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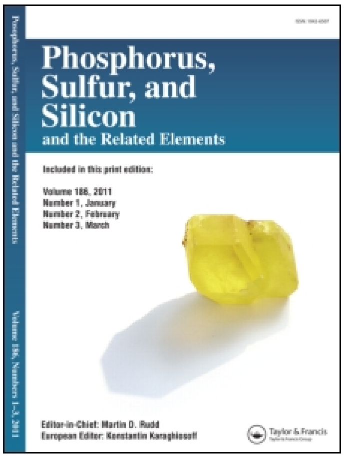

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THE PRESENT STATE OF THE CHEMISTRY OF CYCLOSILANES

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THE PRESENT STATE OF THE CHEMISTRY OF CYCLOSILANES

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In this review, an overlook of the present state of the chemistry of cyclosilanes is given. Cyclosilanes with organic substituents are old and well-known compounds. Starting with the first investigations by Kipping a small review of the background introduces these cyclic compounds.

In the last decades, developments in this field have become faster. West showed in excellent investigations the important behavior of these compounds to form radical anions by adding electrons and we were able to synthesize the first inorganic substituted cyclosilanes such as halogenated cycles, but also the basic compounds Si_5H_{10} and Si_6H_{12}. The properties of the cyclic silanes were reinvestigated in view of all the new derivatives and also of possible industrial applications. New results in UV-spectroscopy in connection with results of PE-spectroscopy show that these groups of compounds are chromophores. Similar results were found some years ago on polymeric compounds containing such silicon cycles, but in view of new results and in connection with the formation of radical anions, the picture now becomes clearer. After discussion of these new results, the review completes the overlook with a presentation of larger ring systems and cyclic silanes with other additional atoms.

In this plenary lecture in our conference, besides all the sulfur, phosphorus and nitrogen-containing ring systems, I want to tell you that also silicon is able to form cyclic systems. I am very grateful to the organizing committee for the opportunity to tell about these silicon cycles. In this lecture room are very famous chemists, but not all of you are specialists in silicon chemistry; therefore allow me to start my lecture with a small historical review. After this, I want to organize my lecture in two main parts, first the preparation and the chemical properties of cyclosilane and second the physicochemical and spectroscopic properties of these compounds.

The first compound which contains a silicon cycle in the molecule was found by Kipping 1921.[1]

$$Ph_2SiCl_2 \xrightarrow[\text{metal}]{\text{alkali}} (SiPh_2)_n \left\{\begin{array}{ll} & \text{m.p.} \\ n = 4 & 32^\circ \\ n = 5 & 451^\circ \\ n = 6 & 495^\circ \\ n = \text{polymer} & \end{array}\right. \qquad (I)$$

He coupled diphenyldichlorosilane with sodium and found four compounds (I). He was able to separate these compounds, because of different solubilities. The high reactivity of the compound *A* in his nomenclature caused him to propose a structure of a biradical, but later investigations done by Gilman[1] and others found that *A* is a four-membered ring Si_4Ph_8 and the reactivity is caused by the high ring strain. The more soluble compound, he called it *B*, was postulated as a four-membered ring, but later investigations showed, it is the five-membered ring. Compound *C* is very insoluble in all common solvents and investigations therefore were very difficult. It seemed to be that *C* is the six-membered ring, but not before the seventies, chemical evidence and mass spectra confirmed this structure.

All perphenylated cyclosilanes are very stable, also in air and exhibit high melting points. The large phenyl groups are able to shield the sensitive silicon cycle and this seems to be the reason for the high stability. The reactivity is depending on this shielding, on the ring strain and on the solubility in organic solvents. Therefore the four-membered ring is the most sensitive compound and the six-membered ring is the less reactive compound, because of its low solubility. The five-membered ring is best suited for chemical reactions. Its solubility is good in benzene and similar solvents and the stability of the silicon cycle is high enough, because of low ring strain to avoid ring cleavage by chemical reactions.

Kipping had also investigated the reaction of bis-*p*-tolyldichlorosilane[2] and found similar results. But it seems to be necessary to reinvestigate this system and we started investigations in the last weeks (II).

$$(p\text{-tolyl})_2\mathrm{SiCl}_2 \xrightarrow[\text{metal}]{\text{alkali}} [(p\text{-tolyl})_2\mathrm{Si}]_n \tag{II}$$

Before I start to tell you more about the reactivity of phenylated cyclosilanes, let us have a look at methylated cyclosilanes.

The first methylated cyclosilane was found by Burkhard 1949 in a very low yield of 2% beside polymeric material[3] (III).

This polymeric material is today the important starting material for the production of silicon carbide fibers. Changing the reaction conditions, we used lithium in THF and addition of a catalyst led to an increase of the yield up to 70 to 80%. The reaction was carefully investigated by West *et al.* He found beside the six-membered ring also other ring sizes $(\mathrm{SiMe_2})_n$ with $n = 5$–35. A kinetic preference for the formation of a five- and seven-membered ring was found to exist, but there is a thermodynamic preference for the six-membered ring. Short reaction times generally give mainly five- and seven-membered rings, while longer reaction times give predominately the six-membered ring.[4]

reaction with alkali metals

$$\mathrm{Me_2SiCl_2} \longrightarrow (\mathrm{SiMe_2})_n \qquad n = 5,\underline{\underline{6}},7,8 \ldots\ldots n \tag{III}$$

Burghard 1949
West and coworkers
and others

$$\mathrm{Et_2SiCl_2} \longrightarrow (\mathrm{SiEt_2})_2 \qquad n = 4-8 \tag{IV}$$

Carlson and West

$$(\mathrm{tBu,Me})\mathrm{SiCl_2} \longrightarrow (\mathrm{tBuMeSi})_4 \tag{V}$$

different isomers West et al

$$\mathrm{PhMeSiCl_2} \longrightarrow (\mathrm{PhMeSi})_6 \tag{VI}$$

and polymers Hengge, West

Investigations were also done with diethyldichlorosilane[5] (IV). The products obtained from this reaction depend on the alkali metal and the conditions. With two equivalents of lithium in THF the major products are $n = 5$ and 7. With an excess of potassium in THF, the five-membered ring is formed and with sodium in toluene the four-membered ring is the major product. It is remarkable that this four-membered ring is more stable than the methylated cycle.

Other cyclosilanes are rare. Known are four-membered rings with methyl and tertiar butyl groups as substituents.[6] Of these cycles several stereochemical isomers exist and West was able to separate these isomers (V).

A very interesting system is the mixed methyl-phenyl substituted ring system (VI). We found this compound for the first time[7] but also West investigated this system and found other ring sizes and polymeric material,[8] which became of important interest for photosensitive films.

Beside this industrial interest the mixed substituted ring opens the possibility of the formation of isomers and I will tell you later more about these compounds.

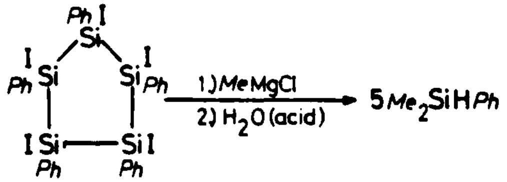
As we started our investigations about cyclosilanes, it is now about 15 years ago, no other and no inorganic substituted cyclosilanes were known. We were interested in these compounds, because I investigated previously the polymeric compound siloxen in which also silicon cycles are included, but coupled with oxygen to a polymeric layer. I was interested in the reason of the color of siloxen derivatives. To learn more about the properties of cyclic silanes, investigation of monomeric cyclosilanes seemed to be necessary.

We started our investigation with phenylated cyclosilanes. It was known from the chemistry of monosilanes that the silicon phenyl bond is split by hydrogen halides. This was investigated by Fritz[9] and others and this reaction gives a good chance also for cyclosilanes. On the other hand, a cleavage of the silicon methyl bond is very difficult and ring cleavage reactions are probable.

Of phenylated compounds, the best-suited ring size was the five-membered ring as I have told you before. Therefore we started our investigation with the five-membered perphenylated ring and tried to split off the phenylgroups by means of HI.

While the four-membered perphenylated ring is destroyed by reaction with HI, the five-membered ring is stable. Some phenyl groups change place with iodine and benzene is formed. The reaction proceeds easily, until five phenyl groups have gone, then it slows down until ultimately 6 to 7 phenyl groups have been removed. With longer reaction times or more drastic conditions, ring cleavage occurs (VII, Figure 1).

$$Si_5Ph_{10} + n\,HI \longrightarrow Si_5Ph_{10-n}I_n + n\,PhH \qquad \text{(VII)}$$



(VIII)

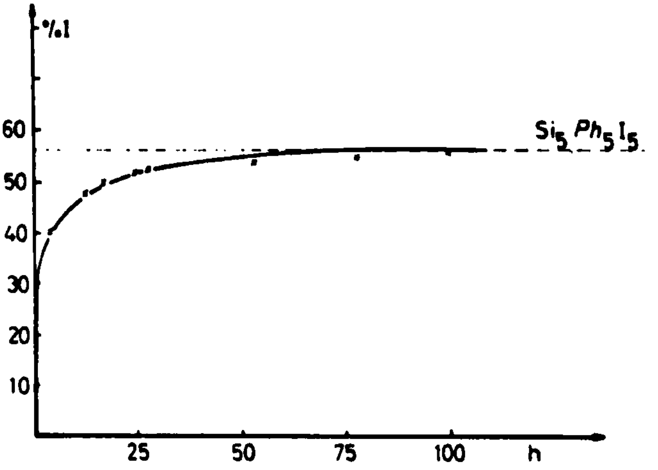
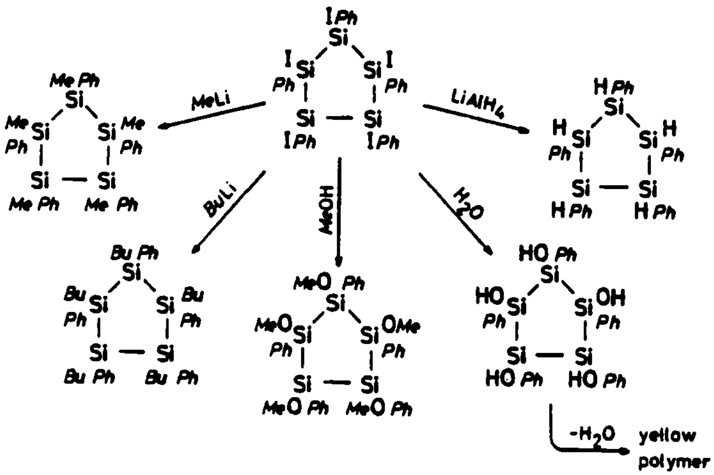


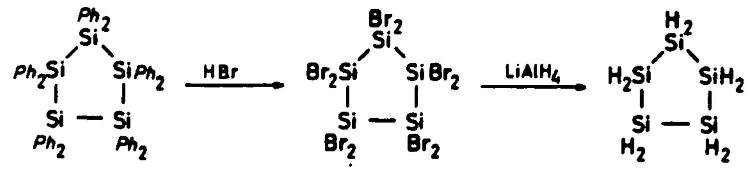
FIGURE 1

The first step, the removal of five phenyl groups yields a well-defined product, pentaphenylpentaiodocyclopentasilane, in which each silicon atom has one iodine atom and one phenyl group. This structure is inferred from the cleavage products of the following Grignard reaction (VIII). The Grignard compound destroys the ring and after acid hydrolysis, a good yield of dimethylphenylsilane demonstrates the proposed structure. The higher iodinated products are probably isomers with various degrees of substitution. The so formed Si-iodine linkages are very reactive, offering the possibility of forming various derivatives[11] (IX).

Methylation to pentamethylpentaphenylpentacyclosilane was effected with methyl-lithium. Butyl and methoxy derivatives are also known. Reduction with $LiAlH_4$ gives the hydrogen compound. In this compound the frequency of Si—H



(IX)



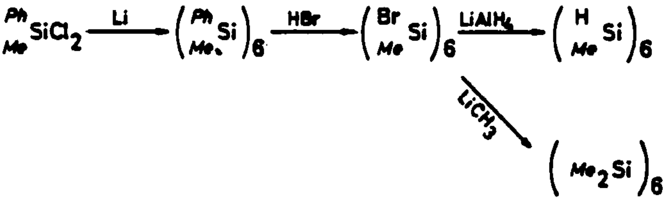
(X)

Kp.: 194°C(extrap.). Fp.: $-10.5°C$.
heat of vap.: 48749 J. mol^{-1} (OK).
$d_4^{20} = 0.963$. $n_D^{20} = 1.6910$.
^1H-NMR (s). $\tau = 6.51$ ppm (TMS).
^{29}Si-NMR(*t*). $\delta = 105.4$ ppm (TMS).
$^1J(^{29}Si{-}H) = 198.8$ HZ.

stretching vibration is very low. Such low frequencies are always observable, if the Si-atom of the SiH bond can be further bonded to at least two other Si-atoms. We found an easy chlorination of the Si—H bond with weak chlorinating agents such as CCl_4 or $CHCl_3$ always occurs, if the frequency is lower than 2100 cm^{-1}. For a silicon chemist, of course, the completely hydrogenated silicon ring would be a particularly interesting compound, because the group of cyclic silicon hydrides was completely unknown. We found now, hydrogen bromide is able to split all phenyl groups from the five-membered cycle is one step in a short time. We made the full brominated Si-cycle Si_5Br_{10} and without difficulties with $LiAlH_4$ the first cyclic silicon hydride Si_5H_{10} is formed (X). Cyclopentasilane is a colorless liquid, the melting point is about $-10°C$, the boiling point 190°C. The compound ignites in air spontaneously, after longer time or on exposure to light, it decomposes to SiH_4 and polymer $(SiH)_n$.[12]

After these results in the five-membered ring chemistry, we tried the same reaction with the six-membered ring. Investigation is very difficult, because the ring is not very soluble in any organic solvent and its reactivity is very low. No reaction occurs with iodine, basic compounds etc.. With HBr in the case of the six-membered ring, we are able to split only half of the phenyl groups from the cycle and we obtained hexabromohexaphenylcyclohexasilane. Stronger reaction conditions split the ring. A reduction with lithium aluminumhydride is possible and yields the compound $Si_6Ph_6H_6$.[13](XI).

$$Si_6Ph_{12} \xrightarrow{HBr} Si_6Ph_6Br_6 \xrightarrow{LiAlH_4} Si_6Ph_6H_6 \qquad (XI)$$



(XII)

Another way to form a ring with two different substituents is the following: In a Wurtz-like synthesis one can get[8,13] hexaphenylhexamethylcyclohexasilane from the reaction of methylphenyldichlorosilane with lithium. To confirm the structure we treated it with hydrogen bromide and it yielded the hexabromide (XII). This hexabromide reacts with Li—methyl to the known dodecamethylcyclohexasilane which is identical with the original compound, yielded by the reaction of dimethyldichlorosilane with sodium/potassium alloy or lithium.

With $LiAlH_4$ the corresponding hydride was obtained. This compound forms several diastereomers, which can be seen in different NMR proton spectra. West showed,[8] that one of the diastereomers of phenylmethylcyclohexasilane, the compound with the maximal distance between the phenyl groups is preferred. This compound shows different solubility in hexane and can be isolated from the other isomers.

We used the splitting reaction of the Si—phenyl bond with HBr, as I have shown you before also with this stereochemical isomer. This yielded hexabromohexamethylhexacyclosilane and after hydrogenation, the corresponding hydride $Si_6H_6Me_6$ shows a complete rearrangement and the formation of many isomers. It seems to be necessary to investigate this reaction mechanism in more detail to understand the reaction.[14]

In all these investigations about the six-membered cycle, we were not able to split all substituents from the ring.

These difficulties of the cleavage of the phenyl-silicon linkage in case of the six-membered ring caused us to investigate this cleavage reaction in detail. A variation is given with changing the hydrogen halide. But neither HI nor HCl instead of HBr shows a quantitative cleavage of all phenyl groups from the Si_6-cycle.

What is the reaction mechanism of this cleavage? No investigation was done about this cleavage reaction in nonaquous solution, but similar investigations done by Eaborn[15] showed an electrophilic reaction. So, we started an investigation with pure HBr and measured the cleavage rates of the silicon phenyl bond with various substituted phenyl groups. The measurements were done by means of NMR spectroscopy.[16]

A series with increase of cleavage rates, based to diphenyldimethylsilane is given in Figure 2; you can see the best rates are given with *p*-tolyl- and cumyl groups, a perfluorinated phenyl ring can not be split off from a silicon atom.

If we see these results in connection with the Hammet constant, we observe a good linear correlation and so we can say also in non-aquous solution, the cleavage reaction in question is an electrophilic reaction.

This result let us expect that the cleavage of tolyl-substituted cycles would be easier, but on the other hand, an electrophilic reaction is also influenced by use of catalysts. This second way seems to be more convenient and we tried to use aluminum chloride with HCl for the cleavage.

The success was outstanding. All phenyl groups of the perphenylated six-membered ring were split in a short time in benzene solution.[17] No sealed tube was necessary; the reaction is simple to do also with larger amounts. The so formed Si_6Cl_{12} can be purified by sublimation; it is a white powder, of course very sensitive to air and moisture. The same reaction is possible with $AlBr_3$/HBr to form Si_6Br_{12} and also with the five-membered cycle (XIII).

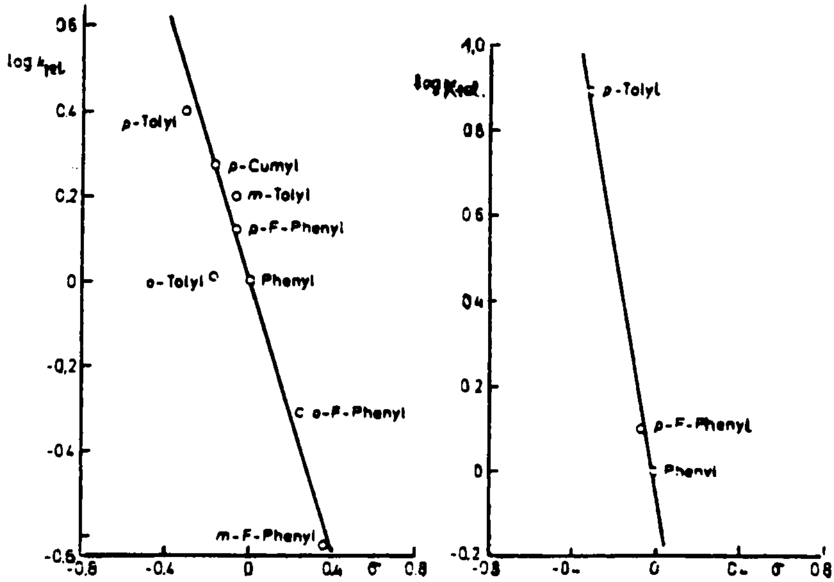
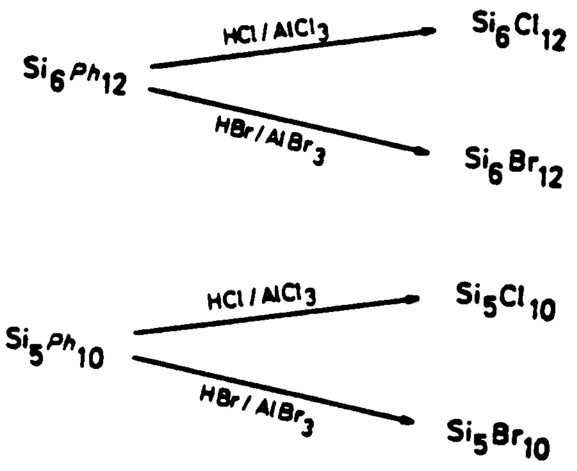


FIGURE 2

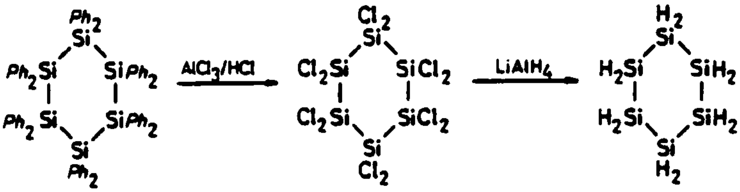
With $LiAlH_4$ we were able to get the corresponding cyclic silicon hydride Si_6H_{12}, the second known cyclic silicon-hydride (XIV)[18]. Because of smaller vapor density, the compound is less sensitive in comparison to Si_5H_{10}, but it ignites in air spontaneously also. It is a colorless liquid, the measured data are summarized in the table.

I have told you now some results about five- and six-membered rings. But also the four-membered ring, a system with high ring strain, gives the possibility for interesting investigations.

The synthesis of octaphenylcyclotetrasilane is complicated, because in the reaction of diphenyldichlorosilane with alkali-metal different ring sizes are formed and the



(XIII)



(XIV)

Mp = 16.5°C. Bp = 232°C.
^{1}H-NMR: (s) $\tau = 6.53$ ppm (TMS).
^{29}Si-NMR: (t) $\delta = 107.5$ ppm (TMS).
$^1J(^{29}\mathrm{Si{-}H})$: 195 HZ.

separation of the four-membered ring is troublesome and the yield low. For the preparation of disilane derivatives, which cannot be prepared in a Wurtz-like synthesis, we developed a new electrochemical method, which is also suitable for the preparation of the perphenylated four-membered cyclosilane.[19,20]

$$2R_3\mathrm{SiCl} \xrightarrow{+2e^-} R_3\mathrm{Si} - \mathrm{Si}R_3 + 2\,\mathrm{Cl}^- \qquad \text{(XV)}$$

$$R = \mathrm{CH_3}, \mathrm{C_6H_5}$$

solvent: 1,2-dimethoxyethane.
supporting electrolyte: tetrabutylammonium perchlorate.
terminal voltage: 50 V.
current density: 1.5 mA/cm^2.
cathode material: Pt.
anode material: Hg, Cd.
H-shaped cell with glass frit diaphragm.

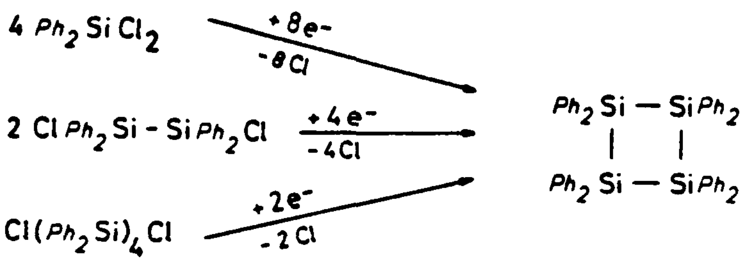
If one electrolyzes trimethylchlorosilane or triphenylchlorosilane in a divided cell, one can observe the cathodic formation of hexamethyldisilane or hexaphenyldisilane in nearly 100% current yield. It is remarkable that an electrolysis of a mixture of triphenyl- and trimethylchlorodisilane yields only the asymmetric triphenyltrimethyldisilane (XV).

After many experiments, we know today the limitation of this reaction. The electrolysis for the formation of SiSi linkages is possible only if we use aryl groups on the silicon atom (except the trimethylsilylgroup) or the compound formed is insoluble in the dimethoxyethane solvent. So, for example we were able to synthesize symmetric and asymmetric disilanes with fluorophenyl groups. It is not possible to synthesize such compounds by Wurtz synthesis, because of the reactivity of the fluorine with alkali metals and the compounds were unknown.

Electrolysis of diphenyldichlorosilane yields only the four-membered ring beside polymeric material. The synthesis is also possible, starting with 1,2-dichlorotetraphenyldisilane or with 1,4-dichlorooctaphenyltetrasilane (XVI). In the same way, we were able to isolate octakis (*p*-fluorophenyl) cyclotetrasilane (XVII).

But let us now see more about the chemistry of the four-membered ring.

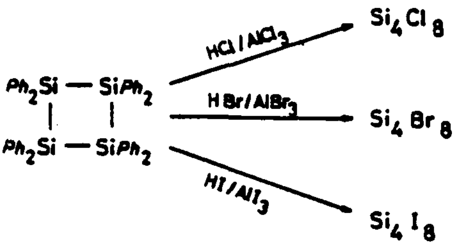
Starting from octaphenylcyclotetrasilane, it was possible under mild reaction conditions to split off the phenylgroups without a ring cleavage by use of our



(XVI)

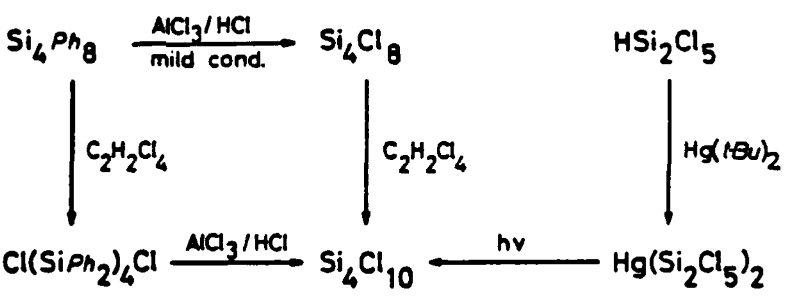
$$4\,(p\text{-F-C}_6H_4)_2SiCl_2 \xrightarrow{+8e^-} [(p\text{-F-C}_6H_4)_2Si]_4 + 8\,Cl^- \quad \text{(XVII)}$$

method with HX/AlX_3 and we were able to isolate Si_4Cl_8,[21] Si_4Br_8[22] and Si_4I_8.[23] The ring structure were proved by mass spectra and vibrational spectra (XVIII).[24]



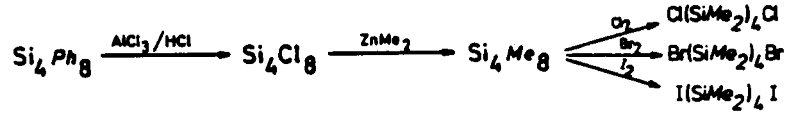
(XVIII)

The new cyclic chloride opens the possibility to synthesize the linear isomer of octachlorotetrasilane.[25] This simple compound was unknown in a pure state, it was prepared only in a mixture with the branched isomer. Splitting of the cyclic chloride Si_4Cl_8 with $C_2H_2Cl_4$ yields n-Si_4Cl_{10}. We prepared this compound in other ways too. One can split the ring first and then split off the phenyl groups. A completely different route was a synthesis, starting with pentachlorodisilane via the mercury compound and its decomposition in light (XIX).



(XIX)

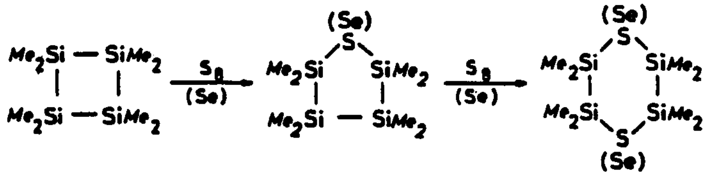
New aspects of the chemistry of the permethylated cyclosilane were given by a new synthesis route. Up to now only very small amounts of this compound were available and the separation from other ring sizes was possible only by use of chromatographic methods.



yield: 40%, Fp.: 40° (dec.).
^{1}H: $\delta = 0.32$ ppm (TMS).
^{29}Si (H): $\delta = -27.72$ ppm (TMS).
$^{2}J(SiH)$: 6.41 Hz.
$^{3}J(SiH)$: 3.36 Hz.
^{13}C (H): $\delta = -5{,}31$ ppm (TMS).
$^{1}J(SiC)$: 37,1 Hz.

(XX)

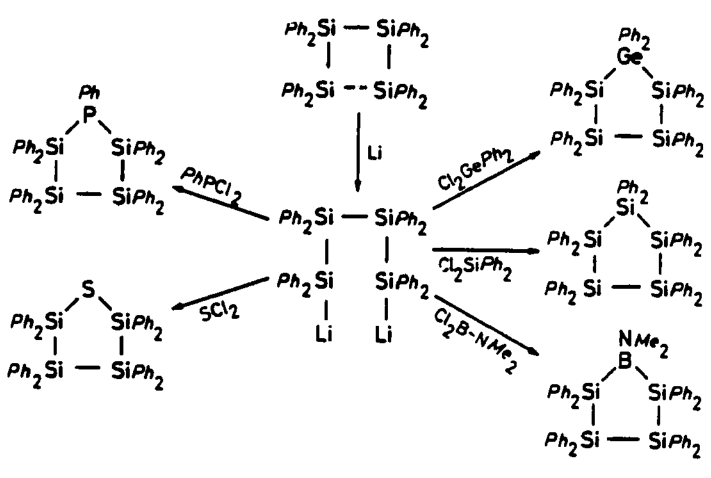
We found it is possible to methylate the Si—Cl bond with dimethylzinc at low temperature[26] and so, octamethylcyclotetrasilane is now available in preparative amounts (XX). The methylation is also possible by use of trimethylaluminum instead of the expensive and hard to prepare dimethylzinc, but only in the presence of small amounts of zinc chloride.[27] An intermediate formation of dimethylzinc seems to be probable during the reaction. The availability of larger amounts of the methylated four-membered ring makes it possible to start different investigations with this compound. We were able to split the ring with halogens; this is a good and new way to form four-membered chains with halogen atoms on the ends of the chain.[27] Insertion reactions with sulfur and selenium yielded the heterocyclic silanes Si_4S and Si_4Se (XXI) and in a second step rings with two sulfur or two selenium atoms, respectively.[28,29]



(XXI)

Other heterocycles were formed, starting with the perphenylated cycle.

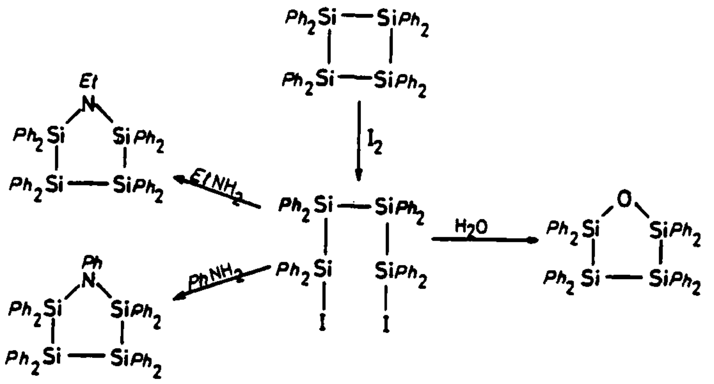
The perphenylated four-membered cycle Si_4Ph_8 is easily split by lithium. This was found by Gilman[1] many years ago. For following reactions it is not essential to



(XXII)

isolate the compound, but we found it is possible to do this in form of an adduct with two THF-molecules.[30]

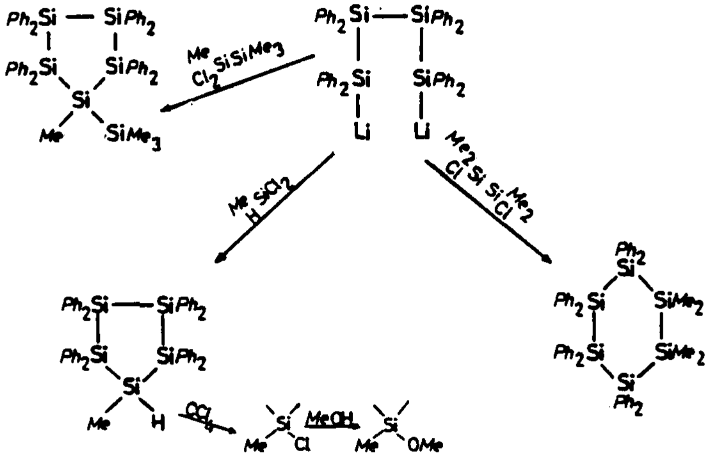
The dilithium compound opens the possibility of ring extension reactions, as well for isocyclic as for heterocyclic silanes (XXII), respectively.[30, 31] In this way we were able to synthesize some heterocyclic silanes and you see in Scheme XXIII also the other way, the opening of the ring with iodine to form other heterocyclic silanes.[30] In all these reactions, the yield is low and the preferred reaction is the back-formation of the four-membered ring. This led to the conclusion that the two lithium atoms are very close together and one has only the chance for a ring extension if one uses a small group or atom for the reaction.



(XXIII)

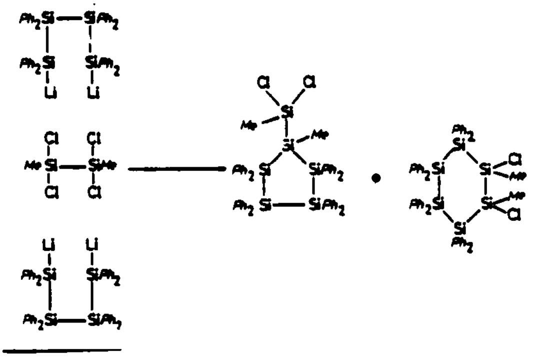
In this view, we can understand some results of ring-extension reactions of isocyclic silanes. The dilithium compound reacts with dichloromethylsilane to the expected five-membered ring; chlorination and methoxylation yields derivatives of the five-membered ring. 1,1-dichlorotetramethyldisilane reacts to the expected five-membered ring with a side chain, but with 1,2-dichlorotetramethyldisilane the six-membered ring is obtained only in a very low yield (XXIV).[32, 33]

On the other hand 1,1,2,2-tetrachlorodimethyldisilane yields only a mixture of five- and six-membered rings favoring the five-membered ring. We don't find a



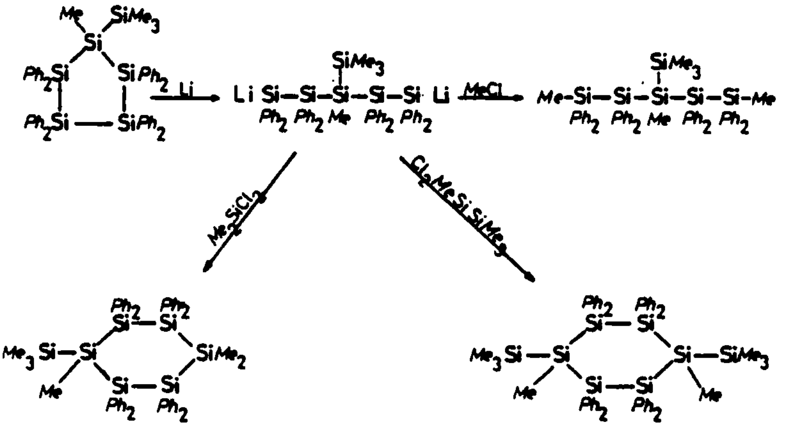
(XXIV)

bicyclic system and it seems to be that all the phenyl groups lead to steric hindrance (XXV):[32]

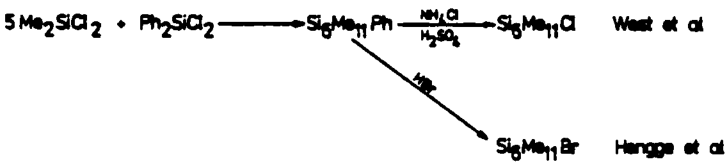


(XXV)

One reaction of all the reactions shown yielded a ring with a silicon-containing side chain. This cycle can be cleaved with lithium again and in respect to the known facts of the simple disilane chemistry, that cleavage is preferred with phenylated SiSi bonds, it occurs mainly on a defined SiSi bond and after methylation with methyl chloride, a new branched hexasilane was obtained. Instead of methylation one can add 1,1-dichlorotetramethyldisilane to the branched Li compound and a six-membered ring with two side chains is obtained. With a simple dichlorodimethylsilane, a six-membered ring with only one side chain is formed.[33,34]



For the preparation of cyclic silanes with side chains or for the preparation of polycyclic compounds a ring system with only one functional group would be an extremely interesting compound. In connection with the described splitting reaction of a phenyl group from a silicon framework, the six-membered ring with one phenyl and eleven methyl groups as substituents would be the best starting material. West has described this compound,[35] made in a cocondensation of dimethyl- and methylphenyldisilane in a yield of ~ 70%, but after many detailed investigations, we were not able to reproduce this yield. Only very small amounts of this compound were observed besides many by-products.



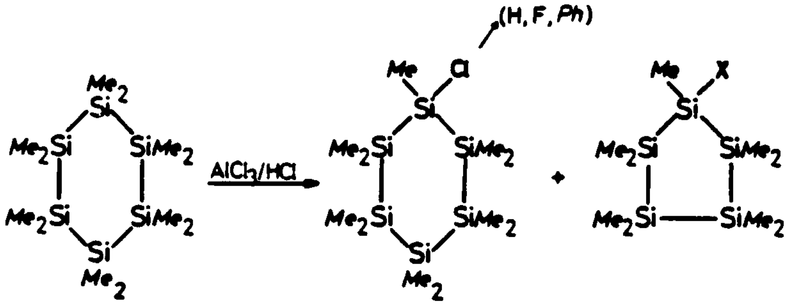
It is possible to change the phenyl groups by different methods, but the low yield of the first reaction makes this synthesis very troublesome.

Another way to split one methyl group from the permethylated ring is the reaction with trichlorosilane in presence of platinum compounds as a catalyst, but also in this way we find low yields and many side products.[36]

$$Si_6Me_{12} \xrightarrow[H_2[PtCl_6]]{HSiCl_3} Si_6Me_{11}Cl + \text{side products} \qquad \text{Hengge et al}$$

Kumada[37] was able to split one methyl group from dodecamethylcyclohexasilane by action of $HCl/AlCl_3$. Also in this reaction (XXVI) many side reactions occur, for example the formation of a five-membered ring.[38] The heterogenic reaction is strongly dependent on reaction conditions, on the quality and the surface of the $AlCl_3$. If the reaction time is too short, only starting material is obtained, if it is too long, higher chlorinated products are yielded. The reaction time is therefore very important and we controlled this time by gas chromatography to optimize the yield.

$$Si_6Me_{12} \xrightarrow[\text{Cyclohexane}]{HCl/AlCl_3} Si_6Me_{11}Cl + \text{side products} \qquad \text{Kumada et al}$$

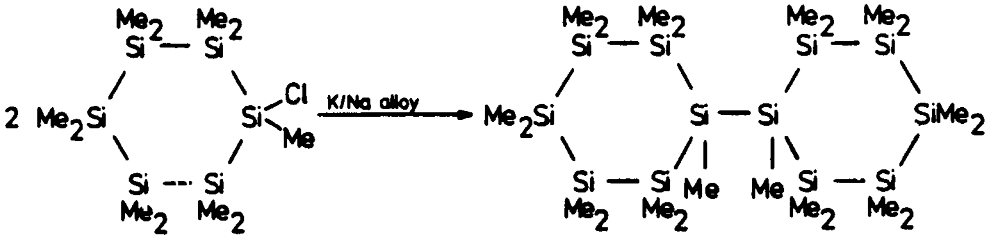


(XXVI)

$X = Cl, SiMe_3, SiClMe_2$.

So we have now available this monochlorinated compound in larger amounts and we started new investigations with this compound just in the past few months. A first result shows the formation (XXVII) of a bicyclic cyclosilane from a coupling reaction with sodium/potassium alloy. The monochlorinated cyclosilane opens the possibility of many new syntheses and we will investigate these in the near future.

After I have shown you the results of the chemistry, the reactivity and the chemical properties of cyclic silanes, I will start my second part of my lecture, to tell



m/e = 666. (XXVII)

you more about the physicochemical properties of these compounds. What is known about the structures of these compounds?

The structure of the five-membered cyclosilane shows a nonplanar ring system. An X-ray diffraction was made of the perphenylated compound. Parkanyi *et al.*[39] in Budapest found a ring system, very similar to cyclopentane, where the phenyl groups are in the position you can see on Figure 3.

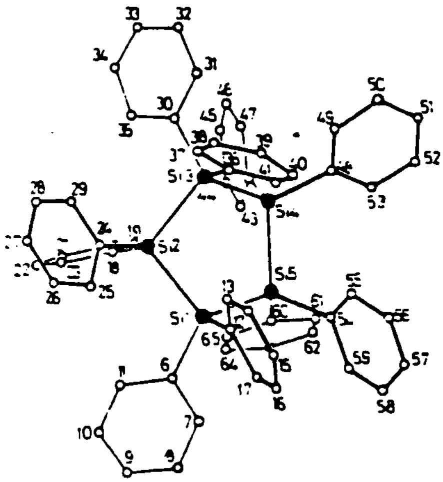
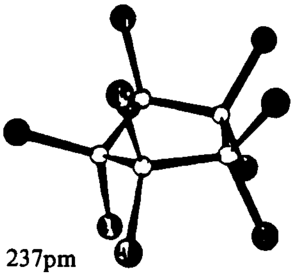


FIGURE 3

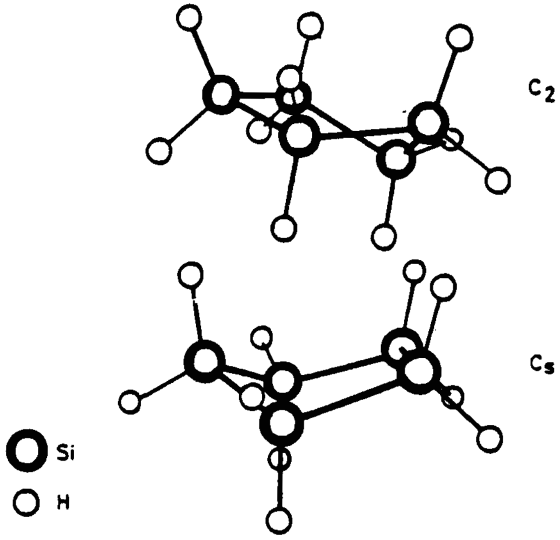
A very similar Si_5 ring structure was found upon X-ray diffraction of perhalogenated cyclopentasilanes such as Si_5Br_{10} and Si_5I_{10}. The investigations were done in Graz at low temperature and in the U.S. at room temperature and independently gave the same results (Figure 4).[40]



Si—Si = 237pm
Si—I = 243pm

FIGURE 4

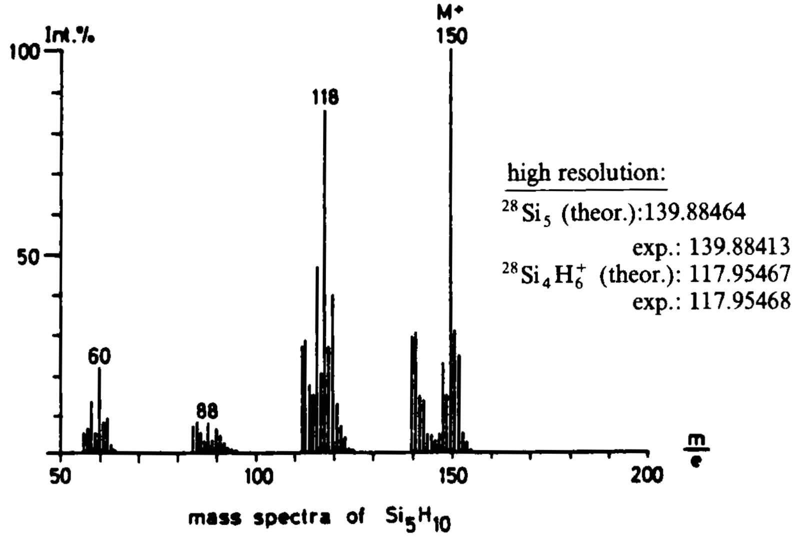
The results are also in complete agreement with an electron diffraction investigation,[41] which we have done together with Zusanne Smith in Oslo. She found a nonplanar structure, but she was not able to distinguish between two nonplanar structures either the envelope form with C_s-symmetry or the chairlike form with C_2-symmetry. The calculation of the molecular energy shows no difference between these two forms. The energy of a planar form was estimated to be 1.2-2.2 kcal · mol^{-1} higher.



r SiSi = 234.2(3) pm.
r SiH = 149.6(6) pm.
∢HSiH = 105.3 (29)°
∢SiSiSi = 104.3(7)°.

FIGURE 5

Very interesting is the mass spectrum of Si_5H_{10}.[12] You can see in Figure 6 the expected parent peak and a series of fragments, formed by separation of SiH_4 units. Masses near the parent peak can be explained by abstraction of hydrogen, one after another until a mass of 140. The mass 140 can only be explained by an Si_5 framework. High resolution mass spectra show:



high resolution:
$^{28}Si_5$ (theor.):139.88464
exp.: 139.88413
$^{28}Si_4H_6^+$ (theor.): 117.95467
exp.: 117.95468

FIGURE 6

The mass 140 is really the Si_5 particle, but also other observed mass peaks such as 118 show the expected composition exactly. So, the proposed fragmentation seems to be proved. The appearance of a Si_5 particle was surprising and shows the high stability of a Si_5 framework.

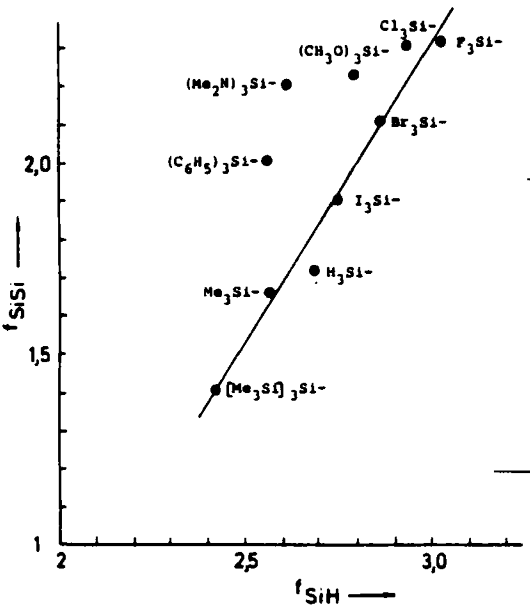
Raman and infrared spectra of all the known cyclopentasilane derivatives have been measured and assigned. It would take too much time to present all the figures, but all data are published.[12,42,43]

Some important modes:

Ra (fl.)	IR (nujol)	
2135 s,b,p		ν_{as} SiH_2
	2141 vs	ν_s SiH_2
926 w,p		δ_s SiH_2
464 m		ν
408 w,sh	406 m	ν SiSi
382 vs,p		ν_s (cycle)

$f_{SiSi} = 1{,}68$ N/cm, $f_{SiH} = 2{,}62$ N/cm.

A complete normal coordinate analysis of Si_5H_{10}, done by Prof. Höfler in Graz, has been performed using isotopic data from Si_5D_{10}. The SiSi stretching force constant is calculated to be 1.68 N/cm. Selection rules point out cyclopentasilane is not planar and undergoes a rapid pseudorotation, analogous to cyclopentene.[42] The Si—H vibration signals the same SiSi force constant of about 1.68 N/cm in view of a SiH/SiSi-comparison. Let me explain this comparison very briefly.[44] Force constant calculations are only possible with small molecules. Larger substituents or strong mutual influence of the vibrations makes the calculation too difficult or



$X_3Si\text{-}SiX_3$	f_{SiSi}	X_3SiH → SiH	X_3SiH f_{SiH}
Me_6Si_2	1.65	2118	2.58
H_6Si_2	1.7	2175	2.71
J_6Si_2	1.9	2190	2.75
Br_6Si_2	2.1	2236	2.87
Cl_6Si_2	2.3	2258	2.92
F_6Si_2	2.3	2318	3.08
$(C_6H_5)_6Si_2$	2.0	2126	2.59
$(Me_3O)_6Si_2$	2.2	2203	2.78
$(Me_2N)_6Si_2$	~ 2.2	2110	2.58
$(Me_3Si)_6Si_2$	1.4	2056	2.42

FIGURE 7

impossible. But the electronic condition of a silicon atom can be proved by the half of the molecule saturated by hydrogen. The SiH stretching vibration is not influenced by coupling effects, the SiH-force constant is only a function of the electronic state of the silicon atom. So, the SiH stretching vibration is a good indicator for the force constant of an SiSi bond. You see a nearly linear dependence between the two force constants in similar compounds but some small differences between more different substituents like phenyl or nitrogen, which have strong additional bond effects between silicon and the substituent.

We proved this method on different substituted disilanes and found in all examples a good connection between the calculated and the estimated amounts of the force constants.

The results of the structure of the five-membered ring are also in good agreement with the proton ^{1}H-NMR-signal; it shows a sharp singlet without changing the form at −40°C (Figure 8).

The nonplanar structure found let us understand the NMR results of the partially phenylated compound $Si_5Ph_5H_5$, which I have shown you before. A five-membered ring with 2 × 5 substituents includes the possibility of several conformations. A possible method to see the arrangement of the H-atoms is the NMR investigation.

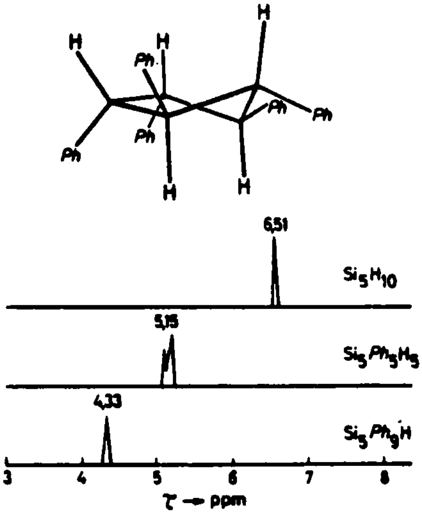
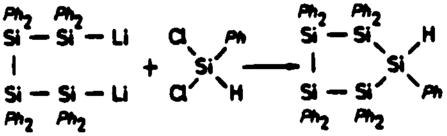


FIGURE 8



(XXVIII)

The NMR spectra of $Si_5Ph_5H_5$ shows two singlets with a ratio 2 : 3. All investigated samples show the same ratio. On the other hand, Si_5H_{10} shows only one singlet, shifted to high field. A compound with the composition Si_5Ph_9H shows one singlet at lower field. The synthesis of this compound was possible by another method, as you can see in (XXVIII).[45]

A conformation of the compound $Si_5Ph_5H_5$ which is shown in the Figure 8 would explain the NMR results. This conformation is also the probable one in view of the formation reaction.

What is known about the structure of the six-membered ring? An X-ray diffraction was made of the methylated[46] and the phenylated[47] ring and both show a chair form of the ring as in cyclohexane (Figure 9).

IR- and Raman data show us the cycle seems to be not planar, the expected chair form is in agreement with the observed modes:[49]

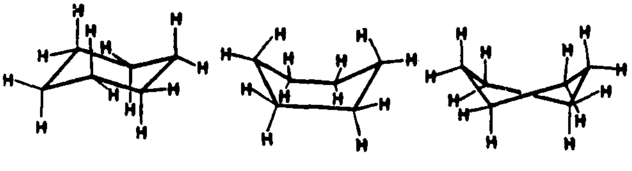


FIGURE 9

some important modes:

Ra (fl.)	IR (nujol)	
2128 s,b,p		ν SiH
	2120 vs	ν SiH
893 m		δ SiH
455		ν SiSi
—	384 m	ν SiSi
350 vs,p	—	ν_s SiSi

$f_{SiSi} = 1.63$ N/cm,

$f_{SiH} = 2.59$ N/cm.

Electron diffraction study shows[43] that the molecule exists predominantly in a chair form, but at the investigation temperature of 130°C, it can not be excluded that the molecule is partly in a boat or in a twist form. The energy differences between the three forms are very low, about one or two kcal · mol^{-1} which is significantly lower than in the corresponding hydrocarbons. These low differences are also in agreement with theoretical investigations done by Mislow and coworkers, which were done before we had found the compound Si_6H_{12}.

The mass spectra, shown in Figure 10, gives the right parent peak and similar to the five-membered cycle, a mass fragment Si_6; also in this case, the silicon framework seems to be very stable.[18]

The perphenylated four-membered ring was also investigated by X-ray diffraction.[50] The results exhibit a folded ring with a fold angle of 12.7° (Figure 11). A different fold angle was found in case of *tert.*-butyl-methylsubstituted ring systems.[51] So, it seems to be that the fold angle is dependent on the size of the substituents. Because of our new synthesis of the methylated four-membered ring in larger amounts, we were able to carry out X-ray investigations of this compound.[52] The result (Figure 12) shows an unexpected planar structure of the Si_4 ring in the crystalline state, but an unfinished new electron diffraction investigation led us to expect a small angle of a few degrees. We thought that small substituents lead to small fold angles and bulky substituents to big angles, but in contrast to these consideration P. P. Gaspar found a planar structure in octakis (trimethylsilyl) cyclotetrasilane.[53] Therefore, for the moment we see no rules for the dependence between substituent and fold angle; more investigations are necessary.

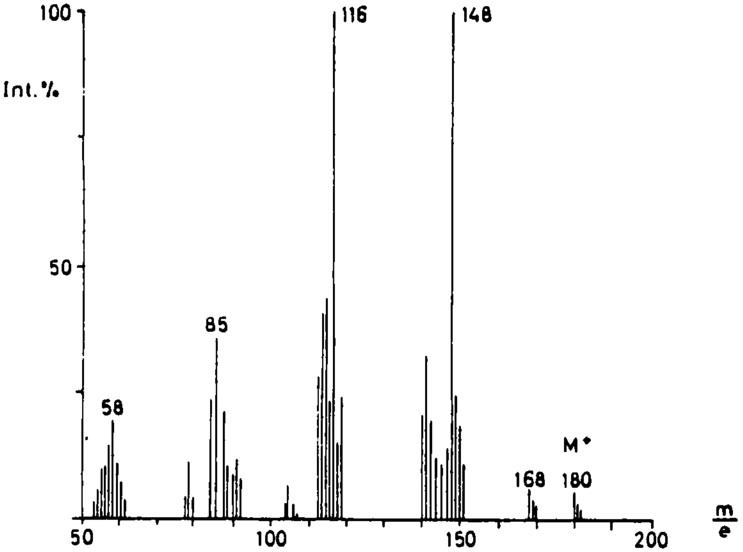
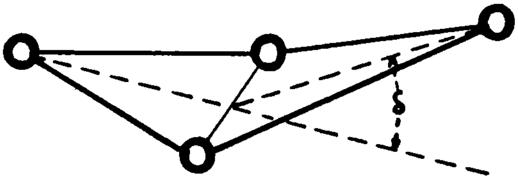


FIGURE 10



	R SiSi[pm]	δ
Si_4Ph_8	237.6(3)	12.7°
$Si_4(t\text{-}Bu)_4Me_4$	237.7(1)	36.8°
$Me_3SiSiMe_3$	234.0(9)	—
Si_6Me_{12}	233.8(4)	—
C_4H_8	—	−35°

FIGURE 11

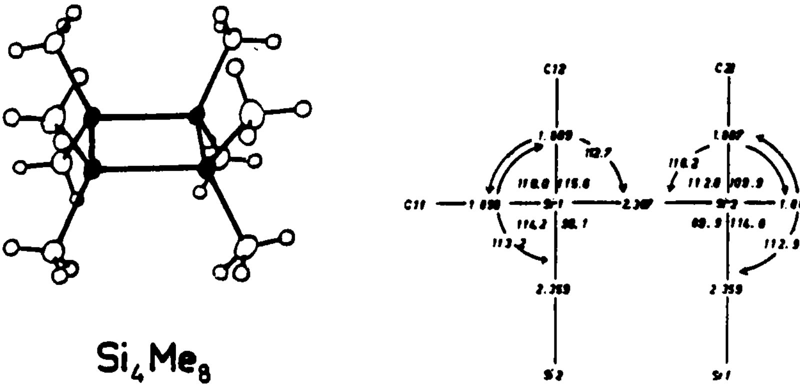

Si_4Me_8

FIGURE 12

^{29}Si-NMR investigations show a clear dependence of the chemical shift not only on the substituents, but also on the ring size.[54] The unstrained five- and six-membered rings show very similar shifts, but the strained four-membered ring shows different values (Figure 13). For the not yet isolated four-membered silicon hydride, one can expect a shift around −80 ppm.

More instructive are the results of the vibrational spectra and the force constants calculations with a complete normal coordinate analysis, done by Dr. Hassler, who is with me in Graz.[24,42,43,48] I will show you only the results and not all the data of the vibrational spectra, all these data are published.

The force constants f(SiSi) of the five- and the six-membered rings are very similar, as are the NMR shifts. The four-membered ring exhibits lower force constants. All SiSi force constants of the cycles are lower than in the corresponding disilane derivatives.

Very interesting is the dependence of the force constants on the substituents. You can see (Figure 14) strong differences between methyl and chloro compounds. Such

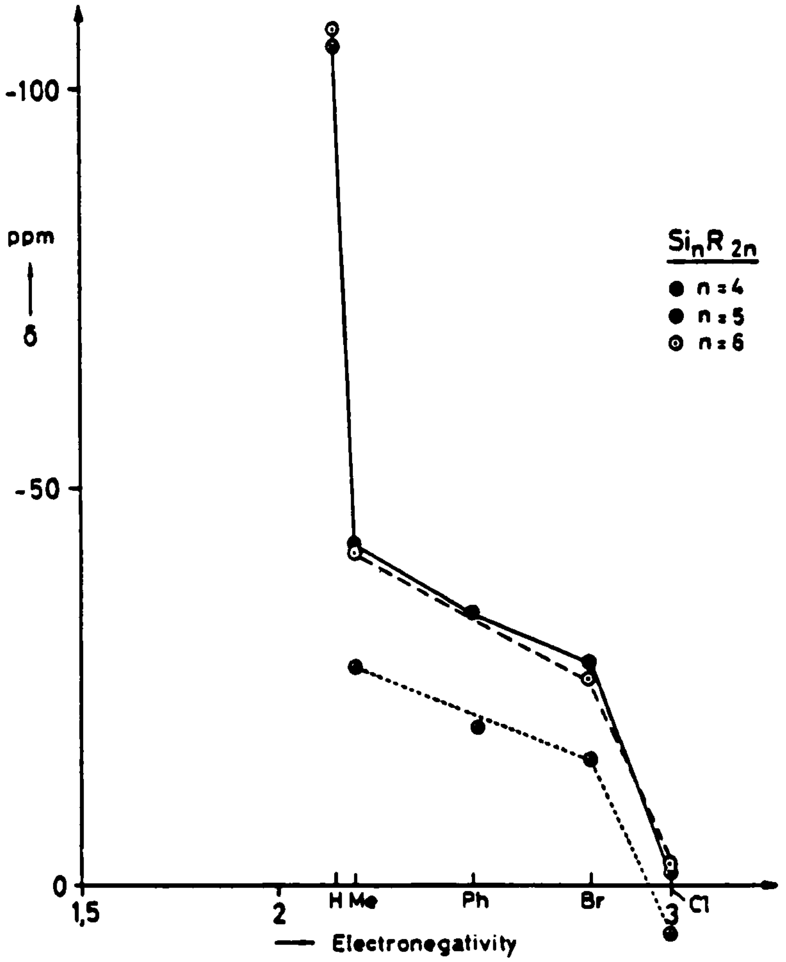


FIGURE 13

differences are known from previous investigations which we have done on disilane derivatives.

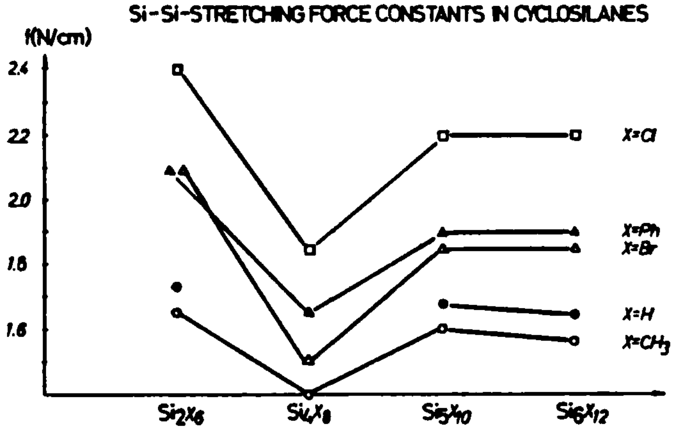


FIGURE 14

We have measured the Raman spectra and the IR spectra and have calculated the force constants by the method of the general valence force field with constraints in the force constant relations.

If we see the disilane Si_2H_6 as the basic compound in which the SiSi bond is a pure single bond, one can see that the methyl group shows a small decrease of the force constant, the series of halides points to a strong increase up to an amount of 2.3 N/cm. Also substituents with strong $d_\pi p_\pi$ effects such methoxy or amines give high force constants:

X_3Si-SiX_3

X	f_{SiSi}
H (D)	1,73
Me (CD_3)	1,65
I	1,9
Br	2,1
Cl	2,3
F	2,3
MeO (CD_3O)	2,25
Me_2N	2,2
Ph	2,0

Me < H < I < Ph < Br < MeO-Me_2N < Cl = F

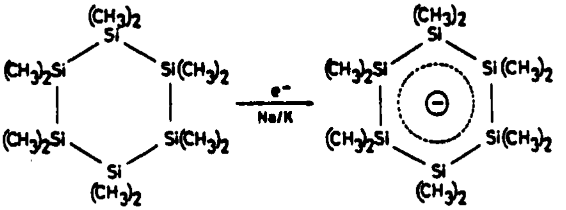
So, we are able to give a series of the substituents as a function of the influence of the SiSi bond strengthening.

In case of cyclosilanes, we found the same series of substituents as for disilanes and we know after some investigations, it is also valid for oligosilanes with longer chains.

Silicon is able to form additional bond effects with different substituents like oxygen or nitrogen. These additional bond effects lead to a higher electron density on the silicon atom. The additional electron density on the silicon atom could suggest different SiSi bond strengths as a function of the substituents.

In the series, the substituents increase in electronegativity and with additional bond effects from the substituents to the silicon atom.

This idea was published in 1963 as a result of investigations about the color of polymeric compounds with SiSi bonds.[55,56] The effects shown let us suppose that a silicon cycle is capable of adding more electrons, a property which stands in marked contrast to saturated organic ring systems. West was the first to prove the existence of a radical anion of cyclic silanes and therefore shows this postulated property directly. In 1965 he discovered (XXIX) that dodecamethylcyclohexasilane adds an electron by reaction with alkali metal or by electrochemical reduction.[57] Subsequently West found this behavior on other cyclic derivatives,[58] Bock and I were able to show the same property on phenylated ring systems,[59] but in a joint investigation, West and I could not successfully generate a radical anion of the hydrogenated cyclosilane Si_5H_{10}. All the radical anions are stable only at low temperature. First esr spectra of the radical anions of permethylcyclosilanes (Figure 15) show that the unpaired electron contacts all the methyl protons equally. Therefore it is delocalized over all of the silicon atoms of the ring.



(XXIX)

West et al (1965)

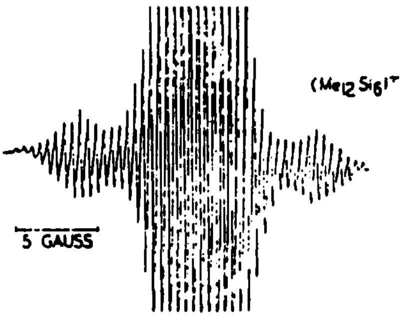
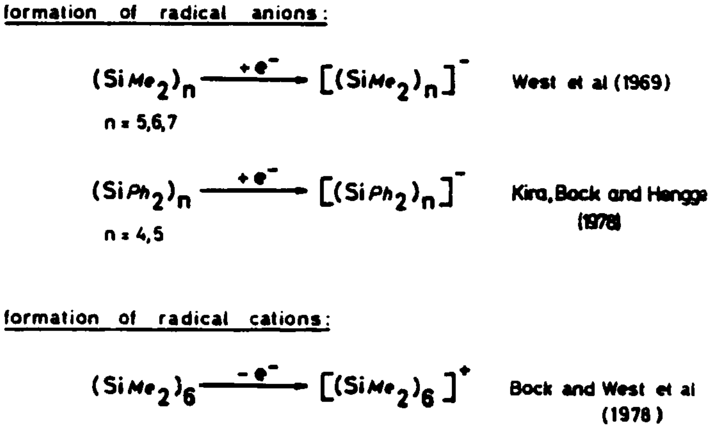


FIGURE 15

More detailed esr investigations, recently done by Wadsworth and West[60] confirmed this fact of a complete delocalization and showed the electron spin density being localized not only in the silicon orbitals but also in mainly s-orbitals of carbon atoms of the substituents.

The results of the esr investigation of perphenylated cyclosilanes show larger *g*-values relative to the permethylated cyclosilanes and no hydrogen coupling hyperfine structure can be resolved. This observation suggests that the odd electron does not enter the phenyl groups and rather is localized within the silicon ring, but new theoretical investigations point out that more than 10% of the electron spin density is localized in the phenyl groups. Also in this case, all phenyl groups seem to be equivalent (XXXI).



(XXX)

(XXXI)

(XXXII)

Due to the results of the esr investigations, the anions of cyclosilanes must either interconvert rapidly between equivalent conformers on the esr time scale of 10^{-5} sec. or have planar structures.

But not only anions are possible from cyclosilanes. In the case of permethylated cyclosilanes, cations were also generated by oxidation with $AlCl_3$ in dichloromethane[61] (XXXII). The redox potential of this mixture is sufficient to oxidize compounds that have a first ionization potential below 8 eV. The esr spectra of the dodecamethylcyclohexasilane cation can be explained by two different sets of six equivalent methyl groups. These results suggest a nonplanar ring structure in a chair cyclohexane conformation and the equilibrium between equivalent chair conformations must be slow in the esr time scale of about 10^{-5} sec. Generally it can be said that cyclosilanes are able to add or lose electrons, forming anions or cations. On the other hand, as I have shown you before, substituents on these cyclosilanes are able to pump more or less electron density to the ring. This behavior might also be apparent in the uv spectra of the derivatives and therefore we measured the uv spectra of some cyclosilane derivatives, recently prepared by our group.

In Figure 16, you can see the uv spectra of some cyclotetrasilane derivatives.[62] The longest wavelength absorption band shows a bathochromic shift, depending on the substituents in the order chlorine < bromine < iodine. This band, very close to the visible region, is only present in the spectra of cyclosilanes bearing substituents like halogens or methoxy groups, but not on methylcyclosilanes, as one can see in Figure 17. We can find this additional band only on derivatives with substituents containing lone electron pairs. At shorter wavelengths we see a very similar absorption system for all derivatives.

Figure 18 shows the influence of the ring size on the uv spectra of cyclosilanes. It was surprising that this additional band shifted to longer wavelength in the order

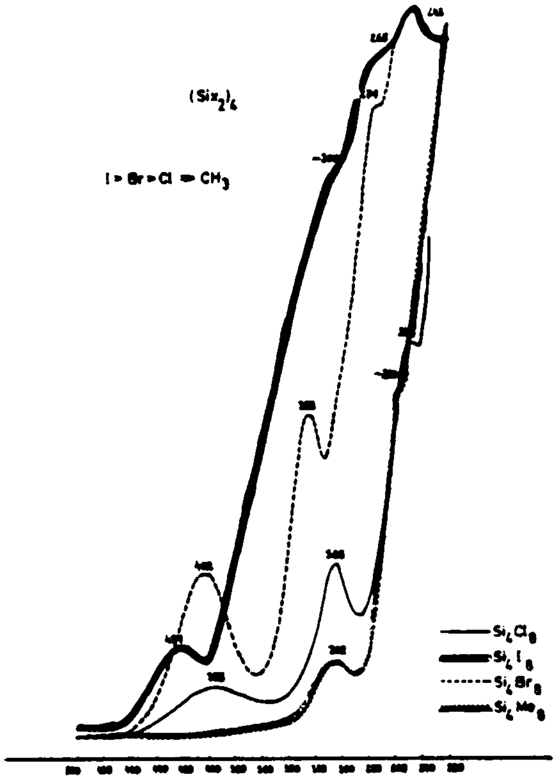


FIGURE 16

$Si_4 > Si_6 > Si_5$ and therefore did not follow the ring size directly as one would expect from the spectra of permethylcyclosilanes (Figure 18). In this context we remembered the results of photoelectron spectroscopy of alkylcyclosilanes.

Here one can find the same order at the first ionization band. So the photoelectron spectra of all the new derivatives turned out to be extremely interesting and we are grateful to Prof. Bock and Dr. Souluki in Frankfurt for recording these spectra.[63] The spectra are well resolved, as one can see on the example of permethylcyclotetrasilane on Figure 19.

All other spectra are very similar in resolution. The additional band at longest wavelength in the uv spectra of cyclosilane derivatives is only present for substituents with lone electron pairs and represents a transition in the term diagram, which is unknown up to now.

Similar to these results, some years ago, Pitt investigated the uv spectra of linear polysilanes and found a longest wavelength transition and associated it with a charge-transfer transition. It seems to be that the new transition found in cyclosilanes is a charge-transfer transition also. If we want to understand this transition as a charge-transfer band, a connection must be made between the first ionization energy of the photoelectron spectra and the uv maximum. In Figure 20, you can see this connection, it is given only with the longest wavelength band and not with the

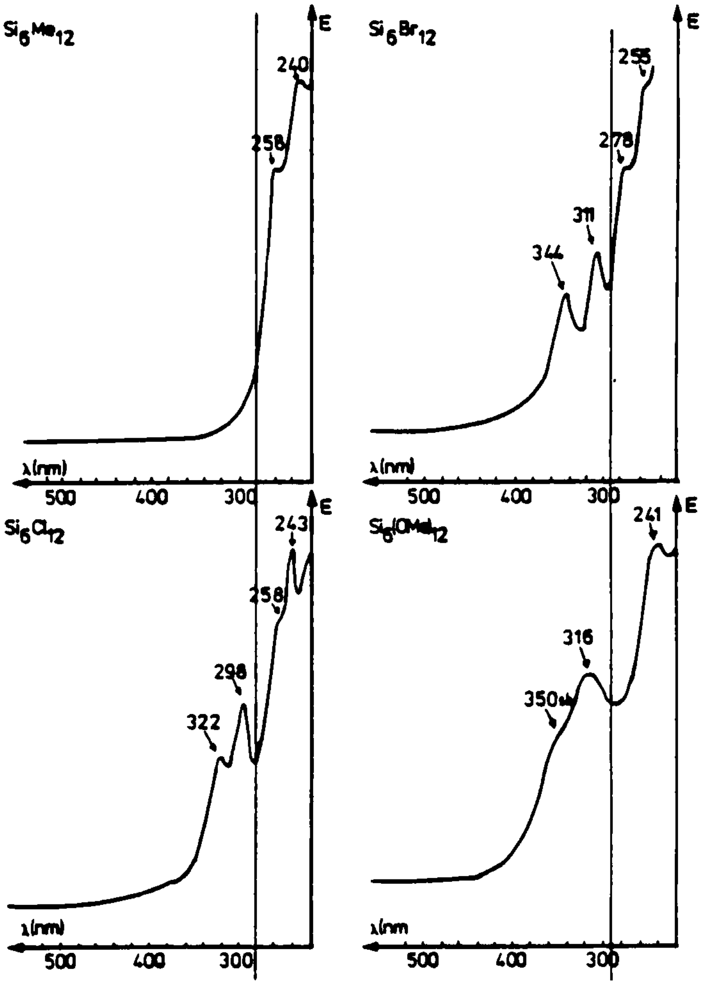


FIGURE 17

shorter bands of the uv spectra. So, it would be possible that this longest wavelength band is a σ-n* transition. To check this postulation, MNDO calculations are necessary and we started a theoretical investigation together with Prof. Bock in Frankfurt. First results seem to confirm this idea of a charge-transfer transition.

We have seen, that this band in question is shifted to the visible region and bromine and iodine derivatives are colored light yellow.

In larger polycyclic ring systems or polymeric compounds with larger SiSi-frameworks, this band also appears in the visible region and therefore is responsible for the color of polymeric compounds. But it seems to be that this charge-transfer band is not only occurring in cyclic silanes, but also on long chains.

Nefedow at al in 1968[64] showed that linear polysilanes are also able to form radical anions. Together with the fact that long linear Si-chains are also colored, these observations suggest that Si-chains have similar properties like Si-cycles, being

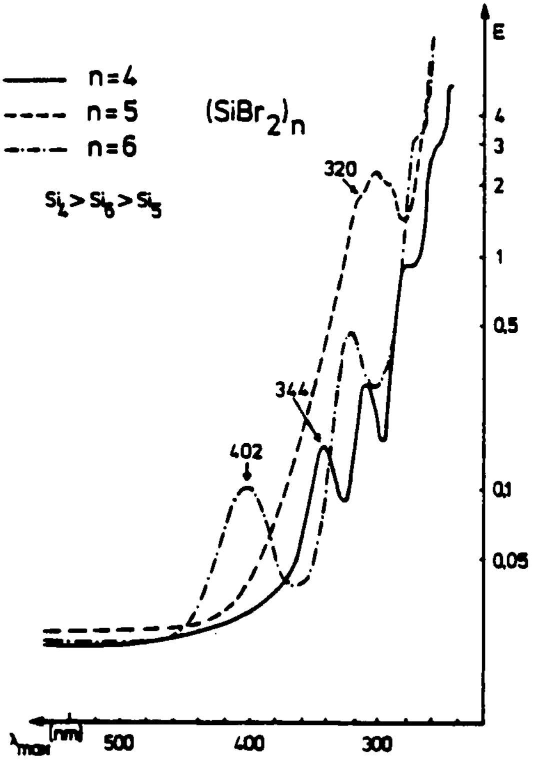


FIGURE 18

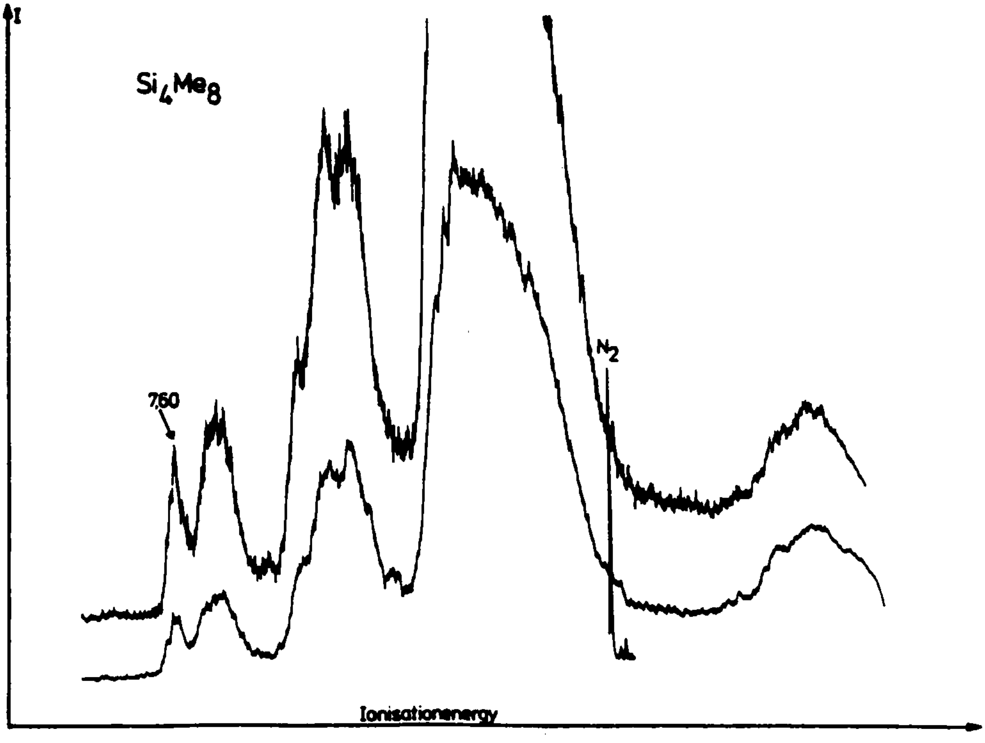
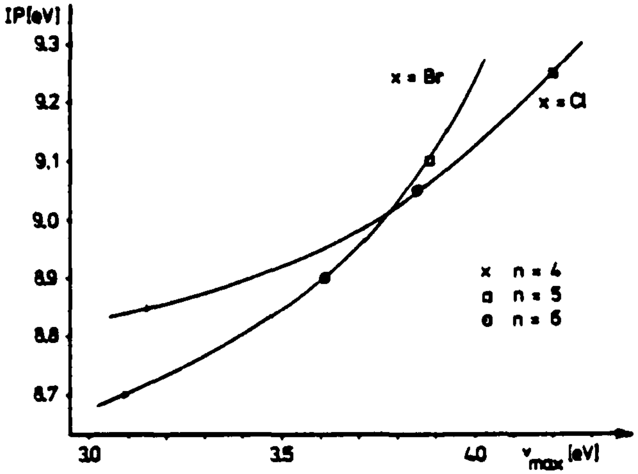


FIGURE 19



First IP's vs first UV-absorption bands of $(SiCl_2)_n$ and $(SiBr_2)_n$

First Ionization Potentials (eV)[63]

Si_4Cl_8	8.85	Si_4Br_8	8.7	Si_4Me_8	7.60
Si_5Cl_{10}	9.25	Si_5Br_{10}	9.1	Si_5Me_{10}	7.94
Si_6Cl_{12}	9.05	Si_6Br_{12}	8.9	Si_6Me_{12}	7.79

FIGURE 20

able to add or to lose electrons. This behavior directly leads us to the properties of semiconducting elementary silicon. But more investigations are necessary to clear up the properties of this fascinating field of silicon chemistry, the change of the properties going from simple monosilanes to cyclic and chainlike molecules up to polymeric structures and elementary silicon.

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