

Unstable Silicon Analogs of Unsaturated Compounds

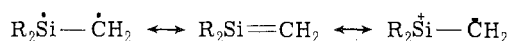
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Received July 25, 1973

Silicon and carbon belong to group IVB of the periodic table, and both have the same constitution of valence shell electrons: C $1s^2 2s^2 2p^2$, Si: $1s^2 2s^2 2p^6 3s^2 3p^2$. Most compounds of silicon have a formal valence number of four due to the transition of one 3s electron to a 3p orbital. Both silicon and carbon readily form single bonds resulting from sp^3 orbital overlap. However, despite the great abundance of stable multiple-bonded compounds of $p_\pi-p_\pi$ type for carbon, there has been a complete absence of them for silicon, although silicon does have d orbitals available for $p_\pi-d_\pi$ bonding.^{1,2}

Until recently silicon analogs of unsaturated compounds were believed to be nonexistent.¹ In this Account we describe the evidence for generation of this new class of organosilicon compounds and discuss their synthetic utility. Our main emphasis is on compounds of silicon which are analogous to olefins and ketones.³ This means that formally, at least, their structure can be described in terms of π -bonded silicon. At present there are no data unequivocally indicating this type of chemical bond with silicon: alternative structures may also be correct.



We do not consider such π -bonded intermediates as :SiO and :SiS, which are discussed in the fairly recent review⁴ on divalent radicals of group IVB.

The first structures with silicon double bonds were assigned to compounds obtained in reactions of ammonia with silicon tetrachloride, trichlorosilane,⁵ etc. ($HN=Si=NH$; $N\equiv SiNH_2$). In 1912 Schlenk and Renning⁶ described the synthesis of a stable compound with a silicon-carbon double bond by dehydration of diphenylmethylsilanol. However, their work was reexamined by Kipping,⁷ who proved that they had been dealing with a mixture of diphenyldimethylsilane, diphenylmethylsilanol and diphenyl. By the end of the second decade of this century, it had become clear that earlier works in which structures with multiple bonds to silicon were assigned to stable compounds were wrong and reactions which lead to formation of double bonds with carbon are

not suitable for synthesis of corresponding compounds of silicon. For example, the loss of water from one molecule of silanol does not occur, but rather the elimination of water from two molecules to form disiloxane. No silicon analogs of olefins can be obtained by dehydrochlorination of chlorosilanes, which are fairly stable and can be distilled without decomposition (even in the presence of quinoline). Some other attempts to prepare stable compounds with multiple bonds involving silicon also failed.^{8,9}

In the late 1940's and early 1950's, the problem of the nonexistence of double-bonded compounds involving silicon began to be considered on the basis of a pictorial presentation of orbitals and quantum mechanical calculations (see below).

In 1952, Andrianov and Sokolov announced¹⁰ the existence of dialkylsilanones as unstable intermediates formed both on heating of organopolysiloxanes up to 150–200° and on gas-phase hydrolysis of dimethyldichlorosilane. The intermediates were observed by mass spectrometry.

Two more claims to stable compounds containing double-bonded silicon were made. These were $Me_3Si-CH=SiMe_2$ ¹¹ and the silicon analog of benzene.¹² Later the first compound appeared to be 1,1,3,3-tetramethyl-1,3-disilacyclobutane which, due to its ability to react with bromine, was wrongly assigned the unsaturated structure.¹³ No confirmation of the second compound's structure has been obtained.¹⁴

In recent years, silicon analogs of unsaturated compounds have come to be considered mainly as short-lived intermediates during the formation of more stable products. Thus, dimethylsilanone was postulated as an intermediate in cleavage of polysiloxanes by the Jozitsh reagent;¹⁵ $MeHSi=CH_2$ was mentioned as only a very minor product of isomerization of dimethylsilylene;¹⁶ and $Me_2Si=CH_2$ was

(1) W. E. Dasent, "Non-existent Compounds," Marcel Dekker, New York, N. Y., 1965.

(2) C. J. Attridge, *Organometal. Chem. Rev.*, **2**, 161 (1967).

(3) N. S. Nametkin, L. E. Gusel'nikov and V. M. Vdovin, communication presented at the 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., 1972.

(4) P. L. Timms, *Prep. Inorg. React.*, **4**, 59 (1968).

(5) L. Gattermann, *Ber.*, **22**, 194 (1889).

(6) W. Schlenk and J. Renning, *Justus Liebigs Ann. Chem.*, **394**, 221 (1912).

(7) F. S. Kipping, *J. Chem. Soc.*, 104 (1927).

(8) See references cited in M. F. Schostakovskij and N. V. Komarov, *J. Prakt. Chem.*, **23**, 208 (1964).

(9) C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p 113.

(10) K. A. Andrianov and N. N. Sokolov, *Dokl. Akad. Nauk SSSR*, **82**, 909 (1952).

(11) G. Fritz and J. Grobe, *Z. Anorg. Chem.*, **311**, 325 (1961).

(12) G. Urry, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(13) R. Muller, R. Köhne, and H. Beyer, *Ber.*, **95**, 3030 (1962).

(14) G. Urry, private communication, cited in ref 9.

(15) Schostakovskij and Komarov.⁸

(16) O. M. Nefedov and M. N. Manakov, *Angew. Chem., Int. Ed. Engl.*, **5**, 1021 (1966).

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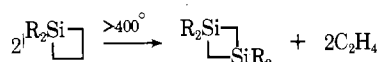
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introduced into the scheme for the mechanism of pyrolysis of tetramethylsilane¹⁷ to explain the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Related to the above are experiments on dechlorination of tris(trichlorosilyl)chloromethane with a silicon-copper alloy.¹⁸ Unfortunately, in all the above cases one deals with complex nonselective processes where other mechanisms are equally possible.

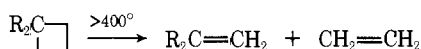
In 1965 we found a selective gas-phase thermal decomposition of monosilacyclobutanes^{19,20} which enabled us to obtain both kinetic and chemical evidence for the existence of silicon olefin analogs as reaction intermediates.²⁰⁻²³ As a result, silicon analogs of unsaturated compounds attracted the attention of chemists, and a series of publications on the subject has subsequently appeared. Below we discuss the results of this new stage in the chemistry of silicon analogs of unsaturated compounds.

Silicon Analogs of Olefins

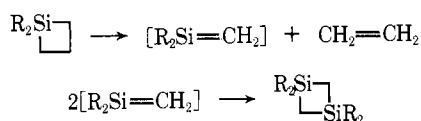
During a study of the pyrolysis of monosilacyclobutanes, we observed the elimination of ethylene and the clean formation of 1,3-disilacyclobutanes^{19,20} in accord with the following scheme.



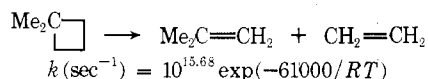
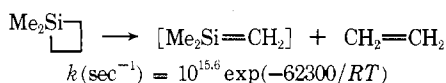
The only products of the thermal decomposition of 1,1-dimethyl-1-silacyclobutane were ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. By analogy with the reaction of cyclobutanes²⁴



we suggested that 1,3-disilacyclobutane was formed from an unstable silicon olefin analog.^{20,21}



Kinetic data^{22,25} appeared to be in good accord with this suggestion, since the Arrhenius parameters of homogeneous unimolecular thermal decomposition of 1,1-dimethyl-1-silacyclobutane²³ and the thermal decomposition of 1,1-dimethylcyclobutane²⁵ were very similar.



(17) G. Fritz, J. Grobe, and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, **7**, 349 (1965).

(18) R. Muller and W. Muller, *Ber.*, **97**, 1111 (1964).

(19) N. S. Nametkin, V. M. Vdovin, L. E. Gusel'nikov, and V. I. Zav'yalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 589 (1966).

(20) N. S. Nametkin, L. E. Gusel'nikov, V. M. Vdovin, P. L. Grinberg, V. I. Zav'yalov, and V. D. Oppengeim, *Dokl. Akad. Nauk SSSR*, **171**, 630 (1966).

(21) L. E. Gusel'nikov, P. L. Grinberg, V. M. Vdovin, and N. S. Nametkin, Symposium on Structure, Reactivity, and Reaction Mechanism of Compounds with Multiple Bonds and Small Rings, Leningrad, 1967, p 149.

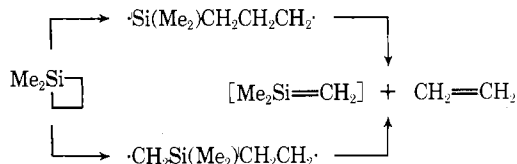
(22) L. E. Gusel'nikov and M. C. Flowers, *Chem. Commun.*, 864 (1967).

(23) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419, 1396 (1968).

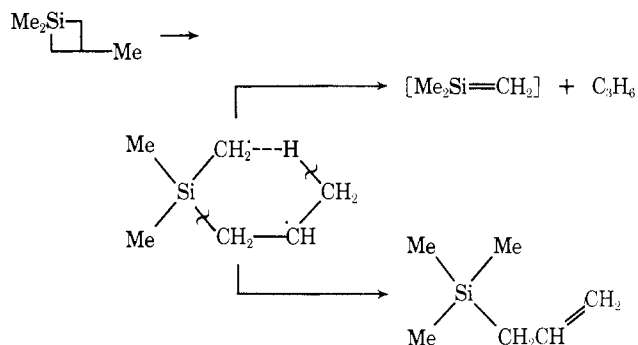
(24) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 148 (1966).

(25) P. S. Rotoli, M.S. Thesis, University of Rochester, 1963.

The biradical mechanism for decomposition is widely accepted for the gas-phase thermal decomposition of cyclobutanes.²⁶ By analogy, for monosilacyclobutane an initial cleavage of either the carbon-carbon or the silicon-carbon bond of a four-membered ring results in the formation of the corresponding biradical intermediates, further decomposition of both radicals leading to ethylene and the silicon analog of isobutene.



Carbon-carbon bond cleavage is in accord with the observed isomerization of 1,1,3-trimethyl-1-silacyclobutane^{27,28} into allyltrimethylsilane, which, occurs together with decomposition.



Because of the short lifetime of a silicon analog of isobutene under conditions normally used, its formation and disappearance processes cannot usually be separated. However, in a flow system at pressures below 1 Torr, cyclodimerization occurs beyond the reactor. So if one places a low-temperature trap in the space where the reactive intermediate exists, it will be condensed along with other products. Following this idea, we have observed the formation of $(\text{Me}_2\text{SiCH}_2)_x$ polymer and the related decrease of 1,1,3,3-tetramethyl-1,3-disilacyclobutane among products (Figure 1) due to polymerization of $\text{Me}_2\text{Si}=\text{CH}_2$ on the cold surface.²⁹

Using our kinetic data on the 1,1-dimethyl-1-silacyclobutane pyrolysis²³ and the data of Davidson, *et al.*, on pyrolysis of trimethylsilane,³⁰ Walsh estimated a value of 30-42 kcal/mol for the π -bond energy in the silicon analog of isobutene.³¹ Barton and McIntosh³² observed a 1407-cm^{-1} band for the products of thermal decomposition of 1,1-dimethyl-1-silacyclobutane trapped at -196° , which in the authors' opinion was due to $\text{Me}_2\text{Si}=\text{CH}_2$ absorption. The ion $[\text{Me}_2\text{SiCH}_2]^+$ is readily formed under electron-impact fragmentation of 1,1-dimethyl-1-silacyclobu-

(26) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(27) R. L. Ushakova, Ph.D. Thesis, Institute of Petrochemical Synthesis, Moscow, 1972.

(28) N. S. Nametkin, R. L. Ushakova, L. E. Gusel'nikov, E. D. Babich, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1676 (1970).

(29) N. S. Nametkin, L. E. Gusel'nikov, E. A. Volnina, E. N. Burdasov, and V. N. Vdovin, *Dokl. Akad. Nauk SSSR*, **214**, 818 (1974).

(30) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. A*, 882 (1971).

(31) R. Walsh, *J. Organometal. Chem.*, **38**, 245 (1972).

(32) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972).

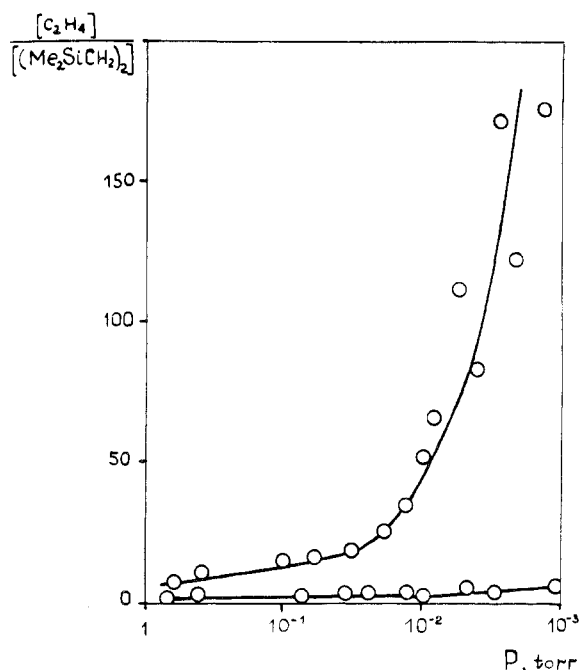
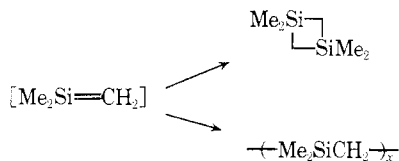


Figure 1. Pyrolysis of 1,1-dimethyl-1-silacyclobutane in a flow system. Dependence of $C_2H_4/(Me_2SiCH_2)_2$ on pressure: (upper curve) distance between pyrolysis and condensation zones 30 mm, (lower curve) 250 mm.

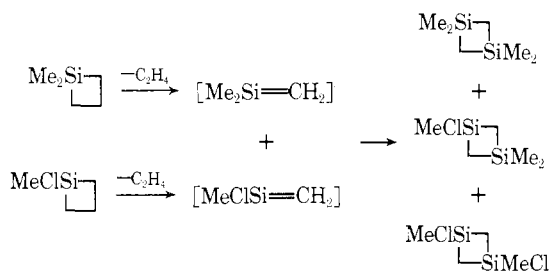
tane^{33,34} (the peak m/e 72 is the most intense one in the mass spectrum).

Some chemical evidence for the existence of silicon analogs of olefins is considered below.

It has already been mentioned that, in the absence of trapping agents, silicon olefin analogs form a dimer in the gas phase and a polymer in the condensed phase.



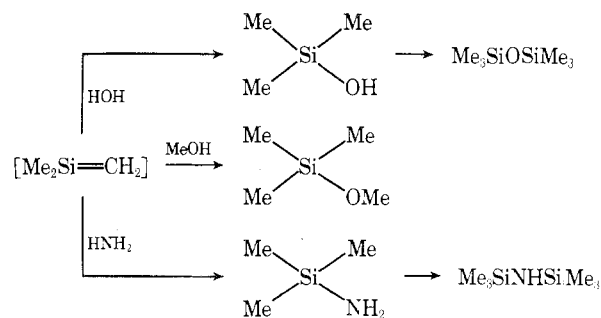
If two different monosilacyclobutanes undergo copyrolysis, products of direct and cross cyclodimerization are formed.^{20,35}



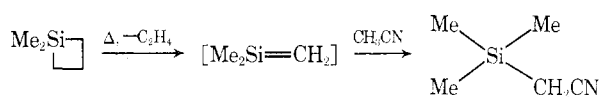
It is significant that among the products we have never observed either "head-to-head" dimers or cyclic trimers.

Trapping agents form adducts with silicon analogs of olefins when they are involved in copyrolysis with

monosilacyclobutanes. We have found that water vapor, ammonia, and alcohols readily form addition products with $Me_2Si=CH_2$.^{22,23}



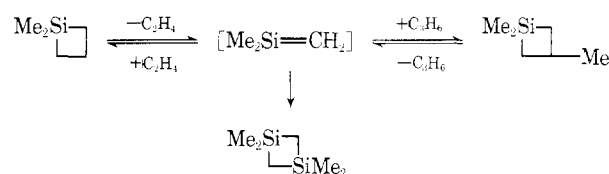
A similar reaction was observed recently with acetonitrile and its derivatives.^{36a}



Another reaction of silicon olefin analogs is cycloaddition to olefins. However, since the rate constant of this reaction is negligible compared to one of cyclodimerization at the temperatures of pyrolysis, the contribution of cycloaddition is noticeable only when the concentration of olefin is much higher than that of the short-lived compound of silicon. For example, the consequence of the contribution of this reaction results in a deviation from the straight line of the first-order plot for the thermal decomposition of 1,1-dimethyl-1-silacyclobutane only at conversion above 60%.²³

Kinetic evidence for the reaction of $Me_2Si=CH_2$ with ethylene has been obtained by pyrolysis of 1,1-dimethyl-1-silacyclobutane in the presence of ethylene.²³ Thus, the apparent first-order rate constant appeared to be dependent on the concentration of ethylene, as predicted by a kinetic scheme including a reversible first step of decomposition.

Chemical evidence for the reversibility of the first step of decomposition of monosilacyclobutanes has also been obtained from the study of copyrolysis of both 1,1-dimethyl-1-silacyclobutane in the presence of excess propene and 1,1,3-trimethyl-1-silacyclobutane with excess ethylene.^{37,38} Apart from the normal decomposition products, 1,1,3-trimethyl-1-silacyclobutane and 1,1-dimethyl-1-silacyclobutane were formed in the first and in the second case, respectively.



(36) (a) R. D. Bush, C. M. Golino, D. N. Roark, and L. H. Sommer, *J. Organometal. Chem.*, **59**, C17 (1973); (b) C. M. Golino, R. D. Bush, N. R. Roark, and L. H. Sommer, *J. Organometal. Chem.*, **66**, 29 (1974); (c) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Amer. Chem. Soc.*, **96**, 614 (1974).

(37) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1840 (1971).

(38) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **201**, 1365 (1971).

(33) N. Ya. Cherniak, R. A. Khmel'nitskiy, T. V. Diakova, V. M. Vdovin, and T. N. Arkhipova, *Zh. Obshch. Khim.*, **36**, 96 (1966).

(34) V. Yu. Orlov, N. S. Nametkin, L. E. Gusel'nikov, and R. L. Ushakova, *Org. Mass Spectrom.*, **6**, 309 (1972).

(35) P. L. Grinberg, Ph.D. Thesis, Institute of Petrochemical Synthesis, Moscow, 1968.

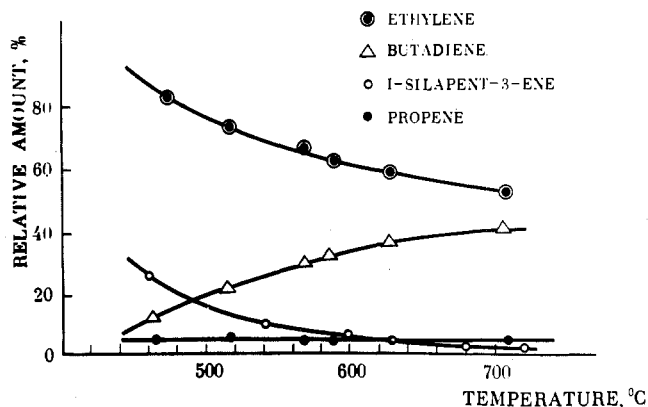
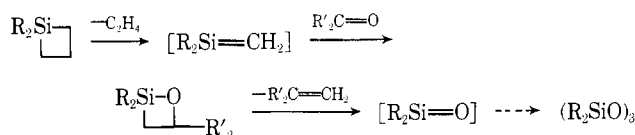
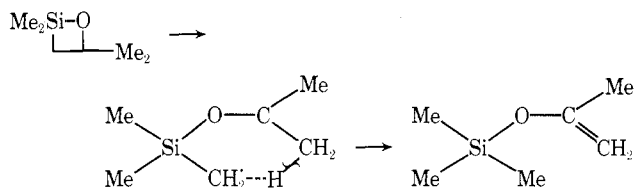


Figure 2. Pyrolysis of 4-silaspiro[3.3]heptane. Dependence of relative amounts of decomposition products on temperature.

Silicon analogs of olefins readily react with compounds containing a carbonyl double bond. Copyrolysis of 1,1-dimethyl-1-silacyclobutane with isobutyl methyl ketone,³⁹ as well as copyrolysis of 1,1-diphenyl-1-silacyclobutane with 2-pentanone, 2-heptanone or benzophenone,⁴⁰ resulted in the formation of cyclosiloxane (mainly trimer), ethylene, and a corresponding new olefin. The following course of reaction has been suggested.



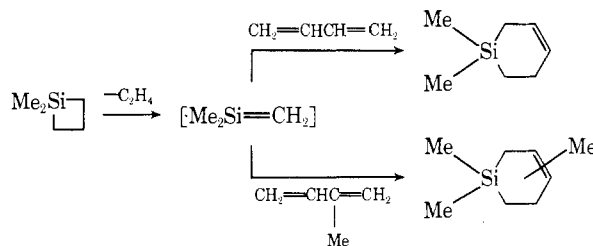
Barton and Kline found that at 600° the adduct of $Me_2Si=CH_2$ and isobutyl methyl ketone was the major product of copyrolysis. A possible 1,2-silaoxetane structure has been assigned to this product. However, we have isolated a similar adduct from pyrolysis of 1,1-dimethyl-1-silacyclobutane with acetone and identified it as isopropenyloxytrimethylsilane. We believe that formation of the latter is due to the isomerization of the silaoxetane resulting from 1,5-hydrogen atom migration in the biradical formed by cleavage of the C-C bond in a four-membered ring which is apparently unstable under reaction conditions.



The mechanism involving the addition of the enol form of ketone to $Me_2Si=CH_2$ ⁴⁰ seems to be less probable. The argument based on the nonoccurrence of the addition reaction in copyrolysis of 1,1-diphenyl-1-silacyclobutane with benzophenone is not conclusive, since in this case 1,5 migration of hydrogen in the biradical is not possible either. Actually, the latest mechanism suggested for this reaction^{36a,b} is fairly similar to ours. A similar reaction of $R_2Si=CH_2$

has recently been realized with the imines $PhCH=NPh$, $Ph_2C=NPh$, and $Ph_2C=NPh$.^{36c}

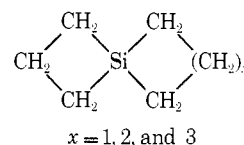
Silicon analogs of olefins readily react as dienophiles in a reaction of the Diels-Alder type. Thus, formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was completely suppressed and the corresponding 1-silacyclohex-3-ene were formed when 1,1-dimethyl-1-silacyclobutane pyrolysis was carried out in the presence of butadiene,³⁸ isoprene,³⁸ or 2,3-dimethylbutadiene.⁴¹



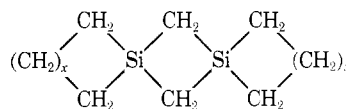
Formation of one adduct in the reaction with butadiene and two adducts with isoprene is in accord with one-step 1,4 cycloaddition.

Hence, there are a number of reactions proving the formation of short-lived silicon olefin analogs in pyrolysis of monosilacyclobutanes. A similar pathway was observed in pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane²⁷ and 1,1-diphenyl-1-silacyclobutane.⁴⁰

Interesting results have been observed when studying the pyrolyses of silaspiroalkanes.



4-Silaspiro[3.4]octane ($x = 2$) and 4-silaspiro[3.4]nonane ($x = 3$) form corresponding 1,3-disilacyclobutanes.



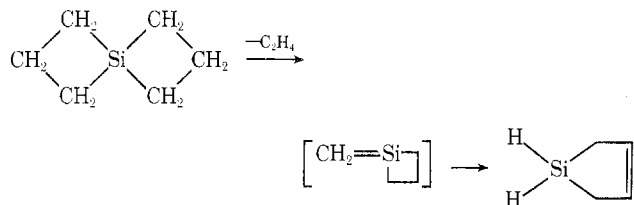
4-Silaspiro[3.3]heptane^{27,42} undergoes an abnormal thermal decomposition. In a flow system on a helium stream, an oily product with a composition corresponding to the loss of ethylene from the starting material is formed. Under low pressure this compound decomposes to hydrogen, ethylene, propene, butadiene, and 1-silacyclohex-3-ene in ratios depending on the temperature of pyrolysis (Figure 2). No 1,3-disilacyclobutane compounds are formed. Deposition of metallic silicon is observed on the reactor wall. We suppose that formation of 1-silacyclohex-3-ene is due to isomerization of silicon analogs of methylenecyclobutane. Further pyrolysis of the isomeric compound could be responsible for other decomposition products.

(39) T. J. Barton and E. Kline, presented at the 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., 1972.

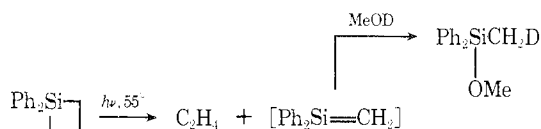
(40) D. N. Roark and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, 167 (1973).

(41) W. J. Bailey and M. S. Kaufman, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract ORGN-55.

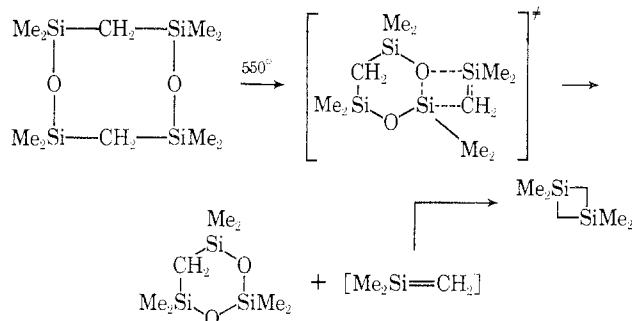
(42) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, V. Yu. Orlov, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, 211, 108 (1973).



Considering gas-phase thermal decomposition of monosilacyclobutanes as the method for generation of silicon analogs of olefins, it should be pointed out that in the series cyclo-(CH₂)₃ER₂ (where E = C, Si, Ge) the selective decomposition to form compounds of the olefin type is typical only for the compounds of carbon and silicon. In the case of the germanium compound⁴³ the reaction is more complex because of the carbenoid decomposition (*i.e.*, formation of Me₂Ge and C₃H₆). Monosilacyclobutanes also seem to be effective sources of silicon analogs of olefins in liquid-phase photolysis.⁴⁴

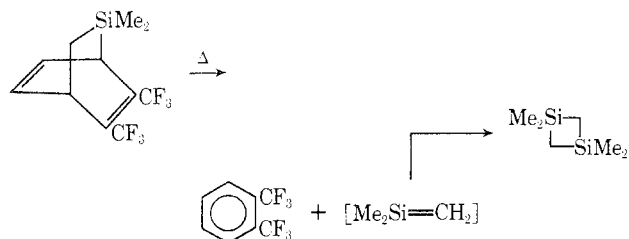


The formation of the silicon analog of isobutene emerges from the study of pyrolysis of eight-membered cyclocarbosiloxanes containing siloxane and silylmethylene fragments.⁴⁵⁻⁴⁷



However, in this case alternative decomposition to dimethylsilylanone also occurs.

Barton and Kline⁴⁸ have found that pyrolysis of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene at 400° results in the formation of Me₂Si=CH₂ according to



(43) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, V. Yu. Orlov, O. V. Kuzmin, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **194**, 1096 (1970).

(44) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, **54** (1973).

(45) N. S. Nametkin, L. E. Gusel'nikov, T. H. Islamov, M. V. Shishkina, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **175**, 136 (1967).

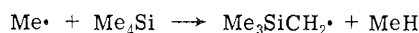
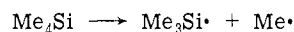
(46) N. S. Nametkin, T. H. Islamov, L. E. Gusel'nikov, A. A. Sobtsov, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **90** (1971).

(47) N. S. Nametkin, T. H. Islamov, L. E. Gusel'nikov, and V. M. Vdovin, *Usp. Khim.*, **41**, 203 (1972).

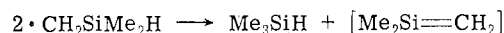
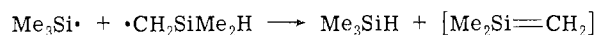
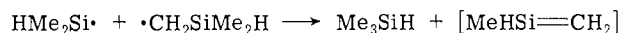
(48) T. J. Barton and E. Kline, *J. Organometal. Chem.*, **42**, C21 (1972).

However, liquid-phase photolysis⁴⁸ of this compound gave only traces of 1,1,3,3-tetramethyl-1,3-disilacyclobutane.

Formation of silicon analogs of olefins has been postulated in gas-phase thermal decomposition of some noncyclic organosilicon compounds, but these reactions are not clean, and the yields of products which may be due to silicon analogs of olefins are usually low. One example is thermal decomposition of tetramethylsilane.¹⁷

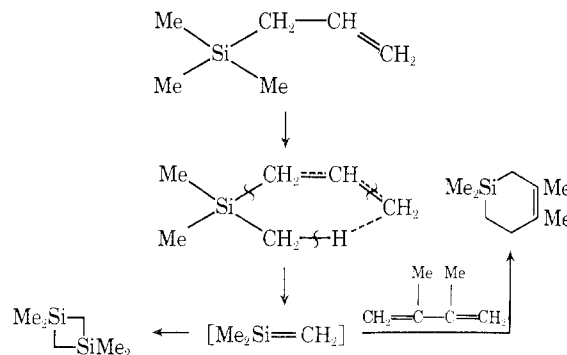


However, Davidson and Lambert^{30,49} have shown that, under pyrolysis conditions, disproportionation of radicals to form a silicon olefin analog is a more favorable process than decomposition.



Cyclodimerization of these intermediates results in the formation of three corresponding 1,3-disilacyclobutanes. As has been estimated recently,⁵⁰ disproportionation is an even more important reaction of silyl radicals than recombination under pyrolysis conditions. The ratio of the rate constants of disproportionation and recombination reactions of trimethylsilyl radicals is 1.2 at 900 K and only 10⁻³ at 300 K.⁵¹

Rather ambiguous results were obtained from studies of the pyrolysis of allyltrimethylsilane. Bailey and Kaufman⁴¹ found that at 600° this compound decomposes to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane together with other products, whereas in the presence of 2,3-dimethylbutadiene a Diels-Alder adduct with 1,1-dimethyl-1-silaethylene is formed.



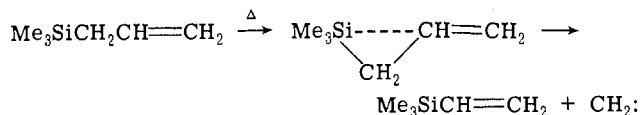
Sakurai, Hosomi, and Kumada⁵² found that decomposition of allyltrimethylsilane occurs even at 500° to form methylene and vinyltrimethylsilane by α elimination, in contrast to the above.

(49) I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc. D*, 1276 (1969).

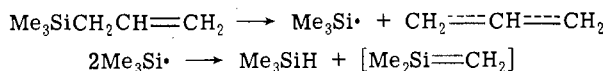
(50) R. P. Clifford, B. G. Gowenlock, C. A. F. Johnson, and J. Stevenson, *J. Organometal. Chem.*, **34**, 53 (1972).

(51) P. Cadman, G. Tilsey, and A. F. Trotman-Dickenson, presented at the Gas Kinetics and Photochemistry Meeting, University College, Cardiff, 1970; see ref 50.

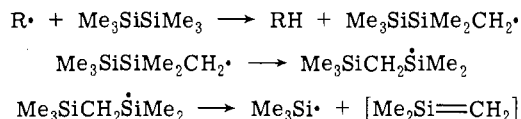
(52) H. Sakurai, A. Hosomi, and M. Kumada, *Chem. Commun.*, 767 (1970).



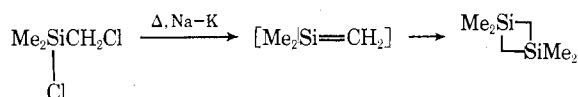
We believe that data presented in ref 41 may be better explained in terms of decomposition of allyl-trimethylsilane to produce trimethylsilyl radical followed by its disproportionation.



$\text{Me}_2\text{Si}=\text{CH}_2$ was also postulated in gas-phase pyrolysis of hexamethyldisilane.⁵³

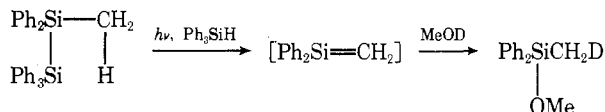


Among other reactions generating intermediate silicon analogs of olefins, gas-phase dechlorination of (chloromethyl)dimethylchlorosilane with sodium-potassium vapors⁵⁴ and vacuum photolysis of meth-



ylsilane^{55,56} should be mentioned.

The idea of the formation of silicon analogs of olefins has been used to explain some liquid-phase reactions. Thus, Kumada, *et al.*,⁵⁷ suggested a $\text{Me}_2\text{Si}=\text{CH}_2$ intermediate resulted from β elimination in the reaction of ethanol with 1-chloromethylpentamethyldisilane, and Jarvie and Rowley⁵⁸ also introduced $\text{Me}_2\text{Si}=\text{CH}_2$ into the mechanism for reaction of dimethylsilylmethylmagnesium bromide with benzophenone. However, in both cases, alternative reaction mechanisms, including no silicon analog of olefin, are equally probable.^{58,59} Besides the work on liquid-phase photolysis of 1,1-diphenyl-1-silacyclobutane⁴⁴ already mentioned, the recent work on photochemical dehydrosilylation of pentaphenylmethyldisilane in the presence of methanol-*d*⁶⁰ is of interest.



Thus as expected, photolysis of $\text{Ph}_2(\text{CD}_3)\text{SiSiPh}_3$ in methanol results in $\text{Ph}_2(\text{CD}_2\text{H})\text{SiOMe}$ and triphenyldeuteriosilane.

(53) I. M. T. Davidson and A. B. Howard, *J. Chem. Soc., Chem. Commun.*, 323 (1973); I. M. T. Davidson, C. Eaborn, and J. M. Simmie, *J. Chem. Soc., Faraday I*, 70, (2) 249 (1974).

(54) P. S. Skell, communication presented at the 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., 1972.

(55) O. P. Strausz, K. Obi, and W. K. Duholke, *J. Amer. Chem. Soc.*, 90, 1359 (1968).

(56) K. Obi, A. Clement, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, 91, 1622 (1969).

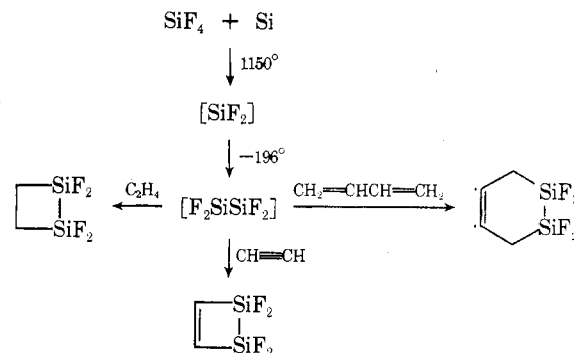
(57) M. Kumada, K. Tamao, M. Ishikawa, and M. Matsumo, *Chem. Commun.*, 614 (1968).

(58) A. W. P. Jarvie and R. J. Rowley, *J. Organometal. Chem.*, 36, C7 (1972).

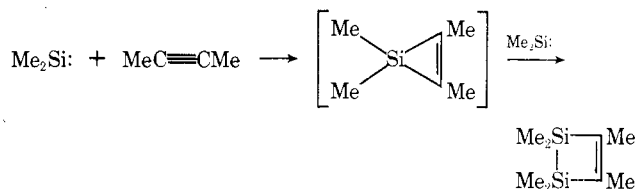
(59) K. Tamao and M. Kumada, *J. Organometal. Chem.*, 30, 349 (1971).

(60) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, 94, 7926 (1972).

Some information has appeared on silicon olefin analogs containing two π -bonded silicon atoms. Considering data on cocondensation of SiF_2 with a number of unsaturated compounds and low-temperature ir and esr spectra of SiF_2 , Margrave, *et al.*,⁶¹ suggested that it forms the diradical, Si_2F_4 , at -196° .

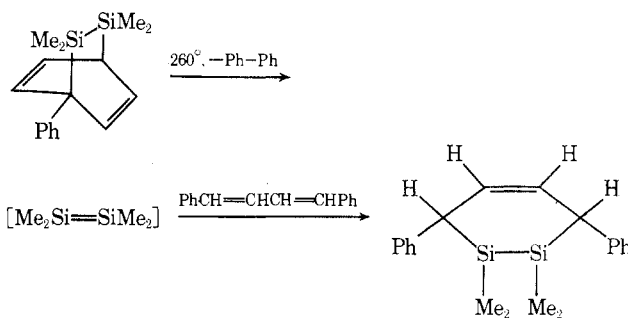


Similar conclusions were reached in studies of reactions of SiF_2 with BF_3 , benzene, propyne, 2-butyne. However, "a reaction mechanism involving diradicals seems doubtful"⁶² when SiF_2 reacts with MeOH , H_2O , H_2S , I_2 , GeH_4 , etc.⁶¹ Although some of the given cyclic structures were criticized⁶³ as not well identified, the recent publication⁶⁴ on the synthesis of hexamethyl-1,2-disila-3-cyclobutene from dimethylsilylene and 2-butyne is in agreement with the above. It is interesting that the reaction took place in a gas-flow system, the proposed mechanism involving no Si_2F_4 .



Moreover, observation of an esr spectrum when SiF_2 (which is originally a singlet) condenses on a cold surface seems not to be considered as evidence for Si_2F_4 . It may be due to the polymeric species, $\cdot\text{SiF}_2(\text{SiF}_2)_n\text{SiF}_2\cdot$, where $n = 1, 2, 3, \dots$, and not necessarily to Si_2F_4 .

Peddle and Roark^{65,66a} found that pyrolysis of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes results in $\text{Me}_2\text{Si}=\text{SiMe}_2$, an unstable intermediate which can



(61) J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 4, 145 (1971), and references therein.

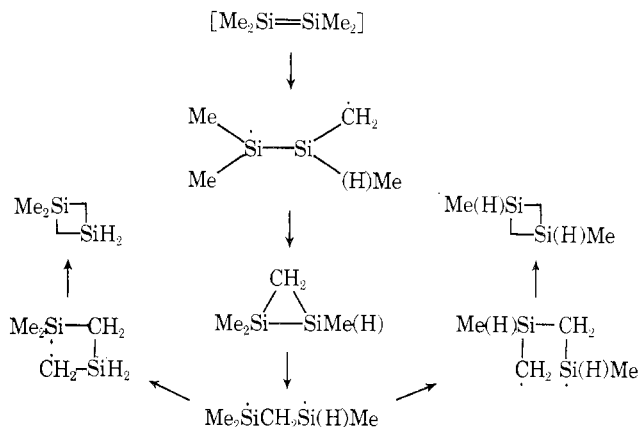
(62) J. L. Margrave, K. G. Sharp, and P. W. Wilson, *Inorg. Nucl. Chem. Lett.*, 5, 995 (1969).

(63) R. Damrauer, *Organometal. Chem. Rev.*, 8, 67 (1972).

(64) W. H. Atwell and J. G. Uhlmann, *J. Organometal. Chem.*, 52, C21 (1973).

be trapped by naphthalene, anthracene, or *trans*-*trans*-1,4-diphenyl-1,3-butadiene to give adducts.

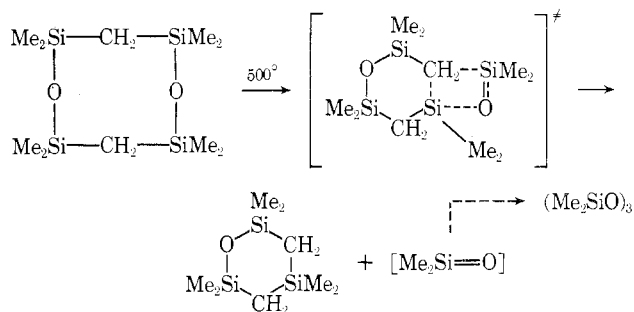
An intense peak corresponding to a π -bonded intermediate is also observed in mass spectra of these compounds. On the other hand, low-pressure pyrolysis in the absence of trapping agents gives 1,1-dimethyl-1,3-disilacyclobutane (30%), 1,3-dimethyl-1,3-disilacyclobutane (10%), and polymer. A reasonable, although unproven, pathway for the formation of 1,3-disilacyclobutanes is suggested.^{66a}



Since $\text{Me}_2\text{Si}=\text{SiMe}_2$ formation occurs in a singlet state by a thermally initiated concerted retrodiene reaction, it may be regarded as having a silicon-silicon π -bond unless steric repulsion of the vicinal methyl groups is greater than the π -bond energy.^{66a} It has been shown recently^{66b} that $\text{Me}_2\text{Si}=\text{SiMe}_2$ results in unstable $\text{Me}_2\text{Si}=\text{O}$ and $\text{Me}_2\text{Si}=\text{CHPh}$ intermediates when pyrolysis is carried out in the presence of benzaldehyde.

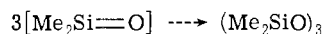
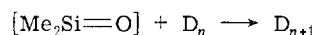
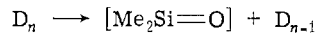
Silicon Analogs of Ketones

Thermal decomposition of eight-membered cyclocarbosiloxanes containing alternative siloxane and silylmethylene groups results in products which are formed by the elimination of monomeric fragments.⁴⁵⁻⁴⁷ One of them is due to the loss of dimethylsilanone.



Similar results were obtained during the study of pyrolysis of cyclosiloxanes, D_n (where $n = 3-7$).^{67,68} Compounds of D_{n-1} appear to be the main products of unimolecular decomposition at a very early stage of the process. Among D_{n+m} type products, the only

product was D_{n+1} . This corresponds to the loss of dimethylsilanone and formation of either a cyclic trimer or the product of insertion into the Si-O bond of starting material to give D_{n+1} .



While the loss of dimethylsilanone is favorable for the cyclic tetramer and pentamer, higher cyclosiloxanes decompose to yield stable D_3 or D_4 . The activation energy for thermal decomposition of D_5 is 61 kcal/mol.

Similar results have been obtained by Davidson and Thompson,⁶⁹ who studied pyrolyses of octamethylcyclotetrasiloxane. The main products, D_3 and D_5 , observed in the ratio 1.3:1, are in accord with the above-mentioned mechanism. The activation energy for the decomposition of D_4 is 71.9 kcal/mol; the lower limit of π -bond energy of dimethylsilanone is estimated to be 38 kcal/mol.

Silanones are also formed upon condensation of silicon monoxide with organic compounds at -196° . However, unlike the above, they undergo an uncontrolled polymerization.⁷⁰ One more route to silanones has been mentioned above in the copyrolysis of silicon analogs of olefins with carbonyl compounds.

Conclusion

As one can see from the results considered above, there is a vast body of data consistent with the idea of the existence of silicon analogs of unsaturated compounds as short-lived, unstable intermediates. More support is lent by mass spectral evidence, which is only briefly mentioned in this Account (such data are discussed in ref 71).

Unlike the unsaturated compounds of carbon, the silicon analogs are highly reactive in bimolecular reactions, and their isolation is difficult. However, they are quite resistant to unimolecular decomposition.

A number of attempts have been made to explain the low π -bond stability for the elements of the third and subsequent rows. Thus, on the basis of pictorial presentations of orbitals, Pitzer⁷² has postulated that low π -bond strength is due to the repulsion of bonding orbitals and filled inner shells of heavier atoms ("inner-shell repulsion").

However, Mulliken^{73,74} concluded from overlap integral calculations that this repulsion is not larger for the third-row elements compared to the second-row elements and hence it may not be the reason for the low π -bond stability. According to Mulliken's concept, nonexistence of stable double-bonded compounds with silicon might be due to the fact that formation of two σ bonds is more favorable than one double bond, *i.e.*, there is a stronger tendency to form polymer rather than unsaturated monomer.

(65) G. J. D. Peddle, D. N. Roark, A. M. Good, and S. G. McGeachin, *J. Amer. Chem. Soc.*, **91**, 2807 (1969).

(66) (a) D. N. Roark and G. J. D. Peddle, *J. Amer. Chem. Soc.*, **94**, 5837 (1972); (b) T. J. Barton and J. A. Kilgour, *ibid.*, **96**, 2278 (1974).

(67) T. Kh. Islamov, Ph.D. Thesis, Institute of Petrochemical Synthesis, Moscow, 1970.

(68) L. E. Gusel'nikov, N. S. Nametkin, T. H. Islamov, A. A. Sobtsov, and V. M. Vdovin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **84** (1971).

(69) I. M. T. Davidson and J. F. Thompson, *Chem. Commun.*, 251 (1971).

(70) E. T. Schashel, D. N. Gray, and P. L. Timms, *J. Organometal. Chem.*, **35**, 69 (1972).

(71) V. Yu. Orlov, *Usp. Khim.*, **42**, 1184 (1973).

(72) K. S. Pitzer, *J. Amer. Chem. Soc.*, **70**, 2140 (1948).

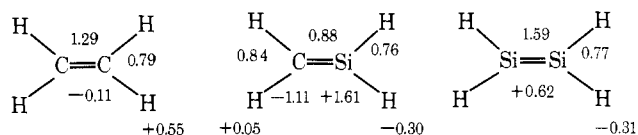
(73) R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 4493 (1950).

(74) R. S. Mulliken, *J. Amer. Chem. Soc.*, **77**, 884 (1955).

Levin, Syrkin, and Dyatkina⁷⁵ estimated the value of p_π - p_π interaction for both carbon and silicon atoms from the heats of sublimation of diamond and silicon and found that the Hückel parameter, β , for silicon is approximately half that of carbon. In the authors' opinion, it may be regarded as a possible reason for nonexistence of stable π -bonded compounds of silicon. Very recently, calculations by Curtis^{76a} for the $\text{H}_2\text{Si}=\text{CH}_2$ and $\text{H}_2\text{Si}=\text{SiH}_2$ molecules, using Hoffmann's EHMO theory, have indicated that the contribution of 3d orbitals to the π -overlap population is high. Moreover, p_π - d_π contribution to the π overlap is larger than p_π - p_π contribution when the valence-state ionization potential of 3d orbitals is taken as -5.50 eV.

	π -overlap population			
	$(p_\pi - p_\pi)$	$(p_\pi - d_\pi)$	$(d_\pi - d_\pi)$	
$\text{CH}_2=\text{SiH}_2$	0.130	0.197	-	= 0.327
$\text{H}_2\text{Si}=\text{SiH}_2$	0.227	0.348	0.038	= 0.663

Total overlap populations and atomic charges in ethylene and its silicon analogs are given below (according to Curtis^{76a}).



(75) A. A. Levin, Ya. K. Syrkin, and M. E. Dyatkina, *Zh. Strukt. Khim.*, **8**, 317 (1967).

(76) (a) M. D. Curtis, communication presented at the 3rd International Symposium on Organosilicon Chemistry, Madison, Wis., 1972; (b) M. D. Curtis, *J. Organometal. Chem.*, **60**, 63 (1973).

Although the EHMO method clearly displays serious deficiencies in the calculations reported,^{76a} the author concluded that silicon-silicon double-bonded compounds should be more stable than silicon-carbon ones. More theoretical studies of the compounds with double-bonded silicon have been done recently,^{76b,77} and significant π -bond order and short bond distances between Si and C strongly indicate a certain stability for silicon analogs of olefins.

Considering the nature of the π bond in silicon analogs of unsaturated carbon compounds, one should mention the recent research⁷⁸ on the structure of silyl radicals. From the esr spectra of $\text{H}_3\text{Si}\cdot$, a pyramidal configuration was deduced. Substitution in the silyl radical of a hydrogen atom by a methyl group affects its geometry very little. It might be that the low tendency to sp^2 hybridization of silicon is responsible for poor π overlap.

Therefore, the nature of the bonds in the silicon analogs of olefins remains an unresolved chemical problem. The technique of low-temperature stabilization of these unstable compounds will no doubt facilitate bonding studies. Further physical studies in gas phase are also needed.

As one can see from data presented, monosilacyclobutanes and 7-silabicyclo- and 7,8-disilabicyclo[2.2.2]octa-2,5-dienes are now the most efficient sources of silicon analogs of olefins. Doubtless the development of new clean reactions resulting in silicon analogs of unsaturated compounds from accessible starting materials will promote the synthetic use of this new type of organosilicon compound.

(77) R. Damrauer and D. R. Williams, *J. Organometal. Chem.*, **66**, 241 (1974).

(78) For references, see R. A. Jackson, *Chem. Soc. Spec. Publ.*, No. 24, 295 (1970).