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THREE-MEMBERED HETEROAROMATIC COMPOUNDS—I*

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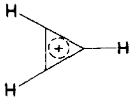
Abstract—A new type of aromatic system, that of three-membered aromatic heterocycles,stabilized by p-p-p or p-p-d conjugation is discussed. The problem of carbenoid or inorganic compounds with electron valent shells similar to that of carbenes has been considered and it has been supposed that their reactions with multiple bonds can be used to obtain three-membered heterocycles. These conclusions are substantiated by the investigation of the reactions of bivalent silicon and germanium derivatives with diphenyl acetylene and acetylene. First representatives of the new type of heterocyclic, three-membered silicon and germanium heterocyclic compounds, have been prepared.

A. *General Considerations*

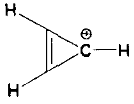
IN all known aromatic heterocycles, the aromatic character is usually associated with a sextet of electrons, similar to that in benzene, the cyclopentadienyl anion or the tropylium cation.

In terms of Hückel's[1] quantum-mechanical considerations and the modern concept on aromaticity,[2–4] cyclic conjugated systems are aromatically stable when the number of π-electrons is $4\,n + 2$ with n being 0, 1, 2, 3, or any other integer.

Thus the sextet of electrons is only one of many electron systems which are known to confer stability. The simplest aromatic system (with $n = 0$) should involve only two π-electrons as represented by the cyclopropenyl cation (I). Indeed, many stable derivatives of this new aromatic system have recently been reported.[5–7]



I



I a

It is evident that similar three-membered heterocyclic systems of type 11 can in general be theoretically deduced by replacing the $>\overset{\oplus}{C}-H$ group in the formula I a by a heteroatom with an available orbital.† This applies particularly to those elements

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* Translated by A. L. Pumpiansky, Moscow.

† The change in energy due to replacement of the isoelectron heteroatom for the CH group is considered by the molecular orbital method as perturbation not affecting the closed or not closed character of the electron shell[1,8]

[1] E. Hückel, *Z. Phys.* **70,** 204 (1931).

[2] W. Baker, *Perspectives in Organic Chemistry* (Edited by A. Todd) p. 28. New York, London.

[3] *Nonbenzenoid Aromatic Compounds* (Edited by G. Ginsburg) New York, London (1960).

[4] M. E. Volpin, *Uspechi Chimii* **29,** 298 (1960).

[5] R. Breslow, *J. Amer. Chem. Soc.* **79,** 5318 (1957); R. Breslow and Chin Yuan, *Ibid.* **80,** 5991 (1958); R. Breslow, R. Haynie and J. Mirra, *Ibid.* **81,** 247 (1959); R. Breslow and R. Peterson, *Ibid.* **82,** 4426 (1960); R. Breslow, and H. Hover *Ibid,* **82,** 2677 (1960).

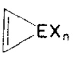
[6] M. E. Volpin, Yu. D. Koreshkov and D. N. Kursanov, *Izv. Akad. Nauk SSSR* 560 (1959); *J. Gen. Chem. U.S.S.R.* **30,** 2877 (1960).

[7] D. G. Farnum and M. Burr, *J. Amer. Chem. Soc.* **82,** 2651 (1960).

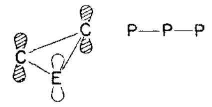
[8] D. A. Bochvar, N. P. Gambaryan, I. V. Stankevich and A. L. Chistyakov, *J. phys. Chem. U.S.S.R.* **32,** 2797 (1958).

whose derivatives of type II have vacant p-orbitals. In the heterocycles thus formed, as in the cyclopropenyl cation, the interaction of three atomic p-orbitals (see Scheme 111) takes place resulting in an aromatic p-p-p-system with two π-electrons in the field of the three nuclei.

A possible alternative worthy of consideration would be the introduction of a heteroatom with a vacant d-orbital into the three-membered cycle. In the resulting p-p-d system interaction of two pπ and one dπ-orbitals may take place.



II

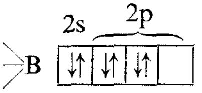


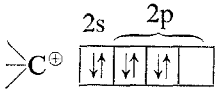
III

As shown by Craig[9] (see also ref.[10]) the interaction of pπ electrons and dπ orbitals in the rings would lead to a considerable gain in energy and the stability of six and eight-membered cyclic phosphoronitrile halides is the result of such a p-d interaction.

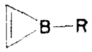
The three-membered aromatic heterocycles of the first type involving p-p-p-interaction should be primarily peculiar to the elements of group III of the Periodic System such as B, Al, Ga, In, Tl with vacant p-orbitals in trivalent state.*

Trivalent boron has the same electron configuration as the carbonium ion

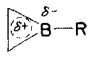




Replacement of atom C^+ by B in Ia should result in an uncharged molecule of boracyclopropenylium (borirene,†) IV. Due to the vacant boron atom orbital being filled on interaction with π-electrons, boron must become markedly 4-covalent and negatively charged, and the carbon atoms must acquire some positive charge. The molecule as such must possess a marked dipole moment and it would be better to express it by formula IVa.



IV



IV a

It is to be expected that such a molecule would be more stable than the aliphatic derivatives of trivalent boron and less affected by bases whilst the double C=C bond would markedly approach the aromatic bond.

Similarly, one might expect the existence of three-membered aromatic heterocycles for Al, Ga, In, and Tl. It seems that the stability of such systems should decrease from Al to Tl with the lessening of the affinity to the electron, extension of the volume of the heteroatom and decrease in the overlapping of 2p-orbitals of the carbon atoms with the larger p-orbital of the heteroatom.

On passing from the elements of the third group of the Periodic System to the fourth, i.e. silicon, germanium, and tin, there appears the possibility of both p-p-p- and p-p-d-interaction in three-membered heterocyclic systems. A simple replacement

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* Only the elements of main groups are considered. The three-membered heterocycles with transition elements will be dealt with in subsequent publications.

† According to Patterson's nomenclature.[11]

[9] D. P. Craig, *Chem. & Ind.* 3 (1958); *J. Chem. Soc.* 997 (1959).

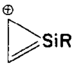
[10] M. J. S. Dewar, E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.* 2423 (1960).

[11] A. M. Patterson and L. T. Capell, *The Ring Index.* New York (1940).

of the carbonium atom C^+ in the formula Ia by Si^+, Ge^+, or Sn^+ may give rise to systems of type V which appear similar to the cycloropenyl systems. However, as shown by numerous investigations, silicon compounds fail to form R_3Si^+ ions and


V

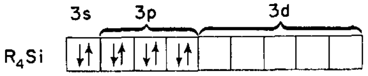

Va

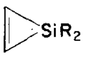

Vb

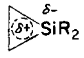
all attempts to obtain these ions or prove their formation in chemical reactions were unsuccessful.[12] On the other hand, it will be noted that the tetracovalent silicon (as well as germanium and tin) do not form stable multiple bonds of the type $\rangle Si{=}X$. All this shows that structures of the type Va and Vb are unstable and make the existence of stable aromatic ions V rather unlikely.

The second alternative is the formation of three-membered cycles with tetracovalent silicon, germanium, and tin that may involve the p-p-d-interaction of π-electrons of the double bond with vacant d-orbitals of the heteroatom. Numerous data on the dipole moments,[13] spectra and reactivity of organo-silicon compounds[12] point to the relative stability of the structures with pentacovalent negatively charged silicon of the type $R_3\overset{\ominus}{Si}{=}C\langle$ produced by the participation of 3d orbitals of silicon.

It is to be expected, that in three-membered cycles of type VI the 2p-electrons of carbon atoms and the 3d-orbital of silicon atom will interact as above leading to the formation of a more stable system which can be conveniently expressed by formula VIa. This interaction should lead to the appearance of a dipole moment directed from carbon to silicon and to the aromatization of the olefin double carbon-carbon bond.




VI


VIa

Similar considerations are applicable to germanium, tin, and to a lesser extent, to lead which could be expected to form aromatic heterocycles of the type VIa.

The delocalization energy in such systems is expected to decrease in the series $Si > Ge > Sn > Pb$ with the lessening of the affinity to the electron and extending the volume of heteroatoms, the transition from the 3d-orbitals to 4d-, 5d- and 6d-orbitals decreasing the extent of their overlapping with 2p-orbitals of carbon atoms.

The above considerations can also be extended to elements of the fifth group of the Periodic System. Thus, substituting the iso-electron atom $\rangle N^+$ for $\rangle C^+$ may lead to the system VII.

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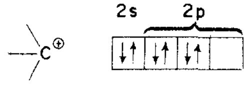
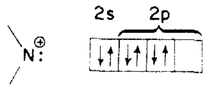
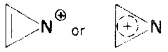
[12] C. Eaborn, *Organosilicon Compounds*. London (1960).

[13] G. N. Kartsev, Ya. K. Syrkin, V. F. Mironov and E. A. Chernyshev, *Dokl. Akad. Nauk SSSR* **122**, 99 (1958).

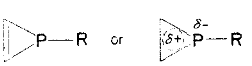




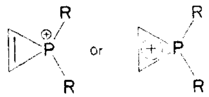


VII

Bearing in mind the affinity to electron $>N^{+}$ being much higher than $>C^{+}$ and, hence, that $>N^{+}$ is less stable, the system VII should be less stable than the derivatives of the cyclopropenyl cation. As nitrogen has no d-orbitals, it cannot partake in p-p-d-interactions,* but in the case of phosphorus (as well as arsenic and antimony) one might expect the existence of p-p-d-systems VIII and IX for valent states of $>P:$ and $>P^{\oplus}$.

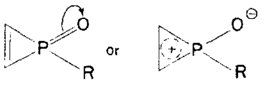


VIII

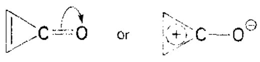


IX

Phosphonium salts of the type IX, where owing to the formation of an aromatic system the positive charge should be delocalized, seem to be stable. It also follows that one can expect the formation of compounds of the type X, peculiar analogs of cyclopropenone XI.



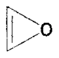
X



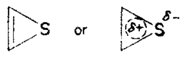
XI

Finally, the same considerations concerning the sixth group of the Periodic System infer that the absence of aromatic properties in acetylene oxide (XII) are due to oxygen lacking d-orbitals. This is substantiated by the properties of its derivatives which are readily hydrogenated, oxidized and isomerized.[14]

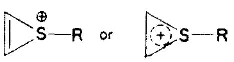
On the other hand, it is evident that rings containing sulphur, selene and tellurium of the type XIII–XVI can be stabilized by p-p-d-interaction.



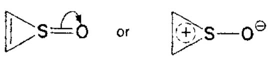
XII



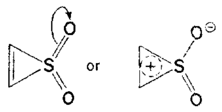
XIII



XIV



XV



XVI

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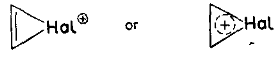
* Compounds of the type $>$NR should therefore have no aromatic properties.

† The above treatment can be also extended to seven-membered heterocyclic systems.

[14] H. H. Schlubach and V. Franzen, *Liebigs Ann.* **577**, 60 (1952).

Similar reasoning suggests that chloronium, bromonium and iodonium cycles of the type XVII may also be stabilized by such an aromatic p-p-d-interaction. Thus, qualitative treatment based on general considerations of the theory of aromaticity



XVII

points to the existence of a great number of various three-membered aromatic heterocycles, stabilized by p-p-p- and p-p-d-interactions.† But qualitative treatment is not sufficient to solve the problem of stability in each of the above systems. The solution should include both the estimation of the p-p-p- and p-p-d-interaction energy stabilizing the system and such factors as the strain in the three-membered ring, the volume of the heteroatom and its electronegativity etc.

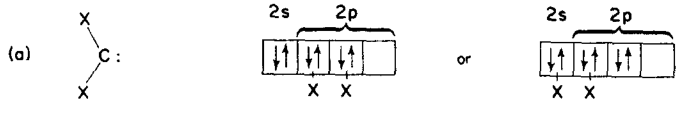
B. *The Routes to Three-membered Heterocycles* V

Carbenes and carbenoids

Though, as shown above, one might expect the existence of various three-membered heteroaromatic compounds, none have as yet been prepared. This seems on the one hand due to the lack of theoretical justification to look for such stable compounds and on the other to the difficulty involved in obtaining such cyclic systems. It suffices to say that even the saturated three-membered heterocycles are as yet known only for an extremely limited number of elements, such as oxygen, nitrogen and sulphur. We therefore deemed it necessary to consider the most general ways to synthesize three-membered heterocyclic compounds.

Of various methods to obtain three-membered carbon rings the most promising is that of cycle formation by the addition of carbenes, unstable derivatives of bivalent carbon, to the double bond (cf. [15]):

The carbene addition to the acetylene triple bond may be used to synthesize unsaturated three-membered cycles either as derivatives of cyclopropene,[16,17] or those of the aromatic cyclopropenyl system.[6] This reactivity of carbenes is due to their electron structure that can be illustrated by the following schemes:



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[15] W. E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.* **76**, 6162 (1959).

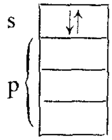
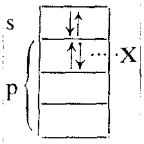
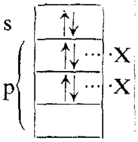
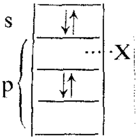
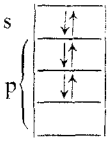
[16] R. Breslow and M. Battiste, *Chem. & Ind.* 1143 (1958).

[17] W. E. Doering and T. Mole, *Tetrahedron* **10**, 65 (1960).

Four valent carbon electrons are involved in the formation of two C-X bonds whilst two free electrons in the ground state can be either shared (a) or unshared (biradical, b), depending on the character of the substituents. Such electron structure of carbenes is responsible for their characteristic property, the ability to form two new covalent bonds in the reaction.

It is accordingly to be expected that such reactivity should be exhibited not only by carbon compounds but also by the derivatives of other elements whose electron valent shell is similar to that of carbenes. These compounds are referred to as "carbenoids". In order that the non-organic or organo-element molecules be similar to carbenes they must fulfil the following requirements:

TABLE 1. CARBENOIDS OR INORGANIC ANALOGS OF CARBENES*

Period	Group				
	II	III	IV	V	VI
	○ :E○ ○ 	○ :EX ○ 	○ $:EX_2$ 	○ :EX ·· 	○ :E: ·· 
2	Be	BX	(CX_2)	NX	O
3	Mg	AlX	SiX_2	PX	S
4	Zn	GaX	GeX_2	AsX	Se
5	Cd	InX	SnX_2	SbX	Te
6	Hg	TlX	PbX_2	BiX	Po

* In general formulas EX_n the electron pairs are symbolized by the sign ":", the available p-orbitals by "○". Conventionally, in all schemes the s-electron pairs are designated as free; all electrons are indicated shared.

(1) The central atom must possess no less than one free pair of s of **p**-electrons (or two unshared electrons)

(2) At least one p-orbital must be vacant (or two electrons must occupy two orbitals)

(3) There must be an absence of vacant d-levels with smaller main quantum number than that of valent p-electrons and p-levels.*

In accordance with these requirements we should expect the atoms of the elements of the second and the sixth group, the monovalent derivatives of the elements of the third and fifth group, and the bivalent derivatives of the elements of the fourth group (see Table 1) to possess carbenoid properties, i.e. to be able to give rise in the reaction to two new covalent bonds. Besides the electroneutral molecules listed in Table 1

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* This refers to transition elements, as these elements with such vacant d-levels cannot form stable bonds between the element and alkyl.

one may also consider as "carbenoids" some ions fulfilling the above requirements, such as the cations

$$\overset{\bigcirc\oplus}{R_2N:},\ \overset{\bigcirc\oplus}{R_2P:},\ \underset{..}{\overset{\bigcirc\oplus}{RO:}},\ \underset{..}{\overset{\bigcirc\oplus}{RS:}},\ \underset{..}{\overset{\bigcirc\oplus}{:Cl:}},\ \underset{..}{\overset{\bigcirc\oplus}{Br:}}\ \text{etc.}$$

Some carbenoids included in Table 1 are quite stable and this allows their reactions to be investigated. On the other hand, such carbenoids as boron, aluminium, nitrogen, and phosphorus derivatives as well as the carbenoid cations mentioned above are rather unstable. One could expect them to be formed as unstable particles in the course of different reactions, similar to the intermediate formation of carbenes themselves which are also unstable under ordinary conditions.

Our review of the literature on the properties and reactions listed in Table 1 of both stable and unstable carbenoids suggests the following:

(1) Similar to carbenes, the carbenoids under review can undergo insertion reactions with the formation of two new bonds.
The general scheme of such reactions for carbenes is:

$$CX_2 + A{-}B \rightarrow A{-}CX_2{-}B$$

Similarly, reactions of carbenoids are according to the general scheme:

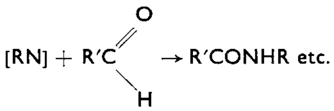
$$EX_n + A{-}B \rightarrow A{-}EX_n{-}B$$

Thus:

$$SiCl_2 + HCl \rightarrow SiHCl_3$$

$$(CH_3)_2Sn + CH_3{-}I \rightarrow (CH_3)_3SnI$$

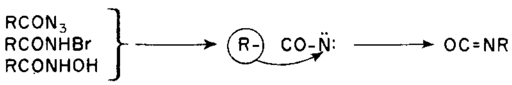
$$Zn + CH_3{-}Br \rightarrow CH_3{-}Zn{-}Br$$



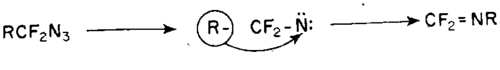
$$[RN] + R'C(=O)H \rightarrow R'CONHR \text{ etc.}$$

(2) Some carbenoids reveal rearrangements similar to the carbenes:

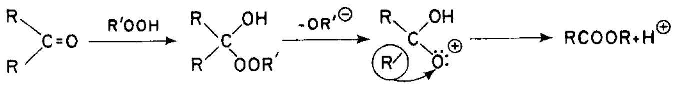
Such are the Curtius, Hofmann and Lossen rearrangements:



The rearrangement of perfluoroazides:[18]



The Bayer-Villiger reaction:



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[18] I. L. Knuniants, E. G. Bykhovskaja and V. N. Frosin, *Dokl. Akad. Nauk SSSR* **132**, 357 (1960).

(3) The least stable carbenoids are those of the first and second periods of the Periodic System, with many unstable carbenoids being as readily polymerized as carbenes.

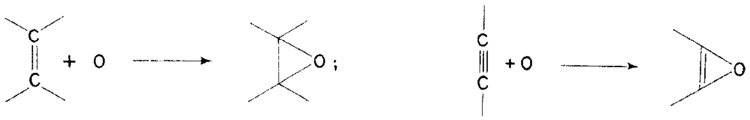
In each group of the periodic system the stability of the electron analogs of carbenes rises with the increase in the atomic number, e.g.

$$SiX_2 < GeX_2 < SnX_2 < PCX_2 \text{ or } AlX < GaX < InX < TlX,$$

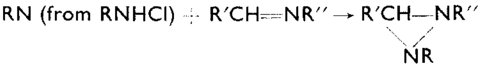
whilst their reactivity in reactions with nucleophilic agents changes in the reverse order.

(4) It is characteristic of carbenes to add to the double or triple carbon-carbon bond producing three-membered cycles.

With carbenoids, however, these reactions are known only for oxygen and nitrogen. Thus, treatment of olefins with peracids or directly with atomic oxygen leads to an ethylene oxide cycle (cf. [14]):

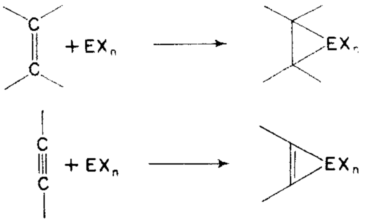


In the case of nitrogen the addition of azacarbene intermediates NH or NR to the bonds C=N has been reported.[19]



$$RN \text{ (from RNHCl)} + R'CH{=}NR'' \rightarrow \underset{NR}{R'CH{-}NR''}$$

The similarity between the electron structure and reactivity of carbenes and their inorganic analogs suggests that not only O and NR, but many other carbenoids, which are sufficiently reactive, would add to the multiple bonds to give three-membered heterocycles, and the reaction of inorganic analogs of carbenes and the acetylene derivatives should be a general method for the synthesis of three-membered aromatic heterocycles, stabilized by conjugation. A systematic investigation of the reactions of carbenoids with olefins and acetylenes in an attempt to find a new synthesis of three-membered heterocycles was therefore undertaken.



C. *Three-membered Germanium Heterocycles*

Confirmation of these conceptions on the existence of three-membered aromatic heterocycles and the analogy between carbenes and carbenoids was first obtained from the study of germanium derivatives.*

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* Cf. preliminary communication.[20]

[19] E. Schmitz, *Angew. Chem.* **71**, 127 (1959); **73**, 55 (1961).

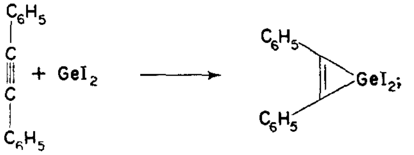
[20] M. E. Volpin and D. N. Kursanov, *Izv. Akad. Nauk SSSR* 1903 (1960).

Although the halogen derivatives of bivalent germanium are more stable than dihalocarbenes, they undergo many reactions similar to those of carbenes:

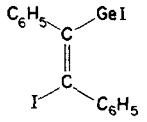
$$GeCl_2 + HCl \rightarrow HGeCl_3;$$
$$GeI_2 + C_2H_5I \rightarrow C_2H_5GeI_3.$$

Carbenoids such as $GeCl_2$, $GeBr_2$ or GeI_2 should react like carbenes with the triple carbon-carbon bond to give three-membered germanium heterocycles stabilized by p-p-p- or p-p-d-conjugation.

In contrast to highly reactive dihalocarbenes, germanium diiodide does not noticeably react with diphenylacetylene either at room temperature or on being moderately heated, but above 200° germanium diiodide adds to diphenylacetylene:

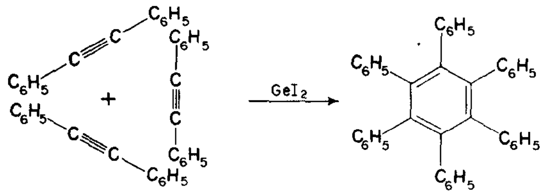


XVIII



XIX

Simultaneously, trimerization reaction of diphenylacetylene to hexaphenylbenzene under the action of GeI_2 takes place.

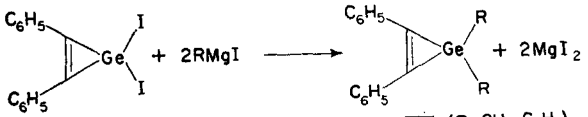


The addition product of germanium diiodide to diphenylacetylene proved to be very stable. It has a high melting point (301–303°), does not oxidize in air, is insoluble in saturated hydrocarbons, ether or water, moderately soluble in benzene and readily in chloroform, acetone and alcohol. This compound could have either structure XVIII or XIX. The properties and reactions of the iodide and its derivatives point to the cyclic structure XVIII and structure XIX may be rejected on the following considerations.

(1) The iodide, as well as its conversion products (see below), are stable in air, do not oxidize even on heating, and add no bromine. This shows that they are derivatives of tetravalent rather than bivalent germanium:

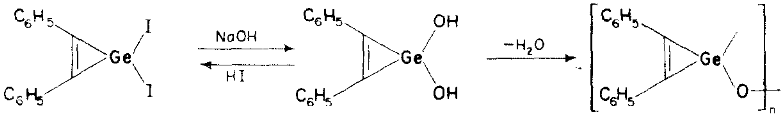
(2) In accordance with structure XVIII both iodine atoms instantly react with $AgNO_3$, are quantitatively titrated with alkali and substituted by alkyls under the action of alkyl magnesium halides, whereas according to structure XIX only one iodine atom (at germanium) should be labile.

The reaction with organo-magnesium compounds proceeds according to the following scheme:



XX ($R = CH_3, C_2H_5$)

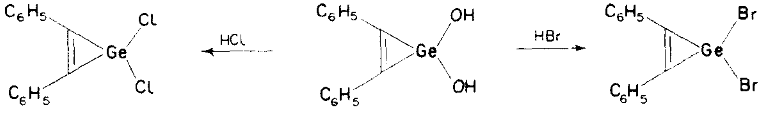
(3) The iodide reaction product with alkali contains hydroxy- and no carbonyl groups, when treated with hydriodic acid it can be reconverted to the starting iodide, this being in accordance with the cyclic structure:



XXI XXII

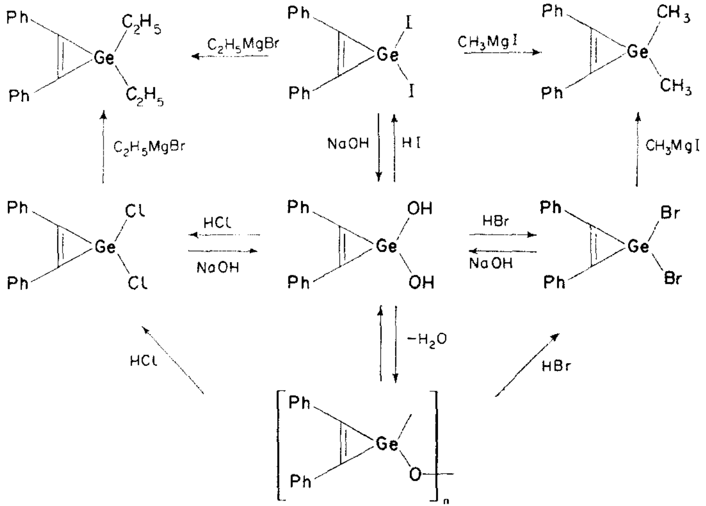
On heating hydroxide XXI it is gradually dehydrated to form a polymeric oxide XXII with a mean molecular weight of about 25,000.

(4) In accordance with the cyclic structure, treatment of hydroxide XXI or oxide XXII with hydrogen chloride or bromide leads respectively to the dichloride XXIII and the dibromide XXIV in high yields.



XXIII XXI XXIV

These halides are similar in properties to iodide XVIII and undergo the same reactions. On treatment with alkali they can be reconverted to the starting hydroxide XXI. The interconversions of substances obtained are represented by the general Scheme 1.



Scheme I

The molecular weight of the compounds produced, estimated cryoscopically in benzene and camphor, and ebullioscopically in benzene, point to a marked association often observed with germanium compounds. More detailed study, carried out with the dimethyl derivative XX ($R = CH_3$) showed the apparent molecular weight to decrease with decreasing concentration of the substances in solution (Fig. 1) and extrapolation to infinite dilution showed the molecular weight to be equal to that calculated for the three-membered monomer of the formula XX ($R = CH_3$). The infra-red evidence also confirms the three-membered cyclic structure of compounds obtained.

(1) Spectra of the germanium derivatives XVIII–XXIV reveal two bands of medium intensity at 1562–1592 cm^{-1} which are assigned to the vibrations of the aromatic bonds of benzene rings and the strongly conjugated multiple bond in the cycle. The intensity of the shorter wavelength (1587–1592 cm^{-1}) sharply increases on transition from halides to dialkyl derivatives. The spectra of all compounds reveal no absorption at 2140–2100 cm^{-1} thus pointing to the absence of triple $C{\equiv}C$ bonds.

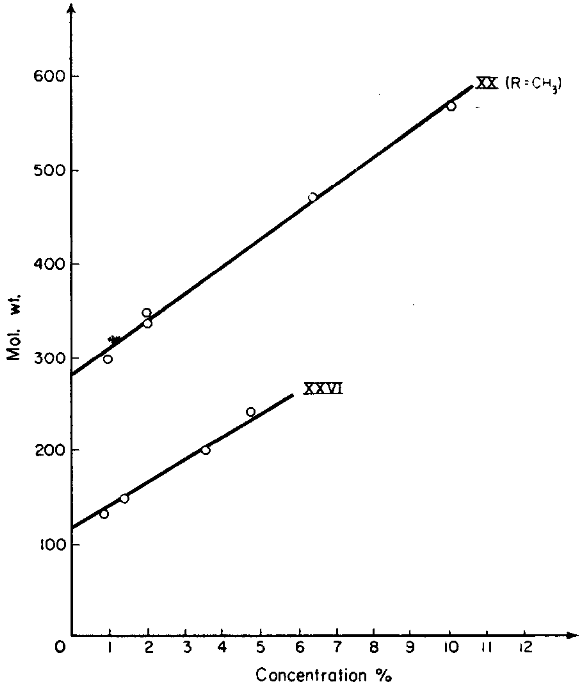


Fig. 1.

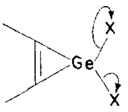
(2) Compounds contain benzene rings (intensive absorption of carbon-hydrogen bond at 3049–3054 cm^{-1}) both rings being monosubstituted (with the characteristic series of four absorption bands at 1680–2000 cm^{-1}).

(3) Spectra of all compounds reveal an absorption band at 500 cm^{-1} in the region of valent vibrations of germanium-carbon bond.

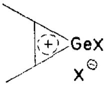
(4) The structure of the dimethyl derivative XX ($R = CH_3$) is substantiated by intensive absorption bands at 582; 600; 802; 825 and 1228^{-1}, assigned to the group $Ge(CH_3)_2$. The spectrum of the diethyl-derivative XX ($R = C_2H_5$) reveals strong absorption at 969, 1010 and 1236 cm^{-1} (group GeC_2H_5) and at 1442 cm^{-1} (deformation vibrations of the $C{-}CH_3$ bond).

(5) The structure of the hydroxide is confirmed by the presence in the infra-red spectra of intensive absorption at 3322 cm^{-1}, characteristic of OH groups and no absorption at 1700 cm^{-1} (no $C{=}O$ groups).

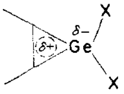
The properties of halides produced such as iodide, bromide, and chloride are in accordance with the covalent structure **A** rather than with the purely ionic structure **B**, though the germanium-halogen bonds appear to be strongly polar.



A



B

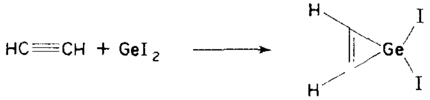


C

On the other hand, a number of properties of these compounds such as high stability (in spite of the presence of a three-membered strained cycle), stability of the system to the action of bromine, alkali and strong acids, and no hydrogen addition with platinum catalyst is in accordance with the suggestion that the heterocycles produced are stabilized by conjugation and are aromatic. The haloderivatives can exhibit both p-p-p-interaction (**B**) and p-p-d-interaction (**C**) and dimethyl derivative—only p-p-d-interaction (**C**). It is evident, that such interactions should primarily result in a marked dipole moment not only in haloderivatives but in the dimethyl derivative of germanium heterocycle as well. This point is being investigated.

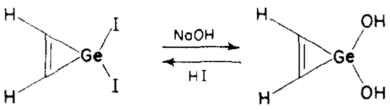
The problem concerning the aromaticity of the new class of heterocycles obtained and their fine structures will be further discussed.

Similar to diphenylacetylene, other compounds with a triple C≡C bond also react with germanium diiodide. Thus the latter adds to acetylene at 140°, following the scheme:

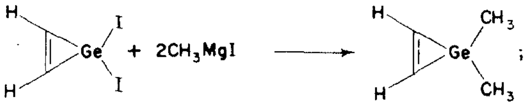


XXV

The addition product of XXV is rather similar in properties to those of XVIII obtained from diphenylacetylene. It is also stable in air, has a high melting point (225–226°) is not soluble in ether and saturated hydrocarbons, reacts with alkali to give the hydroxide:



Compound XXV on treatment with methyl magnesium iodide, the two iodine atoms are substituted by methyl groups:



XXVI

The dimethyl derivative (XXVI) is a colourless liquid, stable in air. Similar to other three-membered germanium derivatives, it is strongly associated in solutions and its apparent molecular weight rises with increasing concentration to that calculated for formula XXVI only at low concentrations of the substance in solution (Fig. 1). Its structure was confirmed by infra-red evidence with the spectrum showing the presence of the group $Ge(CH_3)_2$ (1418, 1243, 824, 807 and 600 cm^{-1}) and the absence of bonds Ge—H and C≡C.

D. *Three-membered Silicon Heterocycles*

As shown above, the bivalent silicon derivatives owing to their electron configuration should exhibit a "carbenoid" reactivity, and react to form two covalent bonds.

Only few bivalent silicon compounds have as yet been reported, all these compounds under usual conditions are polymeric substances involving Si-Si bonds. We expected the unstable bivalent silicon derivatives, if formed in the reaction, to undergo reactions similar to those of carbenes. The alkyl derivatives of bivalent silicon may be obtained as follows:

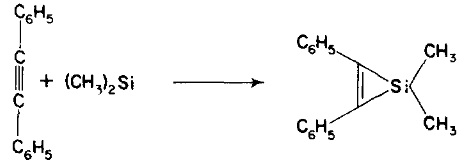
(1) The reactions of dimethylchlorosilane and sodium in boiling xylene:

$$(CH_3)_2SiCl_2 + 2Na \rightarrow (CH_3)_2Si + 2NaCl$$

(2) The thermal splitting of Si-Si bonds in the polymer $[(CH_3)_2Si]_n$ (with n being 55 according to[21]:

$$[(CH_3)_2Si]_n \xrightarrow{t^\circ} n(CH_3)_2Si$$

It was thought that these reactions when carried out in the presence of diphenylacetylene would result in the addition of the intermediate dimethylsilicon $(CH_3)_2$ Si to the triple carbon-carbon bond to give a three-membered ring:



XXVII

Indeed, in both cases the same compound containing silicon, whose composition, molecular weight and infra-red and chemical evidence indicated structure XXVII was isolated. This compound is very stable, melts at 324–328° without decomposition, sublimates under atmospheric pressure above 200° and is not oxidized in air. Compound XX is of a similar structure to the germanium compound, and does not add bromine in carbon tetrachloride. These properties seem to be due to the reduced reactivity of the double bond owing to its interaction with vacant d-orbitals of silicon. As with germanium heterocycles its apparent molecular weight increases with increasing concentration of the compound, being at low concentrations that calculated for the heterocycle XXVII. The structure of the compound was substantiated by the infra-red evidence showing absorption bands at 1248, 795 (the $Si(CH_3)_2$ group), 1600 (the conjugated C═C double bond and aromatic bonds) and 696, 752, 1020, 1065, and 1175 cm^{-1} (monosubstituted phenyl groups).

It has thus been shown that bivalent silicon and germanium derivatives add, as do carbenes, to the multiple bond and the first representatives of a new class of three-membered heterocycles containing silicon and germanium (derivatives of silirene and germirene*) have been prepared. The investigation in this field is being continued.

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* According to Patterson's nomenclature.[11]

[21] C. A. Burkhard, *J. Amer. Chem. Soc.* **71**, 963 (1949).

EXPERIMENTAL

1,1-*Diiodo*-2,3-*diphenylgermirene* (XVIII)

A three-necked flask equipped with a stirrer, reflux and thermometer, was charged with finely ground germanium diiodide (12·0 g, 0·0366 mole) and diphenylacetylene (13·2 g, 0·0732 mole). The mixture was warmed with stirring for 2 hr 15 min at the reaction temperature of 220–230°. After cooling 80 ml of benzene were added and the mixture boiled for 15–20 min to dissolve the reaction products. The hot solution was filtered and the precipitate washed with hot benzene. The precipitate (1·70 g) consisted of a little non reacted GeI_2 and much hexaphenylbenzene; after recrystallization from xylene it had m.p. 430–431°, lit. m.p. 430–432°,[23] 426°.[22] (Found: C, 94·12; H, 5·74. $C_{42}H_{30}$ requires: C, 94·33; H, 5·67%).

The benzene filtrate was cooled and poured with stirring into 200 ml of heptane with almost pure iodide XVIII, m.p. 296–298°, being precipitated. This was filtered off, washed with heptane and pet ether and dried in a vacuum. Yield 5·60 g (30%); after recrystallization from benzene m.p. 301–303° (corr.) (Found: C, 33·18, 33·15; H, 1·93, 2·04; I, 50·29, 50·43; Ge, 14·47, 14·59. $C_{14}H_{10}GeI_2$ requires: C, 33·32; H, 2·00; I, 50·29; Ge, 14·39%).

The compound was soluble in chloroform, acetone, alcohol and hot benzene, slowly soluble in carbon tetrachloride and insoluble in heptane, ether and water. Treatment of the alcohol solution with silver nitrate immediately precipitated silver iodide. The iodide (XVIII) is not hydrogenated in alcohol solution in the presence of Adams platinum catalyst.

In titrations of the iodide in alcohol with alkali (with phenol-phthalein), 0·589 g (1·17 mmoles) of the substance required 2·42 ml of 0·1 N NaOH and 0·530 g (1·05 mmoles) of the substance 2·01 ml of 0·1 N NaOH, the mean being 1·99 ± 0·08 equiv of alkali; indicating that both iodine atoms are titrated with alkali.

The molecular weight of iodide (XVIII) was found cryoscopically to be about 635 in benzene; Calc for the monomer $C_{14}H_{10}GeI_2$ 505; for the dimer $C_{28}H_{20}Ge_2I_4$ 1009.

1,1-*Dihydroxy*-2,3-*diphenylgermirene* (XXI)

Iodide XVIII (5·6 g) was dissolved in warm benzene (50 ml) and shaken with an excess of 10% sodium hydroxide. The white amorphous precipitate was filtered off, washed with water (till no alkali reaction was observed) and dried at 120° to constant weight yielding 2·6 g (82%). The substance was thermally stable, did not melt at 600°, is insoluble in water and most organic solvents, gradually soluble on prolonged boiling in alcohol and could be precipitated with water from the alcoholic solution but recrystallization failed.

(Found: C, 59·96, 60··07; H, 4·33, 4·21; Ge, 25·53, 25·66. $C_{14}H_{12}GeO_2$ requires: C, 59·03; H, 4·25; Ge, 25·49%). Prolonged drying at 110° in vacuum led to considerable dehydration and formation of a polymer oxide of a molecular weight about 25,000 (light scattering in chloroform).

Shaking the hydroxide XXI with conc hydroiodic acid and benzene and evaporating the benzene layer yielded the starting iodide XVIII, m.p. 298° with no depression of the mixed m.p. with an authentic sample.

1,1-*Dichloro*-2,3-*diphenylgermirene* (XXIII)

The heated suspension of 1·25 g of the hydroxide XXI in 40 ml of dry benzene was swept with dry hydrogen chloride until the hydroxide was completely dissolved. Boiling removed most of benzene together with the water evolved during the reaction and the excess hydrogen chloride. The precipitate obtained on cooling was crystallized from benzene yielding the chloride, 1·31 g (89·3%), m.p. 290–292°.

(Found: C, 52·03, 51·97; H, 3·24, 3·05; Ge, 22·40, 22·19; Cl, 22·00. $C_{10}H_{10}GeCl_2$ requires: C, 52·26; H, 3·13; Ge, 22·57; Cl, 22·04%). The action of alkali converted it into the starting hydroxide.

1,1-*Dibromo*-2,3-*diphenylgermirene* (XXIV)

A suspension of 2·60 g of hydroxide XXI in 40 ml of dry benzene was swept for 1 hr with dry

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[22] R. Breslow and P. Gal, *J. Amer. Chem. Soc.* **81**, 4747 (1959).

[23] W. Dielthey and G. Hurtig, *Ber. Dtsch. Chem. Ges.* **67**, 2004 (1934).

hydrogen bromide, the precipitate being thereby partly dissolved and bromide crystals being formed. The solution was then boiled to remove excess hydrogen bromide and benzene. Cooling resulted in white crystals of the bromide XXIV yielding 3·33 g (89 %), m.p. 318–317°, after recrystallization from benzene. (Found: C, 40·92, 40·80; H, 2·45, 2·60; Ge, 17·73, 17·46; Br, 38·85, 39·00. $C_{14}H_{10}GeBr_2$ requires: C, 40·94; H, 2·45; Ge, 17·68; Br, 38·91 %). The action of alkali readily converted it to hydroxide XXI.

1,1-*Dimethyl*-2,3-*diphenylgermirene* (XX, R = CH_3)

An ethereal solution of CH_3MgI, obtained from 2·5 g magnesium and 13·5 g methyl iodide in 30 ml ether was filtered off from unreacted magnesium and dry iodide XVIII (3·0 g) in 130 ml benzene was added with stirring. The mixture was boiled with stirring for 1 hr, left overnight and decomposed by cooling with a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with benzene. The combined benzene and ether solutions were evaporated and the precipitate recrystallized from heptane. The yield of the dimethyl derivative was 1·31 g (78·5 %), m.p. 295°. The substance does not decolorize bromine in carbon tetrachloride or benzene and is not hydrogenated in alcohol in the presence of Adams catalyst.

(Found: C, 68·73, 68·86; H, 5·69, 5·71; Ge, 25·50. $C_{16}H_{16}Ge$ requires: C, 68·41; H, 5·74; Ge, 25·85 %). The molecular weight was found to be 299·9 in camphor, for 1·0 % solution), increasing with increasing concentration of the substance (see Fig. 1); extrapolation to the zero concentration gave the molecular weight as 280, calc. for $C_{16}H_{16}Ge$ 281.

1,1-*Diethyl*-2,3-*diphenylgermirene* (XX, R = C_2H_5)

To a suspension of iodide XVIII (2·5 g, 5 mmoles) in ether was added with stirring an ether solution of 20 mmoles of C_2H_5MgBr (two fold excess). The solution was boiled for 40 min, decomposed by saturated ammonium chloride solution and extracted with benzene, the benzene-ether solution being dried over magnesium sulphate. After removal of solvent, the residue was recrystallized from a large amount of heptane, the yield of pure ethyl derivative being 0·48 g (32 %), m.p. 239–240°. The substance was found to be readily soluble in benzene and slightly soluble in pet ether and alcohol.

(Found: C, 69·89, 69·84; H, 6·85, 6·83; Ge, 23·28, 23·24. $C_{18}H_{20}Ge$ requires: C, 69·97; H, 6·53; Ge, 23·50 %).

1,1-*Diiodogermirene* (XXV)

An autoclave (0·51) was charged with finely powdered germanium diiodide (20 g, 0·06 mole) and abs benzene (15 ml). The air in the autoclave was substituted by nitrogen, and acetylene introduced until the pressure reached 6 atm. The mixture was heated with shaking for 7 hr at 130–140°, then filtered and the filtrate evaporated. The crystals precipitated were filtered, washed with benzene and dried in a vacuum, yielding 4·2 g (19·5 %), m.p. 225–226° (after recrystallization from benzene) (Found: C, 6·83; H, 0·60; I, 72·33; Ge, 20·72. $C_2H_2GeI_2$ requires: C, 6·81; H, 0·57; I, 72·01; Ge, 20·59 %). The yield of iodide depends largely on the purity of the acetylene introduced in the reaction.

1,1-*Dimethylgermirene* (XXVI)

The ether solution of methylmagnesium iodide (0·8 g of magnesium and 4·8 g of methyl iodide in 20 ml of ether) was filtered off from unreacted magnesium and added to iodide XXV (2·9 g, 0·008 mole) in abs benzene (20 ml). The mixture was boiled with stirring for 1 hr, left overnight and decomposed with 10 % aqueous ammonium chloride and the aqueous layer extracted with benzene. The combined benzene-ether solutions were evaporated and the remaining liquid distilled in a vacuum, b.p. 67°/14 mm, n_D^{20} 1·5009, d^{20} 1·2850, yielding 0·78 g (74·3 %). (Found: C, 37·32, 37.22; H, 6·33, 6·39; Ge, 56·62, 56·40, C_4H-Ge requires: C, 37·32; H, 6·26; Ge, 56·41 %).

The molecular weight was found to be 133 (in camphor, for 1·3 % solution), calc. for C_4H_8Ge 129. Infra-red spectra (measured by Leytes): 3080 (w), 2974 (s), 2942 (s), 2920 (s), 2863 (w), 2820 (w), 1537 (very weak), 1418 (m.), 1320 (w.), 1243 (m.), 1120 (m.), 848 (s), 824 (s), 807 (s), 758 (s), 690 (w), 635 (s), 600 (s), 584 (s), 559 (m.), 457 (s).

1,1-*Dimethyl*-2,3-*diphenylsilirene*

A. *The reaction of dimethyldichlorosilane and sodium in the presence of diphenylacetylene.* Sodium (11·5 g) was dispersed with vigorous stirring in boiling xylene (100 ml) then diphenylacetylene (71·2 g) was introduced and dimethyldichlorosilane (24 ml, 0·2 mole) being added dropwise for 20–30 min in a dry nitrogen sweep. After a strongly exothermic reaction, the mixture was boiled for another 30–40 min, filtered and the residue repeatedly extracted with boiling xylene. The xylene solution was evaporated to a small volume and poured into 300–500 ml of n-heptane. The filtered heptane solution was chromatographed on alumina. Evaporation of heptane eluates yielded unreacted diphenylacetylene and a viscous oil that solidified on cooling. Crystallization of the oil from heptane give 3·25 g of a white crystalline substance which was treated with acetone and the acetone solution evaporated to yield 1,2,3-triphenylnaphthalene, m.p. 152–153° (from heptane). The residue insoluble in acetone was 1,1-dimethyl-2,3-diphenylsilirene, yield, 0·12 g (0·5%), m.p. 324–328°. (Found: C, 80·94; 81·00; H, 6·93, 6·88; Si, 11·77. $C_{16}H_{16}Si$ requires: C, 81·30; H, 6·82; Si, 11·88%). The molecular weight was found to be 241 (in camphor, 2·4% solution), calc. for $C_{16}H_{16}Si$ 236.

1,1-dimethyl-2,3-diphenylsilirene is soluble in benzene, xylene, hot heptane and insoluble in alcohol, acetone, ether, nitromethane, water, and cold heptane, it does not decolorize bromine in carbon tetrachloride and sublimates over 200° without decomposition.

B. *Destruction of polydimethylsilane in the presence of diphenylacetylene.* Polydimethylsilane $[(CH_3)_2Si]_{55}$ was prepared according to Burkhard[21] from dimethyldichlorosilane (70 g) and sodium (41 g) in benzene (100 ml). After drying in a vacuum at 75° the yield amounted to 21·5 g.

Polydimethylsilane (2·03 g) and diphenylacetylene (12·5 g) were charged in a flask with a stirrer, nitrogen inlet and reflux fed with water at ≈70°. The mixture was stirred and heated in nitrogen at 250–260° for 7·5 hr. After cooling the mixture was treated with 150 ml of benzene, filtered and benzene removed in a vacuum. The residue was treated with acetone and the undissolved substance was 1,1-dimethyl-2,3-diphenylsilirene, yield, 0·50 g (6·0%), m.p. 324–328°. The mixed m.p. with a sample obtained in experiment A showed no depression.