

1,3,4-Triphenylpyrroline-2,5-dione (9) and 1,3,4-Triphenyl-5-phenyliminopyrrolin-2-one (10).—The reaction using phenyl isocyanate (0.05 mol), diphenylacetylene (0.025 mol), and iron pentacarbonyl (0.025 mol) was carried out in a similar manner as above at 175° for 4 hr, and the products were extracted (benzene) and chromatographed (benzene, fractions 1–5; ethanol, fraction 6). From the first fraction, 0.1 g of π -tetraphenylcyclobutadieneiron tricarbonyl, $\text{Fe}(\text{CO})_3(\text{PhC}_2\text{Ph})_2$ (mp 238° dec), and 0.7 g of the binuclear iron carbonyl complex, $\text{Fe}_2(\text{CO})_6(\text{PhC}_2\text{Ph})_2$ (mp 205° dec), were obtained and recrystallized (benzene-ethanol); no depressions of melting points were observed for each mixture with authentic samples.²² From the second fraction, 0.2 g of 2,3,4,5-tetraphenyl-2,4-cyclopentadiene-1-one (mp 220°) was obtained and recrystallized (benzene); no depression of the melting point was observed for the mixture with the authentic sample.²⁵ From the third fraction, the pyrroline 9 was obtained and recrystallized (benzene-ethanol): yellow needles; 3.3 g; mp 180–181° (lit.²⁶ 178–179°); mass spectrum (70 eV) m/e 325 (M^+), 297 ($\text{M} - \text{CO}$), 206 ($\text{M} - \text{C}_6\text{H}_5\text{NCO}$). From the fourth fraction, the pyrroline 10 was obtained and recrystallized (ethanol): orange crystals; 1.5 g; mp 157–158°; mass spectrum (70 eV) m/e 400 (M^+), 372 ($\text{M} - \text{CO}$), 295 (372 – C_6H_5), 281 ($\text{M} - \text{C}_6\text{H}_5\text{NCO}$), 194 ($\text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5$). From the fifth and sixth fractions, 0.1 g of the cyanurate 4 (mp 294°) and 1.0 g of the urea 5 (mp 239°) were obtained; no depression of melting points were observed for the mixture with the authentic samples.^{23,24}

The pyrroline 10 was also obtained in 48% yield in the reaction using $\text{N,N}'$ -diphenylcarbodiimide (0.0073 mol), diphenylacetylene (0.0073 mol), and iron pentacarbonyl (0.0073 mol) at 185° for 2 hr.

4-(Benzylidene- α -d)-1,3-diphenylhydantoin (1'a).—The hydantoin 1'a was prepared from phenylacetylene-1-d in a similar manner to that used to prepare the hydantoin 1a: white crystals, 60% yield, mp 200°.

Equimolecular Reaction of Phenyl Isocyanate, Diphenylcarbodiimide, Phenylacetylene, and Iron Pentacarbonyl.—A mixture of diphenylcarbodiimide (0.01 mol), phenyl isocyanate (0.01 mol), and iron pentacarbonyl (0.01 mol) was heated to 140° for 30 min. Phenylacetylene was added dropwise to the mixture,

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(26) J. V. Seudi and H. G. Lindwall, *J. Amer. Chem. Soc.*, **57**, 2302 (1935).

and stirring was continued for 2 hr at 140–190°. The products were extracted (benzene), concentrated, and chromatographed (benzene). From the first and second fractions, 1.7 g (67%) of the imidazolidine 7 and 1.4 g (82%) of the hydantoin 1a were obtained, respectively. From the third fraction, 0.2 g (12%) of the benzodiazepinone 11 was obtained and recrystallized (benzene-ethanol): yellow crystals; mp 215–216° (lit.⁶ 202–203°); mass spectrum (70 eV) m/e 340 (M^+), 220 ($\text{M} - \text{PhNCO}$), 192 [$\text{M} - \text{CON}(\text{Ph})\text{CO}$].

Acid Hydrolysis of the Imidazolidines 7 and 8a and the Pyrroline 10.—Either 7, 8a, or 10 (0.5 g) was dissolved in a mixture of 20 ml of ethanol and 10 ml of water, and concentrated hydrochloric acid (10 ml) was added. After refluxing for 10 min on a steam bath, the reaction mixture was cooled, extracted (ethyl ether), dried (MgSO_4), concentrated, and recrystallized (benzene) giving 1a (from 7 and 8a) or 9 (from 10). Hydrolyses were quantitative.

Oxidation of the Hydantoin 1a.—Powdered potassium permanganate (1.3 g) was added over 1 hr to the hydantoin 1a (1.5 g) dissolved in pyridine (20 ml)-water (2 ml) with vigorous stirring; the temperature was held at 18–20°. Water (10 ml) in limited amounts was added to the reaction mixture with stirring, and stirring was continued for 30 min. The solution was made acid to congo red with dilute sulfuric acid and decolorized by sodium hydrogen sulfite. The precipitate was washed with water (30 ml) and ethyl ether (30 ml) and crystallized (benzene-hexane), giving 1.0 g (85%) of white needles of parabanic acid 2: mp 210° (lit.²⁷ 206–207°); ir 1785 and 1740 cm^{-1} ($\text{C}=\text{O}$); mass spectrum (70 eV) m/e 266 (M^+), 119 ($\text{C}_6\text{H}_5\text{NCO}$).

Anal. Calcd for $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_3$: C, 67.66; H, 3.79; N, 10.52. Found: C, 67.67; H, 3.79; N, 10.46.

The filtrate was made acid with concentrated hydrochloric acid and extracted with two 100-ml portions of ether. The ethereal extract was dried (MgSO_4) and concentrated. Benzoic acid (0.2 g) was obtained by crystallization of the residue with hexane: 37% yield; mp 124°; no depression of melting point was observed for the mixture with the authentic sample.

Registry No.—1a, 4514-33-4; 1b, 24707-10-6; 1c, 24707-11-7; 1d, 17858-25-2; 1e, 24707-13-9; 1f, 24704-22-1; 2, 6488-59-1; 7, 24707-15-1; 8a, 24707-16-2; 9, 5191-53-7; 10, 24707-18-4; 11, 4514-34-5.

(27) T. Figeo, *Rec. Trav. Chim. Pays-Bas*, **34**, 289 (1915).

Mass Spectra of Tetraza-3,6-disilacyclohexanes and Silylhydrazines

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The mass spectra of some silylhydrazines and tetraaza-3,6-disilacyclohexanes are presented. Silicon-containing fragments are the most abundant. Characteristic fragmentation modes are the direct and stepwise loss of free radicals and neutral molecules from the molecular and fragment ions. Hydrogen transfer and skeletal rearrangement processes are observed. Evidence for rearrangements of doubly charged ions has been obtained. Two different types of metastable ions are detected which support many fragmentation modes. High-resolution data are in agreement with the proposed fragmentation processes.

Although the interest in organosilicon chemistry has been steadily increasing in recent years, only a limited amount of information is available concerning the mass spectral fragmentation of organosilicon compounds.^{2–7}

(1) (a) The National Chemical Laboratory, Poona; (b) Department of Chemistry, Indian Institute of Technology, Kanpur.

(2) G. Fritz, J. Grobe, and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, **7**, 349 (1965), and references cited therein.

(3) J. J. de Ridder and G. Dijkstra, *Rec. Trav. Chim. Pays-Bas*, **86**, 737 (1967).

(4) J. Tama's and K. U'jsza'szy, *Acta Chim. Acad. Sci. Hung.*, **56**, 125 (1968).

(5) Na. Y. Chernyak, R. A. Khmel'nitskii, T. V. D'yakova, K. S. Pushchevaya, and V. M. Vdovin, *Zh. Obshch. Khim.*, **37**, 917 (1967).

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The mass spectra of trimethylsilyl ethers, amines, and sulfides, derivatives of acids,^{8–10} and siloxanes^{11–13} have been reported.

The information available in literature on the be-

(7) T. H. Kinstle, I. Haidue, and H. Gilman, *Inorg. Chim. Acta*, **3**, 373 (1969), and references cited therein.

(8) J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **32**, 3904 (1967).

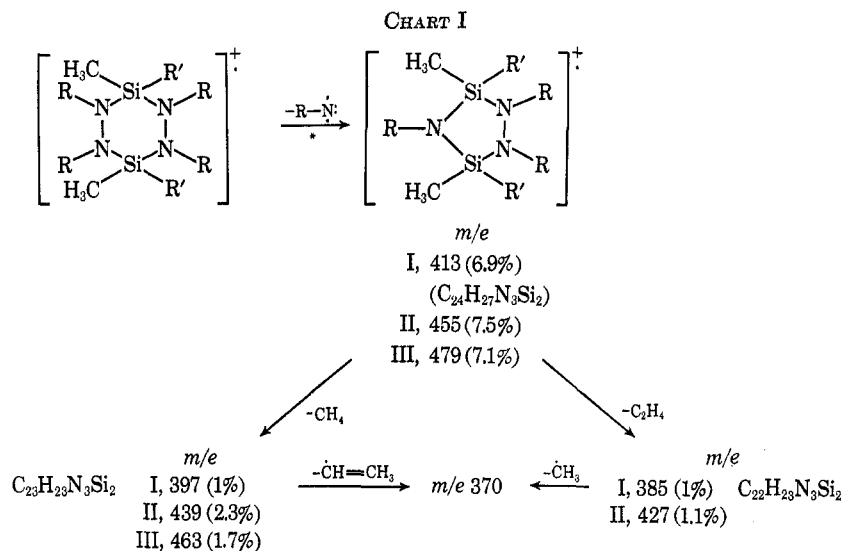
(9) G. H. Draftan, R. M. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 669 (1968), and references cited therein.

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(11) A. G. Brook, A. G. Harrison, and P. F. Jones, *Can. J. Chem.*, **46**, 2862 (1968).

(12) G. Dube and H. Kriegsmann, *Org. Mass Spectrom.*, **1**, 891 (1968).

(13) G. Dube, *Z. Chem.*, **8**, 350 (1968).



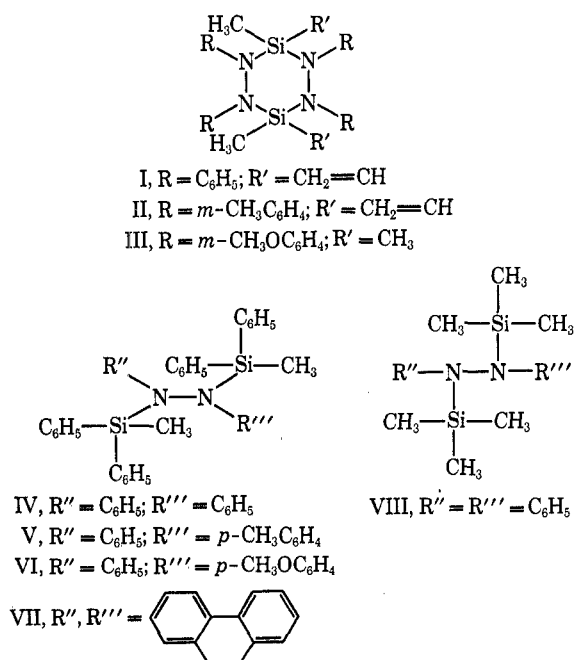
havior of Si-N bond under electron impact is scanty.^{14,15} It has been reported that, in the mass spectra of silazanes, the molecular ion was observed as a minor peak, the base peak being the $M - 15$ ion formed by the loss of a methyl radical. The subsequent fragmentation modes reported are the expulsion of neutral molecules such as methane, ammonia, formaldehyde, and hydrogen chloride. In the present studies, we have examined the mass spectra of a few silicon-nitrogen compounds such as silylhydrazines and tetraaza-3,6-disilacyclohexanes. The tetraaza-3,6-disilacyclohexanes include 1,2,4,5-tetraphenyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (I), 1,2,4,5-tetra(*m*-tolyl)-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (II), and 1,2,4,5-(*m*-anisyl)-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (III). The silylhydrazines that we have studied are

N,N'-diphenyl-N,N'-bis(diphenylmethylsilyl)hydrazine (IV), N-phenyl-N'-(*p*-tolyl)-N,N'-bis(diphenylmethylsilyl)hydrazine (V), N-phenyl-N'-(*p*-anisyl)-N,N'-bis(diphenylmethylsilyl)hydrazine (VI), N,N'-bis(diphenylmethylsilyl)dibenzodihydropyridazine (VII), and N,N'-diphenyl-N,N'-bis(trimethylsilyl)hydrazine (VIII).

Results and Discussion

The mass spectra of the three tetraaza-3,6-disilacyclohexanes (I-III) are shown in Figure 1. Like the mass spectra of cyclosilazanes reported recently,¹⁵ the molecular ion is significant and is the base peak in the spectra of these compounds. Fragments corresponding to direct and/or successive loss of methyl, vinyl, and phenyl radicals are negligible. The loss of phenylnitrene $\text{R}-\text{N} \cdot$ from a molecular ion is a very significant metastable-supported fragmentation mode. The resulting odd-electron ion then appears to eliminate neutral molecules such as methane and ethylene and finally stabilize by expulsion of vinyl and methyl radicals. High-resolution data obtained on peaks at m/e 413, 397, 385, and 370 in the spectrum of compound I support this (Chart I).

From the ion abundances alone it is difficult to establish whether the initial ionization takes place by the loss of a bonding or nonbonding electron.¹⁶ The observed elimination of phenylnitrene can be reasonably explained by assuming that the initial ionization is taking place by the loss of a bonding electron of the Si-N bond, the charge remaining on the silicon atom because of the large difference between the electronegativity of silicon and nitrogen. This is followed by a homolytic cleavage of the N-N bond resulting in the elimination of phenylnitrene. Djerassi, *et al.*,^{17,18} have reported the formation of nitrogen entities with electron sextet as preferred intermediates and product ions in the mass spectra of oximes and N,N-dimethylhydrazones.



(14) J. Silbiger, C. Lifshitz, J. Fuohs and A. Mendelbaum, *J. Amer. Chem. Soc.*, **89**, 4308 (1967), and references cited therein.

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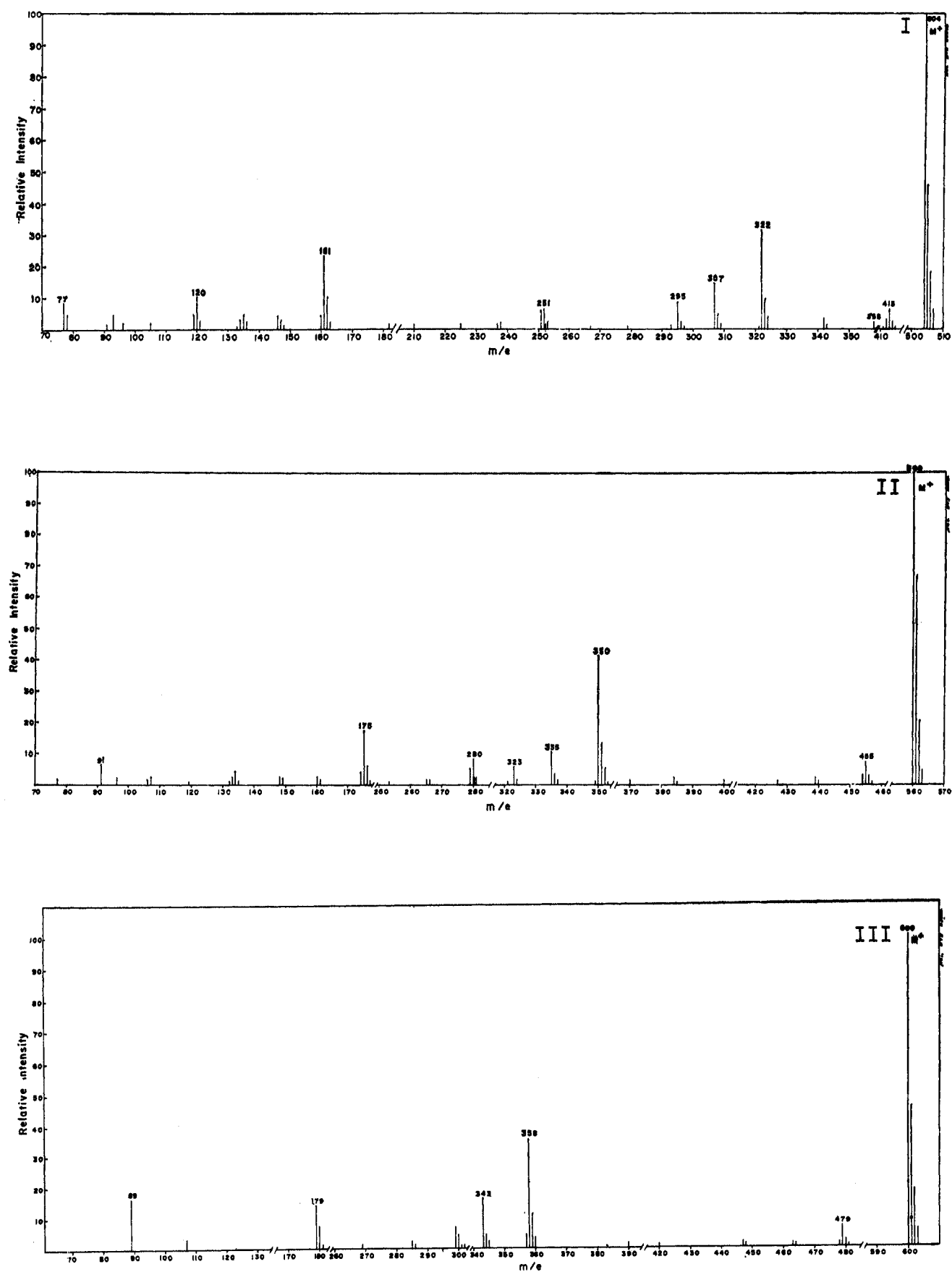
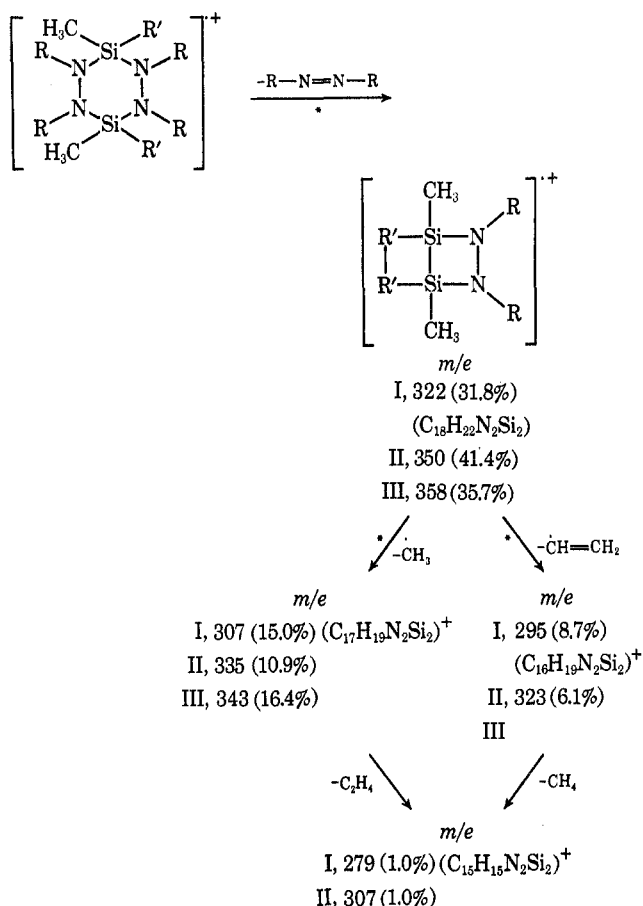


Figure 1.—Mass spectra of 1,2,4,5-tetraphenyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane, (I) 1,2,4,5-tetra(*m*-tolyl)-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (II), and 1,2,4,5-tetra(*m*-anisyl)-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (III).

Photolytic¹⁹ and thermal²⁰ elimination of phenylnitrene is well known. The elimination of phenylnitrene under electron impact appears to be a novel type of fragmentation mode.

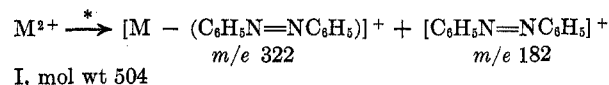
Another fragmentation mode supported by an appropriate metastable peak is the loss of a neutral molecule (RN=NR) from the molecular ion which results in the formation of an odd-electron fragment ion. This fragmentation mode resembles the loss of toluene from the M - 15 ion in the mass spectrum of 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl 1,4-disilin.²¹ It is pertinent to observe that the loss of neutral molecules such as RN=NR was also observed in the thermal decompositions of tetraaza-3,6-disilacyclohexanes.²² Further fragmentation is dominated by the expulsion of free radicals (methyl and vinyl) which leads to the formation of stable even-electron ions. These even-electron ions, in turn, appear to lose neutral molecules such as ethylene or methane. Evidence in support of these fragmentation processes was obtained from accurate mass measurements.



In the mass spectra of benzene²³ and 9,10-diphenylanthracene,²⁴ doubly and triply charged ions have been reported to undergo metastable supported rearrangements. The metastable peak at m/e 411.6 (calcd 411.4) in the spectrum of I has been rationalized by

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 (20) F. P. Lossing, *Ann. N. Y. Acad. Sci.*, **67**, 499 (1957).
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 (22) V. Kalyanaraman and M. V. George, unpublished results.
 (23) W. Higgins and K. R. Jennings, *Chem. Commun.*, 99 (1965).
 (24) K. R. Jennings and A. F. Whittings, *ibid.*, 820 (1967).

assuming the decomposition of the doubly charged molecular ion into two singly charged ions as shown.

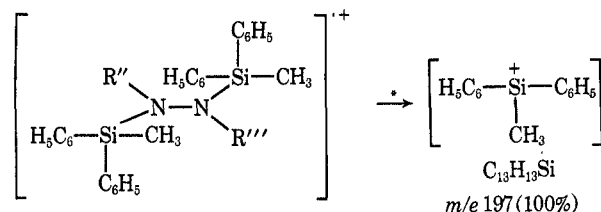


Doubly charged ions have been observed which correspond to the molecular and the M - (RN=NR) ions. These doubly charged ions with integral masses were identified from their isotopic peaks observed at m/e 252.5 and 161.5. High-resolution data also support the elemental compositions assigned to them. This observation can be explained by assuming that the doubly charged molecular ion undergoes the following ion decomposition reaction

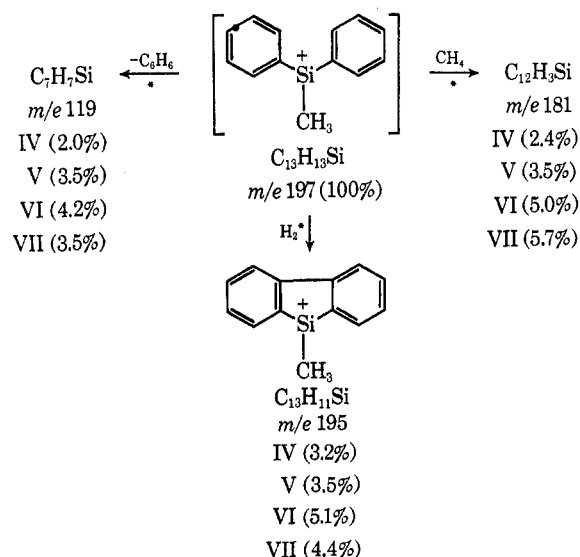


It appears that this fragmentation mode operates in both the singly and doubly charged molecular ions and takes place in a single step.

Figure 2 shows the mass spectra of the compounds IV, V, and VI. It is reasonable to assume that in these compounds, also, the initial ionization takes place by the loss of a bonding electron. This seems to trigger the fragmentation process leading to the formation of the base peak at m/e 197. The M - 197 ion is, however, a minor peak.



The loss of neutral molecules such as H₂, CH₄, and C₆H₆ allows easy degradation paths for the even-electron fragment m/e (197). This gives rise to daughter ions m/e 195, 181, and 119. Compositions of these ions are confirmed from high resolution data.



Loss of two hydrogen atoms in one step by the "ortho coupling" has been shown in the spectra of triphenylphosphine, triphenylarsine, triphenylstibine, diphenyl-

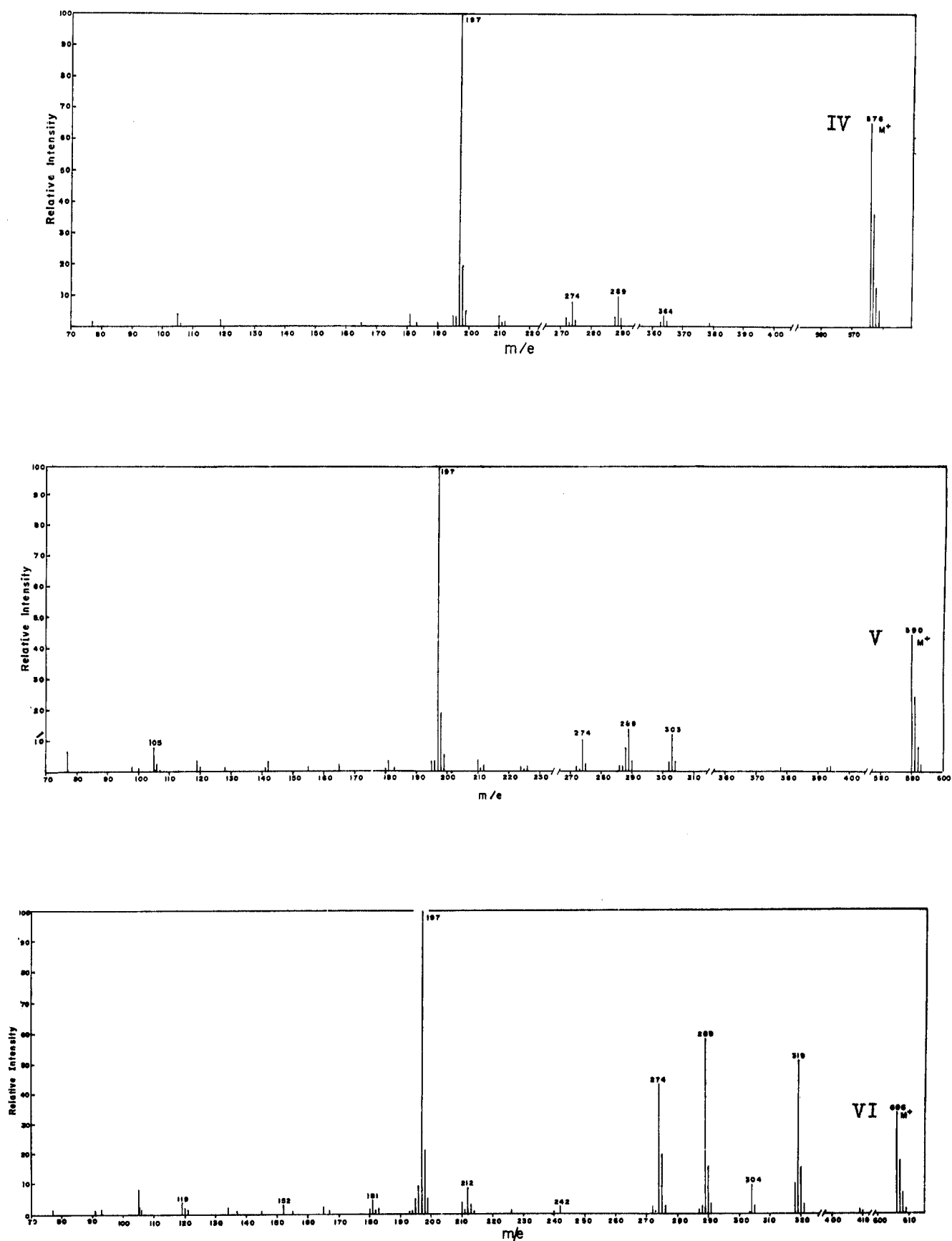
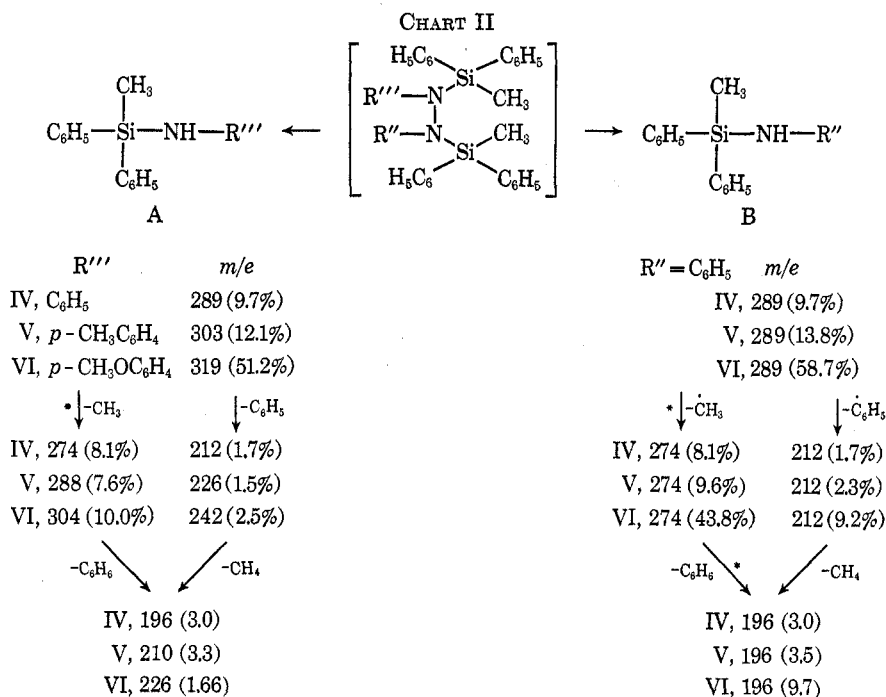


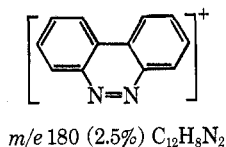
Figure 2.—Mass spectra of *N,N'*-diphenyl-*N,N'*-bis-(diphenylmethylsilyl)hydrazine (IV), *N*-phenyl-*N'*-(*p*-tolyl)-*N,N'*-bis(diphenylmethylsilyl)hydrazine (V), and *N*-phenyl-*N'*-(*p*-anisyl)-*N,N'*-bis(diphenylmethylsilyl)hydrazine (VI).



methane,²⁵ and diphenylamine.²⁶ Elimination of methyl and phenyl radicals from the molecular ion is insignificant. However, the loss of a methyl group is preferred to the loss of a phenyl group attached to a silicon atom.

Simple cleavage of N-N bond in silyhydrazines is not very significant in the spectra of compounds IV to VII. However, cleavage of the N-N bond takes place with hydrogen transfer which results in the formation of odd-electron fragmentation, A and B. Other precursors of these rearrangement ions could not be identified in the absence of appropriate metastable peaks. In compound VIII this rearrangement is not very significant, since the simple cleavage of the N-N bond seems to be preferred over the rearrangement. In the absence of sufficient deuteration data it is difficult to propose any satisfactory mechanism for these rearrangements (see Chart II).

The spectrum of VII is slightly different from those of IV, V, and VI. One of the differences is the stepwise loss of two fragments with mass 197. The driving force for this fragmentation seems to be the formation of a stable aromatic system.

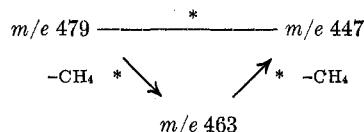


The characteristic peak observed at m/e 289 in the spectra of IV, V, and VI is absent in the spectrum of VII which indicates that the hydrogen rearrangement process is not operating to a significant extent. No rearrangement involving the transfer of alkyl and aryl groups has been observed. The rigidity of the molecule compared with IV, V, and VI may be responsible for the absence of these fragmentation modes in VII.

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The observed values of apparent mass of the metastable ions agreed with calculated values to ± 0.2 mass unit. The metastable peaks were sharp when neutral molecules and radicals were eliminated, and diffuse and broad when silicon-containing fragments were lost. Some metastable peaks observed in the spectra of III, IV, and V can be explained by two-step fragmentation processes, since the fragments lost are not present as single structural units in the parent ion. For example, in compound III it is obvious that the $M - (R-\dot{N}:)$ ion (m/e 479) does not contain any single structural entity



with 32 mass units. Hence, this should involve successive loss of two molecules of methane. Metastable peaks are observed for all these decompositions.

Experimental Section

The mass spectra of compounds I-VIII were recorded on a CEC 21-110B mass spectrometer. The samples were introduced through the direct inlet probe and the ion source was operated between 150 and 200°, the ionizing current was 40 μ A, and the ionizing voltage was 70 eV. The accurate masses of fragments ions were determined by high-resolution mass spectrometry at a resolution of 6000.

The tetraaza-3,6-disilacyclohexanes (I-III) and silyhydrazines (IV-VIII) were prepared according to reported procedures.²⁷⁻²⁹

In the bar spectra of the compounds reported in Figures 1 and 2, intensities of the peaks >1% of the base peak are only reported. The asterisks indicate the observed metastable transitions.

Registry No.—I, 17082-85-8; II, 17082-87-0; III, 17082-89-2; IV, 5994-98-9; V, 15951-44-7; VI, 15951-45-8; VII, 15951-51-6; VIII, 5994-95-6.

(27) S. S. Dua and M. V. George, *J. Organometal. Chem.*, **10**, 219 (1967).

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(29) M. V. George, P. B. Talukdar, and H. Gilman, *ibid.*, **5**, 397 (1966).