C^{1}H_2)^{35}Cl_2$ corresponds to m/e 112, this should have higher abundance than m/e 114 or 116, which contain one or two ^{37}Cl atoms respectively, and it is suggested that the published values may contain a misprint (*i.e.*, for 10 read 100). Similarly, it is suggested that for (IV), where the sequence m/e 85(8), 72(17), 73(100), and 71(6) is given,[10] the correct sequence should read m/e 85(8), 73(17), 72(100), and 71(6), with m/e 72 as base peak in agreement with previous [2] and present work.

Spectra of Compounds (II)—(VIII) *and* (XII).—The silacyclobutanes all show $P^{+\cdot}$ ions, usually in *ca.* 5—12% abundance (Table). The values for (II) and (IV), of 11.74 and 12.18%, respectively, may be compared with the much lower values observed for parent molecular ions from SiH_4 (0.45%) and $SiMe_4$ (0.4%),[5] and with values of between 0.2 and 0.49% found for methylsilanes $SiMe_nH_{4-n}$ (n = 1—3),[11] or for $SiMe_3Et$ (1.18%) and $SiMe_3Pr$ (1.33%).[12] These differences may partly be rationalised if the $P^{+\cdot}$ ions from (II)—(VII) can exist in a relatively stable radical cation form such as (XIII). The cleavage of a Si–C silacyclobutane ring bond to produce ions of type (XIII) with the silicon atom using essentially sp^2 hybridised bonding orbitals seems quite plausible. Moreover, appreciably stable $[P + 1]^+$ ions were found in the spectra of (II), (IV), (V), and (VIII). It is possible to consider these ions as examples of the stable even-electron three-co-ordinate silicon ions often found in high abundance in the spectra of organosilicon compounds.[5] Examples are $[SiH_3]^+$ and $[SiMe_3]^+$, the base-peak ions in the spectra of SiH_4 and $SiMe_4$.

Relative percentage abundance of parent molecular and base-peak ions

Compound	$P^{+\cdot}$	Base peak
(II)	11.74	22.10 [a]
(III)	5.68	47.05 [a]
(IV)	12.18	40.46 [a]
(VIII)	5.05	22.81 [a]
(IX; $R_3M = Ph_3Si$)	11.98	13 94
(IX; $R_3M = Ph_3Ge$)	18.25	18.25
(IX; $R_3M = Me_3Sn$)	5.02	25.73
(X; R = Me)	21.56	30.11
	(0.35) [b]	(0.56)
(X; R = Ph)	16.56	19.46
	(1.05) [b]	(0.25)
(XII)	8.05	29.85

Corresponding to $[P - C_2H_4]^{+\cdot}$ ions. [b] Abundance of doubly charged counterparts.



(XIII)

The fragmentation schemes for (II)—(VII) and (XII) are dominated by the elimination of ethylene from the $P^{+\cdot}$ ions, leading to base-peak odd-electron ions in abundances ranging from 15—47%. In the case of (VIII), loss of ethylene or propylene is almost equal, giving the ions $[P - C_2H_4]^{+\cdot}$ (22.29%) and $[P - C_3H_6]^{+\cdot}$ (21.61%). These decompositions are metastable peak-supported in the spectra of (IV), (VI)—(VIII), or (XII). That olefin-elimination reactions of such importance take place from odd-electron ions is unusual. Almost all the

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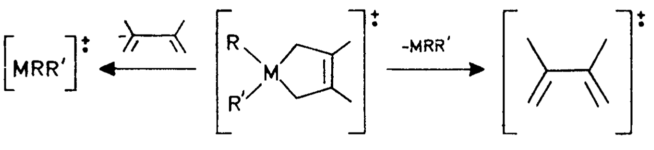
* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue.

[10] R. Damrauer, R. A. Davis, M. T. Burke, R. A. Karn, and G. T. Goodman, *J. Organometallic Chem.*, 1972, **43**, 121.

[11] G. P. Van der Kelen, O. Volders, H. Van Onckelen, and Z. Fecklaut, *Z. anorg. Chem.*, 1965, **338**, 106.

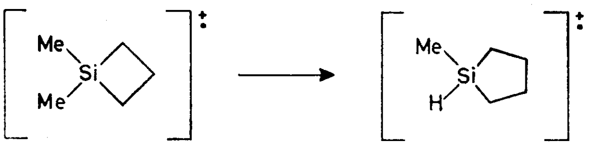
[12] N. Ya. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, and V. M. Vdovin, *J. Gen. Chem.* (*U.S.S.R.*), 1966, **36**, 93.

reported olefin eliminations in the spectra of organosilicon or other main-group 4 element organometallic compounds take place from even-electron ions.[5,6,12-14] An example of this in the present work was the loss of ethylene from $[Si(C_2H_7)]^+$, observed as a metastable peak-supported decomposition, from (IV), (VII), (VIII), or (XII). Previously, the elimination of olefins containing either C(2) and C(3) or C(4) and C(5) have been reported as major, though not dominant, decomposition paths in the spectra of some 1-sila-[15] and 1-germa-cyclopentan-3-ols.[16] However, $P^{+\cdot}$ ions from these compounds were either in very low abundance or absent, and no metastable transitions supporting the suggested eliminations were reported. A number of workers have shown that an important fragmentation path from the $P^{+\cdot}$ ions of 1-sila-[17] and 1-germa-cyclopent-3-enes [7,18] occurs *via* a retro-Diels–Alder type reaction (Scheme 1).

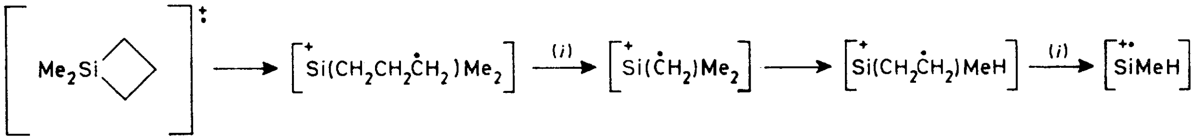


SCHEME 1

The loss of ethylene molecules from $[P - C_2H_4]^{+\cdot}$ in (IV) and both $[P - C_2H_4]^{+\cdot}$ and $[P - C_3H_6]^{+\cdot}$ in (VIII) were interesting metastable peak-supported features in these spectra. The successive elimination of two ethylene molecules strongly suggests some rearrangement involving methylene insertion into an Si–C bond and migration of a hydrogen atom on to silicon leading to ions such as (XIV) [from (IV)] [2] or (XV) (in Scheme 2). A suggestion that the mechanism involves initial silacyclobutane ring expansion has been made mainly on the grounds that the spectra of (IV) and 1-methyl-1-silacyclopentane are closely similar.[2] It is well known that expansion or contraction of cyclopolysilane rings can be either initiated by u.v. irradiation or take place through a cationic mechanism.[19] However, in the mass spectra of (II)—(VIII) and (XII), the evidence of successive specific olefin loss and the high abundance of $P^{+\cdot}$ ions support a scheme involving initial cleavage of a strained Si–C(ring) bond leading to stable three-co-ordinate silicon ions (Scheme 2). It is noteworthy that the metastable-supported successive elimination of two ethylene molecules from the $[P - \dot{C}H_3]^+$ ion and the loss of ethylene from $[P - \dot{C}_2H_5]^+$ were found in the spectrum of $SiMe_2Et$.[12] Similar processes were observed for other silanes including $SiMe_3Pr$ and $SiMeEt_2H$.[12]



(XIV)



(XV)

SCHEME 2 (*i*), $-C_2H_4$.

Other metastable peak-supported fragmentations in the spectra of (IV)—(VIII) and (XII) involve loss of hydrogen atoms or molecules and hydrocarbon species. From (V) and (VI), loss of CH_2O from the $[P - C_2H_4]^{+\cdot}$ ion was observed. Most fragment ions in the spectra of (II)—(VIII) and (XII) appear to retain one or both of the Si–X bonds (X = H, Cl, Me, or OMe).

Spectra of Compounds (IX).—The spectra are characterised by abundant $P^{+\cdot}$ ions (Table) and most ion current is carried by ions produced with cleavage of the Si–M bond. With regard to the latter observation, there is analogy with other compounds such as $Ph_3SiSiMe_3$, $Ph_3SiSiEt_3$, $Ph_3GeSiEt_3$,[20] $Ph_3GeSiMe_3$,[5] and $Me_3SiSnMe_3$,[9] rather than with compounds (II)—(VIII). Another feature in common with the compounds (IX) is the transfer of R groups from M to Si giving ions such as $[SiMePh_2]^+$ in 3.88 and 9.40% abundance when R_3M = Ph_3Si and Ph_3Ge respectively, or $[SiMe_3]^+$ in 5.49% abundance when R = Me_3Sn. Ions formed by group transfer from Si to M were much less abundant. A number of ions reported for $Ph_3SiSiMe_3$ and $Ph_3SiSiEt_3$ were also observed for (IX; R_3M = Ph_3Si), but their relative abundances are considerably different, indicating significant disparity in fragmentation modes. For example, the ratios of $[P]^{+\cdot}$: $[SiPh_3]^+$: $[SiPh_2]^{+\cdot}$ were 1 : 4.45 : 0.37, 1 : 5.18 : 0.26, and 1 : 0.79 : 1.16, respectively. The rearranged ion $[SiPh_3H]^{+\cdot}$, found in the spectrum of (IX; R_3M = Ph_3Si) in 5.24% abundance,

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[13] J. J. de Ridder and G. Dijkstra, *Rec. Trav. chim.*, 1967, **86**, 737.

[14] D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc.* (*A*), 1967, 1759.

[15] C. Lageot, J. C. Maire, P. Mazerolles, and G. Manuel, *J. Organometallic Chem.*, 1973, **60**, 55.

[16] C. Lageot, J. C. Maire, G. Manuel, and P. Mazerolles, *J. Organometallic Chem.*, 1973, **54**, 131.

[17] V. N. Bockharev, A. N. Polivanov, N. G. Komalenkova, S. A. Bashkirova, and E. A. Chernyshev, *J. Gen. Chem.* (*U.S.S.R.*), 1973, **43**, 784.

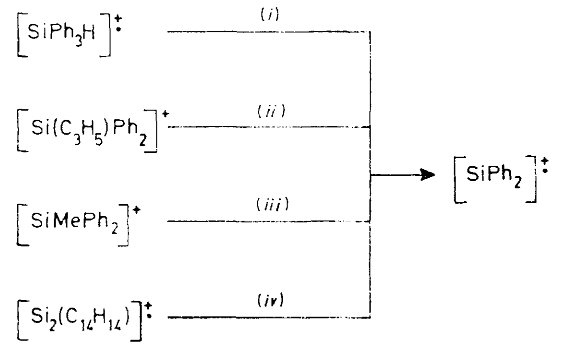
[18] C. Lageot, J. C. Maire, P. Rivière, M. Massol, and J. Barrau, *J. Organometallic Chem.*, 1974, **66**, 49.

[19] C. Lageot, J. C. Maire, M. Ishikawa, and M. Kumada, *J. Organometallic Chem.*, 1973, **57**, C39 and refs. therein.

[20] D. B. Chambers and F. Glockling, *J. Chem. Soc.* (*A*), 1968, 735.

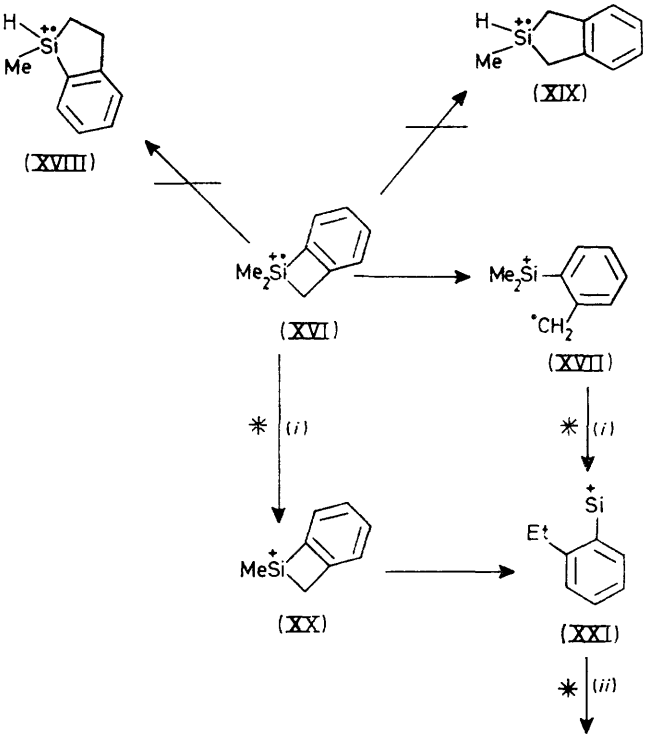
was not observed for $Ph_3SiSiMe_3$ or $Ph_3SiSiEt_3$. This is not due to contamination of our sample by triphenylsilane because the analysis of (IX; $R_3M = Ph_3Si$) and its physical properties were entirely satisfactory and the fragmentation pattern and metastable peaks reported [21] for $SiPh_3H$ were not compatible with our spectrum.

Perhaps the most striking difference between the spectra of (IX) and those of the silacyclobutanes discussed above is the absence ($R_3M = Ph_3Si$ and Me_3Sn) or very low abundance ($R_3M = Ph_3Ge$, 0.33%) of the $[P - C_2H_4]^{+\cdot}$ ion. Apparently there are several other more favourable fragmentation paths, but it is difficult to distinguish any one path as being particularly dominant. In the spectrum of (IX; $R_3M = Ph_3Si$), for example, the base-peak ion is $[SiPh_2]^{+\cdot}$. Metastable-peak evidence supports four modes of formation of this ion from other reasonably abundant ions (Scheme 3). The base-peak ions in the spectra of (IX; $R_3M = Ph_3Ge$ and Me_3Sn) were $P^{+\cdot}$ and $[SnMe]^+$, respectively. Most of the metastable-supported fragmentations concern the loss of hydrocarbon groups such as C_2H_2, $C_6H_5\cdot$, $C_3H_5\cdot$, or $CH_3\cdot$, but the loss of $SiMe_2(C_3H_6)$ from the $[P - \dot{C}H_3]^+$ ion of (IX; $R_3M = Me_3Sn$) was also observed.



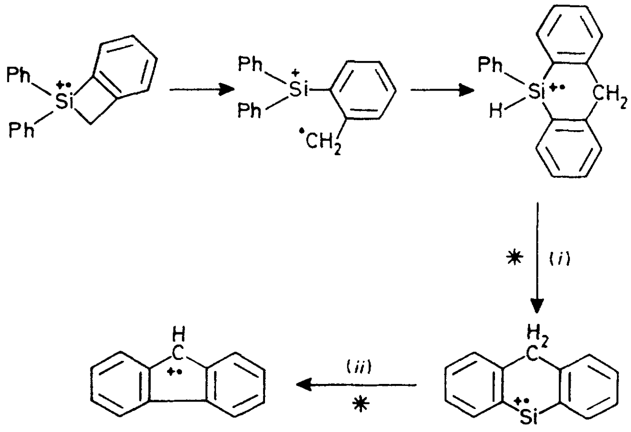
SCHEME 3 (*i*), $-C_6H_6$; (*ii*), $-\dot{C}_3H_5$; (*iii*), $-\dot{C}H_3$; (*iv*), $-Si(C_2H_4)$.

Spectra of Compounds (X) *and* (XI).—$P^{+\cdot}$ Ions are the second most abundant ions in the spectra of (X) and (XI) (Table). The base-peak ions from these compounds are $[P - \dot{C}H_3]^+$, $[P - C_6H_6]^{+\cdot}$, and $[P - \dot{C}H_3]^+$, respectively. Loss of ethylene was not observed from the $P^{+\cdot}$ ions, but ethylene was lost from the $[P - \dot{C}H_3]^+$ ions of (X; R = Me) and (XI), and $SiH\cdot$ from $[P - C_6H_6]^{+\cdot}$ in (X; R = Ph). These observations are rationalised by suggesting that fragmentations of the $P^{+\cdot}$ ions involve considerable rearrangements. In the case of (X; R = Me), the $P^{+\cdot}$ ion may have structure (XVI) (Scheme 4), rearranging to the relatively stable (XVII). The ion at *m/e* 120, $[Si(C_7H_8)]^{+\cdot}$, formed by the elimination of ethylene from a ring-expanded rearranged $P^{+\cdot}$ ion (XVIII), was not found, which argues against an initial ring expansion. An alternative ring-expanded rearranged $P^{+\cdot}$ ion, (XIX), is also discounted since ions at *m/e* 104, $[C_8H_8]^{+\cdot}$, and *m/e* 44, $[Si(CH_4)]^+$, were not found in any significant amount, *i.e.* <0.25%. These ions would have been the expected fragmentation products of (XIX),



SCHEME 4 (*i*), $-\dot{C}H_3$; (*ii*), $-C_2H_4$.

by comparison with the reported spectra of 1-silacyclopent-3-ene derivatives [17] (Scheme 1). With the elimination of olefin from the $P^{+\cdot}$ ion precluded by the presence of the aromatic ring system the loss of a methyl radical from (XVI) may give the relatively stable three-coordinate silicon ion (XX) and (XXI) which, on elimination of ethylene, gives the $[SiPh]^+$ ion, found in 6.32% abundance (Scheme 4). For (X; R = Ph), the suggested decompositions are shown in Scheme 5.



SCHEME 5 (*i*), $-C_6H_6$; (*ii*), $-\dot{S}iH$.

Other metastable peak-supported fragmentations in the spectra of (X) and (XI) involve elimination of hydrocarbon groups, such as C_2H_2, C_2H_4, $\dot{C}H_2$, $\dot{C}H_3$, or CH_4,

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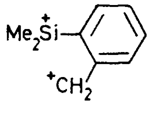
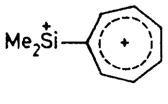
[21] R. R. Schrieke and B. O. West, *Austral. J. Chem.*, 1969, **22**, 49.

or hydrogen atoms or molecules. However, some, such as the loss of SiPhH from the $P^{+\cdot}$ ion and $C_{13}H_{10}$ from $[P - \dot{H}]^+$ of (X; R = Ph), involve more complex species. An unusually broad band of overlapping metastable transitions extending for over four mass units from *m/e* 138 was found in the spectrum of (X; R = Ph). These transitions may be associated with several decompositions including the production of the ions at *m/e* 196—192 from several ions in the region *m/e* 272—267, or ions at *m/e* 166 and 165 from *m/e* 196—194, or *m/e* 152 from either *m/e* 166 or 165. The metastable peak at *m/e* 138.4, corresponding to the elimination of benzene from $P^{+\cdot}$, was the only one intense enough for an unambiguous assignment to be made.

Relatively abundant double-charged counterparts of $P^{+\cdot}$ ions and the base-peak ions were a feature of the spectra of these compounds (Table). The stability of



(XXII)



(XXIII)

these ions may be enhanced if the heterocyclic ring is cleaved and some separation of charge is achieved. Ions such as, for example, (XXII) or (XXIII) from (X; R = Me), may be important in this stabilisation. The metastable-supported decomposition of P^{2+} of (X; R = Ph) by loss of C_6H_6 to give $[Si(C_{13}H_{10})]^{2+}$ was also observed.

EXPERIMENTAL

The organosilicon heterocycles (II)—(IV), (VI)—(VIII), and (X)—(XII) were prepared by standard methods [22-24] and checked for purity by i.r., ^1H n.m.r., and g.l.c. analysis. Compound (V) (b.p. 126—128 °C), synthesised by the action of trimethyl orthoformate on (III), was a generous gift from Dow Corning Ltd. (Barry). The silacyclobutanes (IX) containing metal–metal bonds were prepared [25] by reaction between (VII) and the appropriate lithium reagent ($LiMR_3$).

Mass spectra were recorded on an A.E.I. MS9 mass spectrometer operating with a 70 eV electron beam,* 8 kV accelerating voltage, and an ion-source temperature of between 100 and 150 °C. Liquids and low-melting solid samples were introduced directly into the ion source *via* an all-glass ' direct-inlet ' probe. The flow rate into the source was controlled by a ' Rotaflow ' tap between the source and sample holder and, if necessary, by immersing the sample holder in a cooling bath. Higher-melting solids were introduced by the direct-insertion probe. Relative abundances were calculated by standard procedures.[9]

We thank Miss Choi-Kwan Yuen for assistance with the syntheses.

[5/832 *Received, 5th May*, 1975]

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* 1 eV ≈ 1.60×10^{-19} J.

[22] R. Damrauer, *Organometallic Chem. Rev.*, 1972, **A8**, 67.

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