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STRUCTURE AND PROPERTIES OF UNSATURATED GERMANIUM HETEROCYCLES

M. E. VOL'PIN, V. G. DULOVA, YU. T. STRUCHKOV, N. K. BOKIY AND D. N. KURSANOV
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
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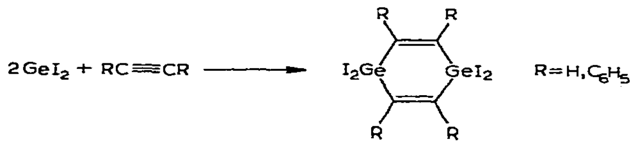
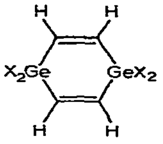
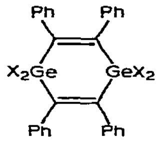
We have previously undertaken a comparison of the properties of divalent germanium and silicon derivatives with those of their carbene electron analogues and found that germanium diiodide is capable of adding to the tertiary carbon–carbon bond[1,2] to form cyclic compounds that were tentatively assigned a three-membered structure. Later, the mass spectrometric investigation of Johnson and Gohlke[3] and our electronographic and X-ray data[4] have shown these compounds to have the structure of unsaturated six-membered heterocycles. The reaction, therefore, of gemanium diiodide with acetylene and tolane may be pictured as follows:



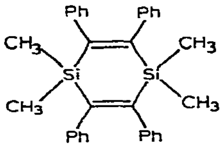
By substituting other groups for iodine it was possible to synthesize the following derivatives of these heterocycles, of general formula I and II



I



II



III

with $X = Cl, Br, OH, CH_3, C_2H_5, C_4H_9, C_6H_5$.

The structure of these compounds and their crystalline geometric molecular parameters were determined by an X-ray study of three substances I ($X = Cl$[4], I and C_6H_5[5]) and of their silicon analogue III, previously described[1,6,7].

All four compounds have the structure of six-membered unsaturated heterocycles. Interatomic distances and bond angles are given in Figs 1, 2 and 3*. In all four cases the molecules occupy symmetry centers so that only a half-molecule is independent crystallographically.

Within experimental accuracy the germanium heterocycles are planar. On

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* The molecules I ($X = C_6H_5$), and III, are projected onto the crystal *ab* plane, the molecule I ($X = I$)—onto the *ac* plane.

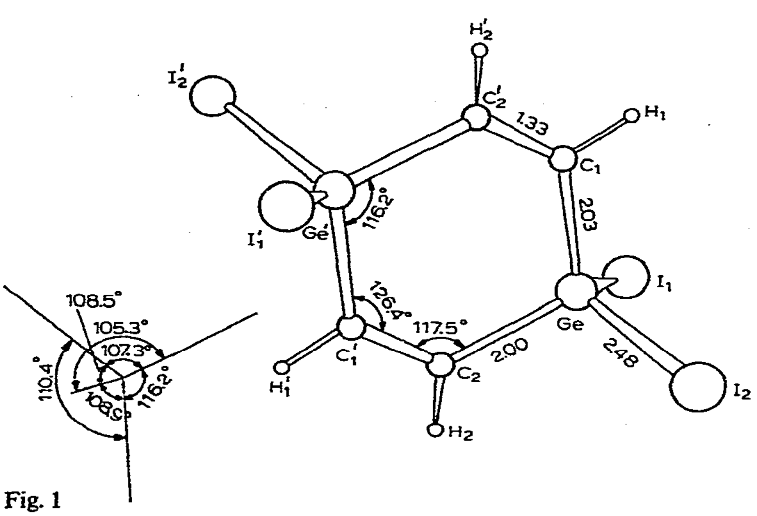

Fig. 1

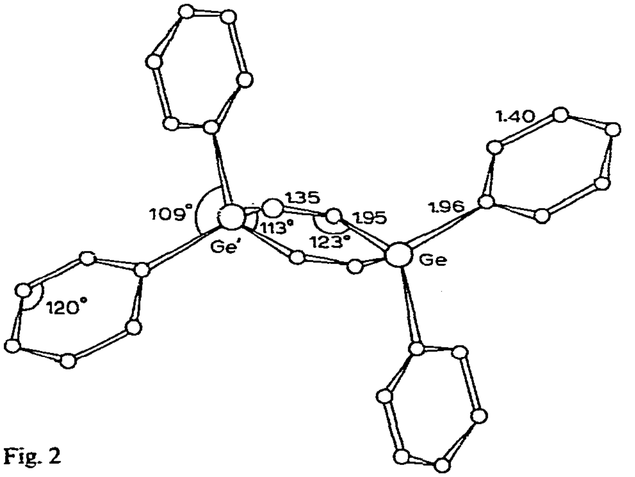

Fig. 2

the other hand there is strong steric hindrance between substituents in the silicon cycle. This overcrowding brings about a distortion of exocyclic bond angles at the atoms C(1) and C(2) (C(5) C(1) C(2) and C(11) C(2) C(1) being increased, SiC(1) C(5) and SiC(2) C(11) diminished) and also leads to displacement of the phenyl rings and of the heterocyclic carbon atoms with them out of the heterocycle mean plane in the opposite sense. This results in a chair-like conformation of the heterocycle. The diplacements are, however, rather small—0.02_4 Å for Si and 0.06_5 Å for C.

The bond distances of the heteroatoms (Si–C, 1.89 and 1.87 Å; Ge–C, 1.98 Å in I with X = Cl and 1.95, 1.96 Å with $X = C_6H_5$; Ge–Cl, 2.15 Å; Ge–I, 2.48 Å*) are in agreement with the mean values for single bonds found previously in other compounds, such as: Si–C, 1.88–1.93 Å; Ge–C, 1.93–1.98 Å; Ge–Cl, 2.08–2.15 Å; Ge–I,

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* The values given in the rest of this paper of all crystallographically independent, chemically equivalent molecular parameters are averages.

2.47–2.51 Å. It should be noted that the exo- and intracyclic heteroatom-carbon bonds are of equal length. The C=C distance is 1.35 Å in I (X = Cl and C_6H_5), and 1.30 Å in III, *e.g.*, corresponding to the normal double-bond length. Silicon and germanium atoms in the compounds investigated have the tetrahedral valence configuration. However, the sum of the normal bond angles of heteroatoms (109.5°) and of carbon atoms (120°) in the cycle is only 699° instead of 720° for a planar hexagon. Therefore, the tendency to planarity results in distortion of angles C–C–Ge(Si) (123° in I with X = C_6H_5; 125° in III) and also of angles C–Ge–C in the germanium compound (113° in I with X = C_6H_5). For I (X = I), the angle distortion follows a similar pattern, C–C–Ge angles being 121.5°; C–Ge–C angles – 116°*. The electron diffraction study of the chloride of I (X = Cl) in the vapour phase by Vilkov and Mastryukov[8] is in good agreement with corresponding X-ray evidence. The results obtained by the same authors on the methyl derivative of I (X = CH_3) remain, however, unaccounted for. The authors believe them to be characteristic of a three-membered cycle only[9,10]. On the other hand, mass-spectral evidence, molecular weight determination in the vapour phase[11] as well as the chemical properties given below, are all in agreement with a six-membered structure. The same is true of the measurement of the spin–spin coupling constant of ^{13}C–H of the vinyl and methyl groups for I (X = CH_3). Both values found, 167 and 128 c/s, correspond to the usual values for sp^2 hybridisation in the former, and for sp^3 in the latter case.

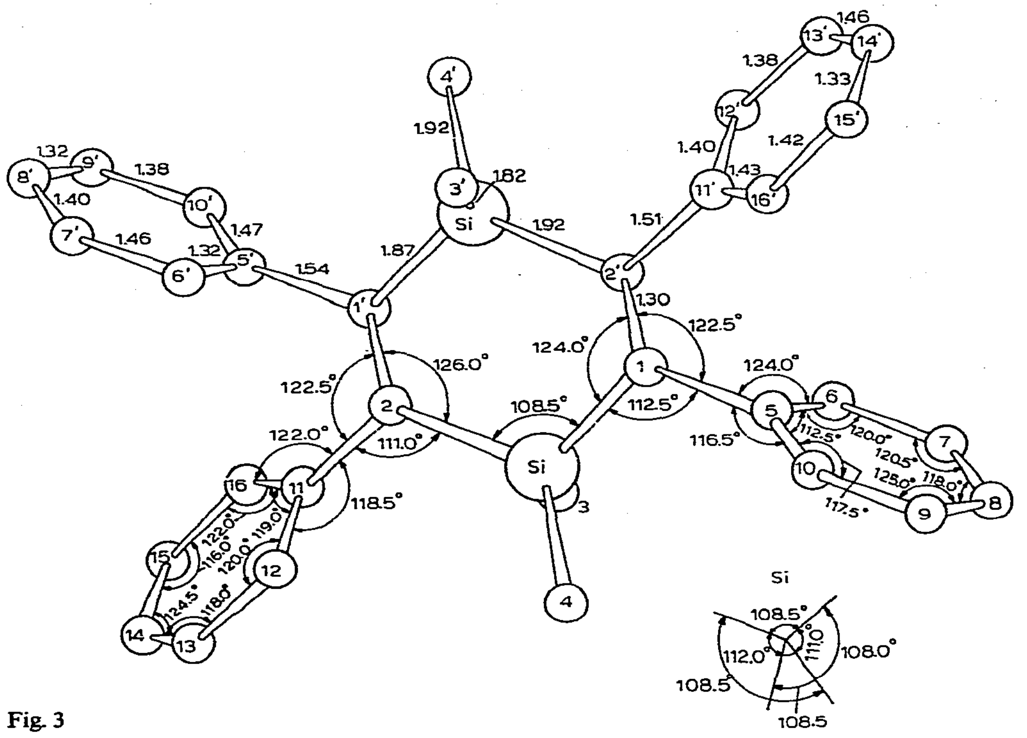

Fig. 3

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* These values are approximate due to the presence of iodine heavy atom and decomposition of crystals during X-ray exposure.

In addition to the structural investigation, we have studied these compounds by NMR and optical spectroscopy (infrared, Raman, and ultraviolet spectra). Chemical shifts of protons at the double bond in the NMR spectra for compounds I ($X=CH_3$, I, and Cl) were 6.95, 7.02, and 7.32 ppm, respectively*, *i.e.*, they are in a lower field than in the case of the open-chain compounds $(CH_3)_3GeCH{=}CHGe(CH_3)_3$ (IV), and $Cl_3GeCH{=}CHGeCl_3$ (V), the corresponding values of which are 6.1 and 6.95 ppm[12]. A comparison of the optical spectra of the cyclic compounds and those of the similar compounds, IV and V, shows them to have a similar vibration frequency of the double bond in the Raman spectra; for the methyl derivative of I ($X=CH_3$) it is 1557 cm^{-1} [13], for the chloride of I ($X=Cl$) it is 1550 cm^{-1} [14] and for IV and V, 1560 and 1550 cm^{-1}, respectively. The absorption band intensity for I ($X=CH_3$) of 110 units in the cyclohexane scale is, however, four times that of IV, the latter being 25 units[15]. The absorption maximum of I ($X=CH_3$) in the UV spectrum (206 $m\mu$[13]) undergoes a bathochromic shift compared to IV (195 $m\mu$[16]).

The frequency of the intensive polarised band in the Raman spectrum of I ($X=CH_3$) assigned to symmetric pulsation vibration of Ge–C bonds is very small (535 cm^{-1} [13]) in comparison with similar frequencies of other compounds (*e.g.*, 572 cm^{-1} for $(CH_3)_4Ge$).

The calculation of frequencies and modes of normal vibrations for the six-membered model of cycle I ($X = Cl$) due to Galpern and Mayanz[14] proved to be in good agreement with experimental data.

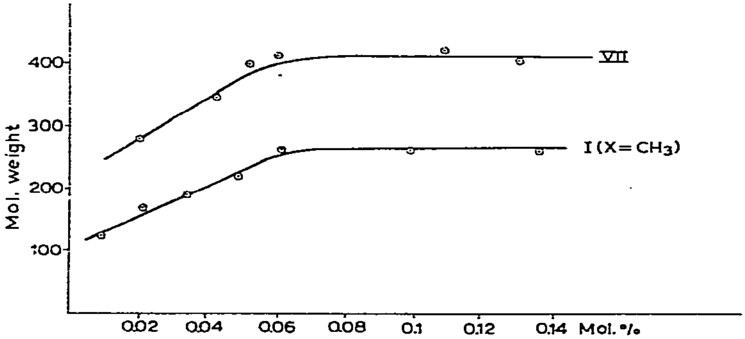

Fig. 4

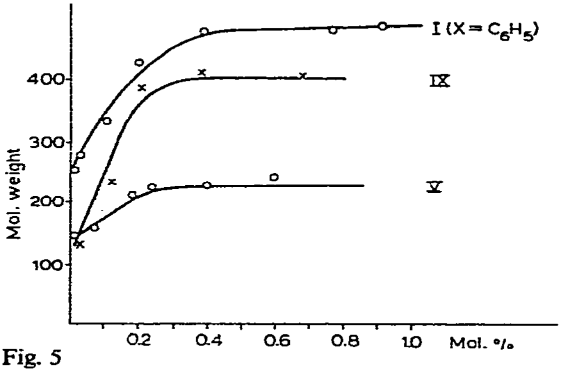

Fig. 5

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* The NMR spectra were obtained in CCl_4 solution on a Hitachi-Perkin-Elmer H-60 employing δ-scale.

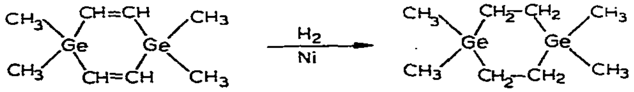
In our previous cryscopic molecular weight determinations of compounds I ($X = CH_3$), II ($X = CH_3$) and III in benzene and camphor[1] we have observed an unusual dependence of the molecular weight on concentration in the conventionally used concentration range (0.1–1 wt.%). At low concentrations, the molecular weight was half the true molecular weight. As the concentration was increased the normal value was reached only at 1–2 wt.%[*].

In order to find out to what extent the cryoscopic approach to this type of compounds could be applied we have determined the molecular weight of five compounds in benzene over a wide range of concentrations (I ($X = CH_3$), I ($X = C_6H_5$), VI, VII, X) and of three compounds in camphor (I ($X = CH_3$), II ($X = CH_3$), VI) see Figs. 4 and 5.

In all cases studied, the concentration limit was found to be between 1 and 2 wt.%. Above this limit, the molecular weight did not change and corresponded to the value calculated for structure I; below this limit the value determined depended on the concentration. Such an anomaly is not only characteristic of germanium and silicon heterocycles. Thus, in the cryoscopic molecular weight determination of diphenyl, dibenzyl, dinaphthyl and tolane (in benzene) the values measured at concentrations below 1% are dependent on concentration, the minimum value being 50% of the true one. Molecular weight determinations of three heterocycles, I ($R = CH_3$ and C_6H_5) and X, by isothermal distillation gave normal values corresponding to structure I.

The chemical behaviour of the germanium heterocycles was studied by hydrogenation, bromination, hydroxylation (Prevost reaction) and by the Diels-Alder reaction.

Hydrogenation of I ($X = CH_3$) on Raney nickel leads to absorption of 2 moles of hydrogen.



VI

The compound isolated was shown by NMR spectrum to have two singlets at $\delta = 0.1$ ppm and 1.2 ppm, characteristic of the chemical shifts of the methyl and methylene group, respectively. The protons are in a ~3 to 2 ratio. The infrared spectrum of this compound closely resembles that of a similar saturated six-membered silicon heterocycle[17].

In the reaction of the methyl derivative of I ($X = CH_3$) with bromine, products of bromine addition either to one (VII) or both double bonds (VIII) were isolated.

The NMR spectrum of the dibromide (VII) contains three types of protons at $\delta = 0.45$ ppm (CH_3 group) 3.97 ppm (CHBr group), and 7.0 ppm (=CH), the integral intensity ratio being 1 : 1 : 6.5.

The spectrum of the tetrabromide (VIII) contains only two singlets at $\delta = 0.7$ and 4.15 ppm and the integral intensity ratio is 2.8 : 1, respectively. In the infrared

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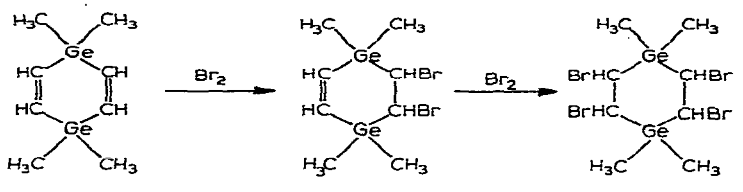
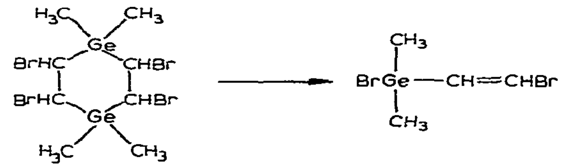
[*] This anomaly has led us previously to an erroneous conclusion as to the true molecular weight of these compounds.


VII VIII

spectra there is no absorption band in the region of double-bond vibrations.

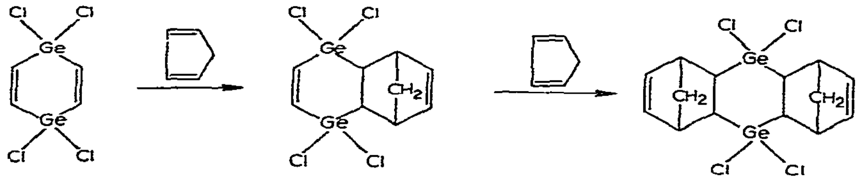
Compounds VII and VIII readily undergo the reaction of β-elimination on heating (as with other compounds having halogen in the β-position to the heteroatom) to form vinyl compounds according to the following scheme:


(IX)

As a result of the formation of IX, the infrared spectrum reveals two characteristic intensive bands assigned to the vibration of the organogermanium compound, *i.e.*, that of the double band at 1510 cm^{-1}, and of the vinyl C–H bond at 2990 cm^{-1}. The NMR spectrum shows peaks corresponding to protons at the double bond at $\delta = 7.08$ and 6.56 ppm with the proton ratio ~ 1 to 1, and to the methyl-group protons at 0.92 ppm.

β-Elimination takes place also by the action of aqueous and alcoholic solutions of $AgNO_3$ and $Hg(NO_3)_2$ on VII and VIII. In either case, half the available bromine can be titrated, showing that bromine is bound to germanium.

Three compounds I ($X = CH_3$, C_6H_5, and Cl) were investigated to exemplify the ability of multiple bonds to undergo the Diels–Alder reaction. Of these, only the chloride proved to be a good dienophile resulting in adducts with cyclopentadiene. Just as with benzoquinone, cyclopentadiene addition to chloride I ($X = Cl$) proceeds stepwise and, depending on the amount of cyclopentadiene, it is possible to isolate either the monoadduct (X) or the diadduct (XI). Neither the methyl nor the phenyl derivative I ($X = CH_3$, C_6H_5) give adducts, even on prolonged heating up to 160°.


X XI

Similarly to 1,1,4,4-tetramethylcyclohexadiene-2,5[18], the methyl derivative I ($X = CH_3$) undergoes hydroxylation (Prevost reaction). Interaction of this derivative (1 mole) with the same amount of a complex of silver benzoate and iodine gives rise to an adduct with one double bond.

Our study of the addition products of germanium diiodide to the triple bond has shown that with germanium compounds this process ultimately is different from that of the carbenes. Unlike the dihalocarbenes which give the cyclopropene compound by a triple bond reaction[19], divalent Ge and Si give six-membered heterocycles having a structure similar to 1,4-cyclohexadiene. This does not exclude the possibility that at the initial reaction stage, GeX_2 and $(CH_3)_2Si$ are added to acetylene and tolane to form three-membered heterocycles that can be further dimerised, as is the case on the heating and UV irradiation of cyclopropene[20,21]. Gilman *et al.*[22] suggest the intermediate formation of a three-membered unsaturated silicon heterocycle with subsequent dimerisation. Skell and Goldstein[23] believe that the synthesis of vinylsilane from $C_2H_5(CH_3)Si(CH_2Cl)_2$ proceeds *via* an unstable, saturated three-membered cycle containing a silicon atom.

The reaction of germanium diiodide with acetylene enables hitherto unknown unsaturated heterocycles to be prepared. These are of interest as germanium analogues of cyclohexadiene-1,4 with alternating double bonds and heteroatoms with available *d*-orbitals. By analogy with phosphonitryl halides there is the possibility of p_π–d_π conjugation. Many data obtained (bond length, angles, chemical properties) point to an absence of a marked p_π–d_π interaction in the class of compounds studied. However, a comparison of the spectral characteristics of I ($X = CH_3$) with those for the linear compound, $(CH_3)_3GeCH{=}CHGe(CH_3)_3$, the double bond of which is also between two heteroatoms, shows that the cyclic system is characterised by additional effects manifested by a marked increase in intensity of the band corresponding to the multiple bond vibration in the Raman spectrum of I ($X = CH_3$), the bathochromic shift of maximum absorption corresponding to the π–π-transfer in the UV spectrum, lowering of the frequency of the symmetric pulsation vibration of the Ge–C bond, and by the chemical shift in the NMR spectrum to the field of conjugated systems.

EXPERIMENTAL

Compounds I ($X = I$ and CH_3) were obtained by a procedure described elsewhere[2].

1,1,4,4-*Tetraphenyl*-1,4-*digermanacyclohexadiene*-2,5

This compound was prepared similarly to I ($X = CH_3$)[1] from the iodide I ($X = I$) and phenylmagnesium bromide; m.p. 149–150° (from benzene). (Found: C, 65.57, 65.55; H, 4.80, 4.80; Ge, 28.26, 28.56%. Molecular weight 475, determined by cryoscopy in benzene, see Fig. 5; 499 by isothermal distillation. $C_{28}H_{24}Ge_2$ calcd.: C, 66.50; H, 4.75; Ge, 28.75%. Molecular weight 505.)

Tetramethyldigermanacyclohexane, (*V*)

1.3 g (5 mmole) of I ($X = CH_3$) were dissolved in 15 ml of alcohol. On mixing with the Raney nickel the solution absorbed 246 ml of hydrogen to yield, after removal of alcohol, 1.1 g of a substance b.p. 79–80° at 14 mm, n_D^{20} 1.4861. (Found: C, 36.74, 36.80; H, 7.71, 7.90; Ge 54.85, 54.70%. Molecular weight 281, isothermal distillation in CH_2Cl_2. $C_8H_{20}Ge_2$ calcd.: C, 36.77; H, 7.71; Ge, 55.58%. Molecular weight, 261.2.)

2,3-Dibromo-1,4-digermanacyclohexene-5, (VII)

To a cooled solution of 0.4455 (1.7 mmole) of I ($X = CH_3$) in CCl_4 (20 ml) was added dropwise, 7.1 ml (1.7 mmole) of 0.487 *N* bromine solution in CCl_4. The mixture was decolorised after 30 min at −5°, the solvent partly evaporated *in vacuo* at low temperatures, and 0.52 g (70.6%) of precipitate filtered off and dried *in vacuo*. After purification of the compound by dissolving it in CCl_4 and evaporating part of the solvent, the melting point was found to be 72–74°. (Found: C, 23.02, 23.29; H, 3.82, 3.84; Ge, 34.04, 34.77; Br, 38,46, 38.14; Br′ estimated by mercurometric titration, 20.05, 20.42%. Molecular weight 410, determined cryoscopically in benzene, see Fig. 4. $C_8H_{16}Br_2Ge_2$ calcd.: C, 23.03; H, 3.84; Ge, 34.80; Br, 38.30; Br′ 19.15%. Molecular weight, 417.)

Tetrabromodigermanacyclohexane, (VIII)

This compound was prepared by the above procedure from 0.2918 g (1.13 mmole) of I ($X = CH_3$) and 9.3 ml (2.26 mmole) of a 0.487 *N* solution of bromine; m.p. 145–149°. The same compound was also obtained from 0.3202 g (0.77 mmole) of VII and 3.1 ml (0.77 mmole) of a 0.487 *N* solution of bromine. (Found: C, 16.85, 17.02; H, 2,86, 2.95; Ge, 24.83, 24.69; Br, 55.32, 55.14; Br′ mercurometric and argentometric titration 29.02, 28.82%. Molecular weight, 542 determined cryoscopically in benzene. $C_8H_{16}Br_4Ge_2$ calcd.: C, 16.64; H, 2.79; Ge, 25.16; Br, 55.39; Br′, 27.69%. Molecular weight, 576.8.)

Adduct IX

To a boiling benzene solution of 1.02 g (1.5 mmole) of chloride I ($X = Cl$), was slowly added dropwise, 0.1 g (0.75 mmole) of cyclopentadiene dissolved in benzene. The mixture was boiled for 15 min and cooled, when a white crystalline substance sparingly soluble in cold benzene was obtained. Recrystallisation from benzene gave 0.82 g (73%) of the compound, m.p. 175–177°. (Found: C, 26.79, 27.02; H, 2.39, 2.34; Ge, 35.27, 35.66; Cl, 34.50, 34.51%. Molecular weight, 413.9, determined cryoscopically in benzene, see Fig. 5. $C_9H_{10}Ge_2Cl_2$ calcd.: C, 26.67; H, 2.49; Ge, 35.83; Cl, 35.00. Molecular weight, 405.2.)

Adduct X

This adduct was prepared from I ($X = CH_3$) in excess cyclopentadiene by the above procedure, m.p. 264–265° (from benzene). The same compound was obtained also by the reaction of the monoadduct IX with cyclopentadiene. (Found: C, 35.51, 35.40; H, 3.56, 3.52; Ge, 29.27, 31.20; Cl, 29.65, 30.96%. Molecular weight 456, isothermal distillation in CH_2Cl_2. $C_{14}H_{16}Ge_2Cl_2$ calcd.: C, 35.13; H, 3.34; Ge, 31.86; Cl, 29.65%. Molecular weight, 478.)

Prevost product

A solution of iodine (0.65 g) in absolute benzene (10 ml) was added with stirring to silver benzoate (0.6 g) and 0.65 g of I ($X = CH_3$) was then added quickly to the mixture. The mixture was stirred for 4 h, washed with water and a 10% solution of sodium carbonate and bisulfite, dried over Na_2SO_4 and the benzene removed *in vacuo* at a low temperature, to yield finally a syrupy mass. (Found: C, 35.62; H, 4.56; Ge, 29.48; I, 23.86%. $C_{15}H_{25}O_2Ge_2I$ calcd.: C, 35.64; H, 4.19; Ge, 28.72; I, 25.11%.)

X-ray analysis

Crystal data of the compounds investigated are given in Table 1.

The structure of I (X = Cl) has been determined previously in projections[4]; those of I (X = I and C_6H_5) and III—in three dimensions by the Patterson and Fourier methods. X-ray exposures for I (X = C_6H_5) and III were taken by the Weissenberg method on the copper radiation to give about 1300 and 1100 independent non-zero reflections, respectively. For I (X = I) retigraph photographs taken with molybdenum radiation contain about 350 reflections.

The structure of I (X = C_6H_5) was refined by least squares with subsidiary conditions[24], the final value of the reliability factor *R*, being 13.6%. The structures of III and I (X = I) were refined by least squares with individual isotropic temperature factors up to R-values of 16.1 and 15.3%, respectively.

TABLE 1

	a(*Å*)	*b*(*Å*)	*c*(*Å*)	*α*°	*β*°	*γ*°	*v*(*Å*)	*d, found (calcd.)*	*N*	*Space gr.*
$Cl_2Ge(CH)_4GeCl_2$	6.2_6	7.4_4	12.1_6	—	$107._5$	—	540	2.13 (2.10)	2	$P2_1/C$
$I_2Ge(CH)_4GeI_2$	8.5_6	7.3_4	10.8_9	—	$92._5$	—	679	— (3.45)	2	$P2_1/C$
$(C_6H_5)_2Ge(CH)_4Ge(C_6H_5)_2$	11.5_4	10.9_3	10.2_4	$97._5$	$106._0$	$99._5$	1217	1.36 (1.38)	2	P_1
$(CH_3)_2Si(CC_6H_5)_4Si(CH_3)_2$	12.6_1	9.2_4	6.3_2	$110._{10}$	$95._5$	$92._0$	686	1.14 (1.14)	1	P_1

ACKNOWLEDGEMENTS

The authors thank L. A. LEITES and P. V. PETROVSKY for work on the infrared, Raman, and NMR spectra and their interest in the discussion of the data obtained.

SUMMARY

The structure of the unsaturated six-membered germanium heterocycles is studied by X-ray and other physical methods. The chemical reactions of these compounds (hydrogenation, bromination, Diels–Alder reactions) are investigated.

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