# THE STRUCTURE OF "SILIRENES" AND "GERMIRENES"*

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(Received August 13th, 1964)

During the past few years considerable research effort has been devoted to investigations into multiple bond formation between carbon and the other atoms of group IV. Bonding of this type between silicon and carbon has received particular attention. Undoubtedly the position of silicon with respect to carbon in the periodic table and the similarity in behavior of some of their compounds have, amongst other stimuli, encouraged such research. In the realm of pure double bond formation, *i.e.* $p_\pi$–$p_\pi$ orbital interactions, the record has been one of dismal failure. All attempts to form stable silicon-to-carbon double bonds[1–3] or to incorporate silicon as an integral part of a $p_\pi$-aromatic system[4,5] have been unsuccessful[6–8]. Attempts to form double bonds between carbon and germanium have not been reported. Reasons for the inability of these elements to form such bonds have been summarized by Eaborn[9]. Perhaps the most cogent of these is that the energy needed to compress the central $\sigma$-bond to obtain reasonable $\pi$-orbital overlap is not compensated for adequately by the energy gain from overlap.

Even more extensive investigations have been made into the possibility that silicon or germanium can participate in multiple bond formation involving one of their empty *d*-orbitals and a filled *p*-orbital of an element of the first row. Here efforts have been attended by some success, albeit limited. The results of investigations by Benkeser and Krysiak[10] on the dissociation constants of *para*-substituted trimethylsilyl anilines, phenols and benzoic acids, are best interpreted in terms of some dative $\pi$-bonding between the benzene ring and the empty 3*d*-orbitals of silicon. Related work by Chatt and Williams[11] on the dissociation constants of acids of the type $p$-$R_3MC_6H_4CO_2H$ ($R = CH_3$ or $C_2H_5$; $M = C$, Si or Ge) revealed that $\pi$-bonding of this type opposed the normal electron releasing effects of the $R_3M$ group where $M = Si$ or Ge although little difference could be observed between the effects of silicon and germanium. The magnitude of such dative $\pi$-bonding has been investigated by Benkeser *et al.*[12], who studied the rates of alkylation and acylation of certain silicon and germanium compounds. They concluded that the conjugative effects for these two elements were weak and of the same magnitude. Other experimental research work[13–15] on the comparative magnitudes of the latter effect for silicon and germanium has pointed to a greater amount of $\pi$-bonding by silicon than by germanium**. The

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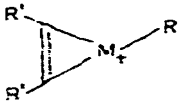
[*] Some of the results in this paper were the subject of a preliminary communication by us in *Tetrahedron Letters*, (1962) 1291.

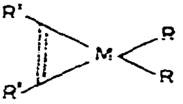
[**] The results of more recent work by Bedford *et al.*[16], support this conclusion. These investigators studied the ESR spectra of the anions of phenyltrimethylsilane and phenyltrimethylgermane and concluded that silicon was much more capable of conjugating with an aromatic system than was germanium.

concensus of opinion, however, appears to have been, that while $p_\pi$–$d_\pi$ bonding* can occur between silicon or germanium and carbon the magnitude of the effect is rather small (in the ground state). However, in the past few years the appearance of a series of articles by Vol'pin *et al.*[19], seemed to contradict this viewpoint completely.

The latter workers discussed at length the problem of stabilization of three-membered aromatic heterocycles. They considered two types of systems, one represented by (I) in which three *p*-orbitals are involved, and the other of type (II) where two *p*-orbitals and a *d*-orbital are utilized. In both instances, Huckel's aromaticity rule[20]—that stable systems should have $4n + 2$ electrons—was invoked wherein $n = 0$. Whereas there is ample evidence that systems of type (I) obey Huckel's rule (although sofar, only where M = C) and are very stable[21], the applicability of this rule to systems involving orbitals other than *p*, has been seriously questioned[22]. In addition in systems involving both $2p_\pi$- and $3d_\pi$-orbitals, extensive overlap cannot be expected not merely because of the disparity in the symmetries of these two types of orbitals, but largely because of the compactness $2p_\pi$ orbitals[18].



(I)



(II)

From several points of view then the claims by Vol'pin *et al.*[19], to have prepared examples of the system (II) (M = Si and Ge) were most interesting. Here were systems supposedly, in which $p_\pi$–$d_\pi$ interactions were large enough to permit extensive electron delocalization around the ring thus giving rise to enough overlap energy to compensate for the angle strain and bond compression that must occur in heterocycles of this type.

However, quite apart from the doubt that the above empirical observations threw on these structures, the three discrepancies cited below, which appeared in the Russian papers led us to reinvestigate the nature of their products.

*a*) The aromatic character of these materials was based on the stability of the ring systems to bromine, heat, and aerial oxidation. In addition, in the case of the dihalogermanium compounds (II; R = halogen), the stability of the ring to alkali and strong mineral acid was also cited.

These properties with the exception of inertness to bromine are common to many organogermanium and organosilicon compounds. For instance tetraalkyl- and tetraarylsilanes are extremely stable to heat and oxidation[23], some of the latter compounds withstanding distillation in air at temperatures[24] above 500°. Similar properties have been noted for organogermanium compounds[25]. The resistance of dihalogermanes to further alkyl or aryl cleavage by strong acids or bases has been well documented.

With regard to the action of bromine on (II) (M = Ge; R = $CH_3$; R' = $C_6H_5$), our results are at variance with those of Vol'pin. We have found that while the absorption of bromine is not rapid, one equivalent is taken up in forty minutes and a second equivalent is absorbed in an additional two and one half hours, at room temperature in carbon tetrachloride. Attempts to obtain a crystalline product after the addition

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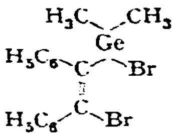
* Excellent theoretical discussions of $p_\pi$–$d_\pi$ bonding can be found in the papers of Craig *et al.*[17], and Jaffé[18].

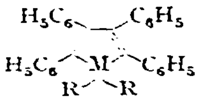
of one equivalent of bromine were fruitless, only a glassy substance together with some starting material being isolated. Nevertheless after the absorption of two equivalents of bromine it was possible to isolate, in low yield, a substance of m.p. 134–6°. This compound gave poor analytical results but its mass spectrum leaves little doubt that it has structure (III). Although the major peaks in the spectrum correspond accurately to the fragmentation pattern of tolane[26], a very broad multiplet of low intensity at approximately mass 440 represents the parent ion. Its multiplicity is that which is expected for a molecule containing one germanium and two bromine atoms. An additional peak, again of low intensity, at *m/e* 361 helps confirm structure


(III)

(III) since the loss of Br (Ge–Br fission) from this molecule is to be expected.

It should be noted that in addition to its origin from a molecule such as (II) (M = Ge; R = $CH_3$; R′ = $C_6H_5$) ,it is possible for (III) to arise by symmetrical cleavage of a dimer of (II).

*b*) One of the methods used to prepare the silirene derivative (II) (M = Si; R = $CH_3$; R′ = $C_6H_5$)—that of reacting dichlorodimethylsilane with sodium in the presence of tolane—was very similar to that used by ourselves[27] and others[28] for the preparation of the metalloles (IV). This suggested that the silirene and the germirenes might possibly be siloles and germoles despite the excellent elemental analytical data

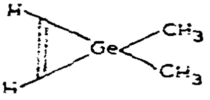

(IV)

presented by the Russians. In addition, the formation of the silirene was accompanied by some 1,2,3-triphenylnaphthalene. The latter material we had often observed during the preparation of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene from tolane and lithium[27–29].

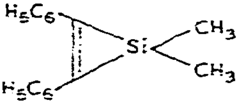
In order to distinguish between such structures as (II) or (IV) for the germanium compounds, the iodide (II) (M = Ge; R = I; R′ = $C_6H_5$) was analyzed by X-ray absorption and fluorescence techniques for germanium and iodine. The values obtained were in good agreement with those obtained by Vol'pin *et al.*[19]. Correlative results were obtained when (II) (M = Ge; R = $CH_3$; R′ = $C_6H_5$) was analyzed for germanium. The nuclear magnetic resonance spectrum of the latter compound showed aromatic proton absorption at 418 cps and aliphatic proton absorption at 12 cps downfield from tetramethylsilane at 0 cps. However, integration did not give an exact 1:1 correspondence for these two types of hydrogen, possibly because of secondary splitting of the aliphatic protons by some of the germanium isotopes. Better results were obtained with (II) (M = Ge; R′ = $C_6H_5$; R = $C_2H_5$). Here the methyl proton to aromatic proton ratio (absorptions occurring at 65 and 45 cps and at 420 cps respectively) approximated 1:1 quite closely.

These results then eliminated from contention structures such as (IV) (M = Ge) for the germanium compounds.

*c*) The molecular weight cited (635) for the iodide (II; R = I; R′ = $C_6H_5$) was determined cryoscopically in benzene and was in poor agreement with the theoretical value (505). Also, the dimethyl derivative (II; R = $CH_3$, R′ = $C_6H_5$) was determined by the Russians to have a molecular weight of 299.9 at 1 % concentration in camphor which rose to 600 at higher concentrations (10 %). In the latter case they were able to obtain an accurate value only by extrapolation to zero concentration of the solute. Similar results were recorded for (V) and (VI). In addition, ebullioscopic molecular weight determinations were claimed to verify all these data but no specific results were given. The variations in molecular weight were ascribed to "a marked association often observed with germanium compounds".



(V)



(VI)

While such a comment may be applicable to inorganic compounds of germanium in an ionizing solvent and perhaps even to (II) (R′ = $C_6H_5$; R = I; M = Ge), it scarcely can be extended to cover purely organic compounds of germanium. Moreover, the presence of a dipole, which one might expect in such three-membered ring compounds, would not necessarily lead to strong molecular association.

A redetermination of the molecular weights of (II) (R = $CH_3$; R′ = $C_6H_5$; M = Ge) in boiling benzene gave inconsistant results but even these did not bear out the Russian claims. At concentrations of 1, 3 and 5 % the values found were 737, 636 and 706 respectively (theory 280.9). Similarly the higher homolog (II) (R = $C_2H_5$; R′ = $C_6H_5$, M = Ge) gave values of 764 and 910 (theory 308.5) at 1 and 2.13 % concentration. Large variations from the theoretical molecular weight have been observed previously for other organic compounds containing an additional group IV element. (The cause of the variation has, however, remained unexplained.) Even taking this into account it did seem that considerably larger molecules were present than the three-membered ring systems claimed by the Russian workers.

Rather than attempt to use the cryoscopic or osmometric methods for molecular weight determinations which again depend on the same thermodynamic properties of solution as the ebullioscopic method, we turned to mass spectrometry for an answer.

The mass spectra of the so-called 1,1-dimethyl-, 1,1-diethyl-, and 1,1-diiodo-2,3-diphenylgermirenes, the 1,1-diiodogermirene and the 1,1-dimethyl-2,3-diphenylsilirene are shown in Figs. 1 to 5 respectively.

### *Mass spectra of germanium compounds*

Perhaps the most significant features of the spectra (Figs. 1–4) of these compounds are *a*) the presence of molecular ion groups at mass values twice those required for the three-membered ring compounds and *b*) the total absence of any ions corresponding to half of these molecular weights.

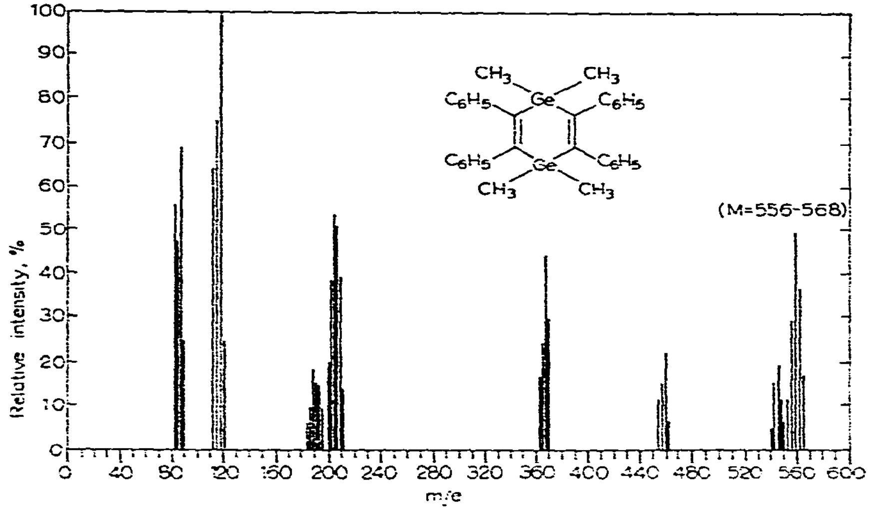
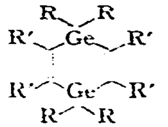


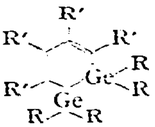
Fig. 1. Mass spectrum of "1,1-dimethyl-2,3-diphenylgermirene".

The possibility that the molecular weights seen in the mass spectra are only apparent and in reality represent tightly bound pairs of molecules of half these molecular weights, that is that they are "dimers by association", seems remote. It appears very unlikely that the energy of such an association would exceed that of a Ge–I or Ge–C bond, which would have to be the case to explain the loss of iodine or methyl at *m/e*'s of *M*-127 and *M*-15 as can be seen in Figs. 1 and 2 respectively. The loss of these particular fragments also helps to eliminate trimeric structures and this is confirmed by the absence of any higher mass ions in the particularly good spectrum of "1,1-diethyl-2,3-diphenylgermirene".

The most probable structures for these materials then appear to be (VII) or (VIII).



(VII)



(VIII)

The mass spectra of the cyclic compounds do not, in themselves, permit a clean distinction to be made between (VII) and (VIII). However, the absence of an ion due to $C_4(C_6H_5)_4^+$ in the phenylated derivatives (*i.e.* R′ = $C_6H_5$) mitigates strongly against structure (VIII). This together with the evidence from bromination reported above leaves no doubt that the germanium compounds must be represented by structure (VII)*.

Other features of the spectra are interesting. For instance one of the preferred fragmentation pathways of (VII) (R = $CH_3$, R′ = $C_6H_5$) seems to proceed as shown on the next page:

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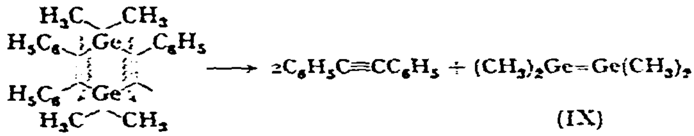
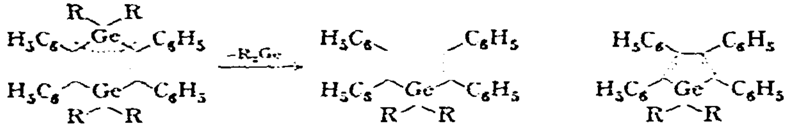
* In a very recent publication Vol'pin *et al.*[30], described an X-ray crystallographic study of "1,1-dichlorogermirene" and conclude also that it has in reality structure (VII) (R = Cl; R′ = H).



(IX)

as evidenced by the intense ion at *m/e* 208, corresponding to (IX). A structure such as this would be expected to have some stability when positively charged[18]. This mode of decomposition is, as expected, also seen in the spectrum (Fig. 2) of the tetraethyl derivative (VII; $R = C_2H_5$; $R' = C_6H_5$) with the corresponding ion of *m/e* 264. The latter compound also shows a fragment at *m/e* 442 resulting from the loss of one molecule of tolane and a similar rupture, accompanied by the loss of a methyl group can be observed for the tetramethyl analog at *m/e* 371.

Another type of cracking that appears to be common to both of these completely alkylated compounds is the extrusion of a dialkylgermanium fragment, *viz.*:



(X) (XI)

However, when $R = CH_3$ the positive ion produced is (X) (*m/e* 460) whereas when $R = C_2H_5$, it is the $GeR_2$ fragment which acquires the positive charge (*m/e* 132), while (X) is the neutral fragment. The possibility that such cracking proceeds to give the closed ring (XI) can be discounted again because of the lack of any $C_4(C_6H_5)_4^+$ fragments in these spectra. The mass spectral cracking patterns of the tetraiodo compounds (Figs. 3 and 4) are similar to one another but differ from those of the tetraalkyl derivatives described above. The spectrum of (VII) ($R = I$; $R' = C_6H_5$)

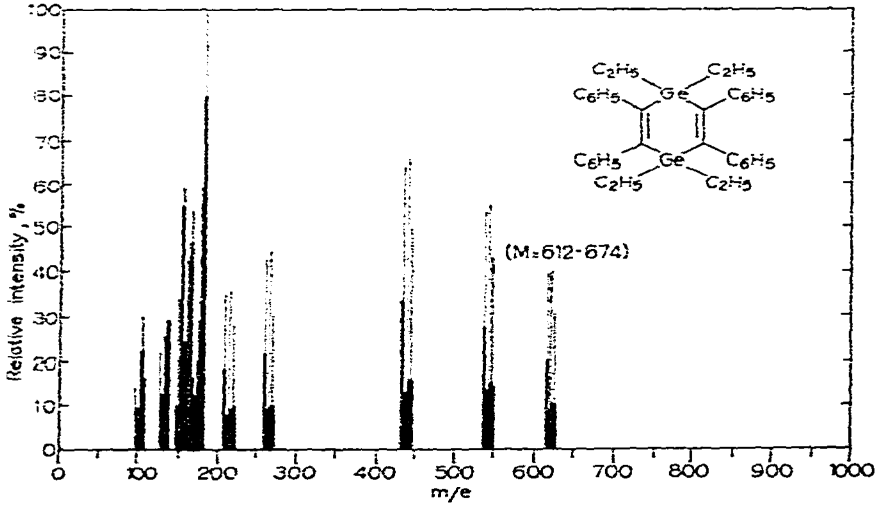


Fig. 2. Mass spectrum of "1,1-diethyl-2,3-diphenylgermirene".

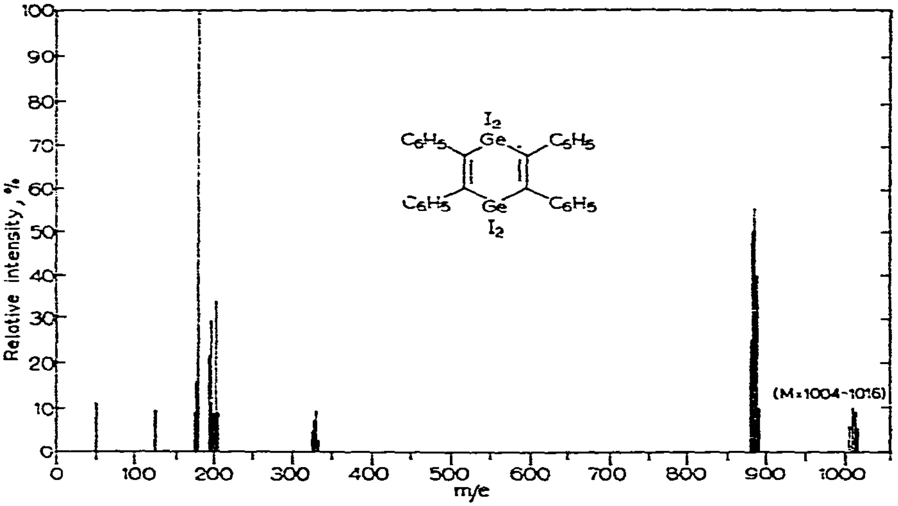


Fig. 3. Mass spectrum of "1,1-diiodo-2,3-diphenylgermirene".

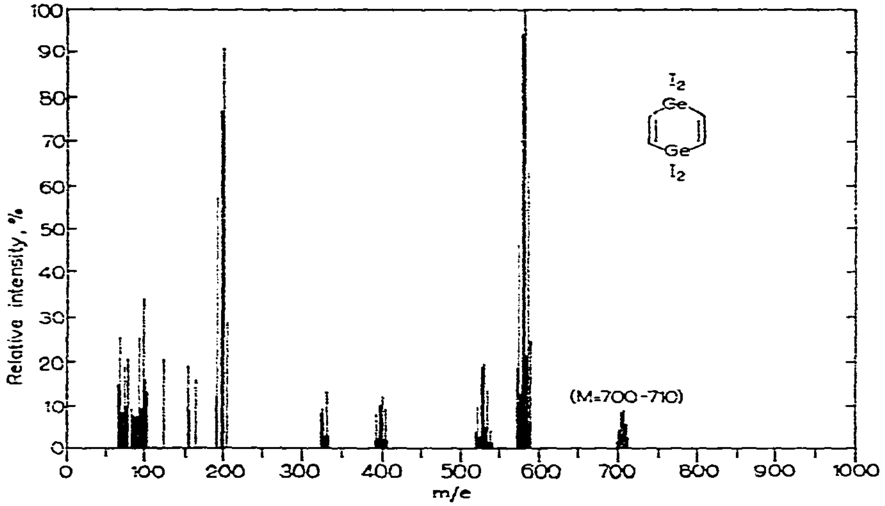


Fig. 4. Mass spectrum of "1,1-diiodogermirene".

is very simple, showing in addition to the molecular ion at *m/e* 1012 only loss of iodine (*M*-127) at *m/e* 885 and peaks for $GeI_2$ (*m/e* 328), GeI (*m/e* 201) and tolane (*m/e* 178). In the spectrum of the simpler heterocycle (VII; R = I; R' = H) similar fragments can be seen, the major peaks representing the molecular ion M (*m/e* 708), M—I (*m/e* 581) and various combinations of Ge with I at *m/e* values of 529 ($Ge_2I_3$), 328 ($GeI_2$) and 201 (GeI).

In conclusion, it should be noted that the lack of symmetrical cleavage of the germanium compounds mitigates strongly against the possible existence of three-membered ring compounds such as (I) or (II) (M = Ge) since one would expect to see them in the mass spectrometer if they had any intrinsic stability.

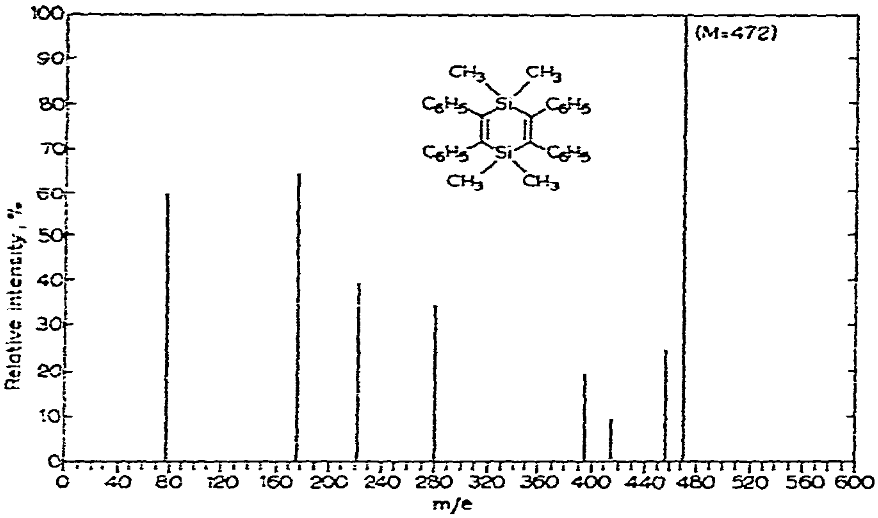
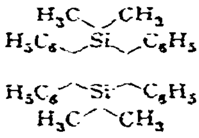
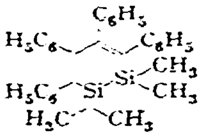


Fig. 5. Mass spectrum of "1,1-dimethyl-2,3-diphenylsilirene".

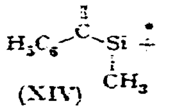
*Mass spectrum of silicon compound*

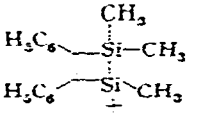
Here again, the presence of an intense molecular ion at *m/e* 472 (Fig. 5) and the lack of any fragment ion of *m/e* 236 is strong evidence against the possibility of the silicon compound having a three-membered ring structure*. The complete absence of a $C_4(C_6H_5)_4^+$ fragment again suggests that the silicon compound must have structure (XII) rather than (XIII).


(XII)


(XIII)

The fragmentation pattern of (XII) is extremely interesting, for here (*cf*. Fig. 1) the extrusion of dimethylsilicon to provide an ion of *m/e* 414 seems to be a minor pathway and collapse across the molecule to give $(CH_3)_2Si\text{-}Si(CH_3)_2$ is unimportant.


(XIV)


(XV)

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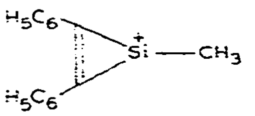
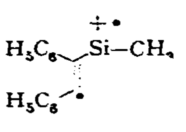
[*] Recently West and Bailey[31] have also conjectured that the silirene, described by the Russian workers, has, in fact, a six-membered ring structure. Their evidence cannot be considered entirely convincing since it consists essentially of only two isopiestic molecular weight determinations. The mass spectral data referred to in their communication was in fact data, from our laboratory relayed to them.

The dominant mode of decomposition appears to be loss of methyl ($M$-15) followed by loss of tolane to give (XIV),—or preferably—(XV) at *m/e* 279.

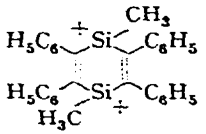
This appears to be followed by the loss of dimethylsilicon to give what may be the 1-methyl-2,3-diphenylsilacyclopropenium ion (XVI) at *m/e* 221, although no attempt was made to observe the metastable ion decompositions which could have provided evidence for or against this specific reaction sequence. It is unlikely that the sequence quoted is the only one which gives rise to the ion fragments observed. Alternate possibilities for the ion at *m/e* 221 are of course, the diradical cation (XVII) and the doubly charged fragment (XVIII). The latter seems improbable in view of the intensity of the peak. However, the likelihood that the fragment is (XVII) cannot be ruled out and a choice between this structure and (XVI) would ultimately depend on knowing something of the energies associated with these two species.



(XVI)



(XVII)



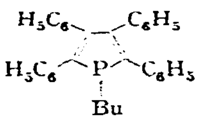
(XVIII)

The conclusions that can be drawn from this spectrum are (*a*) that it seems very improbable that the 1,1-disubstituted silirene can be a very stable entity [otherwise one could expect its formation from (XII) under electron impact] and (*b*) that the silacyclopropenium ion may be a reasonably stable system.

In the light of the mass spectral results the molecular weights of both the germanium and silicon compounds were also determined by osmometry. For (VII) ($R = I$; $R' = C_6H_5$), and (VII) ($R = C_2H_5$; $R' = C_6H_5$) the values obtained were 995 and 621 respectively (required 1009 and 617) whereas for (XII) 474 was found (calcd. 472). These results thus complement the mass spectrometric findings.

A number of attempts were made to extend the scope of this synthesis but most of the research yielded negative results. Hexafluoro-2-butyne could not be induced to react with germanium diiodide at temperatures up to 200°, whereas when phenylacetylene reacted with this iodide, no crystalline product could be isolated from the resultant glass.

The reaction of decaphenylpentastannane[32] with tolane did not proceed below 150° and at higher temperatures led only to tin and tetraphenyltin by disproportionation. Similar results were obtained with dimethyl acetylenedicarboxylate. The reaction of tributylphosphine with tolane in the presence of an iodine catalyst did give a recognizable product. This surprisingly was 1-butyl-2,3-4,5-tetraphenylphosphole (XIX) but the yield was low, being only 3 %. Other reactions which yielded negative results included the reaction of tolane with red phosphorus plus a trace of iodine at 240°, and tolane with triphenylphosphine with the same catalyst at 200°.



(XIX)

Arsenic triiodide or trichloride with tolane at 200° led to only traces of products which were not investigated.

Of the experiments carried out with antimony compounds only that involving triphenylstibine with tolane in boiling diphenyl ether and an iodine catalyst, led to a product. This material analysed well for $C_{20}H_{17}Sb_2$ but so far no structure has been devised to fit these results.

## EXPERIMENTAL

Mass spectra were obtained from a modified 12-107 Bendix time-of-flight mass spectrometer and NMR curves were recorded by a Varian A-60 Spectrometer. Melting points were determined on Fisher-Johns melting point block and are not corrected. All infrared spectra were recorded as Nujol mulls.

The germanium compounds described in this paper were prepared according to the methods of Vol'pin[19]. The latter were found to be completely reproducible only when the germanium iodide used was in the form of nacreous plates. The dimorphic needle-shaped form did not lead to any recognizable products when reacted with tolane.

### *1,1,4,4-Tetraiodo-2,3,5,6-tetraphenyl-1,4-digermin*[19]

This compound had m.p. 302–3° (lit.[19] 301–3°) and exhibited absorption in the ultraviolet spectrum at $\lambda_{max}$ 2600 Å ($\varepsilon$ 2.41 × $10^4$); $\lambda_{max}$ 2850 Å ($\varepsilon$ 2.11 × $10^4$) and at $\lambda_{max}$ 3560 Å ($\varepsilon$ 4.63 × $10^3$). The bonds in its infrared spectrum agreed with those recorded in the literature[19]. (Found: Ge, 14.0; I, 51.0. $C_{28}H_{20}Ge_2I_4$ calcd.: Ge, 14.39; I, 50.29. $C_{28}H_{20}GeI_2$ calcd.: Ge, 10.63; I, 37.17 %.)

### *1,1,4,4-Tetramethyl-2,3,5,6-tetraphenyl-1,4-digermin*

This compound had m.p. 305° (lit.[19] 295°) and exhibited absorption in the ultraviolet spectrum at $\lambda_{max}$ 2270 Å ($\varepsilon$ 4.63 × $10^4$) and $\lambda_{max}$ 2700 Å ($\varepsilon$ 9.5 × $10^3$). (Found: Ge, 26.0. $C_{32}H_{32}Ge_2$ calcd.: Ge, 25.85. $C_{20}H_{26}Ge$ calcd.: Ge, 15.81 %.)

### *The reaction of 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-digermin with bromine*

The germanium compound (0.56 g) in carbon tetrachloride (30 ml) was treated with a solution of bromine (8.2 ml; 0.128 molar in $Br_2$) during 30 minutes, decolorization being complete 10 minutes later. Attempts to isolate a product at this stage were futile, only starting material (0.2 g) and an intractable gummy residue being obtained. These were recombined and rebrominated as above, complete decolorization occurring after 2.5 hours. The solvent was then removed and the residue triturated with a little ether. The crystalline solid (0.1 g) which formed was recrystallized several times from petroleum ether (b.p. 30–60°) to give white crystals, m.p. 134–5°. Mass spectral analysis of this compound showed the molecular weight to be 440. Its infrared spectrum showed significant bands at 6.14, 6.24, 6.30, 10.66, 14.02, 14.31 and 14.46 $\mu$. Absorption in the ultraviolet spectrum occurred at $\lambda_{max}$ 2960 ($\varepsilon$ 2.96 × $10^3$) and $\lambda_{sh}$ 2780 Å ($\varepsilon$ 5.6 × $10^4$) with intense absorption around 2250 Å. Consistent elemental analytical data could not be obtained for this compound and insufficient was available for X-ray absorption or fluorescence analyses.

### *1-Butyl-2,3,4,5-tetraphenylphosphole*

A solution of tributylphosphine (6.0 g) in diphenylacetylene (5.6 g) containing a trace of iodine was heated for 24 hours at 250°. Unreacted tributylphosphine was removed by vacuum distillation and the residue percolated through a column silica gel (150 g). Elution of the column with a 1:1 mixture of petroleum ether (b.p. 30–60°) and benzene (150 ml) led to 0.7 g of crude product. Recrystallization from methylene chloride provided the pure phosphole, m.p. 189–190°. (Found: C, 86.7; H, 7.2; P, 6.4. $C_{32}H_{29}P$ calcd.: C, 86.5; H, 6.6; P, 7.0%.) Its infrared spectrum showed bands at 6.22, 6.34, 6.66, 9.30, 9.70, 10.94, 13.20 and 14.50 $\mu$ and closely resembled that of pentaphenylphosphole[27,28].

### *Reaction of triphenylstibine with diphenylacetylene*

A solution of triphenylstibine (8.8 g) and diphenylacetylene (5.4 g) in diphenyl ether (15 ml) containing a trace of iodine was heated for six hours at 260°. The solution was cooled and a trace of antimony removed by filtration. The bulk of the diphenyl ether was removed by vacuum distillation and the residue taken up in petroleum ether (200 ml; b.p. 30–60°).

On long standing a crystalline precipitate appeared (1.3 g). Recrystallization of a sample from benzene afforded the analytical sample, m.p. 210–211°. (Found: C, 47.4; H, 3.4; Sb, 48.6%.) The infrared spectrum of this material showed bonds at 6.94, 9.35, 9.78, 10.00, 12.80, 13.55, 13.75 and 14.55 $\mu$.

## ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Drs. D. R. Weyenberg and A. E. Bey for a sample of 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilin. They also thank Dr. P. North for the X-ray analyses and Mr. A. A. Carlson for technical assistance.

## SUMMARY

The compounds reported recently by Russian workers as unsaturated three-membered heterocyclic rings containing silicon or germanium are shown to be, in fact, derivatives of the novel ring systems 1,4-disilin and 1,4-digermin.

## REFERENCES

1 R. West, *J. Am. Chem. Soc.*, 76 (1954) 6012.
2 F. S. Kipping, *J. Chem. Soc.*, (1927) 104.
3 G. Fritz and J. Grobe, *Z. Anorg. Allgem. Chem.*, 311 (1961) 325.
4 G. Urry, *Abstracts of 133rd Meeting Am. Chem. Soc.*, San Francisco, April 1958.
5 R. A. Benkeser, R. F. Grossman and G. M. Stanton, *J. Am. Chem. Soc.*, 84 (1962) 4723, 4727.
6 C. Eaborn, *Organosilicon Compounds*, Butterworth, 1960, Footnote p. 113.
7 R. A. Benkeser and G. M. Stanton, *J. Am. Chem. Soc.*, 85 (1963) 834.
8 R. Müller, R. Köhne and H. Beyer, *Chem. Ber.*, 95 (1962) 3030; G. Fritz, W. Kemmerling, G. Sonntag, H. J. Becher, E. A. V. Ebsworth and J. Grobe, *Z. Anorg. Allgem. Chem.*, 321 (1963) 10.
9 See ref. 6, p. 114.
10 R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, 75 (1953) 2421.
11 J. Chatt and A. A. Williams, *J. Chem. Soc.*, (1954) 4403.

12 R. A. Benkeser, C. E. deBoer, R. E. Robinson and D. M. Sauve, *J. Am. Chem. Soc.*, 78 (1956) 682.
13 R. West, R. H. Baney and D. L. Powell, *J. Am. Chem. Soc.*, 82 (1960) 6269.
14 R. West and R. H. Baney, *J. Phys. Chem.*, 64 (1960) 822.
15 W. Gordy, *Discussions Faraday Soc.*, 19 (1955) 14.
16 J. A. Bedford, J. R. Bolton, A. Carrington and R. H. Prince, *Trans. Faraday Soc.*, 59 (1963) 63.
17 D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, (1954) 332; D. P. Craig, *J. Chem. Soc.*, (1959) 997.
18 H. H Jaffé, *J. Phys. Chem.*, 58 (1954) 185.
19 M. E. Vol'pin and D. N. Kursanov, *Izv. Akad. Nauk SSSR*, (1960) 1903; M. E. Vol'pin, Yu. D. Koreshkov and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1961) 1355; M. E. Vol'pin, Yu D. Koreshkov, V. G. Dulova and D. N. Kursanov, *Tetrahedron*, 18 (1962) 107; M. E. Vol'pin and D. N. Kursanov, *Zh. Obshch. Khim.*, 32 (1960) 1455; M. E. Vol'pin, V. G. Dulova and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1963) 727; D. N. Kursanov and M. E. Vol'pin, *Zh. Vses. Khim. Obshchestva im. D.I. Mendeleeva*, 7 (1962) 282.
20 E. Huckel, *Z. Physik*, 70 (1931) 204.
21 R. Breslow, *J. Am. Chem. Soc.*, 79 (1957) 5318; R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, 80 (1958) 5991; R. Breslow, R. Haynie and J. Mirra, *J. Am. Chem. Soc.*, 81 (1959) 247; R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, 82 (1960) 4426; R. Breslow and H. Hover, *J. Am. Chem. Soc.*, 82 (1960) 2672.
22 D. P. Craig, *Theoretical Organic Chemistry*, Butterworth, London, 1959, p. 20.
23 E. Waring, *Trans. Faraday Soc.*, 36 (1940) 1142.
24 L. Spialter, D. C. Priest and C. W. Harris, *J. Am. Chem. Soc.*, 77 (1955) 6227; see also reference 6, p. 122.
25 G. E. Coates, *Organo-Metallic Compounds*, Wiley, New York, 1960, p. 165.
26 R. S. Gohlke, *Uncertified Mass Spectral Data*, The Dow Chemical Company, 1963.
27 F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas and D. S. Lehman, *J. Am. Chem. Soc.*, 82 (1960) 5099.
28 E. H. Braye, W. Hubel and I. Caplier, *J. Am. Chem. Soc.*, 83 (1961) 4406.
29 L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 63 (1941) 1184.
30 M. E. Vol'pin, Yu T. Struchkov, L. J. Vilkov, V. S. Mastryukov, V. G. Dulova and D. N. Kursanov, *Zh. Obshch. Khim.*, 33 (1963) 2067.
31 R. West and R. E. Bailey, *J. Am. Chem. Soc.*, 85 (1963) 2871.
32 W. P. Neumann and K. König, *Angew. Chem., Intern. Ed. Engl.*, 1 (1962) 212.