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Review

CYCLOALKANES CONTAINING HETEROCYCLIC GERMANIUM, TIN AND LEAD

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I. Introduction

Cyclic systems containing one or more Group IV metals are known and have been documented in various general works [1–8]. These Group IV metal cyclic compounds include: (i) systems having only Group IV metal atoms in the ring [9], (ii) those having Group IV metals and other elements such as oxygen, sulfur and nitrogen (with [10] or without [11] carbon), and (iii) those having one or two Group IV metals in a ring with the other ring members being carbon atoms. The scope of this review is limited to the chemistry of germanium, tin and lead cyclic compounds of type (iii), including the corresponding spirocyclic compounds. The literature is surveyed up till June 1972.

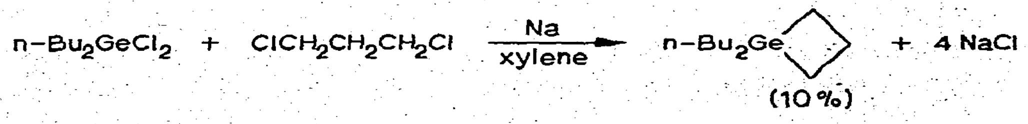
II. Cycloalkanes containing heterocyclic germanium

A. Germacyclobutanes

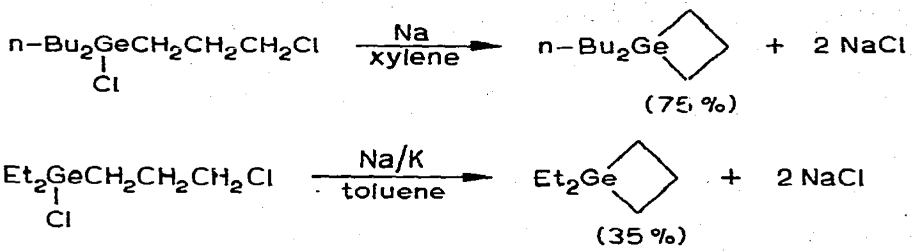
The earlier claims by Vol'pin and coworkers regarding the isolation of germacyclopropene [12–15] have been ruled out, firmly establishing the compound to be a cyclohexadienic derivative containing two germanium atoms in the ring [16–19]. The smallest ring system known contains four members.

1. Preparation

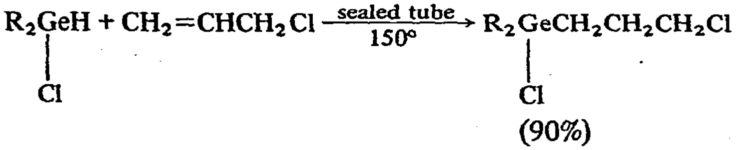
Mazerolles, Lesbre and Dubac reported the first synthesis of germacyclobutanes [20, 21] by a Wurtz type condensation of dialkyldichlorogermanes and 1,3-dichloropropane in the presence of sodium:



The germacyclobutanes were isolated by vapour phase chromatography from the large quantities of polymeric material formed in the reaction (even under high dilution). The compounds [20, 21] were obtained in much better yields by the cyclization of γ-chloropropylchlorogermanes using sodium or a sodium–potassium alloy (23% Na, 77% K) in boiling toluene or xylene:

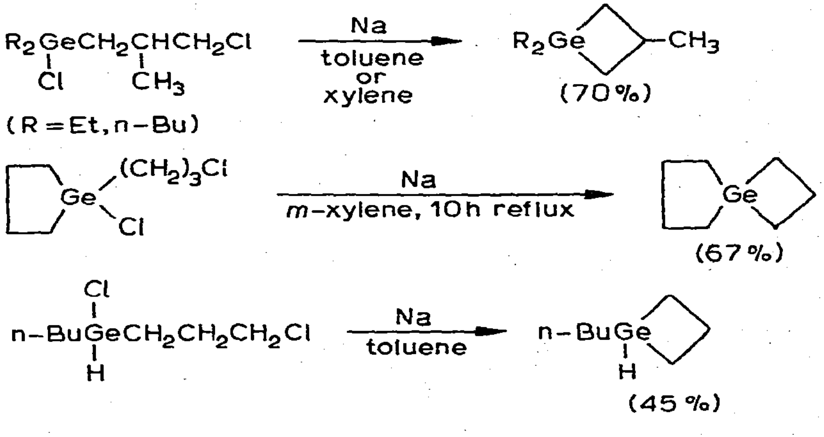


The γ-chloropropylchlorogermanes [22] required for the cyclization could be obtained in high yields via the reaction:

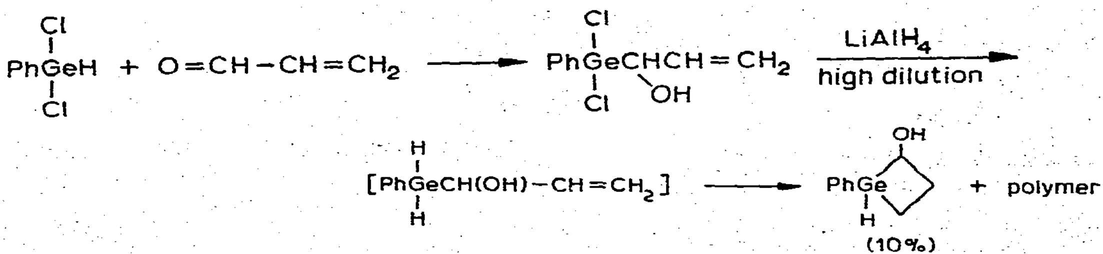


$$R_2\underset{\displaystyle Cl}{Ge}H + CH_2{=}CHCH_2Cl \xrightarrow[150^\circ]{\text{sealed tube}} R_2\underset{\displaystyle \underset{(90\%)}{Cl}}{Ge}CH_2CH_2CH_2Cl$$

The method also permits different substitution patterns [21, 23] in the ring or on germanium:



A more recent synthetic route to germacyclobutanes [24] involves the spontaneous ring closure of 1-germylallyl alcohols:



The hydrogermacyclobutanes [23] undergo a variety of reactions with ring retention (Chart 1) and provide synthetic routes to a number of other germacyclobutanes.

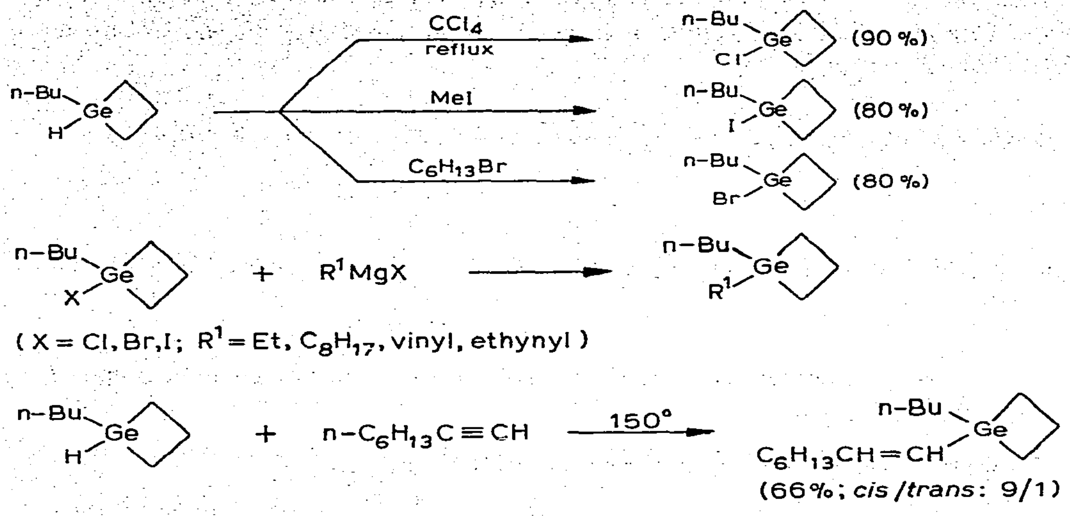

(X = Cl, Br, I; R^1 = Et, C_8H_{17}, vinyl, ethynyl)

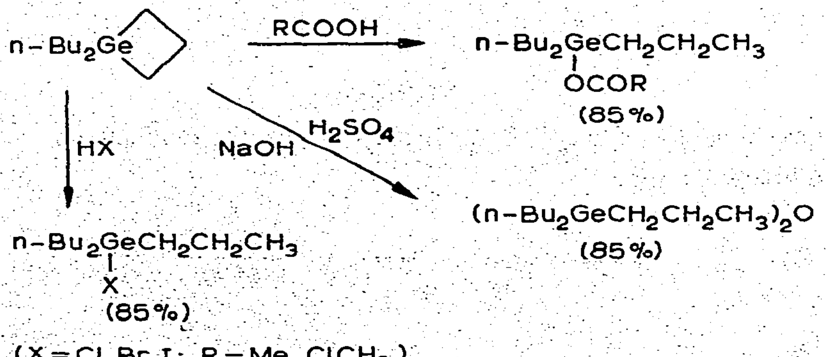
Chart 1. Synthesis of some germacyclobutane derivatives.

2. *Properties and reactions*

The germacyclobutanes so far known are colourless liquids with boiling points higher than those of the linear derivatives containing the same number of carbon atoms, and display notable exhaltations of molecular refraction (ΔMR_D= +0.53 to 0.60) [20, 21] characteristic of small cyclic systems.

The polarizability of the intracyclic germanium—carbon bonds and the ring strain induce high chemical reactivity and both electrophilic and nucleophilic reagents have been shown to cleave the ring. Electrophiles cleave the ring rapidly and quantitatively. Thus halogens react rapidly and exothermically to cleave one intracyclic germanium—carbon bond [21] (e.g. Chart 2).

The acid-catalyzed electrophilic ring opening of germacyclobutanes [20, 21] occurs readily in high yields:


(X = Cl, Br, I; R = Me, $ClCH_2$)

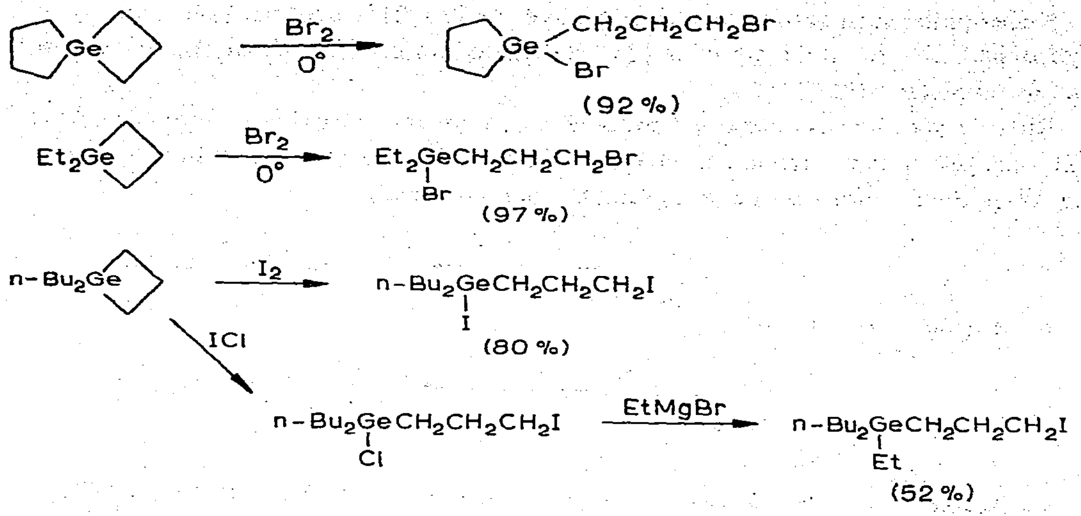


Chart 2. Ring-opening reactions of germacyclobutanes.

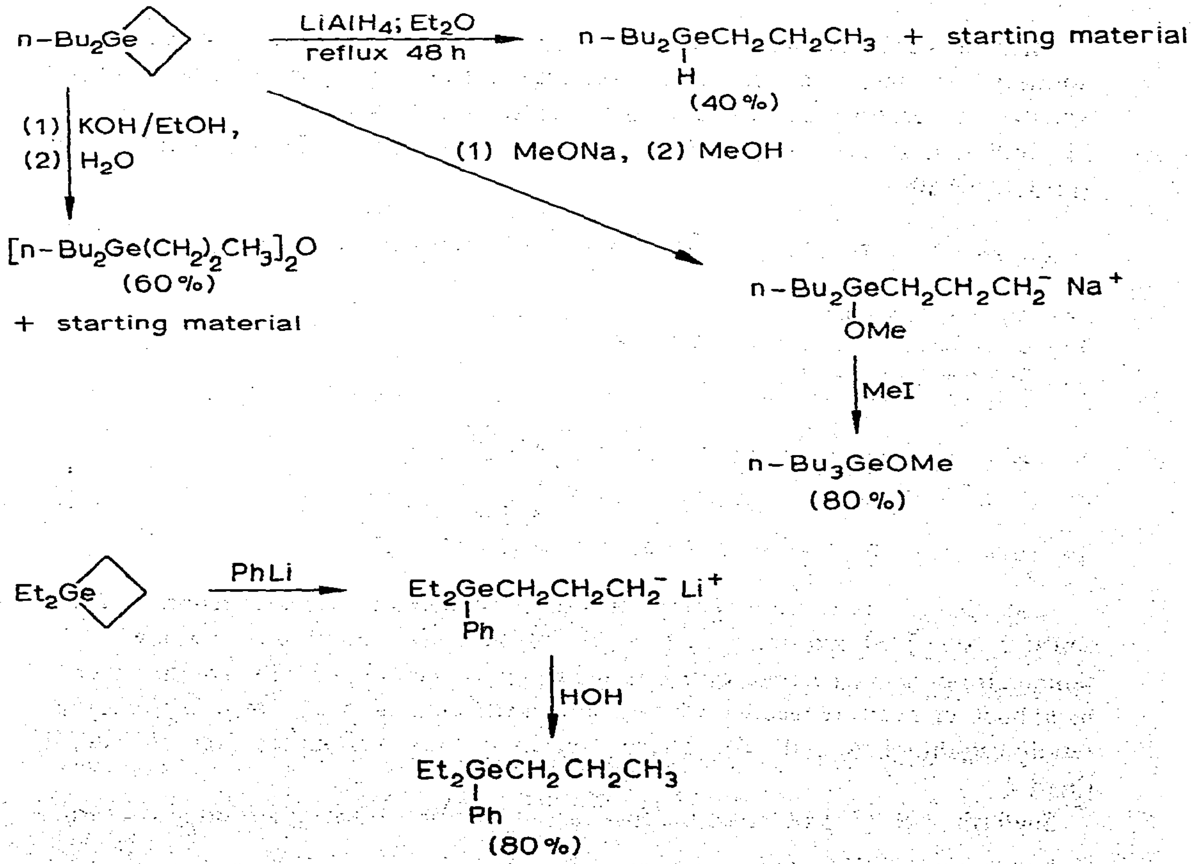
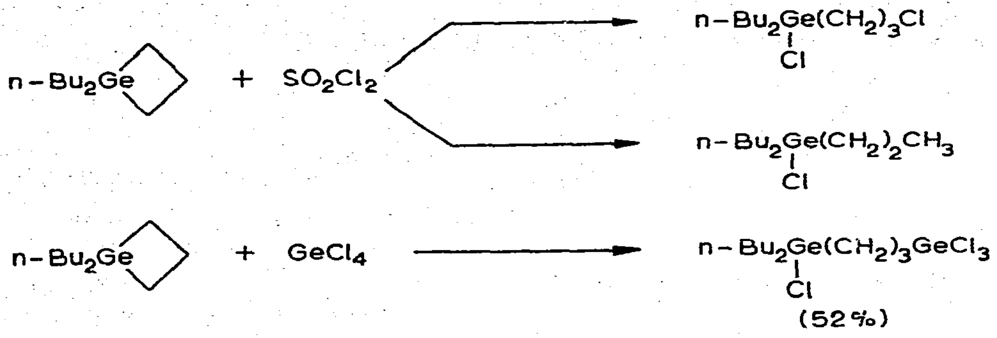


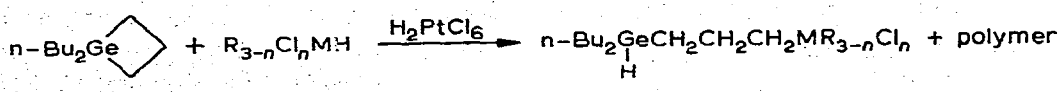
Chart 3. Some reactions of germacyclobutanes.

Nucleophiles such as lithium aluminium hydride [20, 21], alcoholic potassium hydroxide [21], sodium methoxide [23] and phenyllithium [23] cleave the ring slowly and incompletely (see Chart 3).

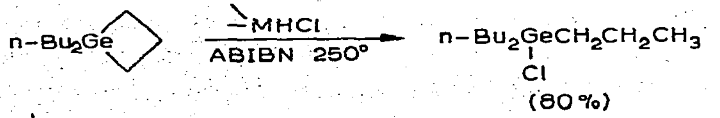
Ring cleavage has also been accomplished by compounds containing a mobile halogen [21] e.g. germanium tetrachloride and sulfuryl chloride. The latter reacts in two different ways (see the reactions with chlorine and hydrochloric acid):



Mazerolles et al. [25–27] reported two different types of ring-opening reactions of germacyclobutanes with organosilicon and organogermanium hydrides depending upon whether the reactions are carried out in the presence of (i) a catalyst [25, 27] e.g. chloroplatinic acid (H_2PtCl_6) or (ii) a free radical initiator [26, 27] e.g. azobis(isobutyronitrile) (ABIBN):



$M = Ge$; $n = 0$; $R = Et$
$M = Si$; $n = 0$; $R_3 = Et_3$, Bu_2Me, Ph_2Me
$M = Si$; $n = 1,2$; $R = Me, Bu$



($MHCl = Bu_2SiHCl$, $MeSiHCl_2$, Et_2GeHCl, Bu_2GeHCl, Cl_3SiH)

A number of insertion reactions leading to ring expansion have been reported. Thus sulfur dioxide [28] and sulfur trioxide [29, 30] have been found to react at low temperatures yielding germaoxathianes and germasultones respectively. On the other hand high temperature reaction with sulfur and selenium has been shown to give germatetrahydro-thiophene and -selenophene respectively [31]. Various reactions are listed in Chart 4.

Seyferth et al. [32] observed the first case of dichlorocarbene insertion into a carbon–

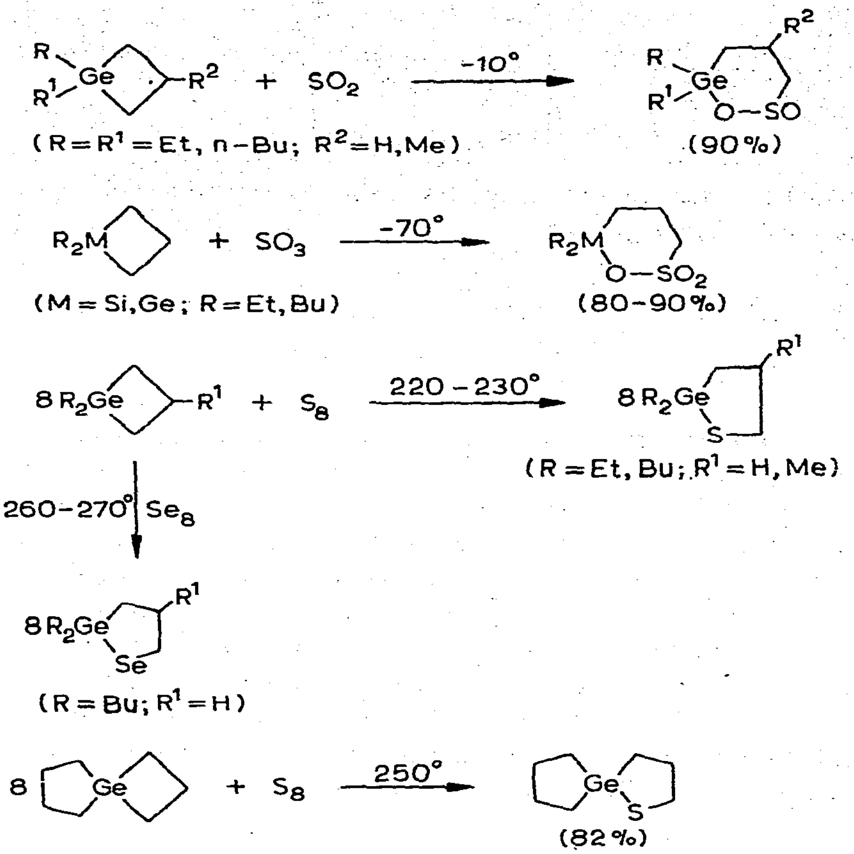
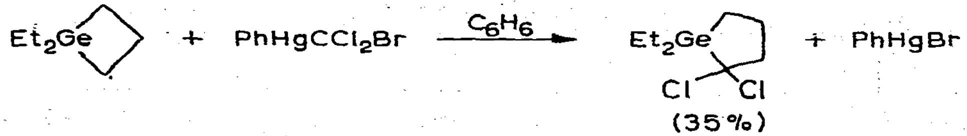


Chart 4. Ring-expansion reactions of germacyclobutanes.

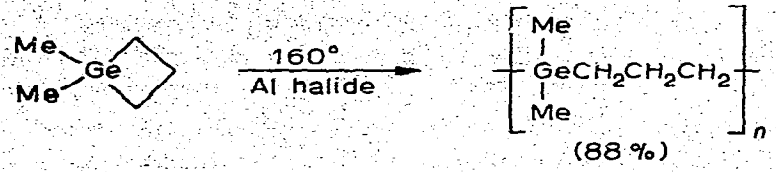
germanium bond when 1,1-diethyl-1-germacyclobutane reacted with phenyl(bromodichloromethyl)mercury in slight excess in benzene solution at reflux:



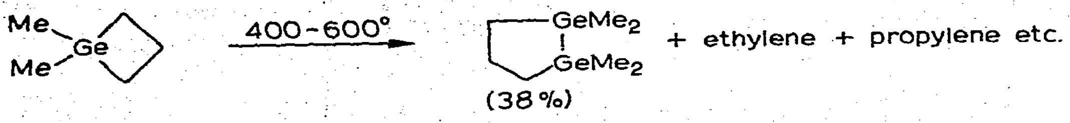
The hydrogermacyclobutanes are more reactive than aliphatic or five- and six-membered ring hydrogermanes. They can be polymerized even without any catalyst, undergo substitution reactions with halogenated derivatives and add to olefins and alkynes without any catalyst [23] (Chart 5).

Unlike germacyclopentane and germacyclohexane derivatives, germacyclobutanes reduce cold alcoholic solutions of silver nitrate and hot solutions of mercuric chloride to the metal [20].

Catalytic polymerization of 1,1-dimethyl-1-germacyclobutane [33] has been shown to yield a high-molecular weight polymer with germanium in the main chain:



Pyrolysis of 1,1-dimethyl-1-germacyclobutane [34] gave a mixture of products (detected by gas chromatography and infrared spectra):



Although more comparative rate studies are needed of the reactivity of germa- and sila-cyclobutanes some tentative conclusions can be drawn from the data already available: (a) Germacyclobutanes seem to be less reactive than the corresponding silacyclobutanes towards nucleophiles; (b) Electrophilic reactions of germacyclobutanes occur more readily than of the silacyclobutanes; (c) Germacyclobutanes like silacyclobutanes, exhibit reducing properties and can be polymerized in the presence of a catalyst or at high temperatures; (d) Hydro-germacyclobutanes as well as -silacyclobutanes are more reactive than the corresponding aliphatic or five- and six-membered ring hydro-germanes or -silanes; (e) The thermal decomposition (400–600°C) of 1,1-dimethyl-1-germacyclobutane differs significantly from that of the silicon analogue in that while the former gives a digermacyclopentane derivative the latter yields a disilacyclobutane derivative [34].

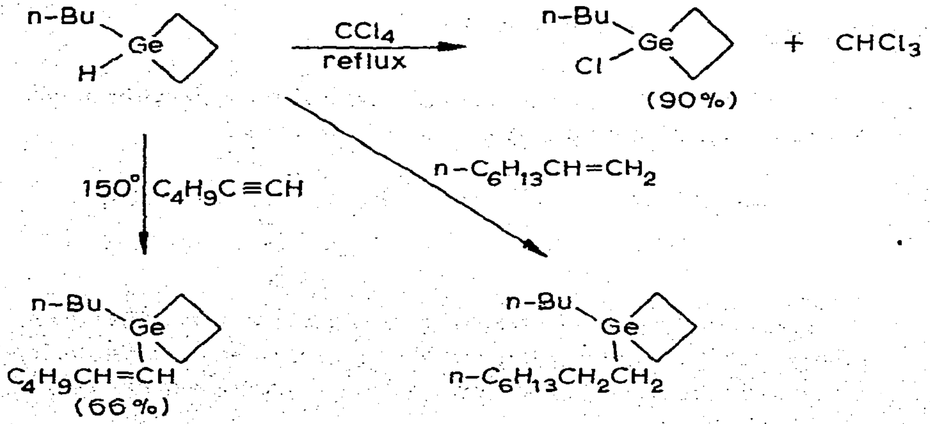
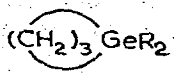
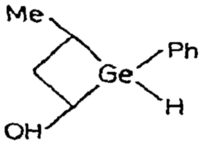


Chart 5. Some reactions of hydrogermacyclobutanes.

3. Spectroscopy

Spectroscopic techniques like IR and PMR have been extensively used to characterize germacyclobutanes as well as various products obtained from their reactions.

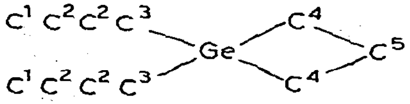
TABLE 1
IR DATA FOR SOME GERMACYCLOBUTANES

Compound	R_2	IR absorption (cm^{-1}) (liquid film)	Assignment	References
 $(CH_2)_3GeR_2$	Me_2	1115^a		34
	Et_2	1114^a		21
	Bu_2	1114^a		21
	$<(CH_2)_4$	1120^a		21
	alkyl, H	$1110-1120^a$ 2020	 ν(GeH)	23
		1125^a		21
		3340 2040	ν(OH) ν(GeH)	24
		3300 2030	ν(OH) ν(GeH)	24

[a] Characteristic of the cyclobutane ring system.

TABLE 2

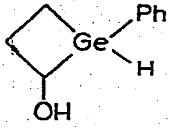
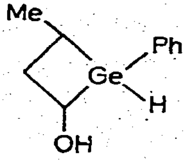
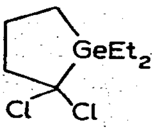
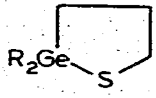
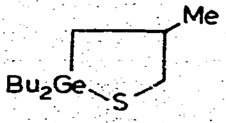
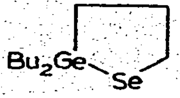
PMR Spectra [25] of



δ (in CCl_4)	Multiplicity	Position
1.9 – 2.4	Quintuplet	C (5) – H
1.4	Triplet	C (4) – H
1.2 – 1.6	Complex	C (2) – H
0.8 – 1.2	Complex	C (3) – H
0.9	Triplet	C (1) – H

An infrared band (1110–1120 cm^{-1}) appears to be characteristic of the germacyclobutane ring system [20, 21, 23, 34], but detailed investigations regarding far-infrared and band assignments (as in the case of silacyclobutanes) have yet to be undertaken. Various infrared absorption bands for germacyclobutanes are summarized in Table 1. In the NMR spectra [21, 25, 31] the germacyclobutane ring protons are deshielded thus enabling the differentiation between cyclobutane ring protons from those belonging to

TABLE 3
PMR DATA FOR SOME GERMACYCLOBUTANES AND THEIR REACTION PRODUCTS

Compound	δ	Multiplicity	Reference
	GeH 4.37 HCO 3.45 CH_2 1.0 – 1.8	multiplets	24
	GeH 4.38 HCO 3.45 CH_3 0.9 – 1.3	multiplets	24
	$EtGeCH_2$ 0.9 – 1.4 ring $GeCH_2CH_2$ 1.6 – 2.1 CH_2CCl_2 2.25	complex multiplet two overlapping doublets	32
 R = Et	α 2.65[a] β 1.90	triplet quintuplet	31
R = Bu	α 2.60 β 1.85	triplet quintuplet	31
$R_2 = -(CH_2)_4-$	α 2.75 β 2.00	triplet	31
	1.8 – 2.9	complex	31
	α 2.70 β 1.90	triplet quintuplet	31

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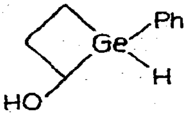
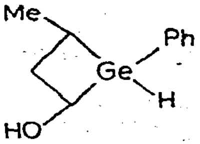
[a] α or β signify the protons on carbon atoms α or β to S or Se.

TABLE 4
PROPERTIES OF GERMACYCLOBUTANES

Compound	R_2	B.p. (°C/mm)	n_D^{20}	d_4^{20}	Other data reported	References
$(CH_2)_3GeR_2$	Me_2	120/760	1.4588[a]	1.1066[a]	IR	33,34
	Et_2	78/80	1.4738	1.0853	IR, mass spectrum	20,21,29,30, 31,32
	Bu_2	112/18	1.4742	1.0163	IR, NMR, mass spectrum	20,21,25,29, 30,31
	Et, Bu	75/13	1.4720	1.0401	IR	23
	Bu, C_8H_{17}	103/0.3	1.4738	0.9799		23
	Bu, $CH{=}CH_2$	80/18	1.4825	1.0506		23
	Bu, $CH{=}CHC_6H_{13}$	75/0.1	1.4828	1.0096		23
	Bu, $C{\equiv}CH$	67/10	1.4822	1.0795		23
	Bu, H	70/25	1.4781	1.0879		23
	Bu, Cl	94/18	1.4900	1.1912		23
	Bu, Br	107/18	1.5157	1.4520		23
	Bu, I	121/18	1.5558	1.6358		23
	Et_2	82/48	1.4682	1.0285		8,28
	Bu_2	113/9	1.4690	0.9937	IR	21
	Bu, Ph	82/0.05	1.5355	1.0909	IR	23
	Bu, H	61/15	1.4701	1.0361		23
	Bu, I	109/15	1.5410	1.5431	IR, NMR	23
		96/0.04			IR, NMR	24
		98–103/0.05			IR, NMR	24
$(CH_2)_3Ge(CH_2)_4$		89/38	1.5185	1.2043	IR	21,31

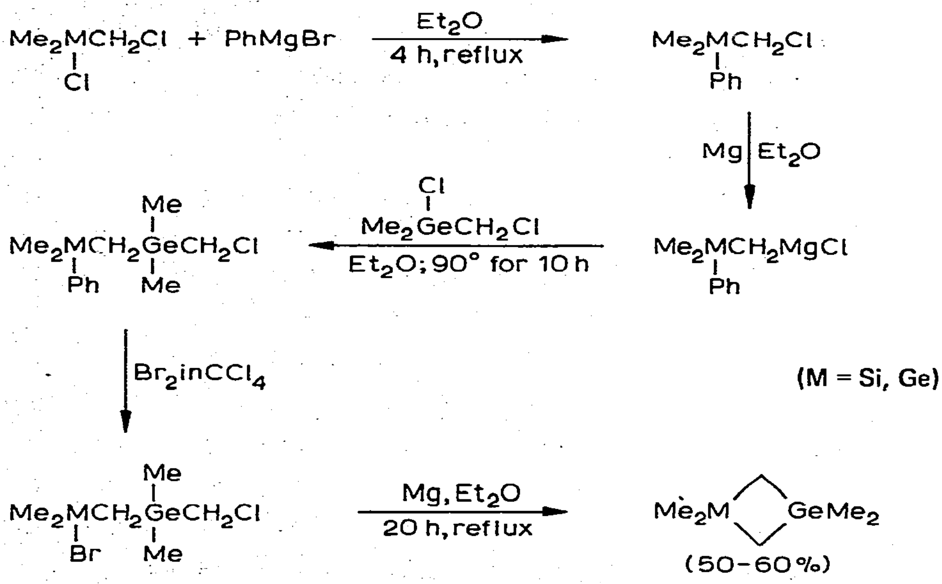
[a] At 25°

an aliphatic chain (see Table 2). PMR data for germacyclobutanes and for some of their reaction products are compiled in Table 3.

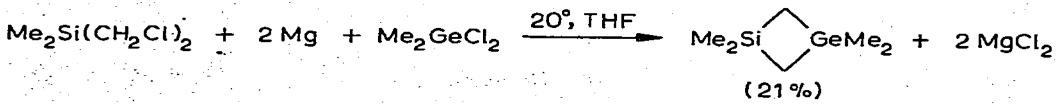
Some physical properties of various germacyclobutanes are summarized in Table 4.

B. Digermacyclobutanes and germasilacyclobutanes

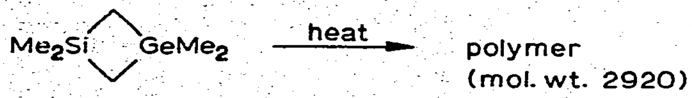
The work on the chemistry of these compounds is very limited and has been carried out since 1969. Mironov and Gar [35, 36] reported the first successful synthesis of 1,1,3,3-tetramethyl-1,3-digermacyclobutane and 1,1,3,3-tetramethyl-1-sila-3-germacyclobutane according to the reaction scheme:



A convenient procedure (from the point of the availability of starting materials) for the preparation of 1,1,3,3,-tetramethyl-1-sila-3-germacyclobutane [37] is to add bis(chloromethyl)dimethylsilane to a well-stirred mixture of dimethyldichlorogermane and high purity magnesium in tetrahydrofuran:



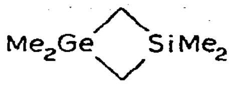
Both the heterocycles (described above) polymerize [36] readily at about 120° with opening of the ring:



but the 1,3-digerma derivative is resistant to vapour phase pyrolysis at 400–600° [34].

Various physical data for these compounds are given in Table 5.

TABLE 5
PROPERTIES OF DIGERMA- AND GERMASILA-CYCLOBUTANE

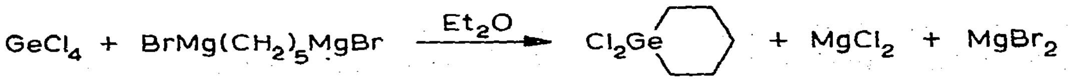
Compound	B.p. (°C/mm)	n_D^{20}	d_4^{20}	Other data reported	References
	65/48	1.4875	1.2929	IR, NMR[a]	35,36,38
	57/60	1.4665	1.0468	IR, NMR[b], mass spectrum	35,36,37,38

[a] δ (in CCl_4) 0.42 (s, Me), 0.64 (s, CH_2).
[b] δ (in CCl_4) 0.16 (s, Me_2Si), 0.40 (s, Me_2Ge), 0.225 (s, CH_2).

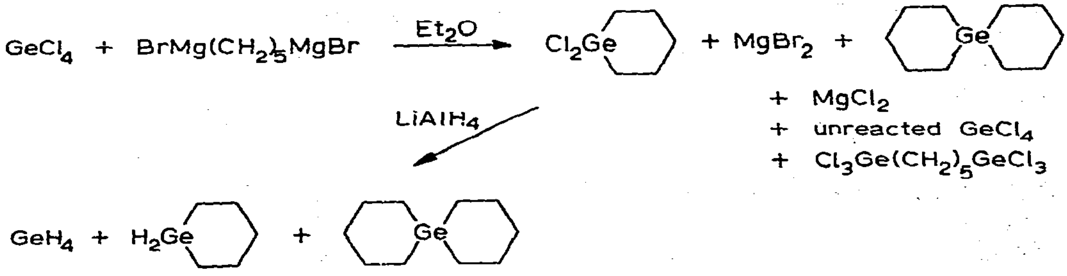
C. Germacyclopentanes and germacyclohexanes

1. Preparation

Schwarz and Reinhardt reported the first preparation of a germacyclohexane derivative [39] using the reaction sequence:



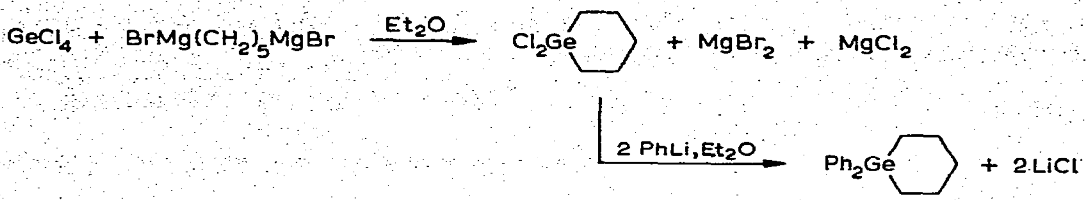
A re-investigation of the above reaction by Mazerolles showed it to give a number of products [40], dichlorogermacyclohexane being one of them:



(gaseous) (b.p. 119°C) (b.p. 109°C/17 mm)

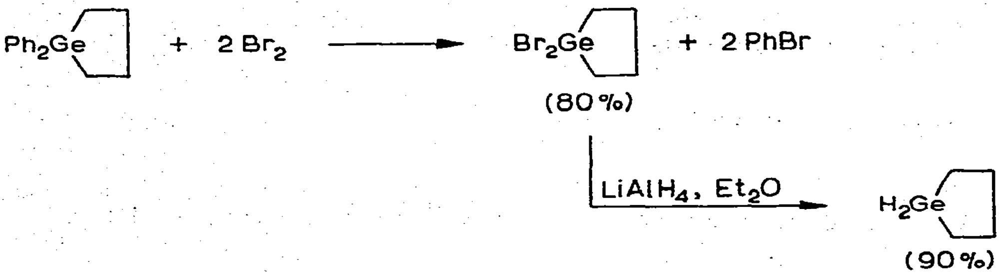
Reduction of the reaction mixture with lithium aluminium hydride gave more volatile hydrogermanes (without affecting the spiran) which could then be separated by distillation. The procedure has been extended to the synthesis of a number of germacyclopentanes [21, 41, 42] and -hexanes [21, 43]:

$$R_2GeX_2 + BrMg(CH_2)_nMgBr \longrightarrow R_2Ge(CH_2)_n + MgBr_2 + MgX_2$$
$$(R = Cl, Me, Et, Ph;\ X = Cl, Br;\ n = 4, 5)$$



The solvent used for these reactions has been found to affect the yields [21].

The germacyclanes obtained by the ring closure reactions mentioned above have been used as starting materials to synthesize a variety of other hydro-, halogeno- or alkyl- and aryl-substituted germacyclanes. Thus diphenylgermacyclopentane could be converted into the dihydro derivative [21] via the reaction scheme:



These hydrogermacyclanes undergo a variety of halogen exchange reactions thereby yielding halogermacyclanes [21, 40]. Some of these reactions are summarized in Chart 6.

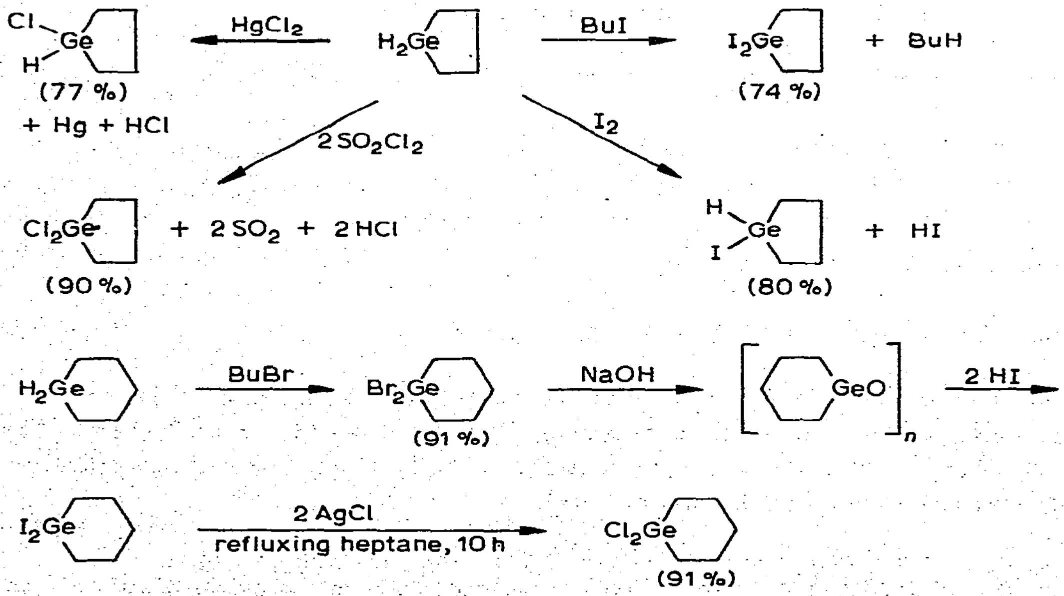


Chart 6. Some reactions of hydrogermacyclanes.

Diphenylgermacyclopentane [21, 40, 41] and dichlorogermacyclohexane [40, 44, 45] undergo a variety of reactions with ring retention and thus are used as excellent starting materials in synthesizing a wide range of germacyclanes. Various reactions are compiled in Chart 7.

Various other routes to germacyclopentane derivatives include: ring expansion reactions [32] of germacyclobutanes, catalytic hydrogenation [46–48] of germacyclopentenes, and the addition reactions [49–52] of diorganogermylenes (R_2Ge:) to olefins (see Chart 8).

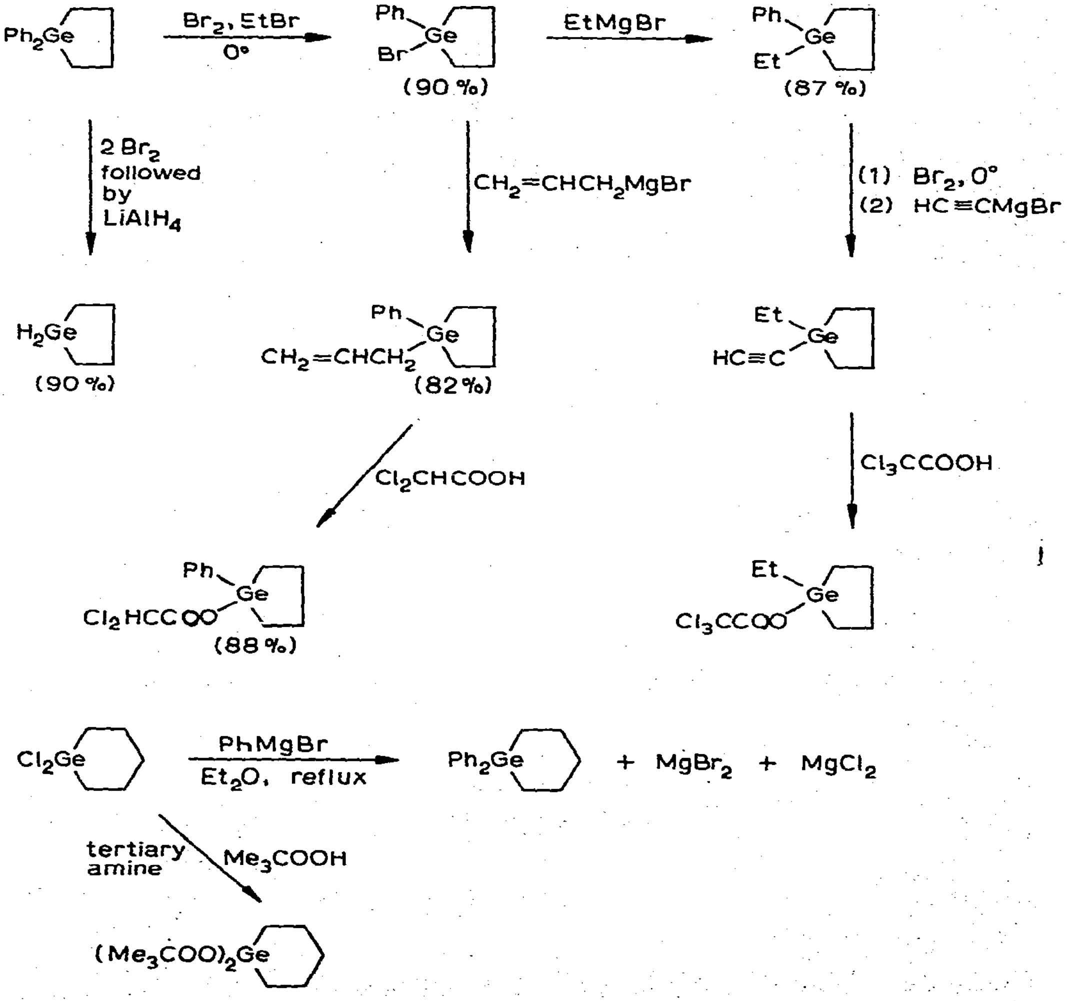


Chart 7. Synthesis of some germacyclopentane and germacyclohexane derivatives.

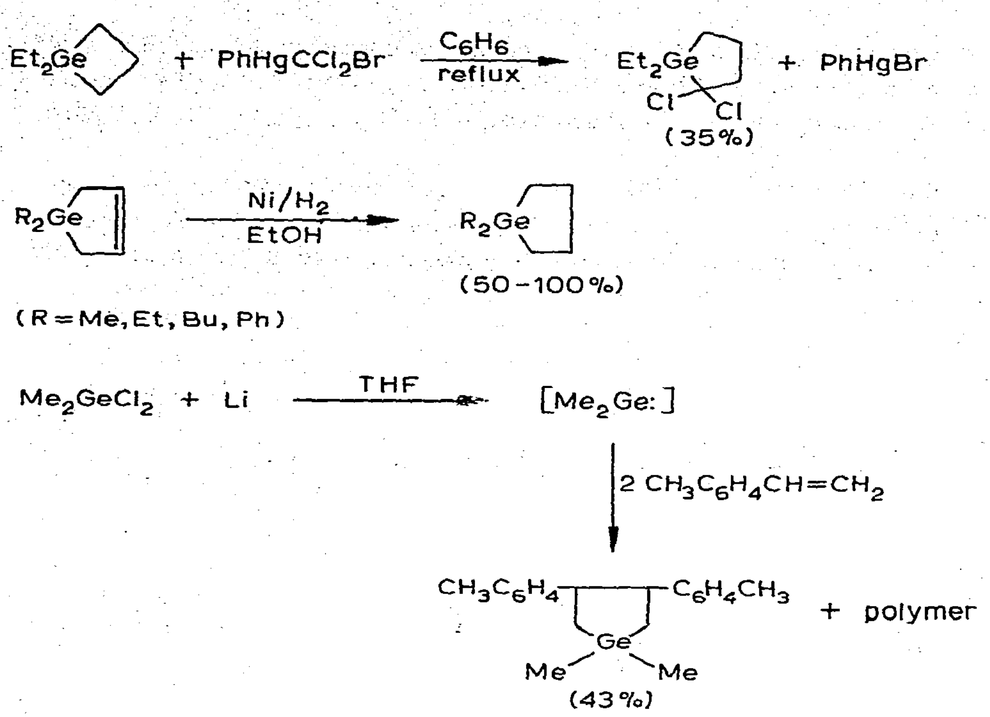


Chart 8. Synthesis of some germacyclopentanes.

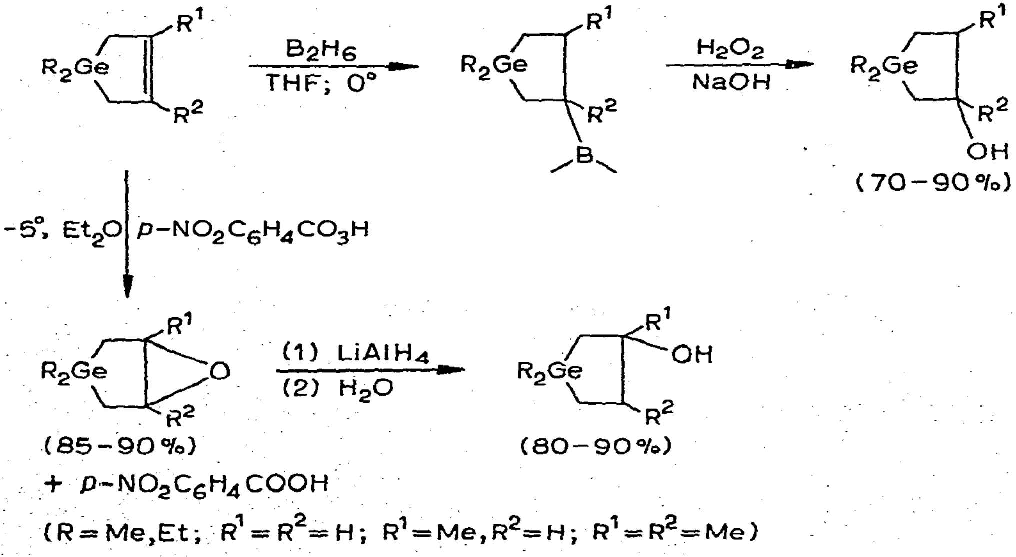
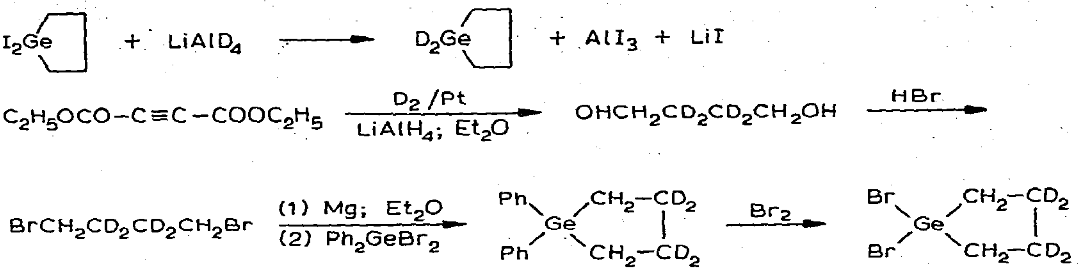


Chart 9. Synthesis of germacyclopentanols.

Deuterated germacyclopentanes containing Ge—D or C—D bonds have been prepared for mass spectroscopic investigations, by the following reactions [53, 54]:

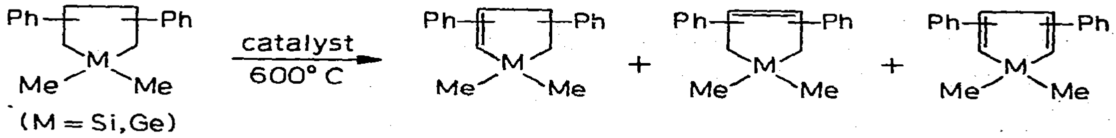


Hydroboration [55, 56] and epoxydation of germacyclopentenes followed by reduction, has been used to synthesize germacyclopentanols in high yields (Chart 9).

2. *Properties and reactions*

The various reactions in the section on preparative routes to diorganogermacyclopentanes show that the ring systems possess great stability. The ring resists many reagents (in contrast to the germacyclobutane ring) e.g. water, oxygen, lithium aluminum hydride, alkyl halides, hydrogen halides but, under more drastic conditions, the ring opening does take place [21, 40]. Some of these reactions are compiled in Chart 10. Diethylgermacyclohexane reacted with concentrated sulfuric acid only above 30—40°C.

In a short communication catalytic dehydrogenation [57] of diorganogerma- and diorganosila-cyclopentanes in the presence of Pt/C (10%) or Al/Cr/K (84/14/2) catalyst has been reported to yield unsaturated derivatives:



Seyferth and coworkers found the insertion of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene to occur at the β-C—H bond of diethylgermacyclohexane [58]. Pyrolysis of the insertion product resulted in germyl-substituted chlorocyclopropane.

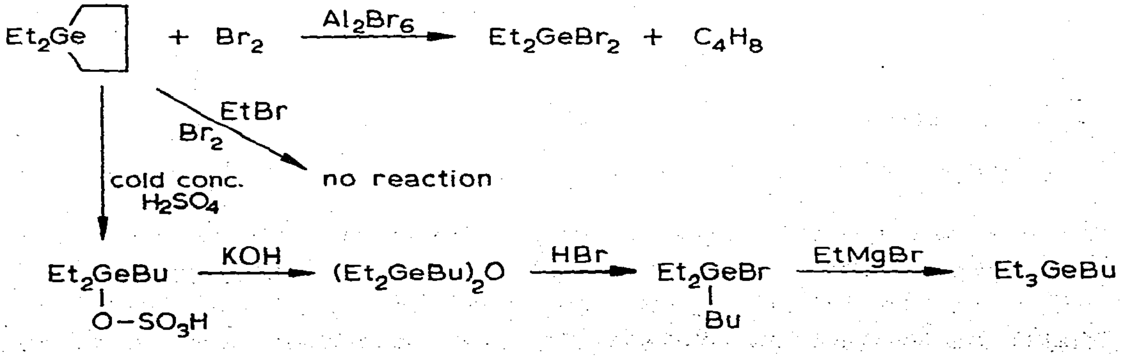
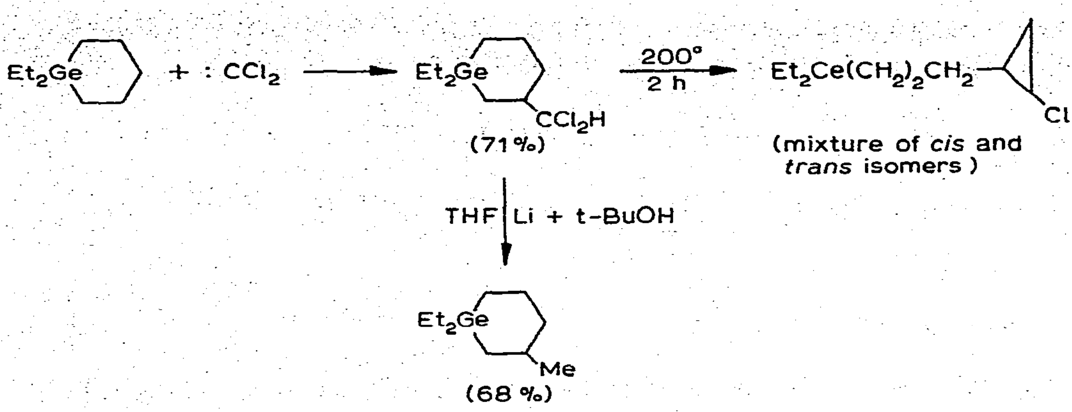
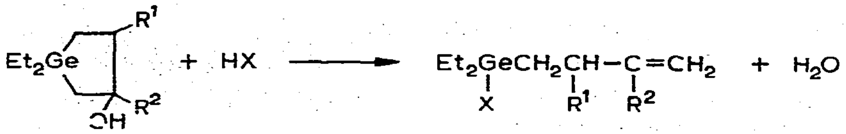


Chart 10. Ring opening reactions of germacyclopentanes.



Dihydrogermacyclanes are liquids which could be distilled without decomposition. They should be stored in an inert atmosphere because of their high sensitivity towards oxygen [40]. Whereas dihydrogermacyclopentane oxidises rapidly in contact with air, the oxidation of dihydrogermacyclohexane takes place in several stages (see Chart 11). Diorganogermacyclopentanols are liquids which could be distilled under reduced pressure without decomposition. They are easily cleaved by protonic acids to give linear olefinic derivatives [59]:



($R^1 = R^2 = H$, Me; $R^1 = Me$, $R^2 = H$; X = F, Cl, Br, I, CH_3COO, Cl_2CHCOO, $ClCH_2COO$)

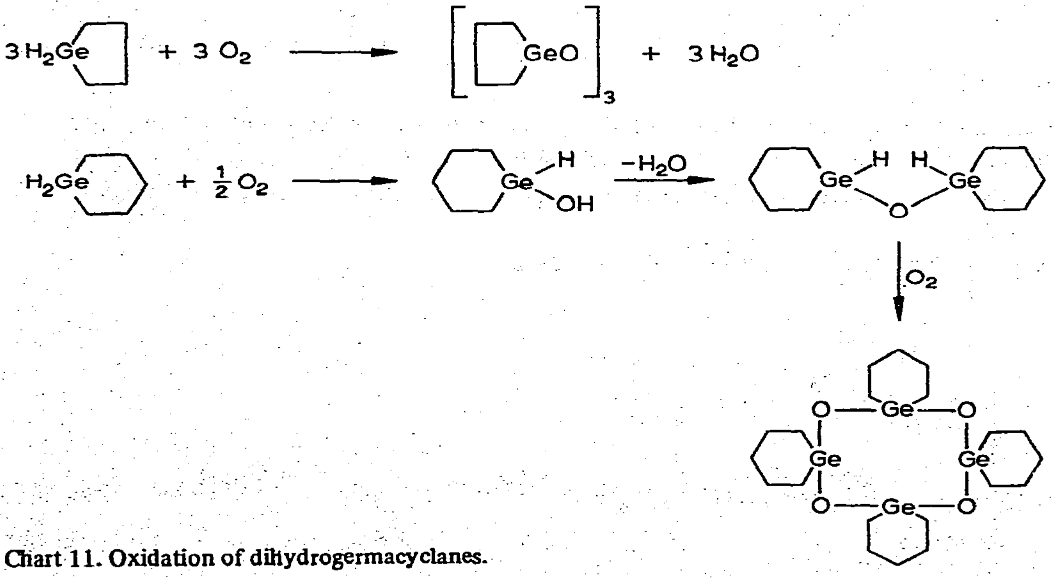


Chart 11. Oxidation of dihydrogermacyclanes.

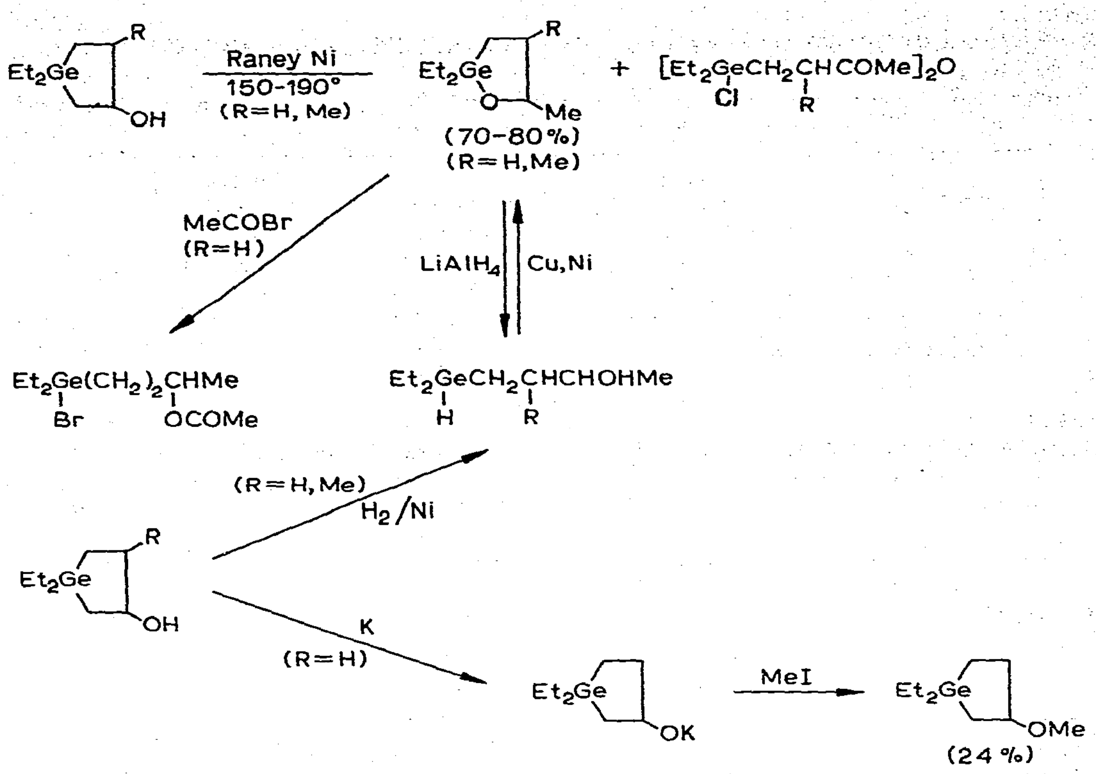
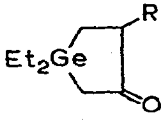


Chart 12. Some reactions of germacyclopentanols and 1-oxa-2-germacyclopentanes.

The rearrangement of germacyclopentanols [60] in the presence of Raney nickel to give 1-oxa-2-germacyclopentanes, as well as some reactions [61] of the latter compounds are given in Chart 12.

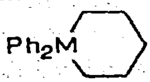
A mechanism involving the intermediate formation of a germacyclopenta-3-one,



has been proposed [60].

3. *Spectroscopy*

Bajer and Post investigated the infrared spectra [43] of six-membered heterocyclic systems:



(M = C, Si, Ge, Sn, Pb) in the region 4000–650 cm^{-1} and observed that in addition to the characteristic metal–phenyl absorptions between 1125–1050 cm^{-1} there occurred a series of three absorption bands at 2650, 990–965 and 910 cm^{-1} (see Table 6). The five-membered heterocycles [64] showed a particularly characteristic pair of bands at approximately 1080 and 1025 cm^{-1}.

TABLE 6

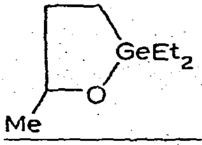
INFRARED ABSORPTION DATA [43] FOR SIX-MEMBERED HETEROCYCLIC SYSTEMS: $Ph_2\widehat{M(CH_2)_5}$

M	ν (cm^{-1})		
C	2640 w[a]	–	905 m
Si	2640 w	987 s	908 s
Ge	2640 w	987 s	913 s
Sn	2640 w	970 s	907 s
Pb	2650 w	965 s	909 s

[a] w, weak; m, medium, s, strong.

TABLE 7

IR DATA FOR SOME GERMACYCLOPENTANE AND GERMACYCLOHEXANE DERIVATIVES

Compound	R_2	IR absorption (cm^{-1}) (liquid film)	References
$\widehat{(CH_2)_4Ge}R_2$	H_2	ν(GeH) 2052s	21,40,65
	H, Cl	ν(GeH) 2081	21
	H, Pr	ν(GeH) 2023	21
	H, Ph	ν(GeH) 2035s	40,65
$\widehat{(CH_2)_5Ge}R_2$	H_2	ν(GeH) 2044s	40,65
	H, Ph	ν(GeH) 2023s	40,65
		ν(GeOC) 1045, 680	60

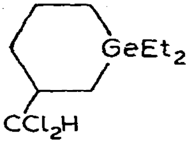
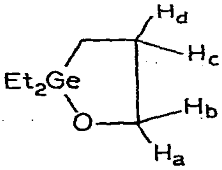
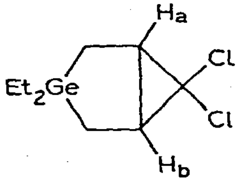
The microwave spectrum [62] of germacyclopentane indicated the molecule to be permanently twisted into a C_2 conformation with a twist angle of 18°.

The infrared (gaseous state, 4000–250 cm^{-1}) and Raman (liquid state) spectrum of germacyclopentane and 1,1-dideutero-1-germacyclopentane have been reported. The large number of polarized Raman lines is conclusive evidence that the molecule (germacyclopentane) is not planar and the data are consistent with the twisted C_2 molecular structure. The 39 fundamental modes of vibration have been assigned for both the compounds [63].

The infrared absorption bands reported for various germacyclopentane and germacyclohexane derivatives are summarized in Table 7.

PMR spectroscopy has been used in the study of various reactions of germacyclanes and in elucidating the structure of the products obtained [60, 61]. Some PMR data for various germacyclanes are given in Table 8.

TABLE 8
PMR DATA FOR GERMACYCLANES

Compound	PMR data[a] (ppm)	References
	δ (CCl_2H) 5.71 (doublet) J 3.0 Hz	58
	δ H_a 3.5 – 4.5[b] δ H_c and H_d 0.7 – 2.2 δ H_b 1.25 δ (Et and CH_2 on Ge) 0.8 – 1.0	60,61
	δ (H_a and H_b) 2.13 (multiplet)	85

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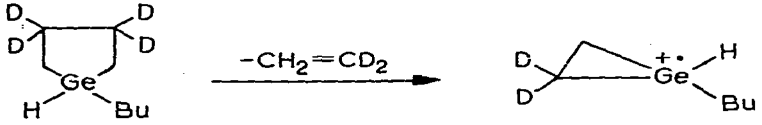
[a] TMS as the standard. [b] C_6D_6 as the solvent.

Mass spectral data [53, 54] for a number of substituted germacyclopentane derivatives and their deuterated analogues have been reported. These spectra are remarkable for the presence of abundant ions which result from fission of one, two, three or occasionally four bonds to the germanium atom with charge retention on the metal-containing species in each instance. Loss of ethylene in these derivatives always is accomplished by elimination of C(2) and C(3):



Some properties of germacyclopentane and germacyclohexane derivatives are summarized in Tables 9 and 10 respectively.

D. Digermacyclanes, germasilacyclanes and germastannacyclanes

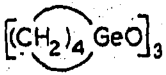
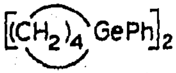
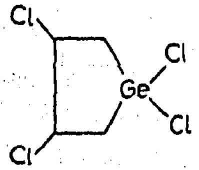
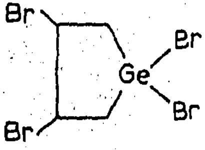
1. Preparation

Mazerolles et al. [66] observed that the action of diethylmercury on 1,3-bis(diethylgermyl)propane leads to a mercury derivative which by pyrolysis, gives a cyclic compound

(continued on p. 349)

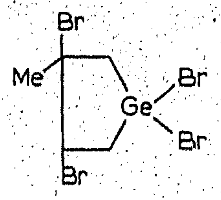
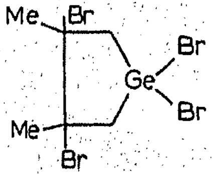
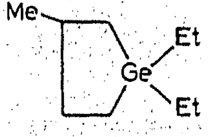
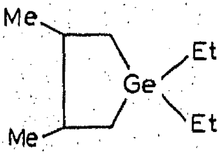
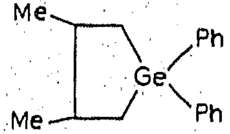
TABLE 9
PROPERTIES OF GERMACYCLOPENTANES

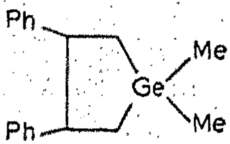
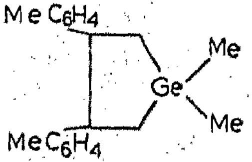
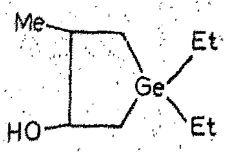
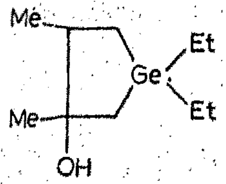
Compound	R_2	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
$(CH_2)_4GeR_2$	Cl_2	94/64	1.5101	1.5239		21,40
	Br_2	97/15	1.5720	2.0806		21,40
	I_2	107/5	1.6770	2.5000		40
	H_2	91–92/760	1.4838	1.2261	IR	21,40,65
	H, Cl	154/745	1.5078	1.4218	IR	21
	H, I	107/48	1.5956	1.9924	IR	40,65
	Cl, $(CH_2)_3Cl$	136–137/12	1.5158	1.3693		21
	Br, $(CH_2)_3Br$	118/1.1	1.5574	1.7933		21
	Br, Et	75/9	1.5201	1.5261		41
	I, Et	113/28	1.5631	1.7450		41
	Br, Pr	92.5/10	1.5153	1.4642		41
	Br, Bu	82/2.2	1.5120	1.4134		41
	Br, Ph	116/0.9	1.5878	1.5438		40
	H, Me	105/760	1.4700	1.1515		8
	H, Pr	89/65	1.4754	1.0995	IR	21
	H, Bu	179/745	1.4756	1.0694		41
	H, Ph	127/30	1.5601	1.2215	IR	40,65
	Me_2	118–119/752		1.0641	PMR	42,46
	Et_2	173–174/750	1.4725	1.0761		40
	Bu_2	123/18	1.4720	1.0142		8
	Ph_2	115/0.2 136/0.4 33	1.5971	1.2189		21,40,41
	Ph, Et	140/20	1.5441	1.1614		41
	Ph, Pr	104/0.8	1.5383	1.1354		41
	Ph, $CH_2CH{=}CH_2$	108/1.7	1.5551	1.1575		21,41
	Et, $C{\equiv}CH$	85/75	1.4862	1.1402		21

	Bu, $C\equiv CH$	101/28	1.4805	1.0737	21
	Et, $C\equiv CCMe_2OH$	100/1.4	1.4910	1.0988	8
	Pr, $(CH_2)_3SCH_2CO_2H$	158/0.25	1.5201	1.2114	41
	Bu, $(CH_2)_2GeEt_3$	131/0.6	1.4940	1.1168	41
	Et, $OCOCCl_3$	102/1.0	1.4992	1.4707	8
	Et, $OCOCHCl_2$	106–107/1.4	1.4949	1.4103	8
	Bu, $OCOCHCl_2$	116/0.9	1.4911	1.3240	8
	Bu, $OCOCH_2Cl$	116/1.4	1.4869	1.2631	8
	Ph, $OCOCHCl_2$	123/0.3	1.5505	1.4290	41
		111/0.2	1.4956	1.1877	41
		166			40
		176/0.6	1.6085	1.3078	41
					77
		73			8

(continued)

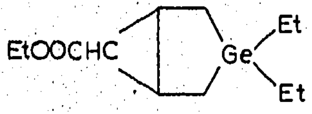
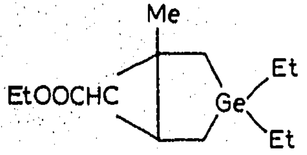
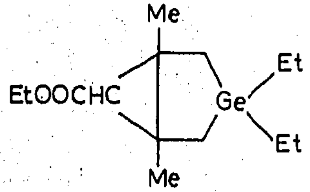
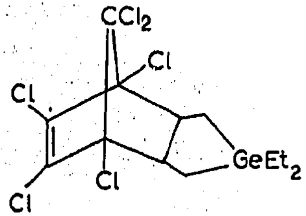
TABLE 9 (continued)

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
		120/0.2	1.6283	2.4994		8
		126 – 127				8
		71.5/14	1.4658	1.0427		55
	*cis*	90/17	1.4733	1.0455		55
	trans	90/17	1.4665	1.0272		55
		156/0.4	1.5853	1.1710		48

	140–141/0.2	1.5920	1.1688	IR	49
	150/0.18	1.5825	1.1346	IR	49
	111/15	1.4944	1.1806		55,59,60
	116.5/16	1.4855	1.1443		55,59,60
	122–125/12	1.4889	1.1272		55,59,60

(continued)

TABLE 9 (continued)

Compound	R₂	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
 *endo*		102/0.7	1.4899	1.1637		55
exo		102/0.7	1.4899	1.1665		55
		92/0.4	1.4850	1.1381		55
 *endo*		94/0.3	1.4844	1.1092		55
exo		94/0.3	1.4862	1.1213		55
		43			IR	55

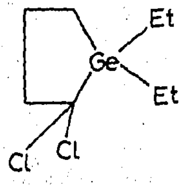
					IR, NMR, n_D^{25} 1.5061	32
$(CH_2)_4Ge(CH_2)_4$		189/760	1.5118	1.1837	IR	40,41,64

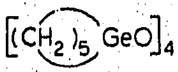
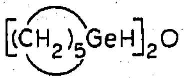
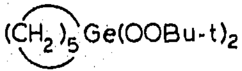
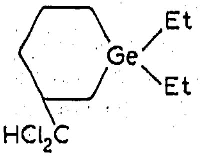
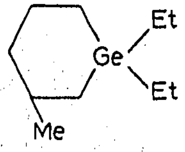
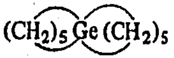
TABLE 10

PROPERTIES OF GERMACYCLOHEXANES

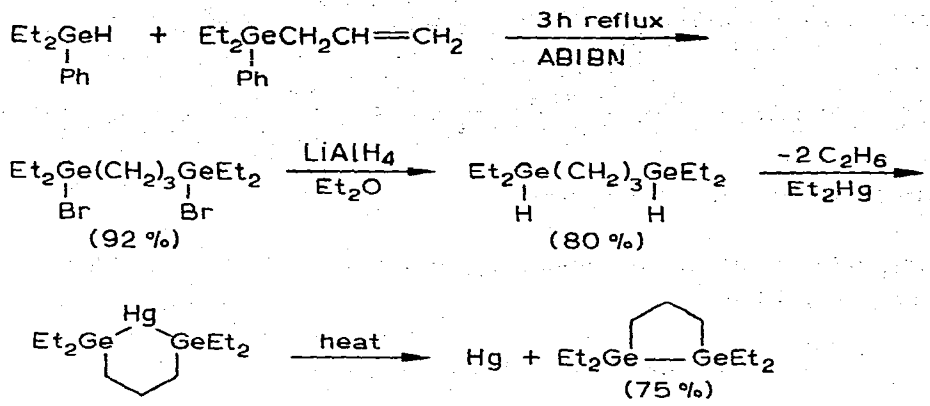
Compound	R_2	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
$(CH_2)_5GeR_2$	Cl_2	99/24	1.5107	1.4675		39,40
	Br_2	115/17	1.5659	1.9775		40
	I_2	108/2	1.6610	2.3698		40
	H_2	119–120/760	1.4835	1.1846	IR	40,65
	I, H	132/58	1.5835	1.8681	IR	40,65
	Br, Ph	125/0.8	1.5828	1.5045		40
	H, Ph	128/14	1.5550	1.1989	IR	40, 65
	Et_2	116–117/72	1.4742	1.0663		39,40,58
	Ph_2	150/1.0	1.5932	1.2061	IR	40,43

(continued)

TABLE 10 (continued)

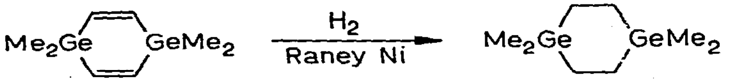
Compound	R_2	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
 $[(CH_2)_5GeO]_4$		144				40
 $[(CH_2)_5GeH]_2O$		130–131/9	1.5085		IR	40,65
 $(CH_2)_5Ge(OOBu\text{-}t)_2$		60/0.001			IR	44,45
					NMR n_D^{25} 1.5025	58
					n_D^{25} 1.4694	58
 $(CH_2)_5Ge(CH_2)_4$		101/23	1.5058	1.1474		40
 $(CH_2)_5Ge(CH_2)_5$		109/17	1.5060	1.1400	IR	40,64

with two adjacent intracyclic germanium atoms:



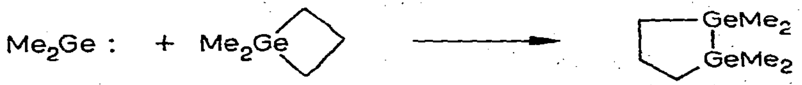
The digermacyclohexane derivative (in 57% yield) is obtained in the same manner from 1,4-bis(diethylgermyl)butane.

The synthesis of digermacyclohexanes has also been accomplished by hydrogenating [67] the corresponding cyclenic derivatives:



The thermal reactions of 1,1-dimethyl-1-germacyclobutane [34] have been carried out in static or pulsed flow systems at temperatures of 400–450° and 550–600° (see under Properties of germacyclobutanes). At a contact time of 12 sec and a temperature of 590° the conversion of 1,1-dimethyl-1-germacyclobutane in the pulsed system was 80% and the yield of 1,1,2,2,-tetramethyl-1,2-digermacyclopentane was 38%:

The product is probably formed by the insertion of the intermediate dimethylgermylene into the Ge–C bond of the four-membered ring:



Henry and Noltes accomplished the first synthesis of a 1-germa-4-stannacyclohexane derivative [68] via the condensation of diphenyldistannane and diphenyldivinylgermane. Similar condensation [40] of dibutyldigermane and diethyldivinylgermane gave a 1,4-digermacyclohexane derivative. The reactions are given in Chart 13.

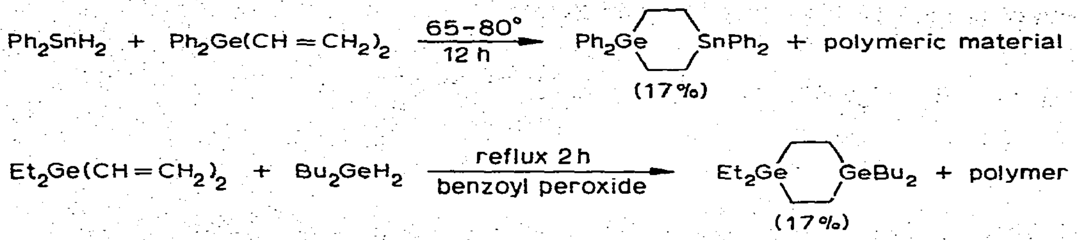
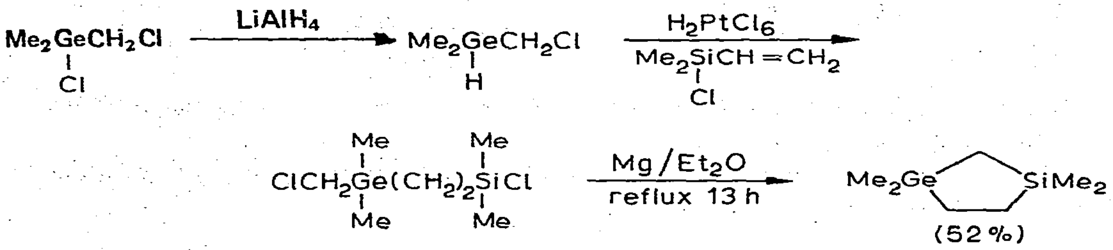


Chart 13. Synthesis of some digermacyclohexane derivatives.

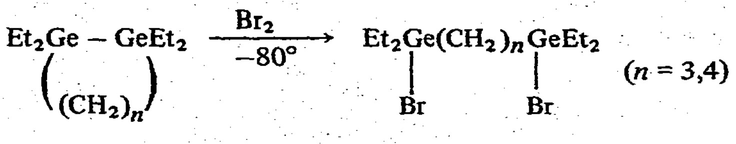
Finally, a good route to these compounds starting from chloro(chloromethyl)dimethylgermane has been reported [36, 69]:



2. *Properties and reactions*

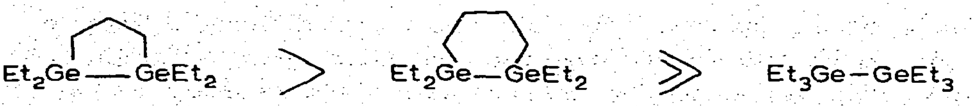
Both 1,1,2,2-tetraethyl-1,2-digermacyclopentane and 1,1,2,2-tetraethyl-1,2-digermacyclohexane are colourless liquids which can be distilled under reduced pressure without decomposition. The cyclopentane derivative oxidises slowly at room temperature, and rapidly at 150° giving a mixture of cyclic oxide and linear polymers [66]. The addition of sulfur and selenium also leads to ring expansion thus yielding a sulfur- or selenium-containing six-membered ring [66] (Chart 14). The analogous digermacyclohexane derivative is more stable and reacts not at all or very slowly with oxygen, sulfur and selenium under similar reaction conditions.

The reaction of these compounds with bromine (at −80°, without any catalyst) results in ring-opening at the Ge–Ge bond.



$$\underset{(CH_2)_n}{Et_2Ge-GeEt_2} \xrightarrow[-80°]{Br_2} \underset{Br}{Et_2Ge}(CH_2)_n\underset{Br}{GeEt_2} \quad (n = 3,4)$$

The ease of cleavage [66] is in the order:



Dichlorocarbene derived from phenylbromodichloromethylmercury has been reported to insert into β-C–H bonds of a number of tetraalkylgermanes; of the trimethylene bridge of

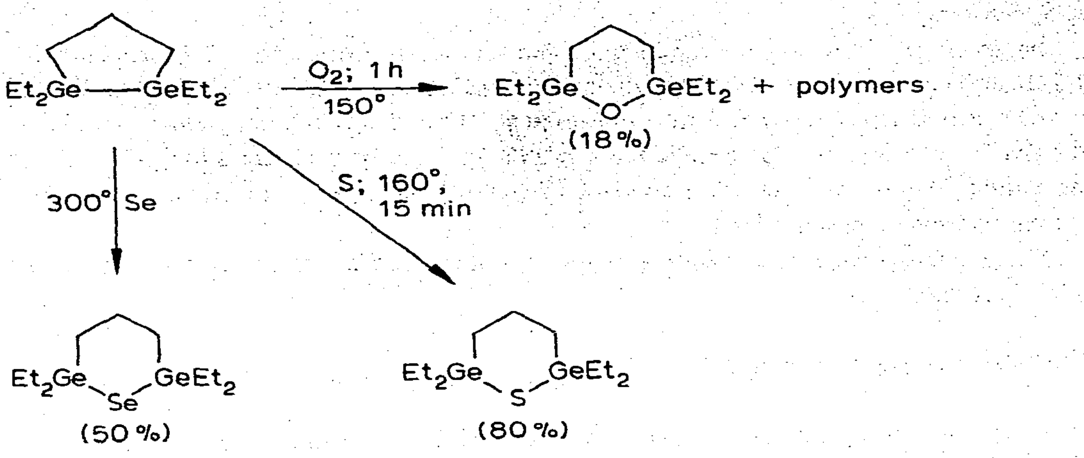


Chart 14. Some reactions of 1,1,2,2-tetraethyl-1,2-digermacyclopentane.

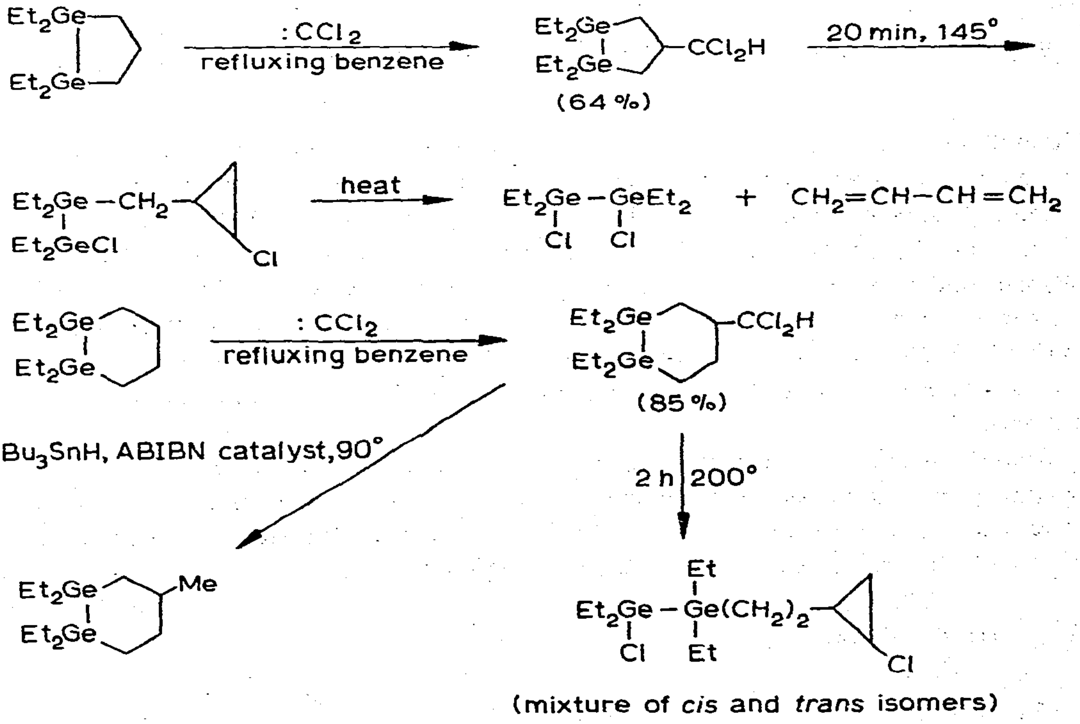


Chart 15. Some reactions of 1,2-digermacyclanes.

1,1,2,2-tetraethyl-1,2-digermacyclopentane and of the tetramethylene bridge of 1,1,2,2-tetraethyl-1,2-digermacyclohexane. Pyrolysis of these insertion products resulted in γ-elimination of Ge–Cl to give germyl-substituted chlorocyclopropanes. The reactions [58] are summarized in Chart 15.

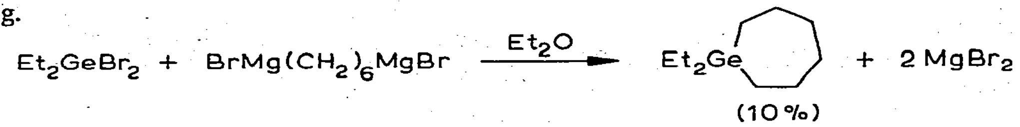
3. Spectroscopy

Nametkin et al. investigated the infrared and Raman spectrum of 1,1,2,2-tetramethyl-1,2-digermacyclopentane [34]. The intense infrared bands at 920, 1010 and 1075 cm^{-1} have been assigned to deformation vibration of C–H bonds of the methylene groups in the five-membered ring. The Raman band at 285 cm^{-1} has been assigned to Ge–Ge stretching. The proton magnetic resonance spectrum [34] is similar to that of the corresponding disila compound [70].

The spectroscopic data and some properties of these derivatives are given in Tables 11 and 12, respectively.

E. Miscellaneous germacycloalkanes

The method using dimagnesium compounds which has been successfully employed for the synthesis of germacyclopentanes and germacyclohexanes when applied to the preparation of medium or large ring systems [8] showed a considerable decrease in the yields e.g.



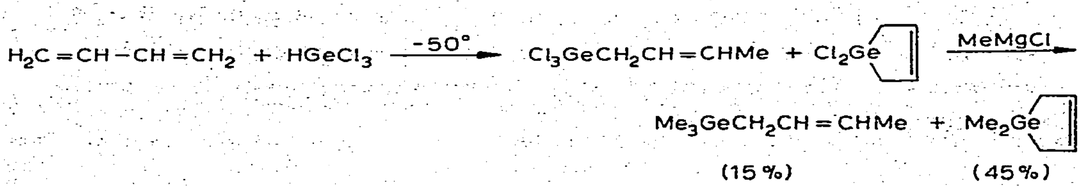
Mazerolles and coworkers investigated the problem and accomplished the synthesis of a number of germamacrocyclic compounds [72–74] by the following methods: (i) the action of sodium on ω-dibromo derivatives of the type $R_2Ge[(CH_2)_4Br]_2$ in various solvents; (ii) the pyrolysis of thorium salts of the type, $[R_2Ge\{(CH_2)_n(COO)\}_2]_2Th$ and (iii) the condensation of diesters of the type, $R_2Ge[(CH_2)_nCOOEt]_2$. The reactions used to prepare the products and their conversion into germamacrocyclic derivatives are given in Chart 16. The reactions of the germaacyloins obtained have been used to synthesize a variety of other germamacrocyclic compounds. Some of these reactions are summarized in Chart 17.

These germamacrocyclic compounds have been claimed to be useful as perfumes [74]. Spectroscopic techniques (IR, NMR and MS) have been used to confirm the structures of germaacyloins and related derivatives [72]. Some infrared data and the properties of these derivatives are given in Tables 13 and 14 respectively.

F. Germacyclopentenes

1. Preparation

Mironov and Gar studied the reactions of trichlorogermane with butadiene and observed [75–77] the presence of a linear and a cyclic product in the reaction mixture:



(continued on p. 356,

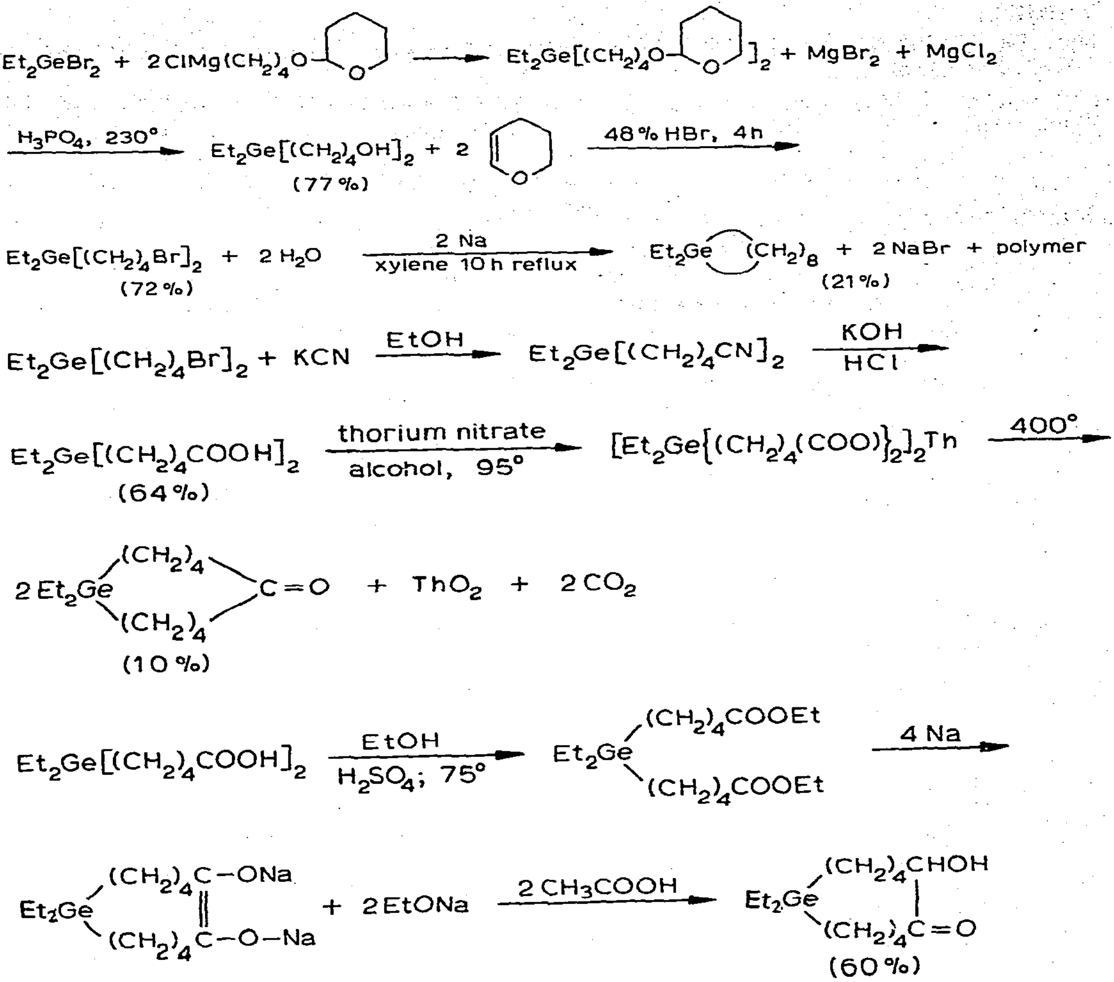


Chart 16. Synthesis of germamacrocyclic derivatives.

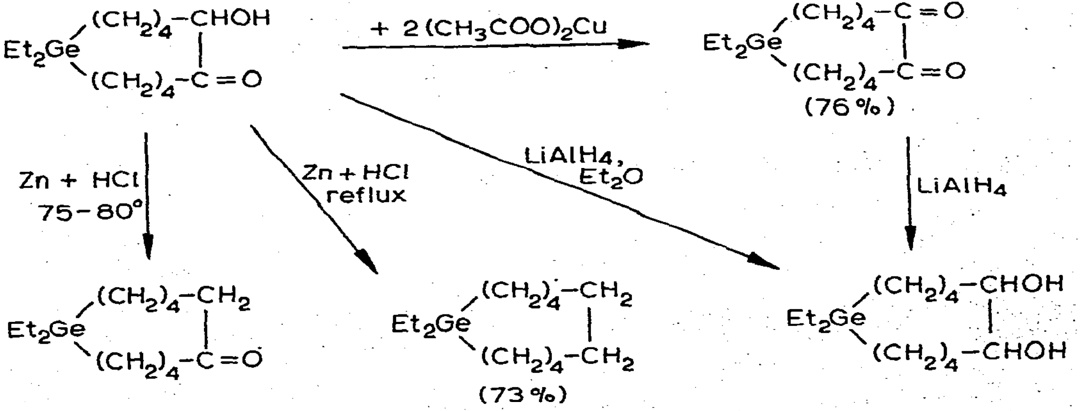
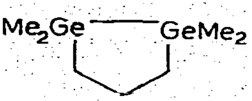
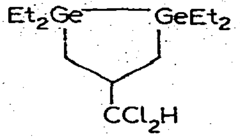
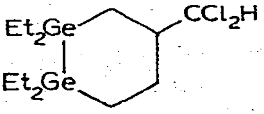
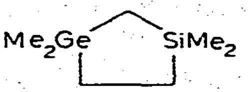
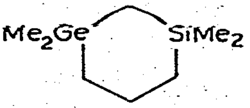
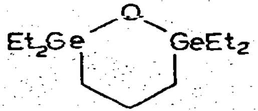
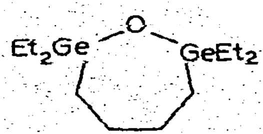


Chart 17. Some reactions of germaacyloins.

TABLE 11

SPECTROSCOPIC DATA FOR DIGERMACYCLANES, GERMASILACYCLANES AND THEIR REACTION PRODUCTS

Compound	IR absorptions (cm^{-1})	PMR[a] data	References
	1075, 1010 and 920 (deformation vibrations of C–H bonds of the CH$_2$ groups in the ring, Raman band at 285 (Ge–Ge stretching)	δ(Me–Ge) 0.25 ppm (singlet) δ(α-CH$_2$) 0.80 ppm (triplet) δ(β-CH$_2$) 1.65 ppm (multiplet)	34
		δ(CCl$_2$H) 5.88 ppm[b] (doublet) J 4.0 Hz	58
		δ(CCl$_2$H) 5.85 ppm[b] (doublet) J 2.8 Hz	58
		δ(CH$_2$) 0.39 ppm δ(MeSi) 0.02 ppm δ(MeGe) 0.20 ppm singlets[c] δ(CH$_2$–CH$_2$) 0.6–0.8 ppm (multiplet)	36
		δ(Ge–CH$_2$–Si) −0.2 ppm δ(MeSi) 0.0 ppm δ(MeGe) 0.15 ppm singlets[c] δ(CH$_2$–CH$_2$–CH$_2$) 0.6–1.8 ppm (multiplet)	36
	ν (Ge–O–Ge) 810		66
	ν (Ge–O–Ge) 820		66

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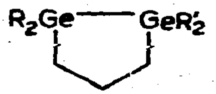
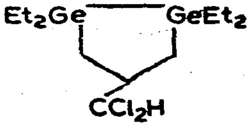
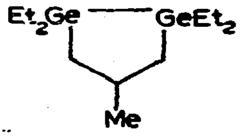
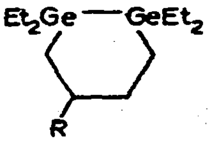
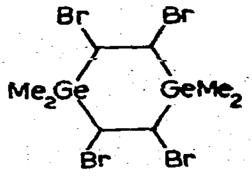
[a] Operating frequency 60 MHz; TMS as the internal standard. [b] As neat liquids. [c] In CCl$_4$.

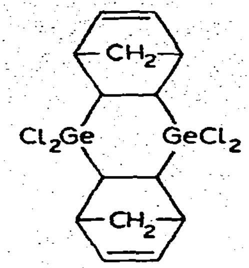
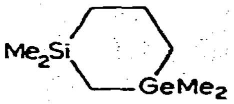
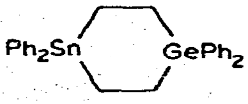
TABLE 12

SOME PROPERTIES OF DIGERMACYCLANES, GERMASILACYCLANES AND GERMASTANNACYCLANES

Compound	R	R′	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
	Me	Me		1.5105	1.2743	IR, NMR, mass spectrum	34
	Et	Et	128/15	1.5159	1.2088		58,66
						NMR	58
						n_D^{25} 1.5071	58
	H		112/25	1.5159	1.1974		58,66
	CCl_2H					NMR	58
	Me					n_D^{25} 1.5080	58
	Me	Me	70–72/12	1.4861			67,71
	Et	Bu	120–122/0.7	1.4932	1.1198		40
			145–149				71

(continued)

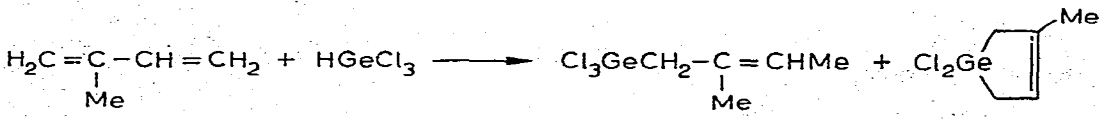
TABLE 12 (continued)

Compound	R	R'	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
			264–265				71
			78/51	1.4652	1.0439	IR, NMR	36,69
			57/10	1.4714	1.0477	NMR	36
			124–125			IR, NMR	68,118, 119

The overall yield of the cyclic compound seems to depend upon the experimental conditions and in some runs about 90% of it was isolated [76]. The formation of the cyclic product has been explained in terms of 1,4-addition of germanium dichloride formed as:

$$HGeCl_3 \rightleftharpoons H^+GeCl_3^- \rightleftharpoons GeCl_2 + HCl$$

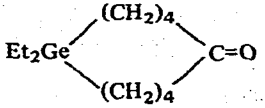
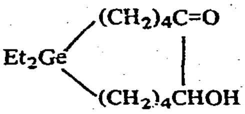
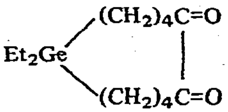
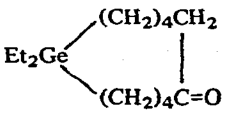
Isoprene reacted analogously but piperylene gave exclusively the linear adduct [77]:



It is interesting to note that the corresponding addition of trichlorosilane to butadiene and other conjugated dienes occurs exclusively by 1,4-addition [78] and requires a catalyst:

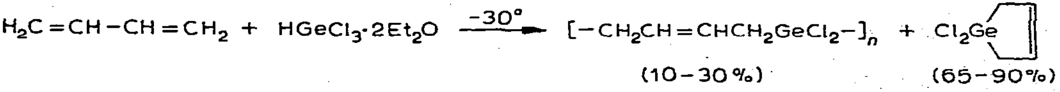
$$H_2C{=}CH{-}CH{=}CH_2 + HSiCl_3 \xrightarrow{Pt/C} CH_3CH{=}CHCH_2SiCl_3$$

TABLE 13
IR DATA FOR GERMAMACROCYCLIC COMPOUNDS [72]

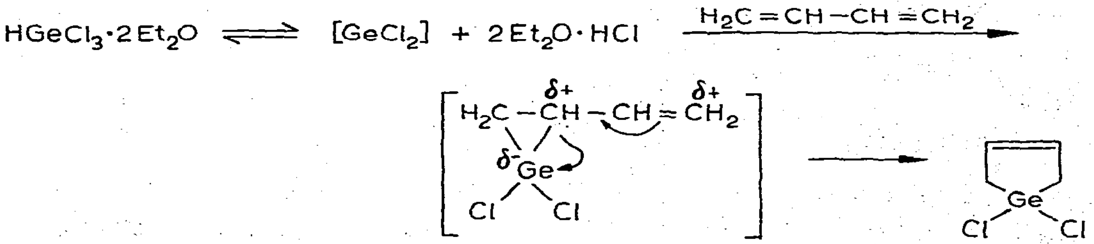
Compound	ν(C=O) (cm^{-1})
	1700
	1720[a]
	1700
	1720

[a] ν(OH) 3500 cm^{-1}.

Nefedov and coworkers found trichlorogermane dietherate to act as a good source of germanium dichloride. With butadiene it gave a germacyclopentene derivative in high yield [79–81]:



The authors suggested the following mechanism for the reaction [79, 80]:



The analogous addition of tribromogermane to butadiene has been reported to give a mixture of linear and cyclic products with the linear derivative predominating [82, 83]:

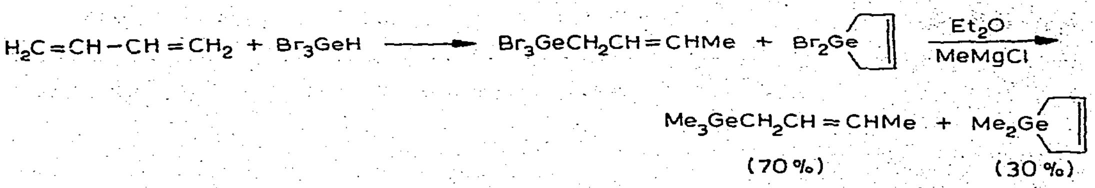
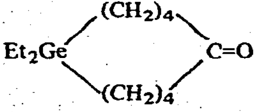
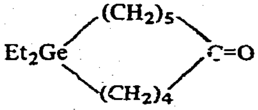
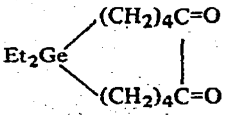
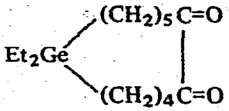
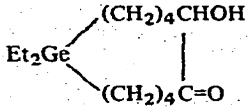
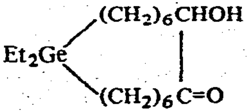
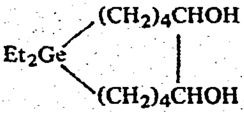
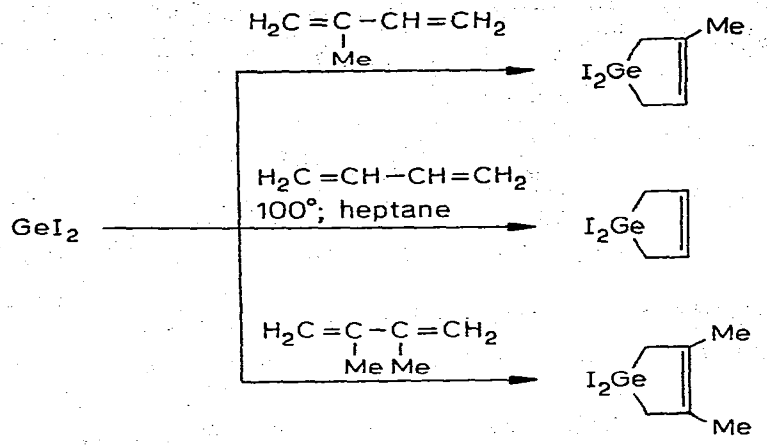


TABLE 14

PROPERTIES OF MISCELLANEOUS GERMACYCLOALKANES

Compounds	R	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	References
	Et	101.5/16	1.4814	1.0641	8
	H	149–150/760	1.4938	1.1694	8
		140			8
		116–117/0.6	1.5008	1.0628	72
		123/1.1	1.5005	1.1096	72
		105/0.1	1.4983	1.1521	72
		140/1	1.4957	1.1188	73
		152/0.6	1.5084	1.1644	72
		190–195/1.5			8,73
			1.5148	1.1529	72
$Et_2Ge(CH_2)_{14}$		135/0.045	1.4918	1.0104	8,73

The addition of germanium(II) iodide to isoprene, butadiene and 2,3-dimethylbutadiene yields diiodogermacyclopentenes [47, 48]:



On the other hand, no reaction occurred with piperylene, 1-phenylbutadiene or tetraphenylbutadiene.

The diiodocyclopentenes obtained as above undergo a variety of reactions [48] e.g. reduction, alkylation or arylation and halogen exchange thus providing various other germacyclopentene derivatives (Chart 18).

Recently Satgé and coworkers have shown the condensation of germanium(II) inter-

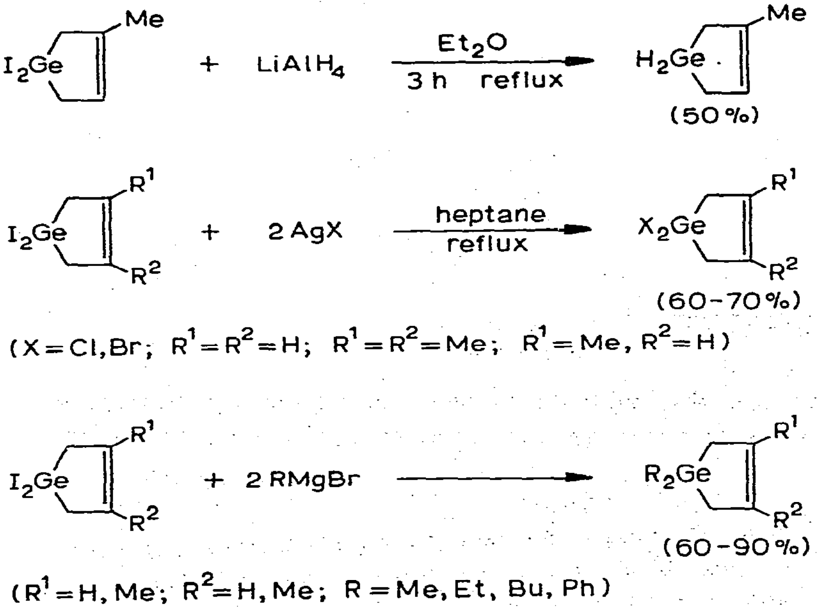
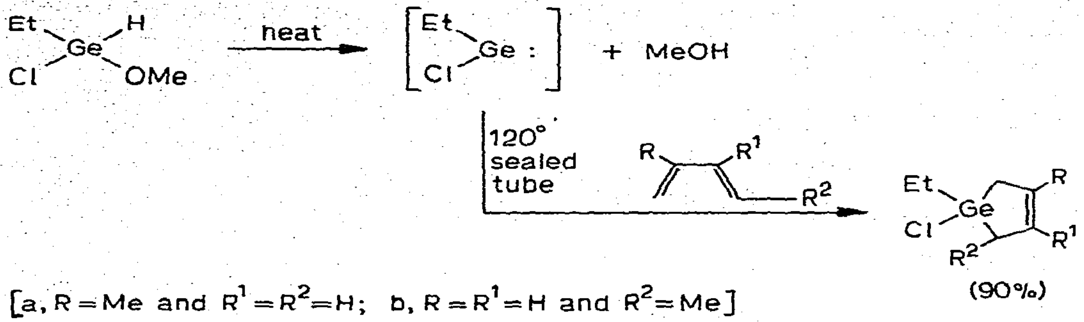


Chart 18. Synthesis of some germacyclopentene derivatives.

mediates with 1,3-dienes to be a convenient and high yield method of synthesizing germacyclopentene derivatives [84]:

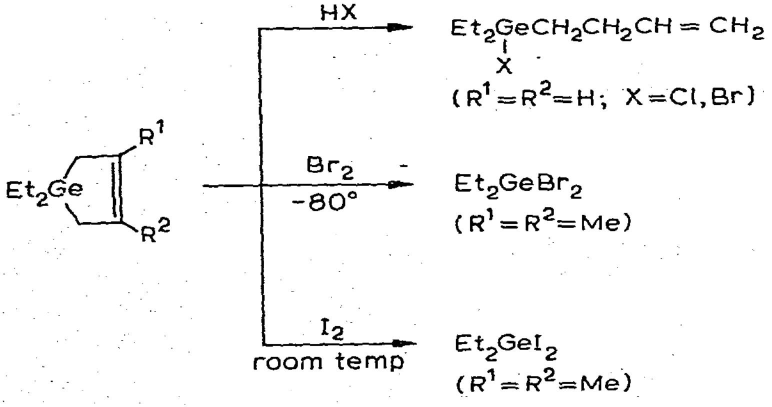


[a, $R = Me$ and $R^1 = R^2 = H$; b, $R = R^1 = H$ and $R^2 = Me$]

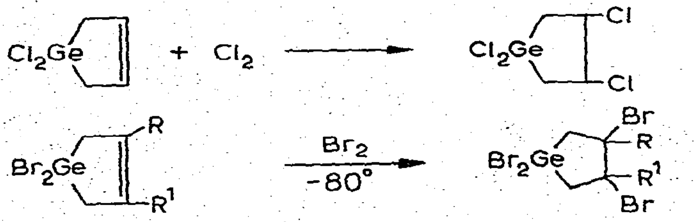
2. Properties and reactions

Diiodogermacyclopentenes have been found to be thermally unstable and only the butadiene derivative could be distilled under vacuum without decomposition. The polymerization of dichlorogermacyclopentene by lithium in tetrahydrofuran or on boiling the compound at 100–120° has been reported [46].

It has been shown [48] that hydrogen halides cleave one intracyclic Ge–C bond of diethylgermacyclopentene giving a diethylhalobutenyl derivative with terminal double bond, whereas halogens simultaneously cleave both the intracyclic Ge–C bonds yielding diethyldihalogermane:

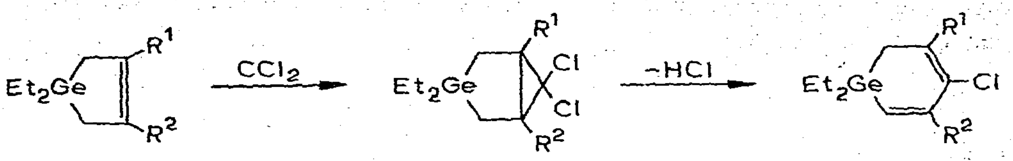


On the other hand, it has been observed that chlorine reacts with dichlorogermacyclopentene [77] and bromine with dibromogermacyclopentenes [8] at the double bond:



($R = R^1 = H, Me$; $R = H$, $R^1 = Me$)

The reaction of dichlorocarbene (generated via $CHCl_3$ + Me_3COK or $PhHgCCl_2Br$) with 1,1-diethyl-1-germa-3-cyclopentenes has been shown to give 3,3-diethyl-6,6-dichloro-3-germabicyclo[3.1.0]hexanes which are not very stable thermally and thus give a germacyclohexadiene derivative [85]:



($R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$ and $R^1 = R^2 = Me$).

The intermediate adduct could only be isolated as a pure substance when $R^1 = R^2 = H$. Methyl substitution on the germacyclopentene C=C bond tends to decrease the stability of the dichlorocarbene adduct.

Some other reactions of germacyclopentene derivatives [46, 48, 55, 84] are summarized in Chart 19.

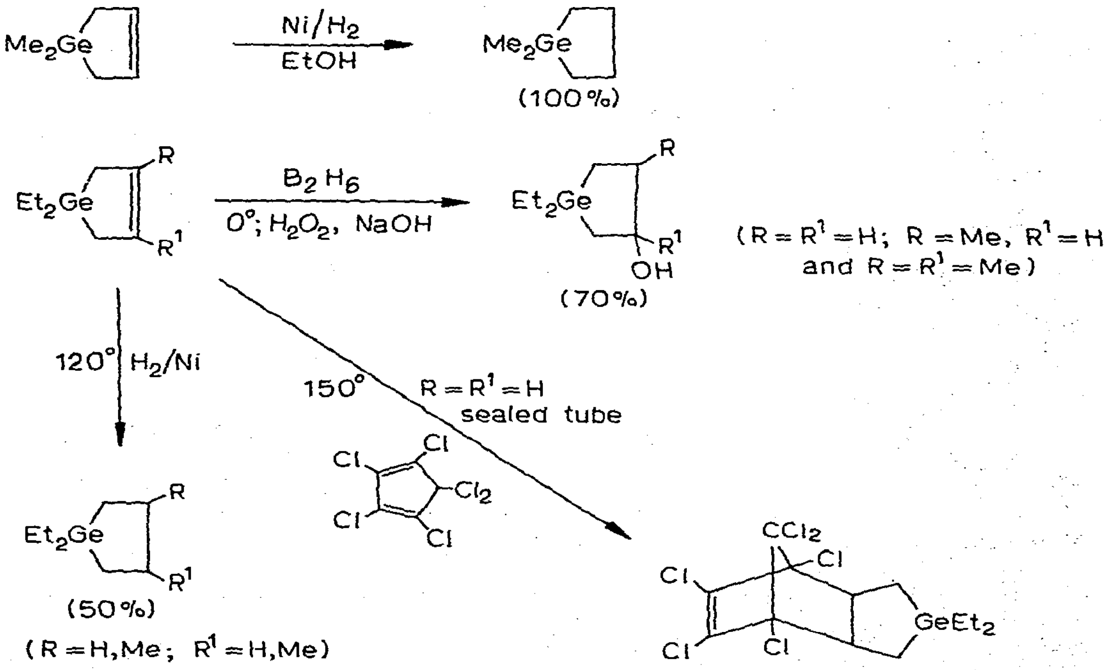


Chart 19. Some reactions of germacyclopentenes.

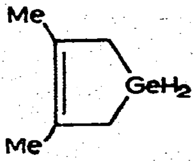
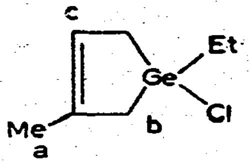
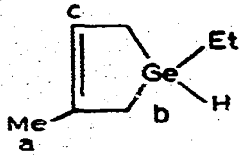
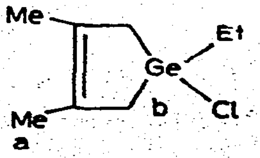
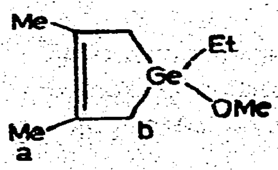
The reactivity of germacyclopentenes appears to be dominated by the nature of the substituents both at the double bond and at the metal atom. The reactions are accompanied either by ring opening or by addition to C=C bonds with preservation of the GeC_4 ring system.

3. Spectroscopy

Various spectroscopic techniques e.g. infrared [46, 48, 77, 83, 84], Raman [46, 76, 77, 83], NMR [77, 84, 85], UV [77] and mass spectroscopy [54] have been used to establish the structures of various germacyclopentenes as well as their reaction products. Some spectroscopic data are given in Table 15, and some properties of germacyclopentenes are summarized in Table 16.

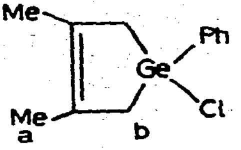
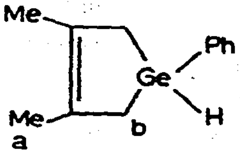
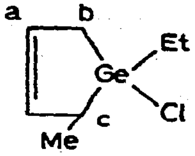
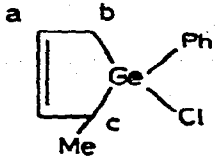
(continued on p. 365)

TABLE 15
SPECTROSCOPIC DATA FOR GERMACYCLOPENTENES

Compound	ν(C=C) (cm^{-1})		δ_a	δ_b	δ_c	(in CCl$_4$)	References
		[5.99 (CH=CH); 1.44 (CH$_2$); 0.90 (Me)]					76,77
	1640	2060^a					48
	1620		1.83	1.75	5.66		84
	1635	2030^a	1.75	1.53	5.54	δ(GeH) 4.33	84
	1650		1.75	1.83			84
	1645	1063^b	1.72	1.58		δ(OMe) 3.35	84

(continued)

TABLE 15 (continued)

Compound	$\nu(C{=}C)$ (cm^{-1})		δ_a	δ_b	δ_c	(in CCl_4)	References
	1640		1.78	2.04			84
	1640	2045[a]	1.74	1.82		δ(GeH) 4.78	84
	1610		5.88	1.70	2.05		84
	1600		6.00	2.01	2.26		84

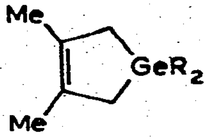
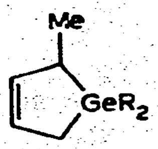
[a] ν(GeH). [b] ν(GeOC).

TABLE 16
PROPERTIES OF GERMACYCLOPENTENES

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
	Cl_2	52/10	1.5223	1.5762	IR, Raman, NMR	46,75,76, 77,80,81
	Br_2	99.5/20.5	1.5880	2.1742	IR, Raman	82,83
	I_2	77/0.2 29				55
	Me_2	119/743	1.4712	1.1273	IR, Raman, NMR	46,75,76, 77,82
	Et_2	65/17	1.4813	1.1013		55,85

(continued)

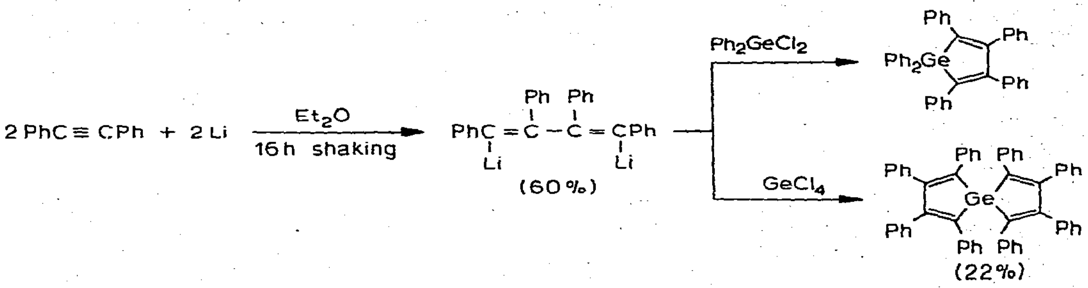
TABLE 16 (continued)

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	n_D^{20}	d_4^{20}	Other data reported	References
	Cl_2	98/34	1.5128	1.4694		48
	Br_2	125/25	1.5825	2.059		48
	I_2		1.6515	2.319		48
	H_2	117/760	1.5212	1.2751		48
	Me_2	139/741	1.4740	1.1041		8
	Et_2	89/24	1.4805	1.0754	Mass spectrum	54,83,85
	Et, H	58/16	1.4870	1.1253	IR, NMR	84
	Et, Cl	100/15	1.5014	1.2701	IR, NMR	84
	Cl_2	120/26	1.5178	1.4249		48
	I_2	32–34				48
	H_2	142/760	1.5025	1.1765		48
	O	190–191				48
	Me_2	71/27	1.4799	1.0902	Mass spectrum	48,54
	Et_2	102/26	1.4850	1.0625	Mass spectrum	48,54,85
	Bu_2	161/36	1.4820	1.0059		48
	Ph_2	142.5/0.25 40–41				48
	Et, Cl	116/20	1.5056	1.2414	IR, NMR	84
	Et, OMe	92/14	1.4832	1.1441	IR, NMR	84
	Ph, F	124/15	1.5390		IR, NMR	84
	Ph, Cl	156/17	1.5610		IR, NMR	84
	Ph, Br	174/15	1.5820		IR, NMR	84
	Ph, I	80/0.04			IR, NMR	84
	Ph, H	94/1.5	1.5605		IR, NMR	84
	Ph, OMe	114/2.0	1.5420		IR, NMR	84
	Et, Cl	112/37	1.4966	1.2442	IR, NMR	84
	Ph, Cl	114/15	1.5590		IR, NMR	84

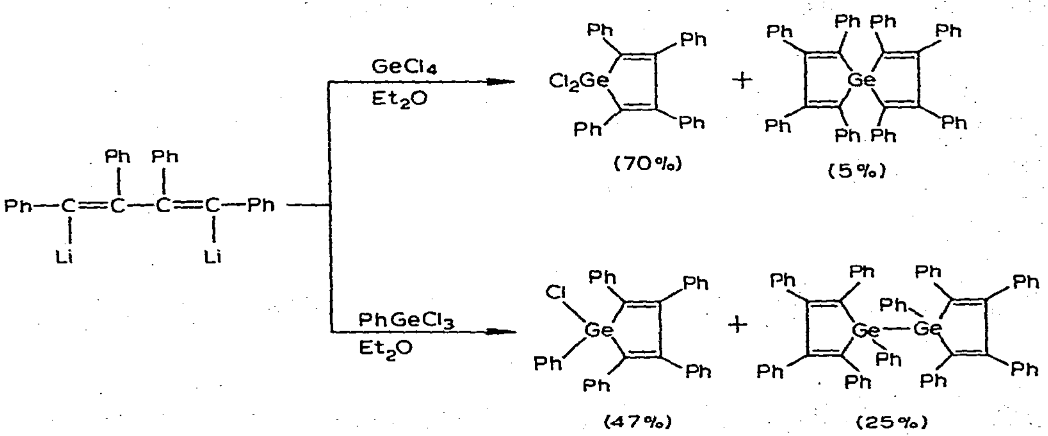
G. *Germacyclopentadienes and germacyclohexadienes*

1. *Preparation*

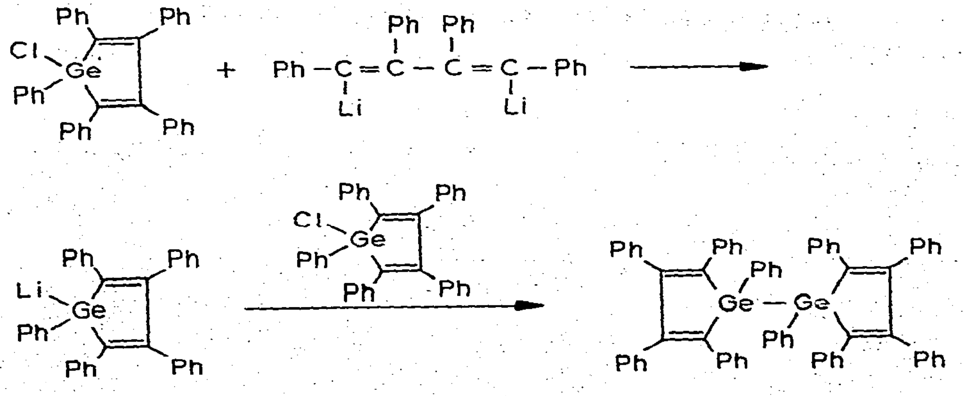
The reaction between germanium tetrachloride or organohalogermanes and 1,4-dilithio-1,2,3,4-tetraphenylbutadiene has been succesfully employed for the synthesis of a number of germacyclopentadiene derivatives [86, 87]:



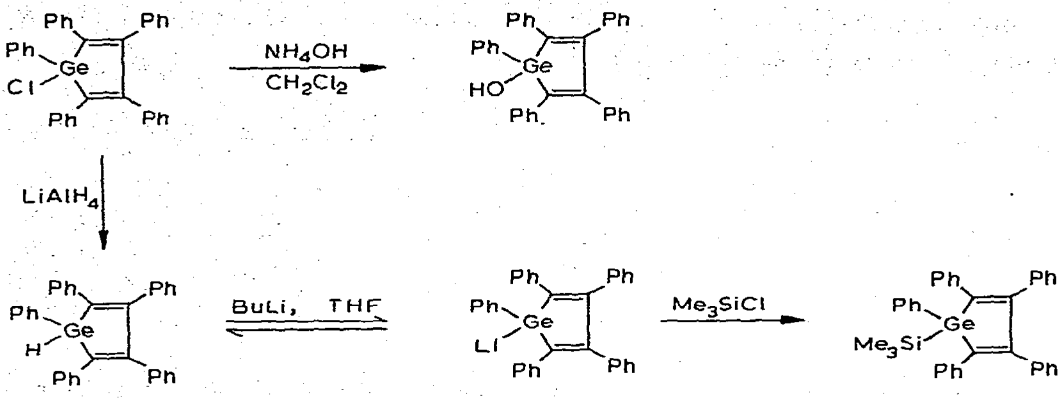
Curtis observed that adding the dilithio reagent to the chlorides $PhGeCl_3$ or $GeCl_4$, rather than vice versa, gave chloro-substituted germacyclopentadienes in good yields [88, 89]:



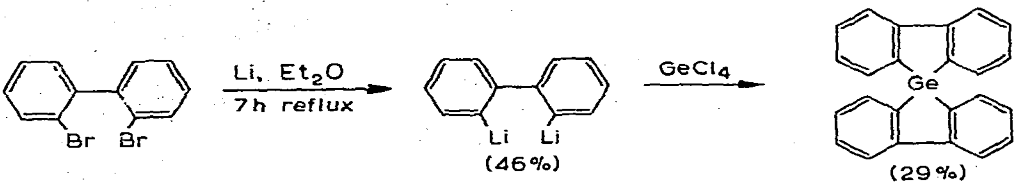
The digerma derivative arises from the halogen–metal exchange sequence:

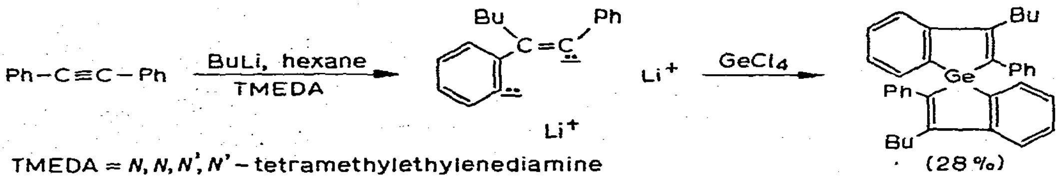


The chloro-substituted germacyclopentadienes undergo certain reactions without ring-opening and thus have been used to synthesize other germacyclopentadiene derivatives [89]:



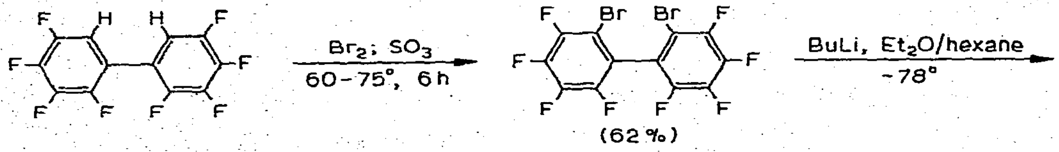
The compounds containing dibenzogermacyclopentadiene [90, 91] and the heterocyclic germanium–indene system [92] have been synthesized by the following reactions:

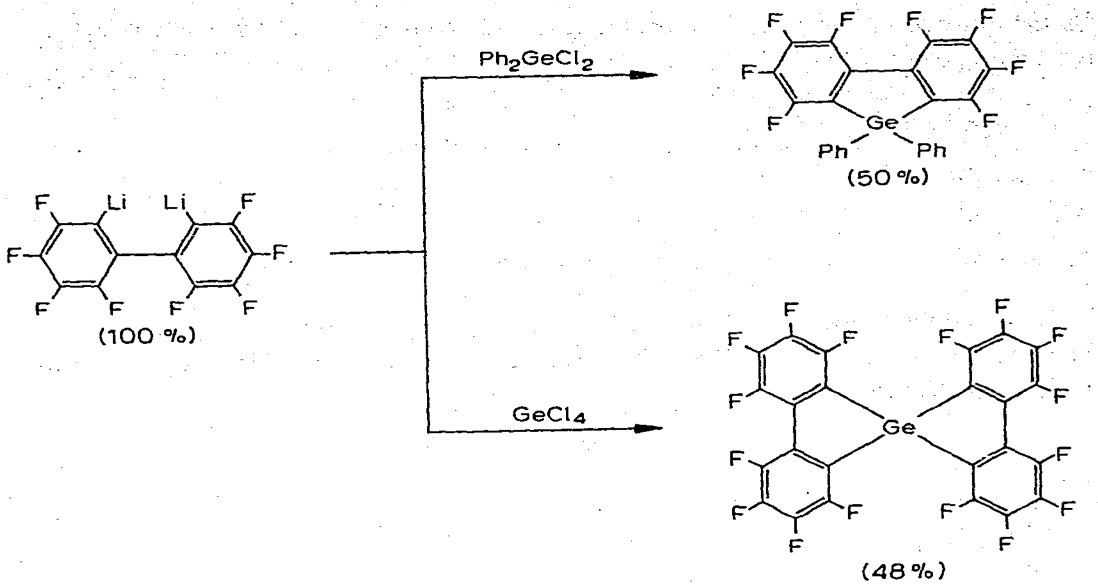




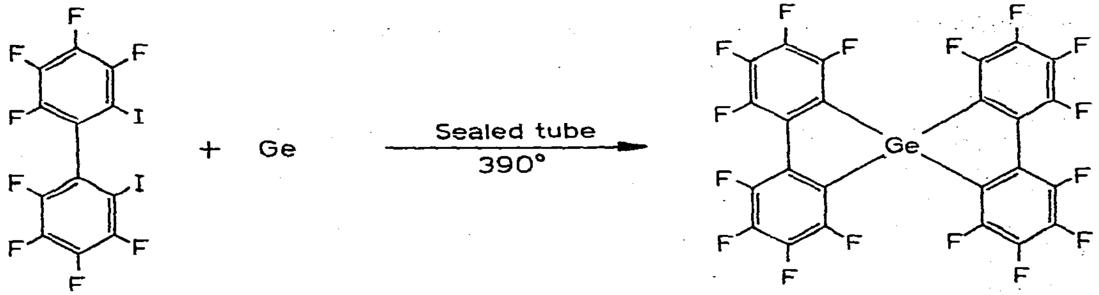
TMEDA = *N*,*N*,*N*′,*N*′–tetramethylethylenediamine

Massey and Cohen studied a number of reactions of 2,2′-disubstituted octafluorobiphenyls [93–95], some of which have been used to synthesize germanium containing heterocyclic compounds:



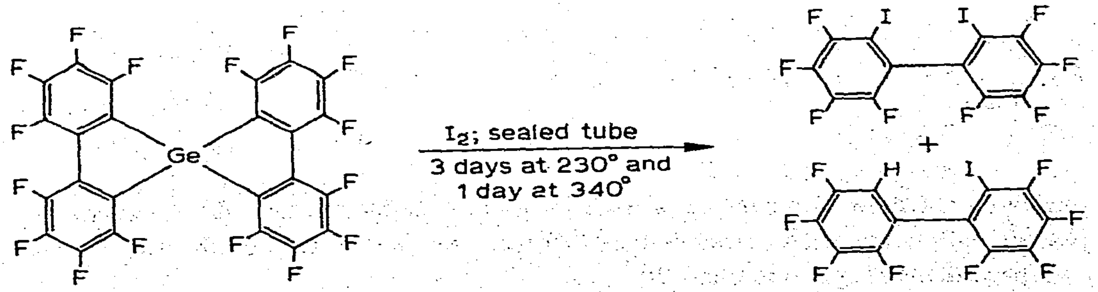


A direct synthesis of the perfluorogermaspiran has also been reported [96]:

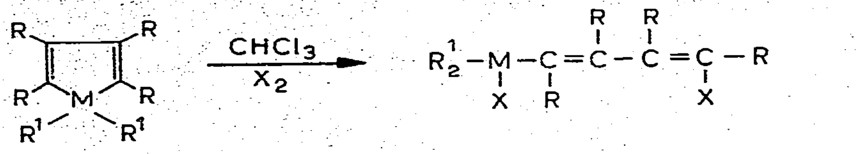


2. *Properties and reactions*

The germacyclopentadienes described above are solids with fairly good thermal stability. Thus bis(octafluoro-2,2'-biphenylyl)germane was recovered almost quantitatively after heating in an evacuated sealed tube for two and a half days at 400° followed by 4 h at 500° when very slight charring was observed [95]. The compound was also slowly cleaved by halogens [95] (partial reaction):

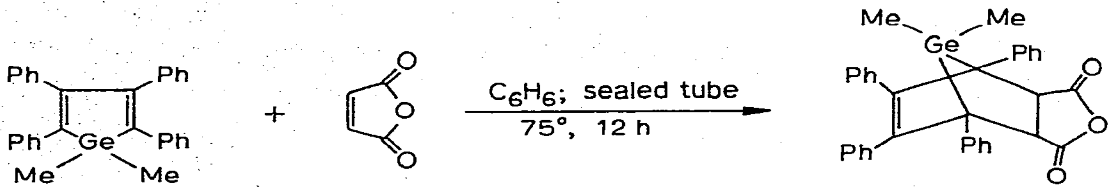


On the other hand, the germacyclopentadienes undergo ring-opening when allowed to react with halogens [97]:

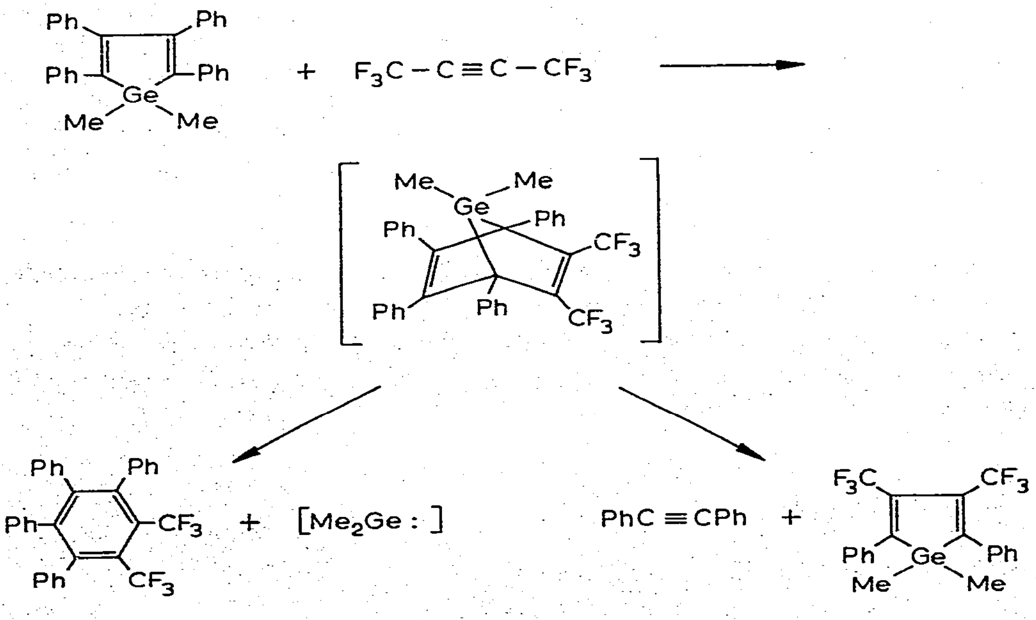


(R and R^1 = alkyl, aryl, cyano etc.; X = Cl Br; M = Ge, Sn, Pb)

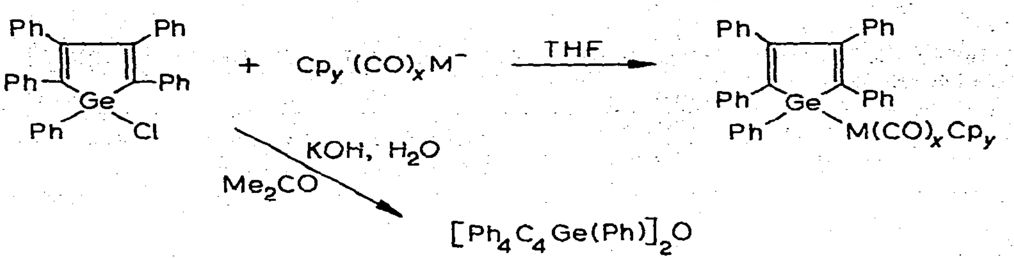
Hota and Willis investigated Diels–Alder type addition reactions of 1,1-dimethyltetraphenylgermacyclopentadiene [98]. The reaction with maleic anhydride gave the expected norbornene adduct:



Attempts to prepare 7-germanorbornadiene adducts by similar addition reactions with acetylenes failed probably because of the instability of the intermediate bicyclic adduct [98]:



Analogous reactions with phenylacetylene [52] and dimethylacetylene dicarboxylate [98, 99] have also been reported. Some other reactions [89] of chloro-substituted germacyclopentadiene are given in Chart 20.

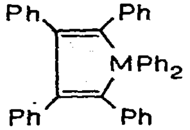


$[M(CO)_xCp_y = Mn(CO)_5;\ Co(CO)_4;\ Fe(CO)_2{-}C_5H_5]$

Chart 20. Some reactions of chloro-substituted germole.

3. *Spectroscopy*

The electrochemical behaviour and ESR results for compounds of the type:



(where M = Si, Ge, Sn) have been reported [100].

Electrochemical reduction showed well-developed reduction curves near −2.6V irrespective of the metal. Partial reduction in all cases gave a radical anion of half-life ~ 1 min.

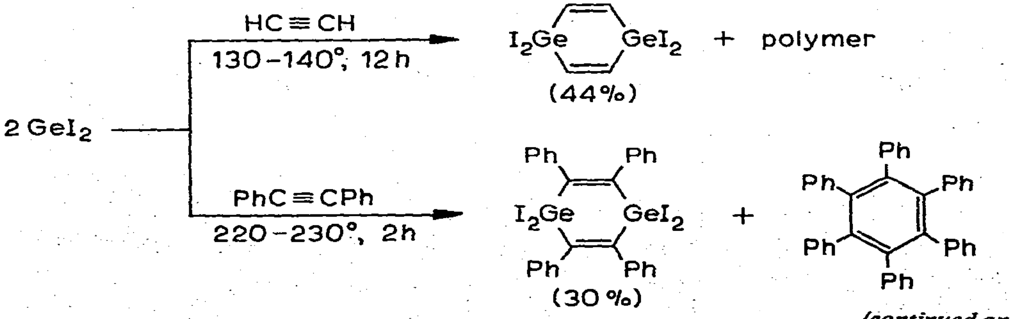
The germacyclohexadienes could be synthesized via the addition of dichlorocarbene to germacyclopentenes [85] (see page 361).

Some properties of germacyclopentadienes and germacyclohexadienes are summarized in Table 17.

H. Digermacyclohexadienes

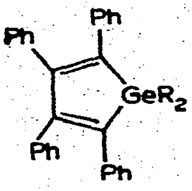
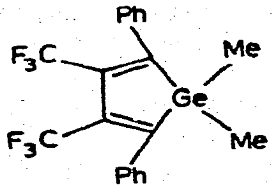
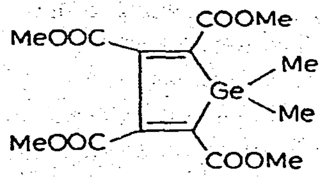
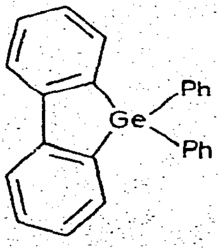
1. *Preparation*

The work of Vol'pin et al. showed that germanium diiodide is capable of adding to the carbon—carbon triple bond [12—15] to form cyclic compounds which were tentatively assigned a three-membered ring structure. Later, the mass spectral investigations by Johnson and Gohlke [16] and X-ray data [67] have shown these compounds to have the structure of unsaturated six-membered heterocycles. The reaction, therefore, of germanium diiodide with acetylene and diphenylacetylene may be pictured as [71]:



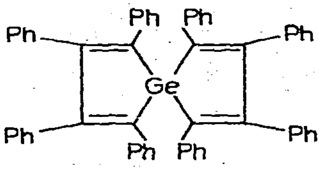
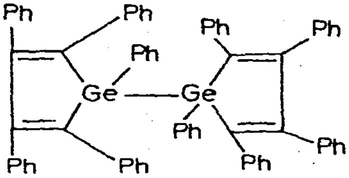
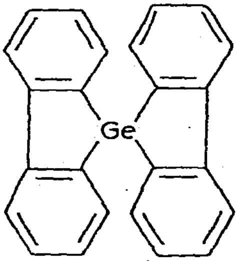
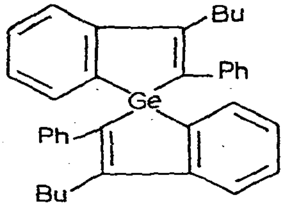
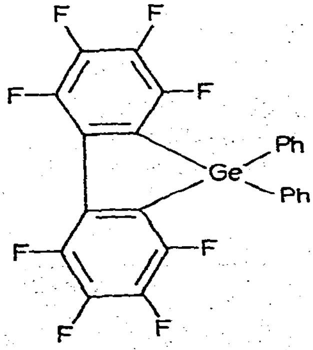
(continued on p. 373)

TABLE 17
PROPERTIES OF GERMACYCLOPENTADIENES, GERMACYCLOHEXADIENES AND GERMACYCLOHEPTADIENES

Compound	R_2	M.p. (°C) or b.p. (°C/mm)	Other data reported	References
	Cl_2	197–199		88,89,97
	H_2	193–195	IR^a	88
	Me_2	179–181	IR, NMR^b mass spectrum	98, 99, 125
	Ph_2	198–199		88,100, 121
	Cl, Ph	210–211		88,89
	H, Ph	187–188	IR^c	88,89
	Me_3Si, Ph	178–180	IR	88,89
	Ph, OH	256–257	IR^d	89
	Ph, $\frac{1}{2}O$	255–257	IR	89
	Ph, $Mn(CO)_5$	144	IR^e	89
	Ph, $Co(CO)_4$	165	IR	89
	Ph, $Fe(CO)_2C_5H_5$	191–193	IR	89
				98
				98
		152–153		91

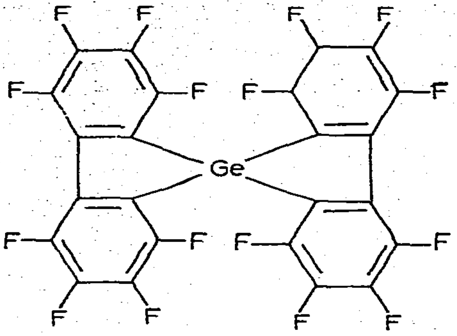
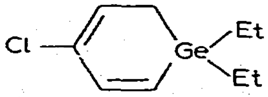
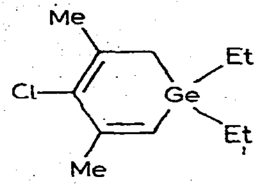
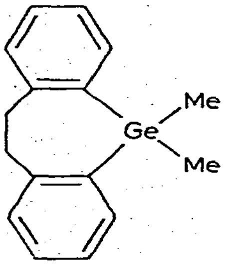
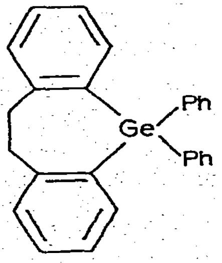
(continued)

TABLE 17 (continued)

Compound	R_2	M.p. (°C) or b.p. (°C/mm)	Other data reported	References
		258–260		86,87,89
		235–236		89
		245–246		90
				92
		139–141	IR	93,94,95

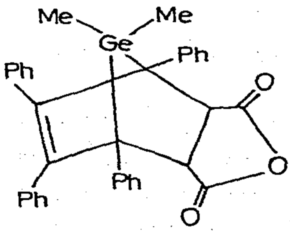
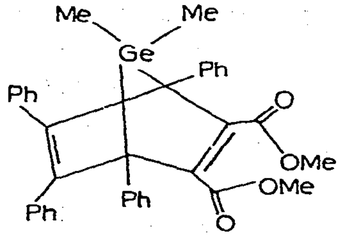
(continued)

TABLE 17 (continued)

Compound	R_2	M.p. (°C) or b.p. (°C/mm)	Other data reported	References
		230.5–232	IR	94,95,96
		76/0.5	IR, NMR	8,85
		100/0.7	IR, NMR, mass spectrum n_D^{20} 1.5211 d_4^{20} 1.1878	8,85
		110–116/0.03	IR, NMR mass spectrum	143
		165–168	IR, NMR mass spectrum	143

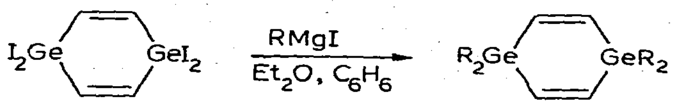
(continued)

TABLE 17 (continued)

Compound	R_2	M.p. (°C) or b.p. (°C/mm)	Other data reported	References
			IR, NMR	98
		100 (dec.)	IR, NMR, mass spectrum	98,99

[a] ν(Ge–H) 2060 cm^{-1}. [b] δ 0.67 (s, Me), 6.9 (m, Ph_4). [c] 2056 cm^{-1}. [d] ν(GeOH) 670 cm^{-1}. [e] ν(CO) 2008, 2014 cm^{-1}.

These could be transformed to the corresponding alkyl or aryl derivatives by reaction with a Grignard reagent:

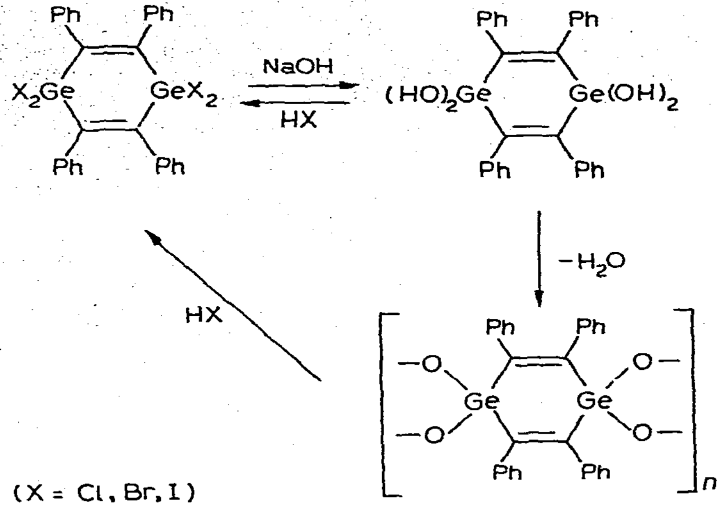


(R = Me, Et, Ph)

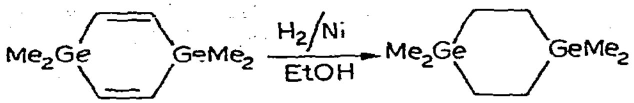
2. *Properties and reactions*

The high thermal stability of these derivatives is apparent from the reaction conditions under which they are synthesized.

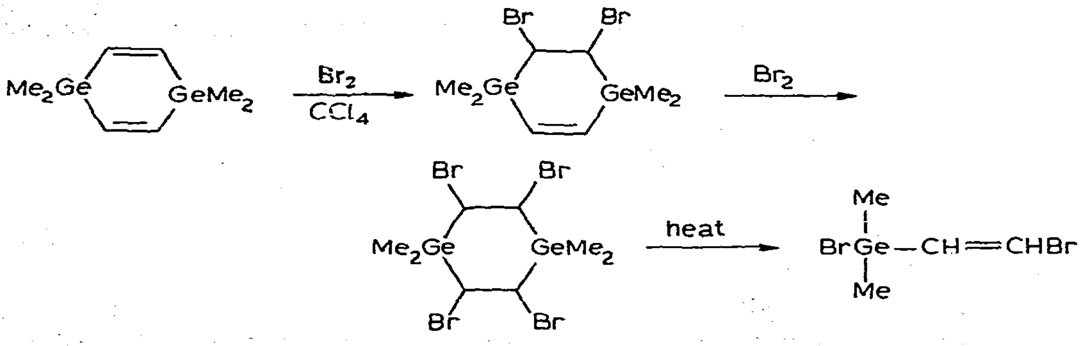
The halogenated derivatives [15] are attacked by sodium hydroxide and the alkyl derivatives could be hydrogenated over Raney nickel [67, 71]:



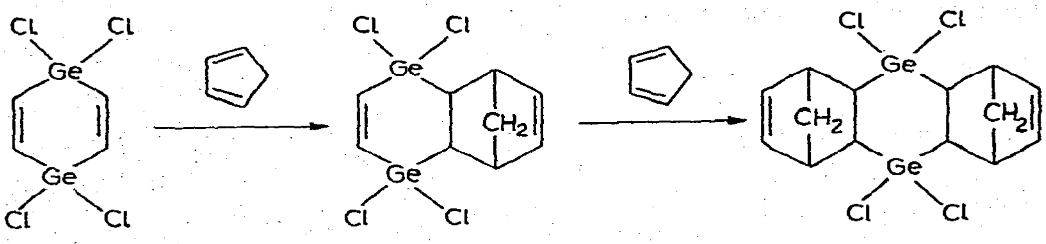
(X = Cl, Br, I)



Bromine adds to the methyl derivative [71] giving dibromide or tetrabromide depending upon the amount used. Both the bromo derivatives undergo β-elimination on heating to form vinyl compounds:

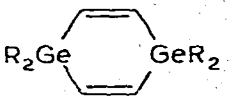


The dichloro derivative has been shown to form adducts with cyclopentadiene [71], whereas the methyl or phenyl derivatives do not add even at 160°:



3. Spectroscopy

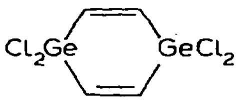
In order to establish the six-membered ring structure of these derivatives (which were tentatively assigned a three-membered ring structure by Vol'pin and coworkers [12, 14]), a number of spectroscopic investigations have been carried out.

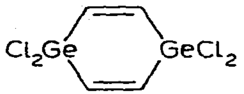
The infrared and Raman spectra of the compounds of the type, 

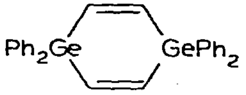
show an absorption band in the 500–600 cm^{-1} region characteristic of the Ge–C bond. In the case of methyl derivative (R = Me) the frequency (535 cm^{-1}) is smaller than in normal methylgermanes (572 cm^{-1} for Me_4Ge). A Raman band for the double bond appears at 1557 for R = Me and at 1550 cm^{-1} for R = Cl [13–15, 19, 71].

The NMR spectrum of the methyl derivative (R = Me) has been shown [13, 71] to consist of two signals with relative areas of 3/1. The chemical shifts of the protons at the double bond have been found to be 6.95, 7.02 and 7.32 ppm for the methyl (R = Me), the iodo (R = I) and the chloro (R = Cl) derivatives respectively.

The mass spectrographic studies of these derivatives [16, 19, 102] proved their six-membered ring structure with the two germanium atoms being in the 1,4-position.

The frequencies and modes of normal vibrations for the compound, 

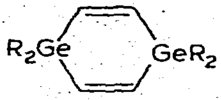
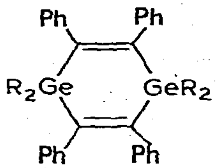
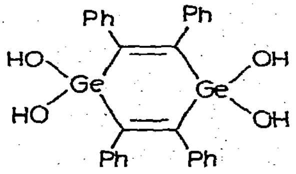
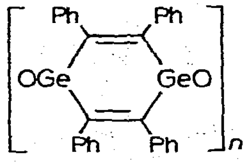
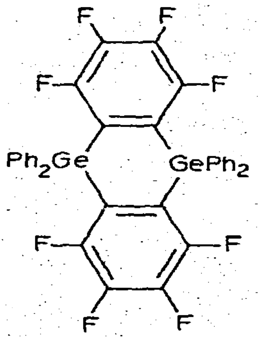
have been calculated. The equilibrium configuration was assumed in which the carbon and germanium atoms form a six-membered planar ring, the C–H bonds lie in the plane, and the $GeCl_2$ planes are perpendicular to this ring [103]. An X-ray investigation gave the bond lengths [67] as: C=C, 1.35; Ge–C, 1.98; Ge–Cl, 2.15Å and the bond angles: C–Ge–C and C–C–Ge about 120°; Cl–Ge–Cl 103°. An electron diffraction study of the molecular structure of 

revealed that the most probable conformation is that of a boat [18]. The crystal structure of 

indicated the six-membered ring to be flat and the configuration at the germanium atoms tetrahedral [104]. Figures 1 and 2 show the structures of 1,1,4,4-tetraiodo- and the 1,1,4,4-tetraphenyl-1,4-digerma-2,5-cyclohexadienes.

Some properties of various digermacyclohexadienes are given in Table 18.

TABLE 18
PROPERTIES OF DIGERMACYCLOHEXADIENES

Compound	R_2	M.p. (°C) or b.p. (°C/mm)	Other data reported	References
	Cl_2	145–146	IR, Raman, NMR, X-Ray, mass spectrum	13,18,67,71,102,103,105
	I_2	225–226	IR, Raman, NMR, mass spectrum, X-Ray	13,18,19,67,71
	Me_2	67/14	IR, Raman, mass spectrum, NMR, UV	13,18,19,71
	Ph_2	149–150	IR, mass spectrum, X-Ray	71,104
	Cl_2	290–292	IR	15
	Br_2	317–318	IR	15
	I_2	301–303	IR, mass spectrum	12,15,19
	Me_2	295	IR, mass spectrum	15,19
	Et_2	239–240	IR, mass spectrum	15,19
			IR	15
				15
		278.5–282.5		101

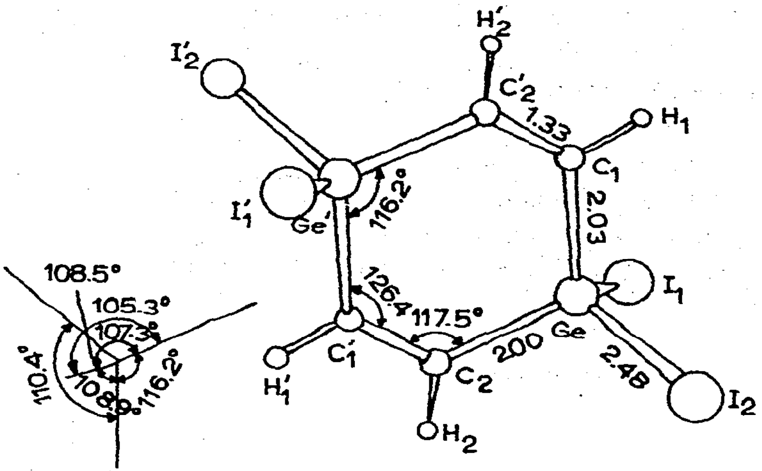


Fig. 1. The structure of 1,1,4,4-tetraiodo-1,4-digerma-2,5-cyclohexadiene

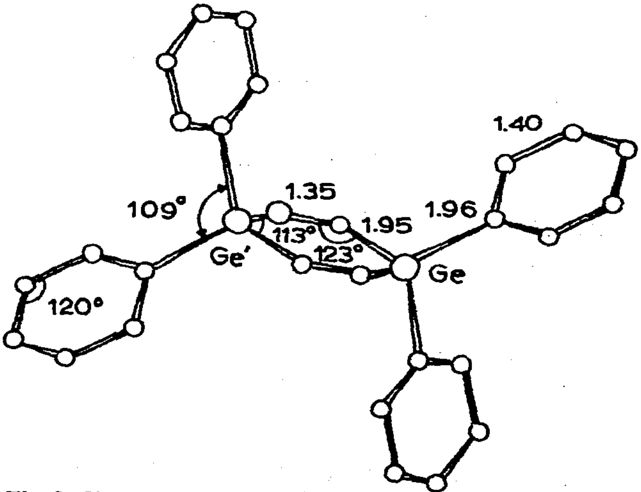
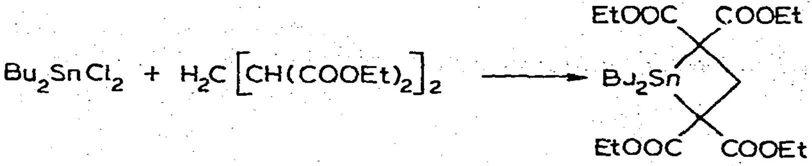


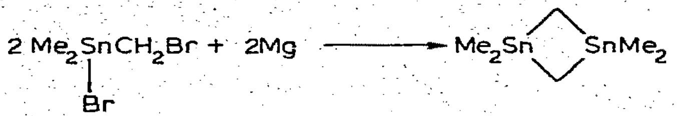
Fig. 2. The structure of 1,1,4,4-tetraphenyl-1,4-digerma-2,5-cyclohexadiene. (Figs. 1 and 2 are reproduced from ref. 71.)

III. Cycloalkanes containing heterocyclic tin

The synthesis of a stannacyclobutane derivative has been patented [106]. The enhanced reactivity of the hydrogen atoms on a carbon attached to electron-withdrawing groups has been utilized in the synthesis:



Also an attempt to synthesize 1,1,3,3-tetramethyl-1,3-distannacyclobutane according to the reaction:



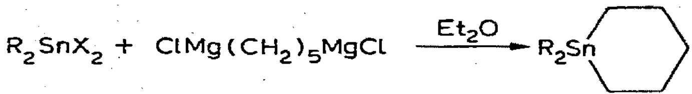
yielded just enough material for an infrared spectrum [107] which was quite similar to that of the corresponding silicon and germanium analogues.

But in general, it is the chemistry of five- and six-membered stannacyclanes which has received much attention.

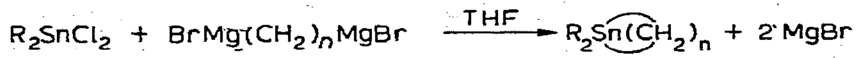
A. Stannacyclopentanes and stannacyclohexanes

1. Preparation

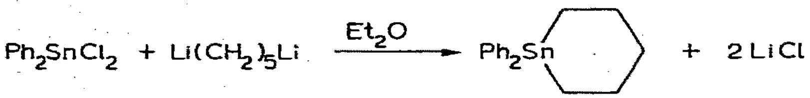
The reactions between diorganotin dihalides and di-Grignard [108, 110] or dilithio [43, 111] reagents have been successfully used for the synthesis of these derivatives:



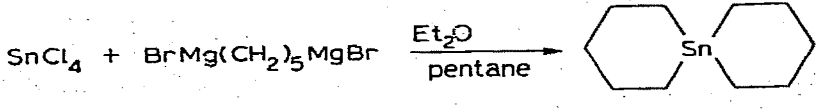
(R = Me, Et; X = Br, I)



$n = 4$, R = Bu, neo-C_5H_{11}; yield 52%
$n = 5$, R = Bu, neo-C_5H_{11}, Ph; yield 27-34%
$n = 6$, R = Me, Et, Ph, neo-C_5H_{11}; yield 10-25%

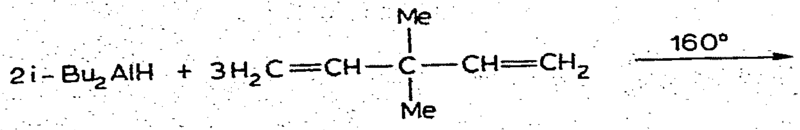


Analogously, using tin tetrachloride the spirocyclic derivatives could be obtained [64, 109]:

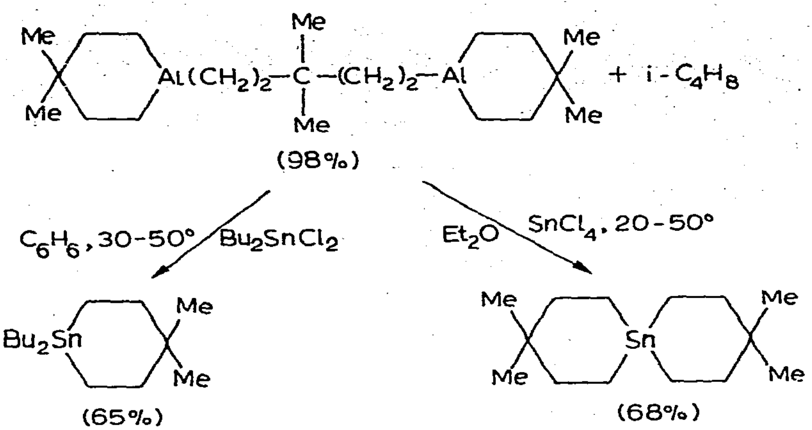


(10-15%)

Polster [112–114] reported the synthesis of a six-membered aluminium heterocycle which on treatment with tin halides gave stannacyclohexanes in high yields:



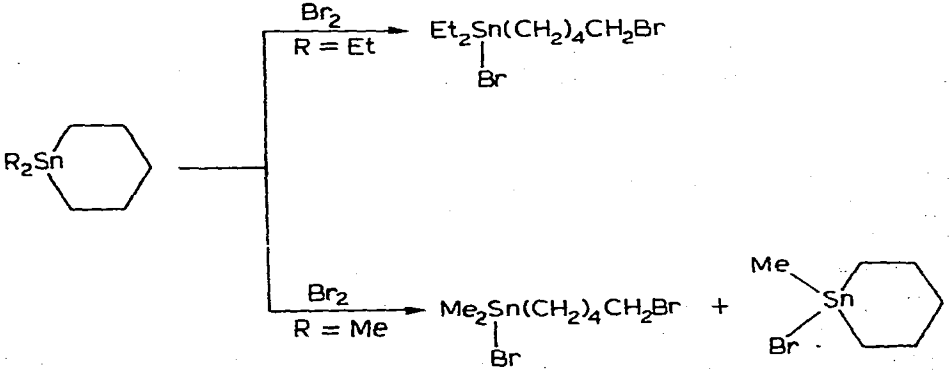
$$2\,i\text{-}Bu_2AlH + 3\,H_2C{=}CH{-}\overset{\displaystyle Me}{\underset{\displaystyle Me}{C}}{-}CH{=}CH_2 \xrightarrow{160^\circ}$$



2. *Properties and reactions*

The 1,1-dimethyl and 1,1-diethyl derivatives of stannacyclohexane are thermally stable and could be distilled in vacuo without decomposition. The unusually (for tetraorganotins) high refractive indices indicate the ring system of these compounds to be strained probably due to the large covalent radius of tin. The atmospheric oxidation of these ring compounds is also unusual for saturated tetraorganotins.

The action of bromine on these stannacyclohexanes proceeds via ring-opening although some tin—methyl bond cleavage is observed in the case of 1,1-dimethyl-1-stannacyclohexane [108]:



The facile reactivity of stannacyclohexanes led Bajer and Post [43, 64] to a detailed study of the reactions of 1,1-diphenylstannacyclohexane. Various reactions are given in Chart 21. Analogous reactions of the spirocyclic derivatives proceed via the rupture of both the rings [64, 112, 115, 116].

Although the halogen derivatives obtained (see Chart 21) provide a convenient route to a large number of 1-substituted stannacyclohexanes, this possibility does not appear to have been much explored.

In general the five- and six-membered cyclic compounds of silicon and germanium are more stable than those of tin.

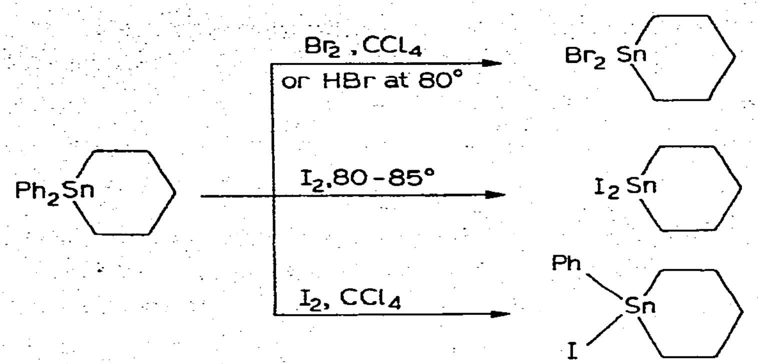
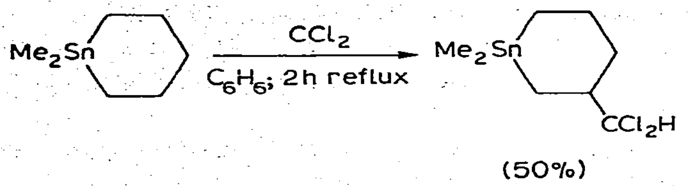
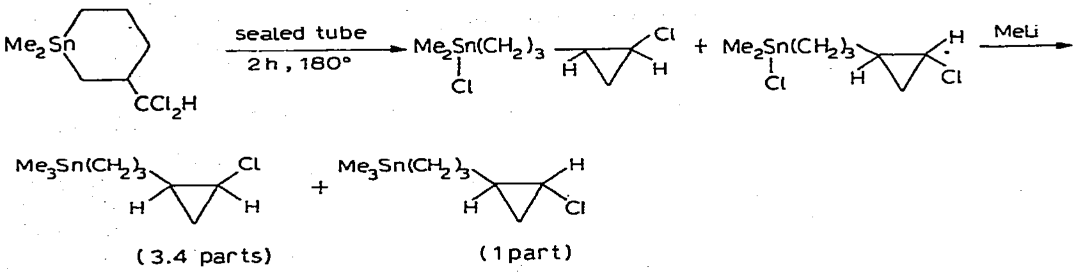


Chart 21. Some reactions of 1,1-diphenyl-1-stannacyclohexane.

Like the corresponding germacyclohexane, 1,1-dimethyl-1-stannacyclohexane has been shown [58, 117] to react with dichlorocarbene (derived from $PhHgCCl_2Br$):



On pyrolysis, the insertion product gives stannyl-substituted chlorocyclopropane:



3. Spectroscopy

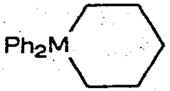
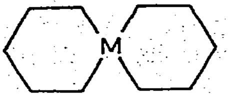
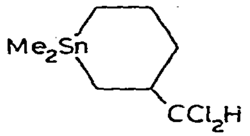
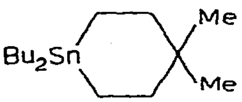
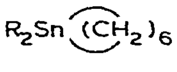
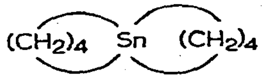
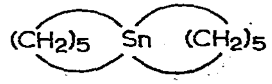
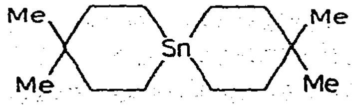
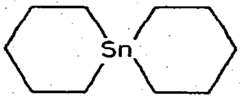
Infrared study of the six-membered heterocyclic system:  (where M = C,Si, Ge,Sn,Pb) has been reported by Bajer and Post [43] (see under germacyclohexanes and Table 6). The spirocyclic derivatives of the type:  (where M = Si,Ge,Sn) show a characteristic infrared band pattern consisting particularly of two strong absorption bands with maxima centered at 990 and 910 cm^{-1}. While the latter band is relatively in-

TABLE 19

PROPERTIES OF STANNACYCLOPENTANE AND STANNACYCLOHEXANE DERIVATIVES

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	Other data reported	References
 $R_2Sn(CH_2)_4$	Bu_2	55/0.04		110
	(neo-$C_5H_{11})_2$	61/0.32		110
 $R_2Sn(CH_2)_5$	Me_2	64/16		108
	Et_2	95/14		108
	Bu_2	87–88/0.4		110
	(neo-$C_5H_{11})_2$	73–73.5/0.08		110
	Ph_2	138–140/0.01 143/0.32	IR	43,110
	Ph, I	219/0.45–0.85	IR	43
	Br_2	166/0.4–0.45	IR	43
1,10-phenanthroline complex		218–220		64
2,2-bipyridyl complex		207–210		64
			n_D^{25} 1.5330	58,117
		71–77/0.0001	n_D^{20} 1.4948	112
 $R_2Sn(CH_2)_6$	Me_2	68/4.6		110
	Et_2	61–63/0.6		110
	(neo-$C_5H_{11})_2$	99.5/0.24		110
	Ph_2	140/0.07		110
		108–110/30	IR, mass spectrum	109
		119–120/10	n_D^{25} 1.5362, IR	64
		75–82/0.0001	n_D^{20} 1.5182	112,113,114, 116

varient (±5 cm^{-1}), the absorption band at 990 cm^{-1} shows both an increased intensity and a shift to a lower frequency of approximately 20 cm^{-1} most noticeable for the tin-containing heterocycle [64].

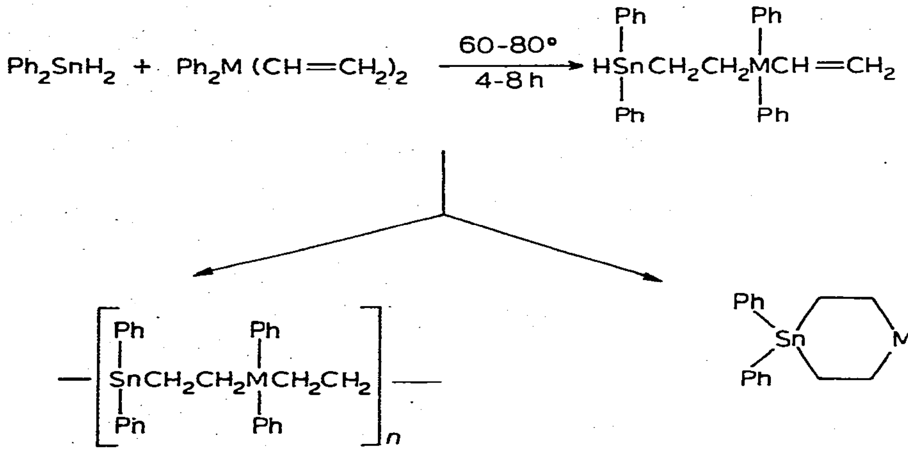
The mass spectrum (under high resolution at 70 eV) of  contained SnH^+ as the only tin hydride ion present in appreciable abundance [109].

Some properties of stannacyclopentanes and stannacyclohexanes are summarized in Table 19.

B. Silastannacyclohexanes and Germastannacyclohexanes

1. Preparation

The hydrostannation of suitable vinyl compounds has been used to synthesize silastanna- and germastannacyclohexanes [68, 118]:



(M = Si, yield 23%; M = Ge, yield 17%)

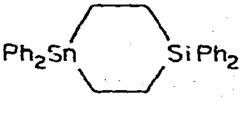
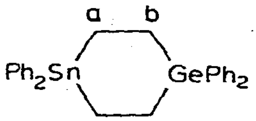
In the above reaction when M = Sn, only low-melting products and insoluble materials were obtained. The analogous lead compound could not be isolated, the reaction resulting in the formation of metallic lead.

2. Properties and spectroscopy

Both the stannacyclohexane derivatives are crystalline solids. These formed 1/1 complexes when recrystallized from cyclic solvents e.g. benzene, toluene, pyridine or dioxane. These weak complexes readily decompose on heating, show the melting point of the parent heterocycle and give the parent heterocycle upon attempted recrystallization from ethanol [68]. Infrared [68] and NMR [119] data for these heterocycles are given in Table 20.

TABLE 20

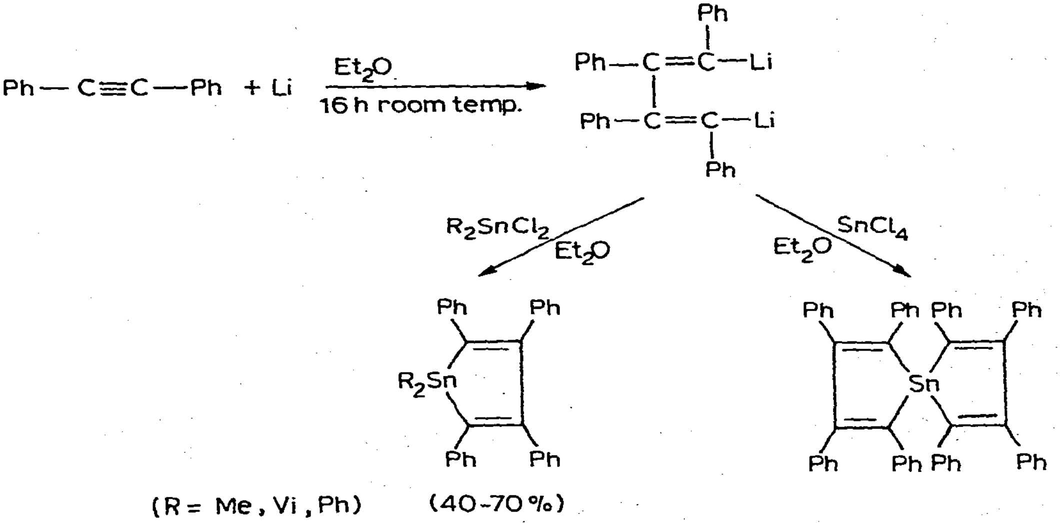
PROPERTIES AND SPECTROSCOPIC DATA OF SILASTANNA- AND GERMASTANNACYCLOHEXANE

Compound	M.p.	ν (cm^{-1})	δ	References
	134–135	Ph–Si 1100 Ph–Sn 1065 CH_2 2860 (doublet)	1.63 (s, CH_2)	68,118,119
	124–125	Ph–Ge 1080 Ph–Sn 1065 CH_2 2860 (doublet)	1.71 (m, CH_2(a)); 1.83 (m, CH_2(b))	68,118,119

C. Stannacyclopentadienes and related derivatives

1. Preparation

The synthesis of stannacyclopentadiene derivatives [86, 87, 120–123] has been achieved via the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (prepared by the dimerization of diphenylacetylene with lithium) with appropriate diorganotin dihalides:



The presence of the dilithio derivative in the *cis,cis*-form seems to be the favourable preferred conformation required for ring closure and thus the success of the synthesis. It is essential that the lithio derivative be added to the halide, as Zavistoski and Zuckerman have shown that the reverse addition leads to alkyl–tin bond cleavage thus giving the spirocyclic derivative [124, 125]:

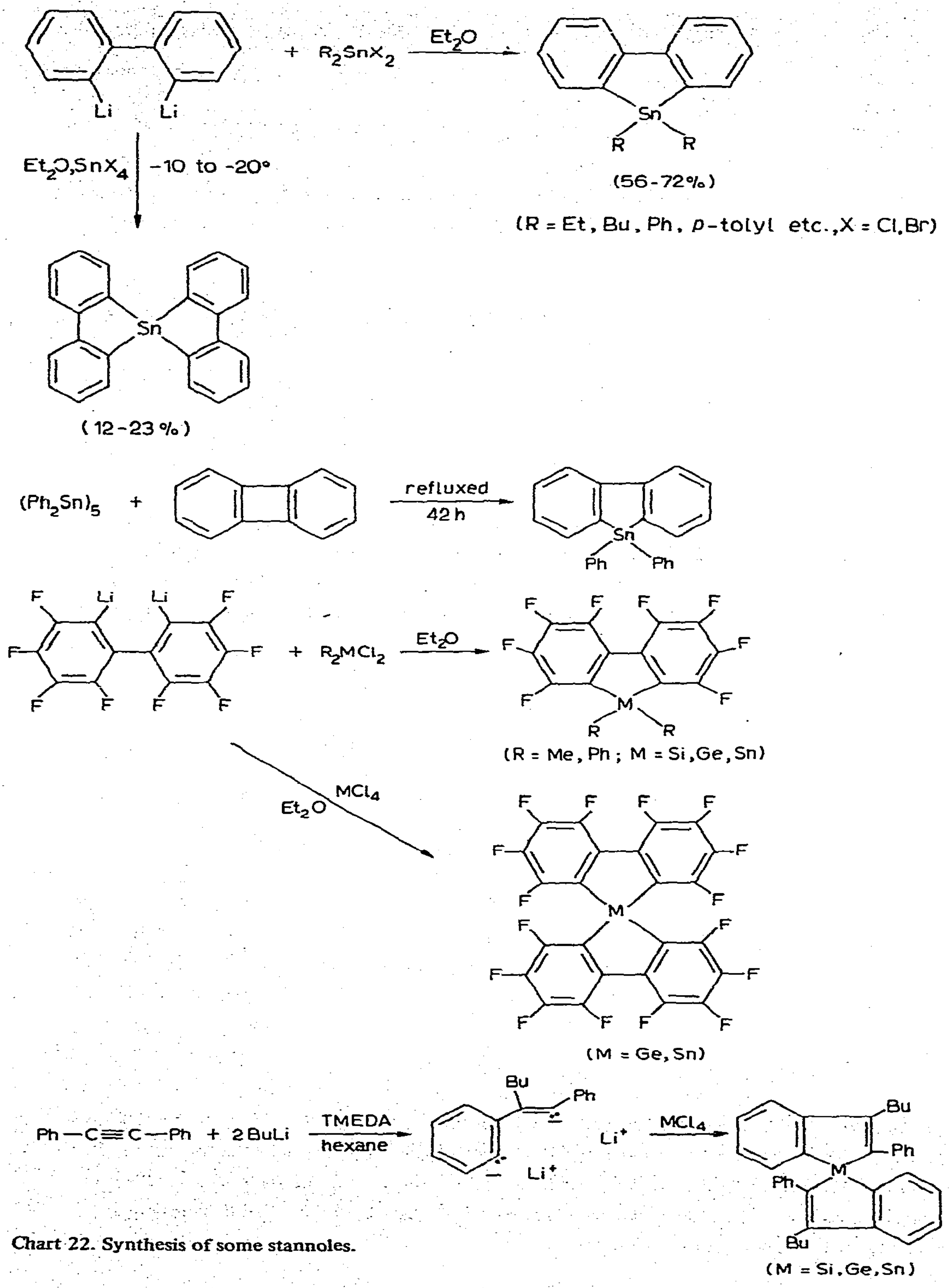
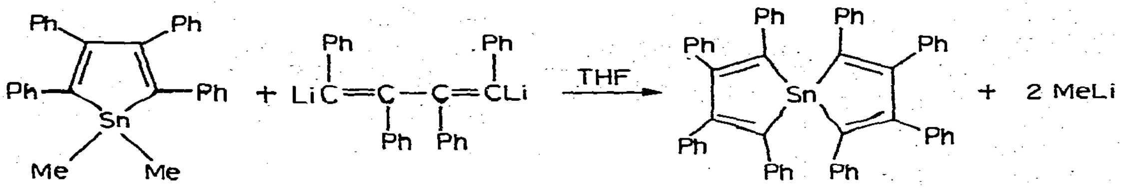


Chart 22. Synthesis of some stannoles.



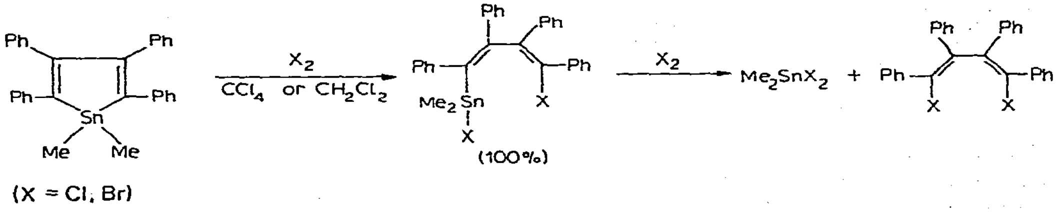
The lability series is R = ethyl, methyl > vinyl > phenyl.

A number of dibenzostannoles [126–128], corresponding fluorinated derivatives [95, 96] and stanna-indene systems [92] have been synthesized. The synthetic routes are compiled in Chart 22.

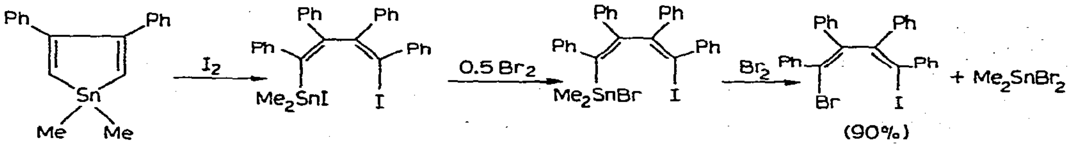
2. *Properties and reactions*

These compounds are well defined colourless crystalline solids of high melting point. Only the hexaphenylstannole is faintly green and fluoresces when solid [123].

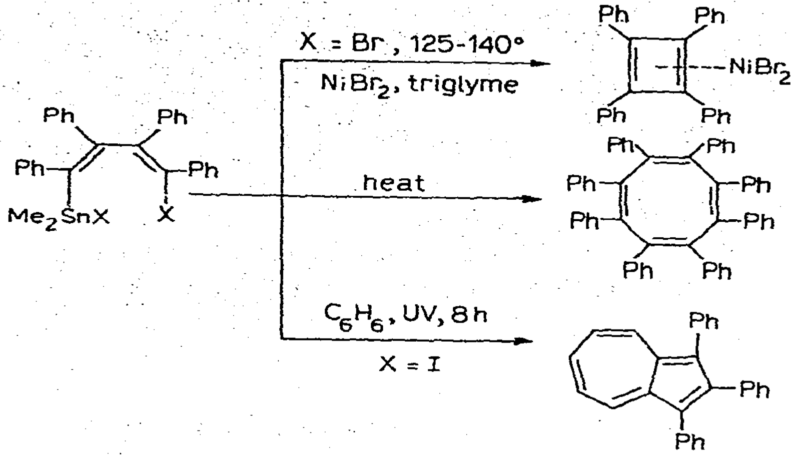
A detailed study of the behaviour of 1,1-dimethyl-2,3,4,5-tetraphenylstannole towards electrophiles, particularly halogens revealed that the cleavage occurs preferentially at the olefin carbon–tin bond and not at methyl–tin bond [97, 129, 130]:



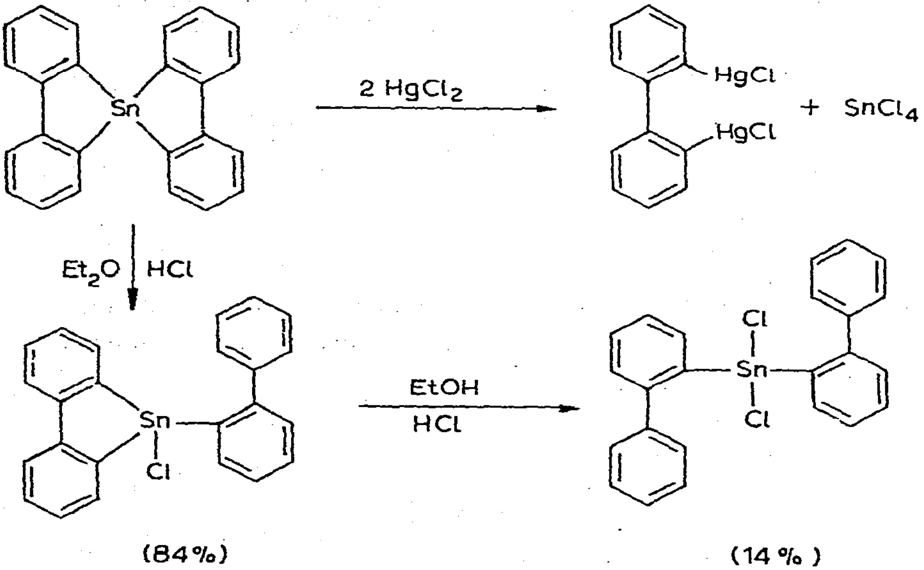
With the weaker electrophile, iodine, further reaction of the stannyl dihalides does not occur up to temperatures of 100° and hence mixed halobutadienes could be synthesized according to the reaction scheme [130]:



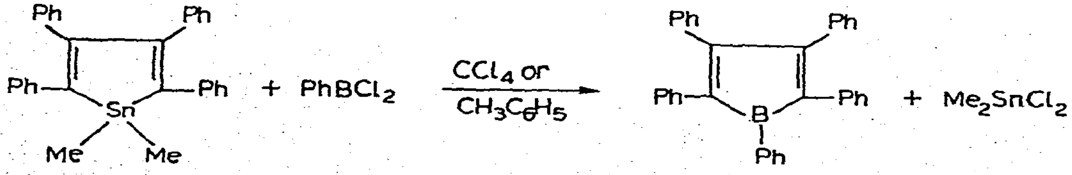
The stannyl derivatives have been found to undergo a variety of reactions leading to some remarkable syntheses [129–133]:



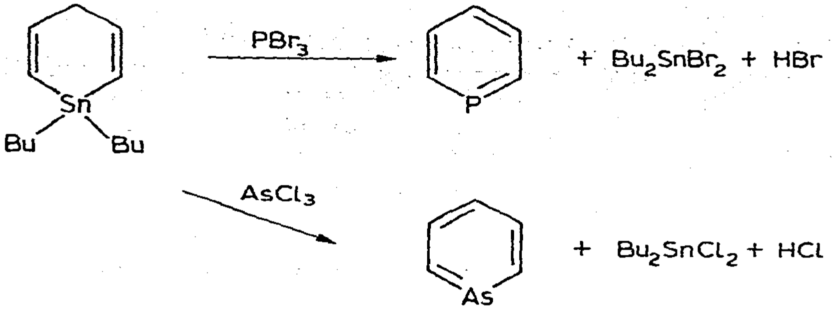
Some reactions of spirobistannole are given below [126]:



Eisch et al. [134] observed the reaction between 1,1-dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene and phenylboron dichloride to proceed via metal–metal exchange:

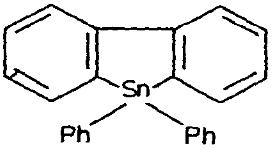


Analogously the reaction of a stannacyclohexadiene derivative [144, 145] with phosphorus or arsenic trihalide has been used to synthesize phosphabenzene or arsabenzene:



3. *Spectroscopy*

The ESR spectrum of the radical anion of 1,1-diphenyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene showed one main line with two satellites due to hyperfine interaction with ^{117,119}Sn species [100].



(I)

The mass spectrum of I showed relatively strong peaks at the positions and with the isotopic distribution expected for (I minus H)$^+$ and (I minus Ph)$^+$; other peaks indicated the presence of $Ph_6Sn_2^+$ and higher molecular weight diphenyltin polymers [128].

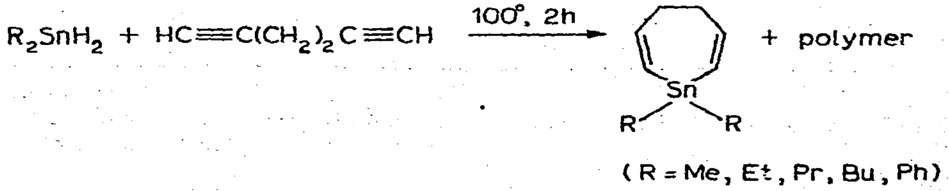
Some properties of these compounds are summarized in Table 21.

D. *Miscellaneous stannacyclanes*

Kuivila and Beumel synthesized several heterocycles containing tin in the seven-membered ring [135, 136]. The synthetic routes are given in Chart 23.

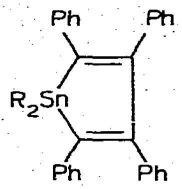
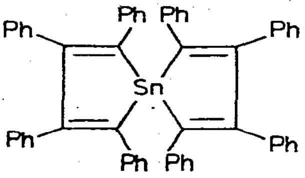
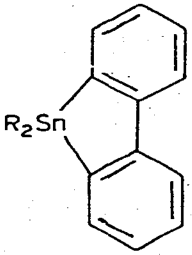
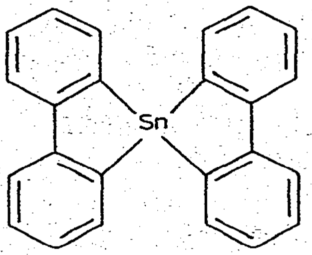
A recent publication [143] claims to have obtained satisfactory yields of stannepins by the direct reaction of the organotin halide with 2,2′-dilithiobibenzyl. Bromination of dimethylstannepin with *N*-bromosuccinimide resulted in the ring cleavage and the formation of 2,2′-dibromobibenzyl [143].

In the polyaddition of diorganotin dihydrides to 1,5-hexadiynes, 1,1-disubstituted stanna-2,6-cycloheptadienes were obtained as by-products (12–28%) [137]:



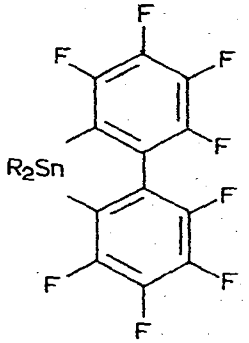
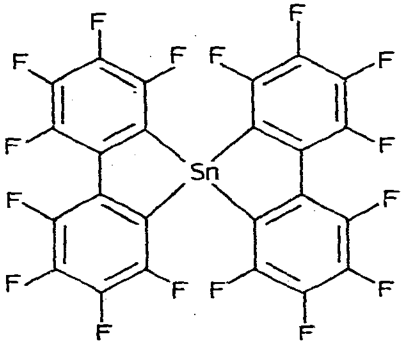
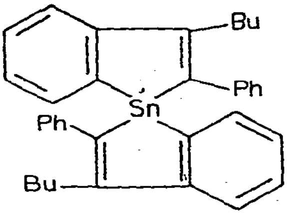
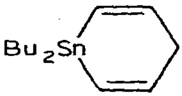
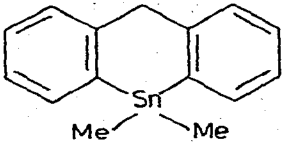
(continued on p. 390)

TABLE 21
PROPERTIES OF STANNACYCLOPENTADIENES AND RELATED DERIVATIVES

Compound	R$_2$	M.p. (°C)	Other data reported	References
	Me$_2$	192–193	ESR, Mössbauer[a]	87,97,100, 125,129–132, 134
	(CH$_2$=CH)$_2$	158–159	Mössbauer[b], IR, mass spectrum	87,125
	Ph$_2$	173–174	Mössbauer[c], ESR	87,97,100, 123,125
		281–282	Mössbauer[d]	87,120,123, 125
	Et$_2$	73	UV, IR	126
	Bu$_2$	56	IR	126
	(cyclo-C$_6$H$_{11}$)$_2$	104	IR	126
	Ph$_2$	141.5	IR, UV, mass spectrum, Mössbauer[e]	126,127,128
	(p-MeC$_6$H$_4$)$_2$	108	IR	126
	(o-PhC$_6$H$_4$)$_2$	196–196.5	IR	126
				126

(continued)

TABLE 21 (continued)

Compound	R_2	M.p. (°C)	Other data reported	References
	Me_2			95
	Ph_2	131–133	IR	95
		227–229	IR	95,96
		141.8–142.5	NMR	92
				144, 145
		64		142

[a] 119m Sn Mössbauer isomer shift (mm·sec^{-1}) with respect to SnO_2 at 77 K 1.23 ± 0.06. [b] 1.25 ± 0.06. [c] 1.19 ± 0.06. [d] 1.30 ± 0.06. [e] 1.20 ± 0.06.

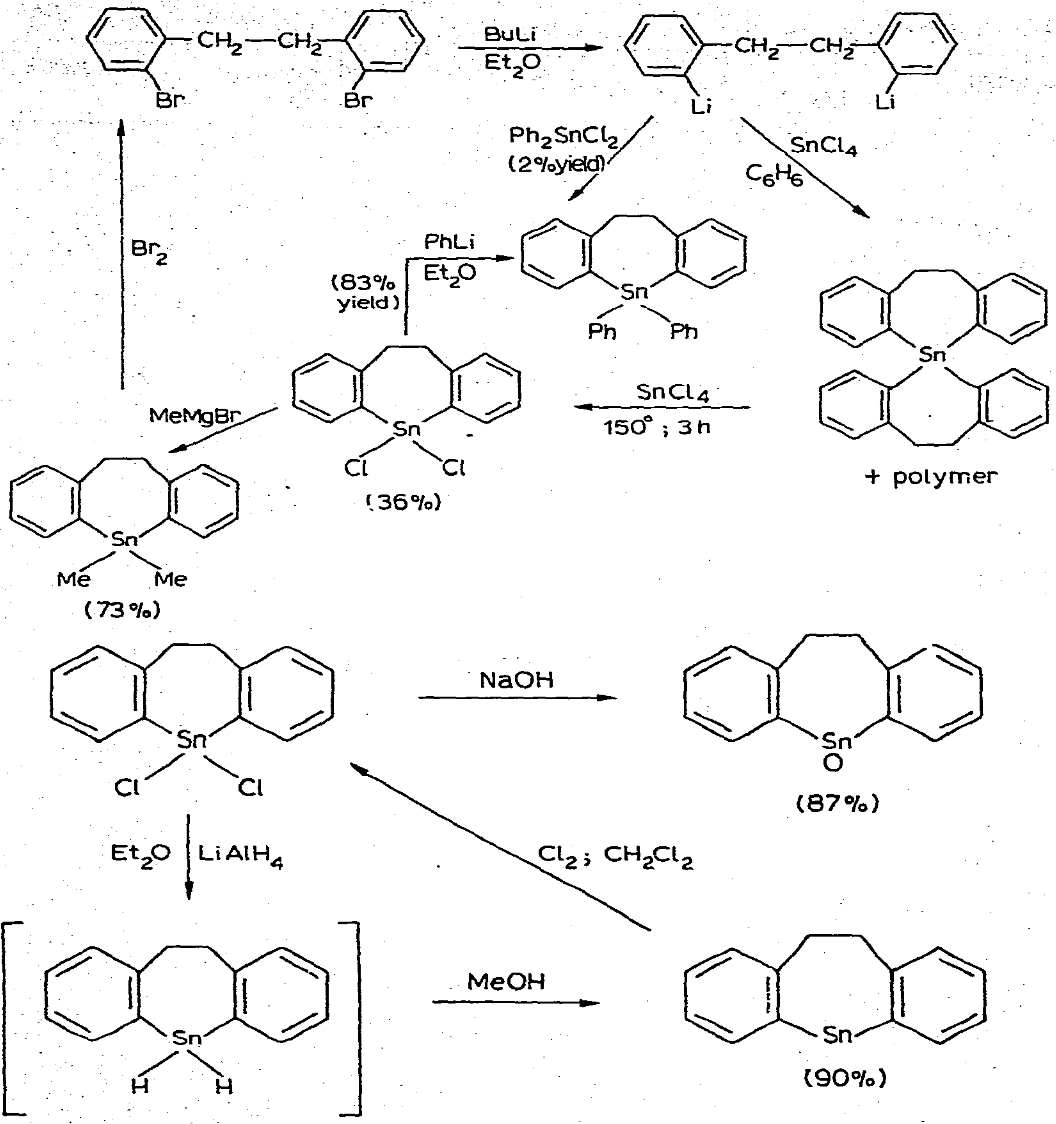
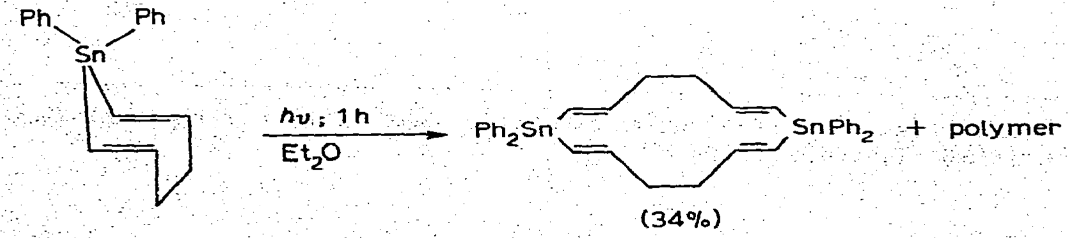


Chart 23. Synthesis of some seven-membered tin-heterocycles.

Photolysis of 1,1-diphenyl-1-stanna-2,6-cycloheptadiene resulted in the ring-expansion yielding a distannacyclotetradecatetraene [138]:



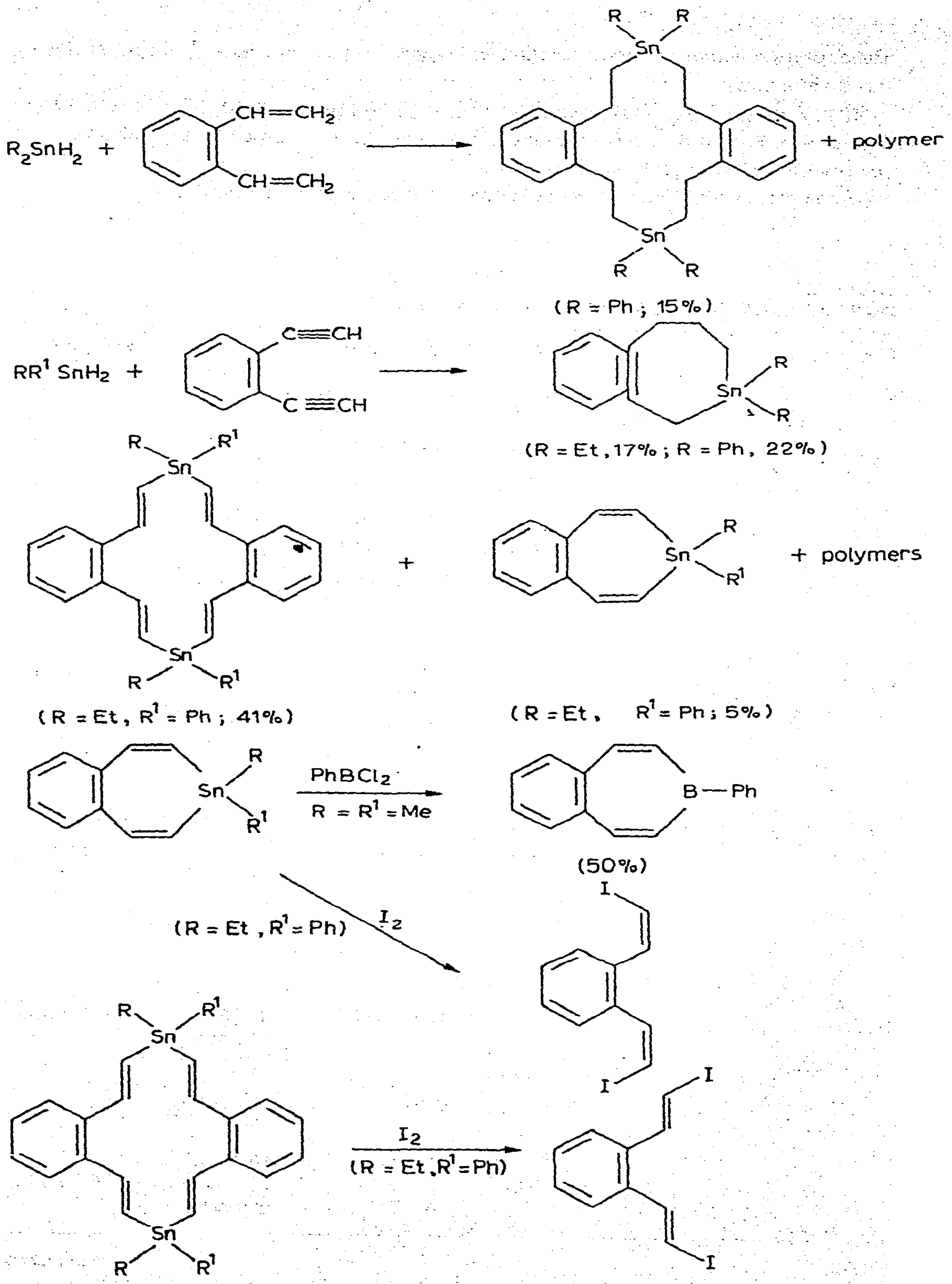


Chart 24. Synthesis and reactions of some seven- and fourteen-membered tin-containing heterocycles.

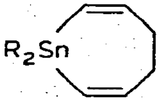
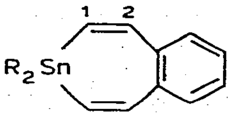
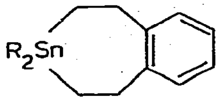
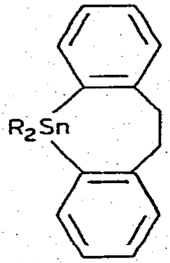
The authors conclude the photoreaction to involve a radical process with fission of the tin–carbon bond.

The syntheses [139, 140], reactions [140, 141] and spectra [140, 141] of seven- and fourteen-membered tin-containing heterocycles have been described by Leusink and coworkers. These are given in Chart 24.

Some properties of miscellaneous stannacyclanes are given in Table 22.

TABLE 22

PROPERTIES OF MISCELLANEOUS STANNACYCLANES

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	Other data reported	References
	Me$_2$	30–32/0.2	n_D^{20} 1.5280	137
	Et$_2$	74–76/5.0	n_D^{20} 1.5308	137
	Pr$_2$	64–65/0.02	n_D^{20} 1.5213	137
	Bu$_2$	90–92/0.08	n_D^{20} 1.5174	137
	Ph$_2$	147–150/0.3	n_D^{20} 1.6226	137,138
	Me$_2$	88–90/0.4 41–42	IR, NMR[a]	139,140,141
	Et$_2$	95–96/0.4	IR, NMR	139,140
	Et, Ph			139,140
	Et$_2$	93–98/0.08	IR, NMR	139,140
	Ph$_2$	98–100		139,140
	Me$_2$	109–120/0.02 130–135/0.2	IR, NMR[b], UV, mass spectrum[d] n_D^{25} 1.6130	135,136,143
	Ph$_2$	138–141 146–147	IR, NMR[c], UV, mass spectrum[e]	135,136,143

(continued)

TABLE 22 (continued)

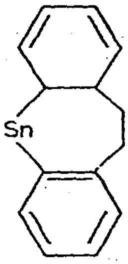
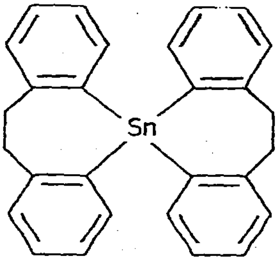
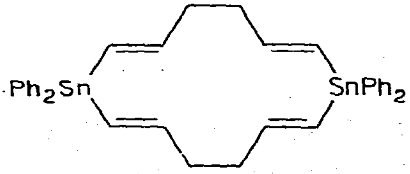
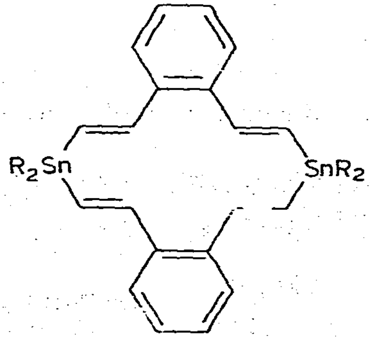
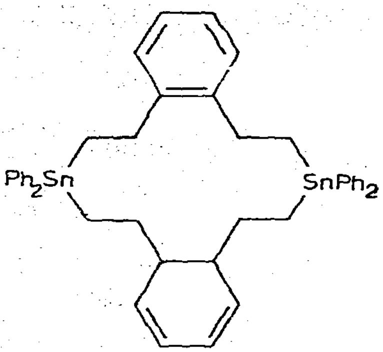
Compound	R_2	B.p. (°C/mm) or m.p. (°C)	Other data reported	References
	Cl_2	106–106.5	UV	135,136
	O			135
	S	274–275		135
				135
				135
		145–146		138
	Ph_2	282–285		139,140
	Et, Ph	184–186		139,140

TABLE 22 (continued)

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	Other data reported	References
		277–282		139,140

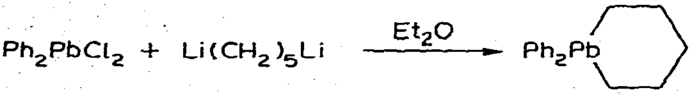
^{a} δ (in CCl_4) 6.32 (H(1)), 7.50 (H(2)), J 14 Hz. ^{b} 7.6–6.8 (m, Ar), 3.1 (s, CH_2), 0.5 (s, Me). ^{c} 7.7–6.9 (m, Ar), 3.17 (s, CH_2). ^{d} Metal-containing fragments: $C_{16}H_{18}Sn^+$, $C_{15}H_{15}Sn^+$, $C_{15}H_{13}Sn^+$, $C_{14}H_{11}Sn^+$, $C_6H_5Sn^+$, etc. ^{e} $C_{26}H_{22}Sn^+$, $C_{20}H_{17}Sn^+$, $C_{14}H_{11}Sn^+$, $C_{14}H_{10}Sn^+$, $C_{12}H_{10}Sn^+$, $C_6H_5Sn^+$, etc.

IV. Cycloalkanes containing heterocyclic lead

The work on the preparation and reactions of compounds with lead in the ring system is very limited. Thus the total number of references is less than twenty, although, 1,1-diethyl-1-plumbacyclohexane was prepared as early as 1916.

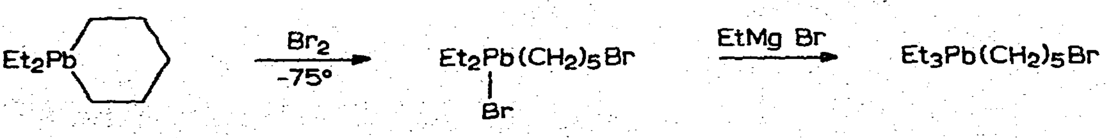
Grüttner and Krause [146] reported the synthesis of 1,1-diethyl-1-plumbacyclohexane according to the reaction:

The analogous diphenylplumbacyclohexane has been prepared by Bajer and Post via the reaction [43]:

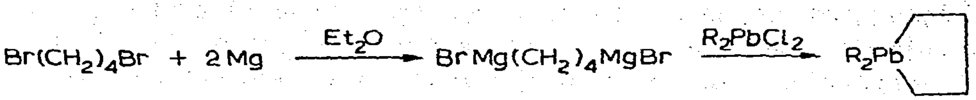


The compound proved to be quite sensitive to light and air, forming a coloured resinous solid.

The diethyl compound was slowly oxidized by air, giving a brown oxygen-containing resin. The cyclohexane ring was cleaved by bromine [146, 147]:

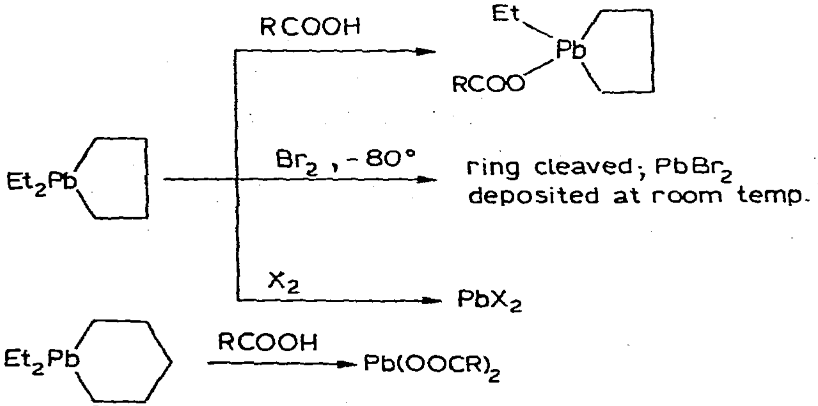


Using the method of Grüttner and Krause, the synthesis of some plumbacyclopentanes has been accomplished [147]:



(R = Et, 70%; R = Ph)

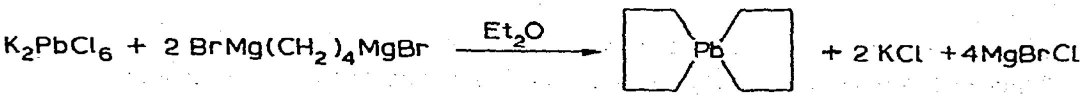
Like 1,1-diethyl-1-plumbacyclohexane, the authors observed a similar ring cleavage of 1,1-diethyl-1-plumbacyclopentane by halogens. However, the reaction with carboxylic acids proceeded without ring-fission in the case of plumbacyclopentane contrary to plumbacyclohexane in which case the ring was ruptured. Various reactions are summarized in Chart 25.



(X = Cl, Br; R = Me, ClCH₂)

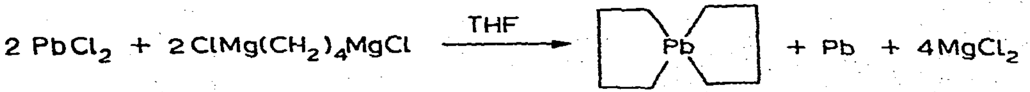
Chart 25. Some reactions of plumbacyclanes.

Potassium hexachloroplumbate [150, 151] has been used as an excellent starting material for the synthesis of organolead compounds. Juenge and Jack accomplished [148] the synthesis of 5-plumbaspiro[4,4]nonane by reaction of tetramethylenedimagnesium dibromide with potassium hexachloroplumbate in diethyl ether:



(~9%)

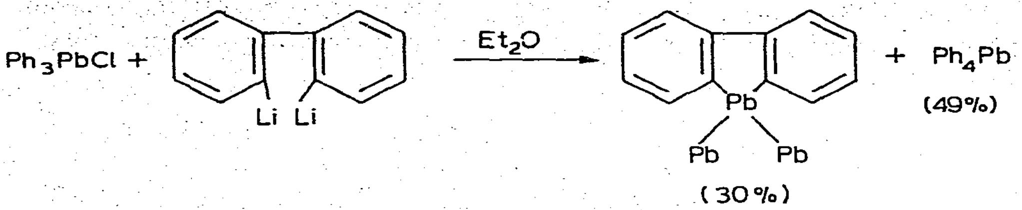
However, Williams [149] claims to have obtained the spirocyclic compound in much better yield by using lead dichloride as the starting material:



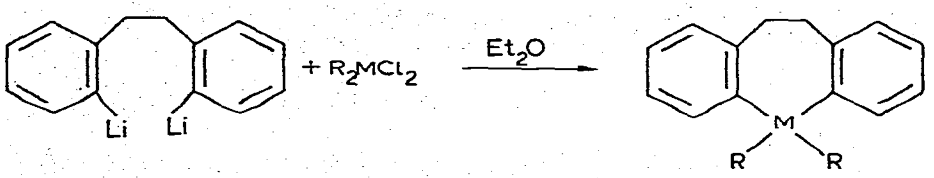
(65%)

The attempt to synthesize 6-plumbaspiro[5,5]undecane via the reaction between potassium hexachloroplumbate and pentamethylenedimagnesium dibromide has been shown to give 1,1-dipentylplumbacyclohexane, probably by incomplete ring closure [148]. The 5-plumbaspiro[4,4]nonane can be polymerized by heating at 120° for several hours, or by storage at 0° for several months, or by refluxing in benzene with benzoyl peroxide. The plumbacyclo-pentane and -hexane did not polymerize under the conditions described above [148].

More stable compounds have resulted from the presence of benzo groups in the molecule. Gelius prepared 9,9-diphenyldibenzoplumbole according to the reaction [127]:

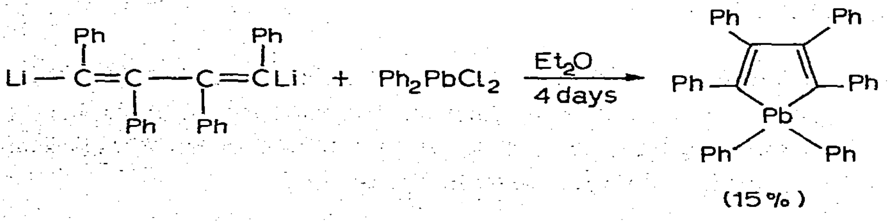


Seven-membered ring systems have been synthesized analogously [143]:



(R = Me, Ph; M = Si, Ge, Sn, Pb)

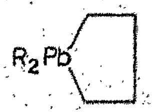
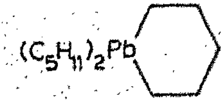
Finally hexaphenylplumbole has been synthesized [97, 125] according to the reaction:



Some properties of various plumbacyclanes are summarized in Table 23.

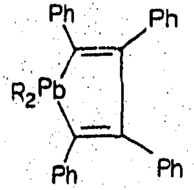
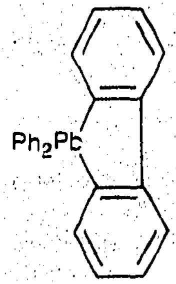
Thus, in conclusion, cycloalkanes containing heterocyclic germanium, tin and lead constitute an interesting class of organometallic compounds. More kinetic work regarding various reactions of these compounds, more detailed spectroscopic investigations and solution of the structural problems should follow in the near future.

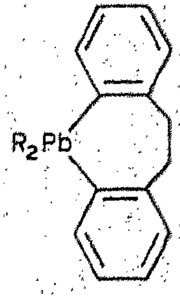
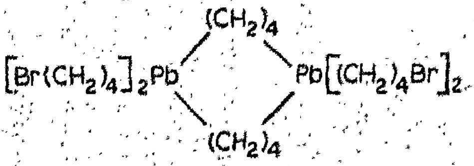
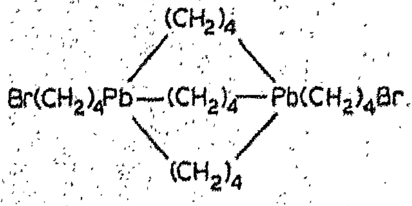
TABLE 23
PROPERTIES OF PLUMBACYCLANES

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	NMR δ (in $CHCl_3$)	Other data reported	References
	Et_2	111/13.5	1.80 (m, β- and γ-CH_2) 1.04–1.64 (Et and α-CH_2)	IR, TLC	146,147,148
	Ph_2			IR	43
	Et_2	31–32/0.18	1.32 (m, α-CH_2) 1.88 (m, β-CH_2) 1.43–1.58 (m, Et)	IR, TLC	147, 148
	Ph_2	145–165/0.5		IR	147
	Et, $MeCO_2$	152–153 (dec.)			147
	Et, $ClCH_2CO_2$	132–133 (dec.)			147
		63–64/1 41–43/0.02	1.61 (m, α-CH_2) 2.11 (m, β-CH_2)	IR, mass spectrum	148,149
		86–87/0.05		IR, NMR	148

(continued)

TABLE 23 (continued)

Compound	R_2	B.p. (°C/mm) or m.p. (°C)	NMR δ (in CCl_4)	Other data reported	References
	Me_2				97
	Ph_2	153–155		IR	97,125
		136–137		UV	127

	Me$_2$	163–165/0.3	6.6–7.7 (m, Ar) 3.0 (s, CH$_2$) 1.05 (s, Me)	IR, mass spectrum	143
	Ph$_2$	163–164	6.7–7.7 (m, Ar) 3.13 (s, CH$_2$)	IR, NMR, mass spectrum	143
					5
					5

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